

M.C.S. (Ex.) 2004

8

Code—04

CHEMISTRY

Time : 3 Hours

Maximum Marks : 150

Note : Attempt *Five* questions in all. All questions carry equal marks. Q. No. 1 is compulsory. Answer *two* questions from Part I and *two* questions from Part II. The parts of the same question must be answered together and must not be interposed between answers to other questions.

1. Write critical notes on any *four* of the following : (4×7½=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.

P.T.O.

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) $[Cr (H_2O)_4 Cl_2] NO_3$
- (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.

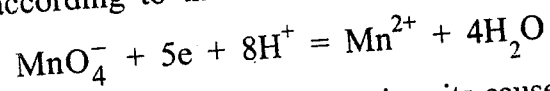
- (b) (i) Derive the following relation :

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

- (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 oxidising 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 ?



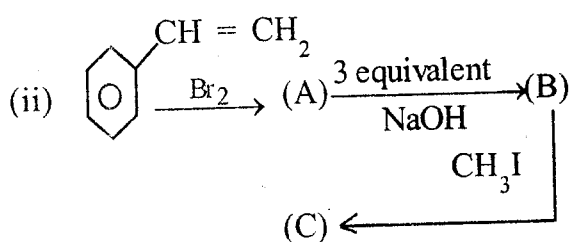
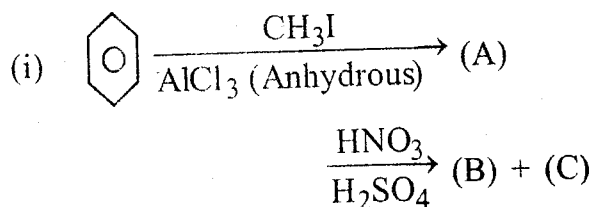
- (b) Describe lanthanide contraction, its causes and consequences.
- (c) Explain the following :
- (i) John Teller effect
- (ii) Fluorescence and phosphorescence. (30)

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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)

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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) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions
 - (ii) Number of fundamental vibrations and coupled vibrations. (30)