

No. of Printed Pages : 3

CS-88/06
CHEMISTRY
Paper-I

Time : 3 Hours]

[Full Marks : 300

- Note :** (1) Candidates should attempt Question No. 1 from Section-A and Question No. 5 from Section-B which are compulsory, and any **three** of the remaining questions, selecting at least one from each Section.
- (2) All questions carry equal marks.

SECTION – A

1. Answer any **three** of the following :
- (a) $[\text{Ni}(\text{CN})_4]^{2-}$ is formed even in excess of CN^- ions but not $[\text{Ni}(\text{CN})_6]^{4-}$.
Explain the reason. 20
 - (b) CaF_2 and CaCl_2 are chemically comparable, their lattice structures are different. – Why ? 20
 - (c) Both MnO_4^- and HgI_2 are of intense colour. – Why ? 20
 - (d) Bond angles in CH_4 , NH_3 and H_2O are different although tetrahedral model is held valid for all of them. Explain the reason. 20
2. (a) What is 'Born-Haber Cycle' ? Describe its applications. 20
- (b) Discuss the geometries of H_3O^+ , ClF_3 and ICl_2^- using VSEPR model for predicting molecular structures. 20
- (c) Describe the structures of oxy acids of P and S. 20
3. (a) Write a brief account of structural principles of silicates. 15
- (b) Define and explain the following : 25
- (i) Lattice Energy
 - (ii) Lanthanide contraction
 - (iii) Electrode potential
 - (iv) Diagonal relations in periodic table
 - (v) Super acids
- (c) Describe the structures of metal carbonyls in general. 20

4. (a) What is nitrogen fixation ? How is N_2 activated by coordination with transition metal ions ? 20
- (b) Describe the structure of active-site of an oxygen uptake protein. 20
- (c) What is Chelate effect in transition metal complexes ? How does it govern thermodynamic stability of complexes ? 20

SECTION – B

5. Answer any **three** of the following :

- (a) Draw and explain phase diagram of KCl + water system. Show that eutectic point is a non-variant point. 20
- (b) (i) What is meant by transport number of an ion in a solution ?
 (ii) The molar conductance of HCl at 0.05 M is $399.09 \times 10^{-4} \text{ m}^2 \cdot \text{mho} \cdot \text{mol}^{-1}$ and the transport number of H^+ ion at this concentration is 0.829. Calculate the ionic molar conductance of H^+ and Cl^- . 20
- (c) The variation of surface tension of an adsorbent is related to the surface excess concentration of a gas by the relation $\gamma - \gamma_0 = a - b\Gamma$
 Where 'a' and 'b' are constants. Show that Gibbs adsorption equation when applied to gas adsorption leads to the Freundlich adsorption equation. 20
- (d) Obtain thermodynamic equation to calculate change in boiling point with pressure. 20

6. (a) A certain gas obeys the equation of state

$$P = (RT/V_m - bT) - a/V_m^3$$

where a and b are constants characteristic of the gas, show that

$$a = 4RT_c V_{m,c}^2/3 \text{ and } b = V_{m,c}/2T_c$$

where $V_{m,c}$ and T_c are the critical volume and temperature, respectively. 20

- (b) Explain why CO and N_2 have the same velocity distribution at the same temperature. 20
- (c) The combustion of 1g of benzene evolves 41.746 kJ of heat at 25 °C.
 (i) Calculate U^0 for combustion of benzene.
 (ii) Calculate $\Delta_f H^0$ (benzene) if $\Delta_f H^0 (CO_2, \text{ gas}) = -393.129 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H^0 (H_2O, \text{ liq}) = -285.577 \text{ kJ} \cdot \text{mol}^{-1}$ 20

7. (a) Show that for a n^{th} order (where $n > 1$) reaction $A \longrightarrow B$, the half life
 $t_{1/2} = 2^{n-1} - 1 / (n - 1) a^{n-1} k$
 Where 'a' is the initial concentration of the reactant and k is the rate constant. 20
- (b) The gas phase reaction $2 \text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ has
 $k = 2.05 \times 10^{13} \exp(-24.65 \text{ kcal.mol}^{-1}/RT) \text{ s}^{-1}$.
 Find $t_{1/2}$ at 323 K. 20
- (c) A first order reaction has rate constant equal to $1.25 \times 10^{-4} \text{ sec}^{-1}$ at 298 K
 and $8.5 \times 10^{-4} \text{ sec}^{-1}$ at 318 K. Calculate the activation energy of the reaction. 20
8. (a) Calculate the efficiency of a heat engine if it is working between 100 °C and
 20 °C. How one can increase the efficiency of heat engine ? 20
- (b) Derive an expression of entropy of mixing of one mole of oxygen gas and
 two moles of hydrogen gas, assuming that no chemical reaction occurs and
 the gas mixture behaves ideally. 20
- (c) Using the equations $dE = TdS - PdV$ and $H = E + PV$, prove that
 $(dE/dS)_P = T - (dT/dP)_S$. 20
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