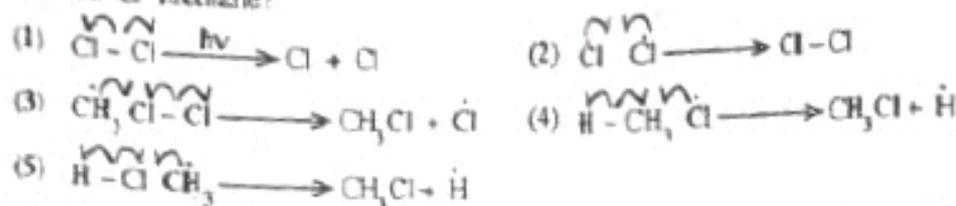


8. Which of the following reactions correctly represents a propagation step in the free radical chlorination reaction of methane?



9. Which of the following statements is false with regard to the chemistry of Aluminium?

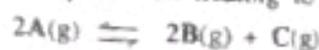
- (1) Aluminium compounds are used as catalysts.
 (2) Aluminium metal reacts with dilute HCl and form H_2 gas.
 (3) The solution formed when solid Aluminium chloride is dissolved in water is basic.
 (4) The shape around the Aluminium atoms in solid Aluminium chloride is tetrahedral.
 (5) Aluminium chloride 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 SF_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.



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) $K_c = \frac{c^2}{(a-2c)^2}$

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

- (1) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is deep blue in colour. (2) $[\text{CrCl}_4]^{2-}$ is pale blue in colour.
 (3) $[\text{NiCl}_4]^{2-}$ is yellow in colour. (4) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is yellow-brown in colour.
 (5) $[\text{CrCl}_6]^{3-}$ 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 $20.00 \text{ kJ mol}^{-1}$. The entropy of vaporization of A in $\text{JK}^{-1} \text{ mol}^{-1}$ at 27°C is,

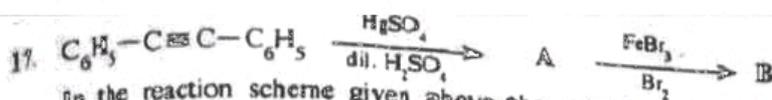
- (1) 0.01 (2) 0.07 (3) 5.66 (4) 14.30 (5) 66.67

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 $1.13 \times 10^5 \text{ Pa}$ pressure was 150.00 cm^3 . Given that the saturated vapour pressure of water is $0.03 \times 10^5 \text{ Pa}$ at 27°C , the mass of O_2 gas collected is, (O = 16)

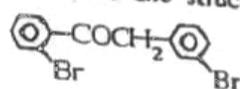
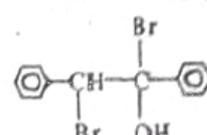
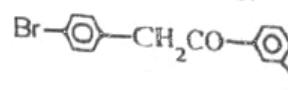
- (1) 0.212 g (2) 0.217 g (3) 198 g (4) 212 g (5) 217 g

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,

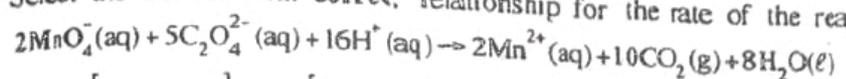
- (1) $a-1$. (2) $a-1/10$. (3) $a+1$. (4) $a-10$. (5) $a+10$.



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

- (1) $C_6H_4(Br)COCH_2C_6H_4(Br)$  (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.



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

$(E_{AgCl(s)/Ag(s)}^\circ = +0.22 V) \quad (E_{Ag^+(aq)/Ag(s)}^\circ = +0.78 V)$

- (1) $+0.22 V, AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ (2) $+0.56 V, Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
- (3) $+1.0 V, AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$ (4) $-0.56 V, Ag^+(aq) + e \rightarrow Ag(s)$
- (5) $-1.0 V, Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

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

- (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 3d-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.



