

CHEMISTRY

1. Write critical notes on any four of the following:

(4x7½=30)

- (a) Heisenberg's uncertainty principle
- (b) Valence bond theory
- (c) Langmuir's adsorption isotherm
- (d) Mechanism of Aldol condensation
- (e) Synthetic and natural rubber
- (f) Isotopic substitution and rotational constants.

PART I

2.(a) Determine the effective atomic number of the central metal atom in the following:

- (i) $K_4 [Ni(CN)_4]$
- (ii) $K_2 Ba [Co(NO_2)_6]$
- (iii) $K_3 [Fe(CN)_6]$
- (iv) $[Cr(H_2O)_4Cl_2] NO_3$

(b) Explain the following:

- (i) H_2O is polar while CO_2 is non-polar
- (ii) $SnCl_2$ and $HgCl_2$ cannot coexist together in an aqueous solution.

- (c)
- (i) Explain bond order and bond strength.
 - (ii) Calculate bond order in H^+_2 and O^{2-}_2

(30)

3.(a) Show that half life period in a first order reaction is independent of initial concentration of the reactant.

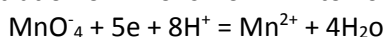
(b) (i) Derive the following relation :

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = \Delta C_p$$

(ii) Derive Clausius-Clapeyron equation and describe its applications.

(C) What is 'radius ratio rule'? How does it help in determining the crystal structure of ionic solids? (30)

4. (a) How much oxidizing power of the couple $MnO_4^- (1M)/Mn^{2+} (1M)$ is decreased on decreasing the concentration of H^+ ions from 1M to 10^{-4} M, if MnO_4^- is reduced according to the following reaction?



(b) Describe lanthanide contraction, its causes and consequences.

(c) Explain the following:

- (i) John Teller effect
- (ii) Fluorescence and phosphorescence.

(30)

PART II

5.(a) Describe Hammond's postulate. Discuss isotope effect and its role in determining reaction mechanism.

(b) Compare the stereochemistry of first order and second order nucleophilic substitution with suitable examples.

(c) Describe the conditions and mechanism of Cannizzaro's reaction. (30)

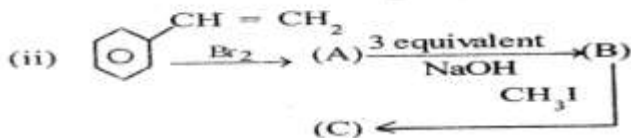
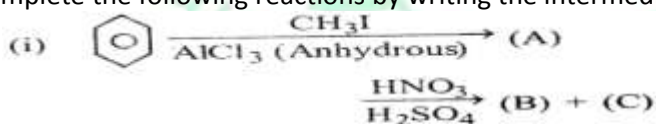
6.(a) Describe osmotic pressure measurement method for the determination of molecular weight of polymers.

(b) Describe preparation and properties of nylon and polyvinyl chloride.

(c) (i) Discuss the mechanism of Pinacol-Pinacolone rearrangement.

(ii) Explain the stability of carbanions and carbenes. Discuss the importance and role of these species also. (30)

7. (a) Complete the following reactions by writing the intermediates and final products:



(b) Describe the factors affecting chemical shifts.

(c) Explain the following:

- (i) $n - \pi^*$ and $\pi - \pi^*$ transitions
- (ii) Number of fundamental vibrations and coupled vibrations.

(30)