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 $890.4 \text{ kJ mol}^{-1}$. When this reaction is carried out under conditions where the water formed is in the vapour state, the enthalpy change is $802.4 \text{ kJ mol}^{-1}$. The enthalpy change (in kJ mol^{-1}) for the reaction $H_2O(l) \rightarrow H_2O(g)$ is,

- (1) -88 (2) -44 (3) 22 (4) 44 (5) 88

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

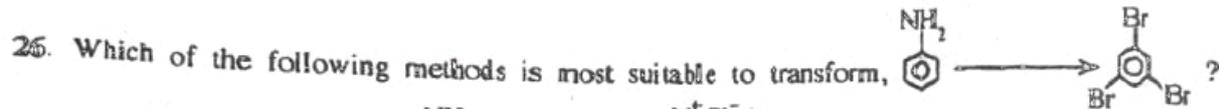
- I. It shows the highest positive oxidation state among the 3d-block elements.
- II. It forms acidic, amphoteric and basic oxides.

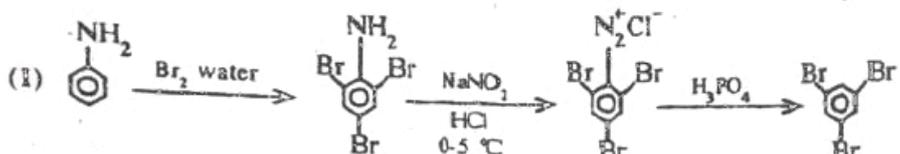
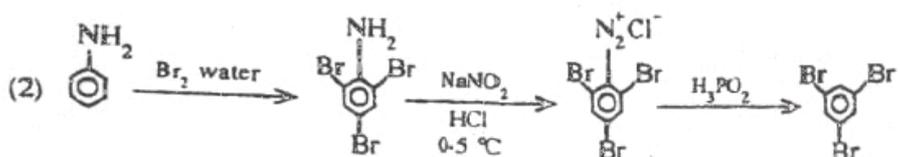
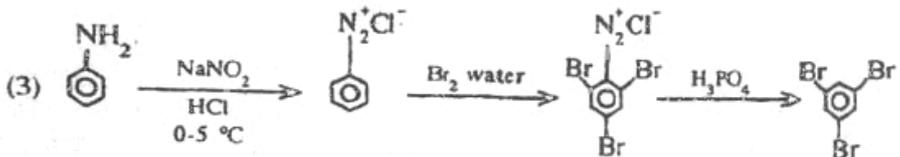
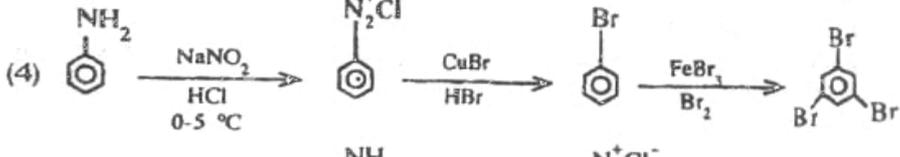
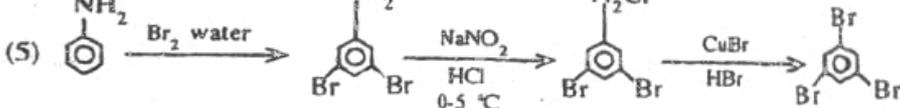
- X is
- (1) Cr (2) Mn (3) Fe (4) Co (5) Zn



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

- (1) $\text{CH}_3-\overset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{COCH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (2) $\text{CH}_3-\overset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CO}_2\text{H}$, $\text{CH}_3\text{COCH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (3) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{COCH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (4) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{COCH}_2\text{CHO}$, $\text{CH}_3\text{COCH}_2\text{CH}_3$
- (5) $\text{CH}_3\overset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\overset{\text{OH}}{\text{CH}}\text{CH}_2\text{CHO}$, $\text{CH}_3\overset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$



- (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?

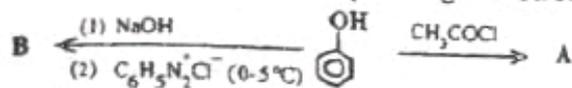
- (1) All elements in Groups I and II react with water and give H_2 gas.
- (2) All elements in Group I react with N_2 gas.
- (3) Mg reacts with both dilute and concentrated H_2SO_4 and give H_2 (g) and SO_2 (g) respectively.
- (4) Li reacts with air and forms a mixture of Li_2O , LiO_2 and Li_3N .
- (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 $\text{Cd(s)}/\text{Cd}^{2+}(\text{aq})$ and $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})$ electrodes?

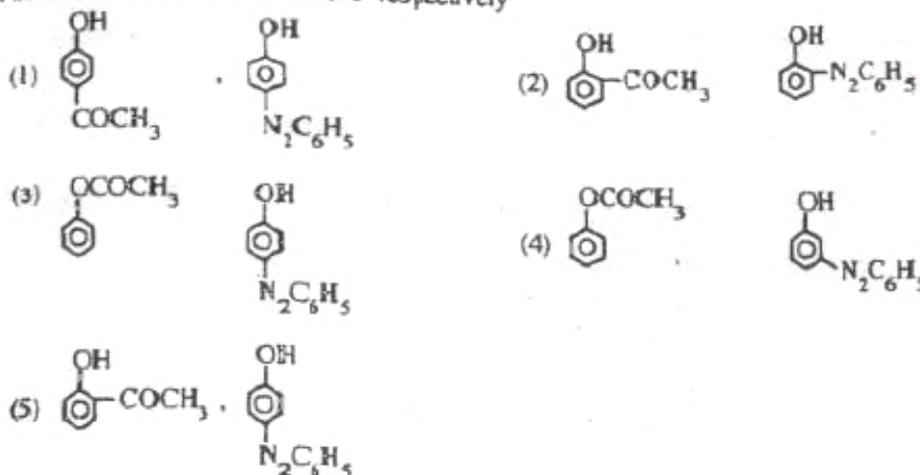
$$E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}, E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ V}$$

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

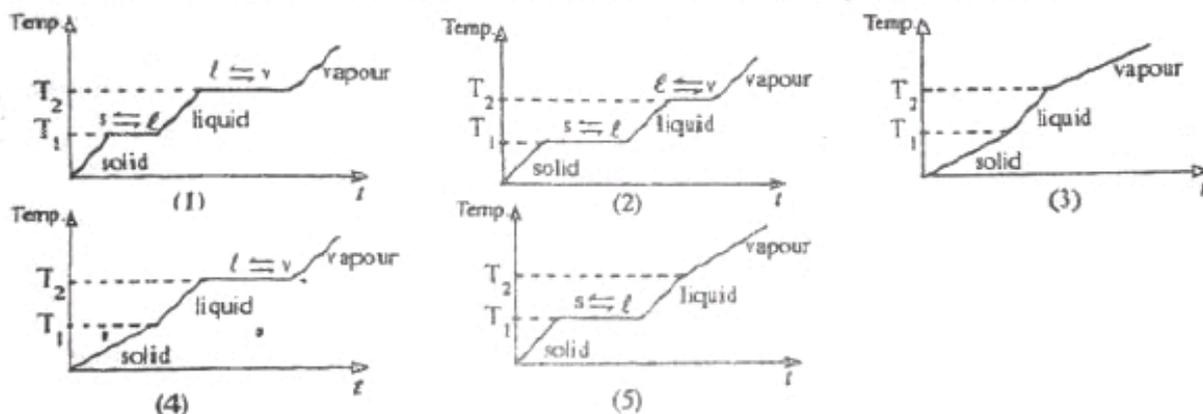
29. Consider the two reactions of phenol given below.



The structures of A and B are respectively



30. For the substance X, the magnitude of the value of ΔH_{fusion} is less than the magnitude of the value of $\Delta H_{\text{vaporization}}$ (i.e. $|\Delta H_{\text{fusion}}| < |\Delta H_{\text{vaporization}}|$). 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

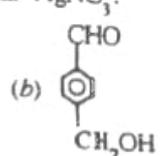
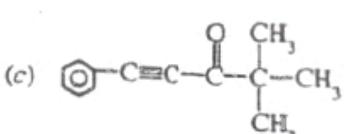
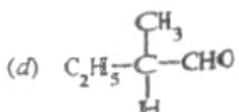
- (1) if only (a) and (b) are correct.
- (2) if only (b) and (c) are correct.
- (3) if only (c) and (d) are correct.
- (4) if only (d) and (a) are correct.
- (5) if any other number or combination of responses is correct.

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, 
- Carbon atoms labelled as a, b, c and d do not lie in a straight line.
 - Carbon atoms labelled as a, b and d are sp^2 , sp and sp^3 hybridized respectively.
 - All carbon, carbon bond lengths of the benzene ring are equal to each other and are longer than the $C\equiv C$ bond length.
 - All carbon, carbon bond lengths of the benzene ring are equal to each other and are shorter than the $C\equiv C$ bond length.
33. Which of the following statements is/are true with regard to the manufacture of NaOH using the mem' and cell?
- During electrolysis $Na^+(aq)$ ions migrate from the cathode compartment to the anode compartment across the membrane.
 - The anode and cathode used are titanium and nickel respectively.
 - High purity NaOH can be prepared by this method.
 - $H_2(g)$ 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?
- The activation energy of the forward reaction in an exothermic process is lower than that of the backward reaction.
 - The activation energy of a slow reaction is less than that of a fast reaction.
 - The activation energy of a given reaction pathway is unaffected by a catalyst.
 - The higher the initial concentration of reactants, the lower the activation energy.
35. Which of the following statements is/are true regarding stereoisomerism?
- A pair of stereoisomers which are mirror images of each other are known as enantiomers.
 - A pair of stereoisomers which are mirror images of each other are known as diastereoisomers.
 - A pair of stereoisomers which are not mirror images of each other are known as enantiomers.
 - 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 $m_l = -2$?
- The electron is in the third main energy level.
 - The electron is in a d orbital.
 - The electron is in a p orbital.
 - 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?
- The increase in temperature increases the activation energy of the reaction.
 - The increase in temperature decreases the activation energy of the reaction.
 - When the temperature increases the number of collisions per unit time per unit volume increases.
 - 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 , of an equilibrium reaction?
- It does not change when the pressure changes.
 - It increases when the concentration of one product is increased.
 - It can change with change in temperature.
 - 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?
- Self condensation with aqueous NaOH.
 - Oxidation with ammoniacal $AgNO_3$.
- 
 - 
 - 
 - 
40. Which of the following statements is/are true regarding polymers?
- PVC is a thermoplastic polymer and does not catch fire easily due to the presence of chlorine.
 - Bakelite is formed by reaction of phenol and formaldehyde in the presence of conc. H_2SO_4 .
 - Urea and formaldehyde react in the presence of conc. H_2SO_4 to form a thermoplastic polymer.
 - 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.	$\text{BaF}_2(\text{s})$ has a higher solubility in an aqueous acid medium than in water	When $\text{BaF}_2(\text{s})$ is dissolved in an acid, due to the formation of HF , the $\text{Ba}^{2+}(\text{aq})$ 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.

Advanced Level 2015 - Chemistry (Paper II)

Part A - Structured Essay

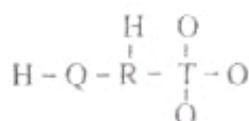
Answer all four questions on the paper itself (Each question carries 10 marks)

1. (a) Consider the following chemical species
 XeF_2 , NO_3^- , SF_6 , Na_2SO_4 , SO_3 , HF

Which one of the above species,

- (i) has both ionic bonds and covalent bonds?
 - (ii) is isoelectronic with BF_3
 - (iii) has a square pyramidal shape?
 - (iv) has an equal number of bonding and non bonding electrons in its most stable structure?
 - (v) has a σ - bond as a result of overlap of a 1s atomic orbital and a 2p atomic orbital?
 - (vi) contains a bond angle of 180° ?
- (b) The compound, $\text{H}_3\text{O}_3\text{QRT}$ shows acidic properties. It loses H^+ to form the anion $[\text{H}_2\text{O}_3\text{QRT}]^-$. 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 $(\text{H}_2\text{O}_3\text{QRT})^-$. Its skeleton is given below



- (i) Identify the elements Q, R and T

Q = R = T =

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

- (iii) Draw six resonance structures for this anion

- (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

Structure of X

- (ii) Write the ground state electronic configuration of X
- (iii) What are the common positive oxidation states of X
- (iv) Write the chemical formulae of the following compounds.
- X_1 :
- X_2 :
- X_3 :
- X_4 :
- X_5 :
- (v) Sketch the most stable structures of X_1 and X_4 , indicate approximate bond angles, in each sketch.
- (vi) Write the balance chemical equation for the reaction of X_1 with acidified potassium permanganate.

- (b) Test tubes labelled A to E contain the following solids (not in order) $Mg(NO_3)_2$, $(NH_4)_2 CO_3$, $(HN_4)_2 SO_4$, 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. colourless, tasteless, non-toxic, triatomic gas with a linear structure.

- (i) Identify solids A to E.

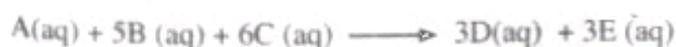
A : B :

C : D :

E :

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

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



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

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

- (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 reactance 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.

.....

- (iii) State the overall order of the reaction

.....

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

.....

- (b) (i) In another experiment, if the concentrations are, $[A]_0 = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[B]_0 = 1.0 \text{ mol dm}^{-3}$, and $[C]_0 = 2.0 \text{ mol dm}^{-3}$, show that the rate expression for the reaction can be given by $\text{rate} = k[A]^2$ (k' is the rate constant of the reaction under these conditions.)

.....

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

.....

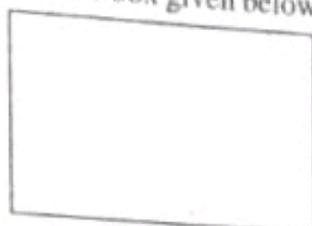
- (ii) In the above (b)(i) experiment, the concentration of A, $[A]$, changes with time (t) according to the following equation, $2.303 \log [A] = -k't + 2.303 \log [A]_0$ ($[A]_0$ is the initial concentration of A). Show that the half-life ($t_{1/2}$) of the reaction is given by $0.693/k'$ and calculate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

.....

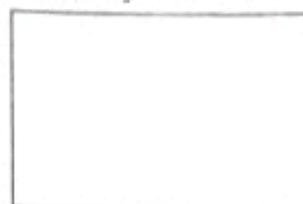
- (a) A, B and C are structural isomers with the molecular formula $C_5H_{11}Br$. All three isomers exhibit optical isomerism, while E and F do not exhibit geometric isomerism. When reacted with alcoholic KOH, A, B and C give D, E and F respectively. D exhibits geometric isomerism, while E and F do not 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)



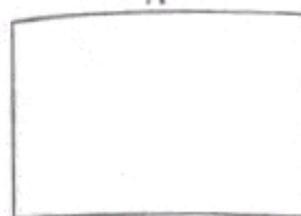
A



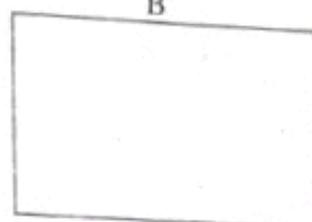
B



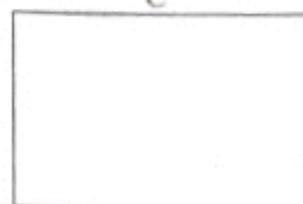
C



D



E

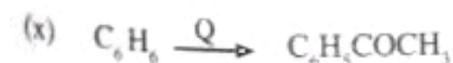
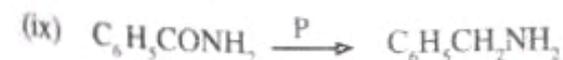
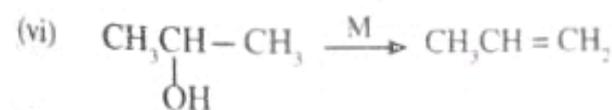
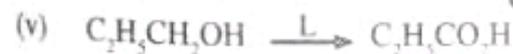
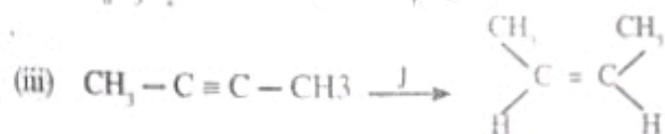


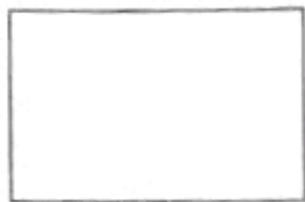
F



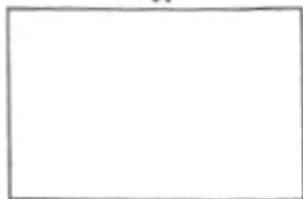
G

- (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

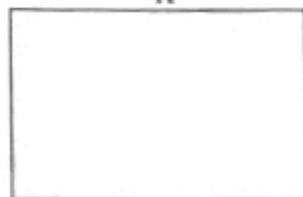




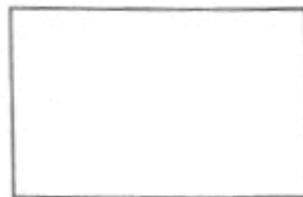
H



K



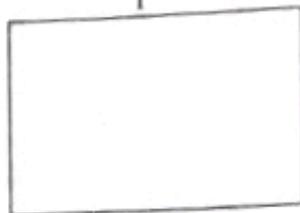
N



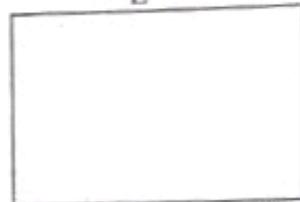
Q



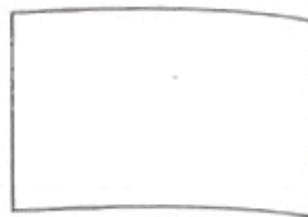
I



L



O



J



M



P

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

රසායන විද්‍යාව II
 இரசாயனவியல் II
 Chemistry II

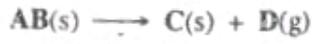


* Universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 * Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

PART B – ESSAY

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

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



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

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
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 dm³ at 930 °C, the system reaches an equilibrium as given below.



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



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 dm³, the partial pressure of D(g) is found to be $7.50 \times 10^5 \text{ Pa}$. 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.
 - I. Some amount of solid C is removed from the system.
 - II. Some amount of gas D is removed from the system.

(10.0 marks)

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. ($X = 110 \text{ g mol}^{-1}$, $A = 40 \text{ g mol}^{-1}$)
- (ii) A completely water soluble solid NaA is added slowly to a 1.00 dm³ aqueous solution containing 0.100 moles of X⁺(aq) and 0.100 moles of Y⁺(aq).
 - I. Predict which of the salts precipitates first. ($K_{sp}(\text{YA}) = 1.80 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$).
 - 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 A⁻(aq), show that the pH of the solution at the equivalence point is given by $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log [A^-(aq)]$.

(You are given that $\text{pH} + \text{pOH} = \text{p}K_w$, $\text{p}K_a + \text{p}K_b = \text{p}K_w$ and $K_b = \frac{[\text{OH}^-(aq)][\text{HA}(aq)]}{[A^-(aq)]}$)

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

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

(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.

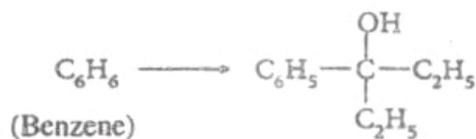
II. Mark the composition (Q) of the vapour phase at temperature T_1 on the phase diagram above.

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)

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



List of chemicals

KMnO₄, PBr₃, Mg, dry ether, CH₃Cl, C₂H₅OH, Anhydrous AlCl₃, conc. H₂SO₄

(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.



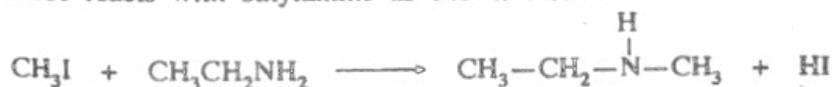
A



B

(7.0 marks)

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



(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.



(3.0 marks)

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, M_1 . On treatment with cold water M_1 gives a clear basic solution, M_2 and a covalent compound, M_3 . M_3 reacts with acidified Ag_2O to give a colourless diatomic gas, M_4 . Excess of M_2 reacts with metal T to give a colourless diatomic gas M_5 , and a water soluble compound, M_6 . The addition of dilute HCl dropwise to an aqueous solution of M_6 gives a white gelatinous precipitate, M_7 which dissolves in excess acid. M_7 does not dissolve in dilute NH_4OH .

- Identify M , M_1 , M_2 , M_3 , M_4 , M_5 , M_6 , M_7 and T .
- Predict the products of the reaction of 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.

- Identify Q and draw the most acceptable Lewis structure for its anion.
- Write balanced chemical equations for the reactions taking place in tests (1), (2) and (3). Indicate the precipitates with an arrow (\downarrow) in the equations.
- Give two uses of Q .

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

(5.0 marks)

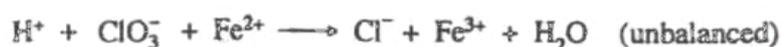
(c) The following procedure was used to determine the percentage by mass of $KClO_3$ and KCl in a mixture X . Mixture X contains $KClO_3$, KCl and a water soluble inert material.

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 $105^\circ C$ 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.



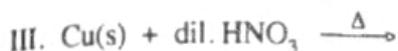
Calculate separately the percentage by mass of $KClO_3$ and KCl in X .

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

(5.0 marks)

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.



(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.

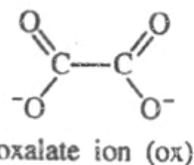
- (i) Special conditions are required to fix N_2 due to its inert nature. Explain why N_2 is inert.
- (ii) State the **two** natural N_2 fixing processes.
- (iii) State the name of the main industrial process used to fix N_2 .
- (iv) Identify the **two** nitrogen compounds that contribute to photochemical 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)

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.

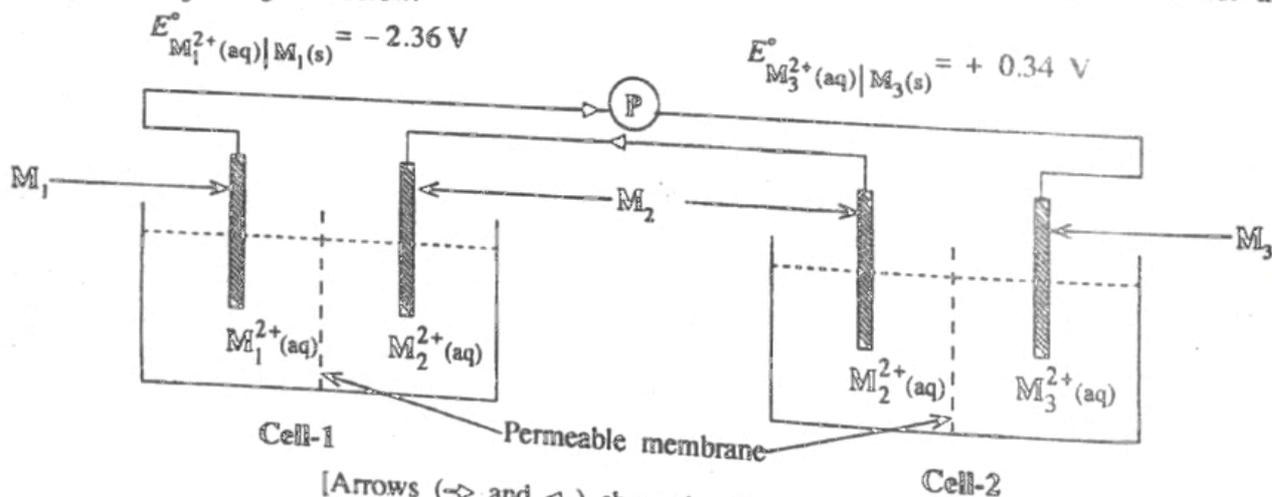


The oxalate ion coordinates the chromium ion through the two negatively charged oxygens to give a complex ion part, E, which has an octahedral geometry. Write the structural formula of E. (The chromium ion in E has the same oxidation state as the chromium in compounds A - D.)

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. M_1 , M_2 and M_3 metals are dipped in aqueous solutions of their own ions $M_1^{2+}(aq)$, $M_2^{2+}(aq)$ and $M_3^{2+}(aq)$, respectively. The concentrations of all solutions are 1.0 mol dm^{-3} . The standard electrode potentials for the metals M_1 and M_3 are given below.



[Arrows (\rightarrow) and (\leftarrow) 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 ($E^\circ_{\text{cell-1}}$) was found to be +1.60 V. Calculate the standard electrode potential ($E^\circ_{M_2^{2+}(aq)|M_2(s)}$) of the $M_2^{2+}(aq)/M_2(s)$ electrode.
- (v) Calculate the electromotive force of cell-2 ($E^\circ_{\text{cell-2}}$)
- (vi) If you are provided only a metal M_4 and a solution of $M_4^{2+}(aq, 1.0 \text{ mol dm}^{-3})$ in addition to the above set up, suggest an experimental method in brief to determine the value of E°