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| <b>CSM – 16/18</b> |
| <b>Chemistry</b>   |
| <b>Paper – I</b>   |

*Time : 3 hours*

*Full Marks : 300*

*The figures in the right-hand margin indicate marks.*

*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and three of the remaining questions, selecting at least one from each Section.*

**SECTION – A**

1. Answer any three of the following :  $20 \times 3 = 60$
- (a) Discuss the types of crystal. In a cubic crystal system, a crystal plane cut through the crystal axes at  $(2a, 2b, 3c)$ . Calculate the Miller indices of this plane.
- (b) What do you mean by co-operative interaction in  $O_2$  affinity of hemoglobin? How do you express this phenomenon by Hill equation and Hill plot?

(c) (i) The rate constant of a 1<sup>st</sup> order reaction is represented by the equation ;  $k \text{ (set}^{-1}\text{)} = 4.5 \times 10^{13} \exp(-105.0 \text{ kJ mole}^{-1}/RT)$ . The above equation can be carried out in the presence of a catalyst that lowers the entropy of activation by  $8.5 \text{ kJ mole}^{-1}$  and lowers the activation energy by  $20.5 \text{ kJ mole}^{-1}$ . Calculate the ratio of rate constant of catalysed reaction to that of the uncatalysed reaction at 350 K.

(ii) The Arrhenius equation for Cis  $\rightleftharpoons$  Trans isomerisation : .

$$k_{\text{Cis}} = 10^{12} \exp(-250.0 \text{ kJ mole}^{-1}/RT)$$

$$k_{\text{Trans}} = 10^{11} \exp(-215.0 \text{ kJ mole}^{-1}/RT)$$

Calculate the temperature at which

$$k_{\text{Cis}} = k_{\text{Trans}}$$

(d) (i) "The number of constituent is not necessarily equivalent to the number of component". Justify the statement giving at least two examples.

- (ii) Show that an aqueous system containing  $K^+$ ,  $Na^+$ ,  $Cl^-$  and  $Br^-$  is a four component system. What will be the number of components when the salts are present in equal amount ?

2. Answer the following :

(a) (i) Define and discuss the physical significance of partial molar volume.

(ii) Calculate the partial molar volume of ethanol at  $25^\circ C$  in 50% mass ethanol-water solution if the density of solution is 0.914 gm/cc and partial molar volume of water is 17.4 cc/mole.  $10+10 = 20$

(b) Show that the probability of finding the particle in a one-dimensional box in the region  $L/4$  and  $3L/4$  is  $\frac{1}{2}$  if  $n$  is even and

$$\frac{1}{2} + \frac{(-1)^K}{n\pi} \text{ if } n \text{ is odd where } n = 2K + 1 \text{ and}$$

$$K = 0, 1, 2, 3, \dots$$

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- (c) Deduce  $\ln f_i = -\frac{Nz_i^2 e^2 K}{2DRT}$  for Debye-Huckel limiting law. Discuss its importance in determining the equivalent conductance of strong electrolytes. 20

3. Answer the following :

- (a) When does a particular substance absorb light in UV-visible region ? How can the concentration of a substance be determined using its characteristics absorption ? Discuss. 20
- (b) Differentiate between protonic and aprotic solvents citing examples in each case. Discuss at least two reactions, in presence of one protonic and aprotic solvent. 20
- (c) Explain the failures of Crystal Field Theory with evidences. Draw a neat Molecular Orbital Diagram of an Octahedral complex considering the ligand group of orbitals and explain the magnetic properties of  $d^3 - d^8$  electron system. 20

4. Answer the following :

(a) Derive the following adsorption equation.

$$\frac{P}{V} = \frac{1}{K_1 V_m} + \frac{P}{V_m}, \text{ the terms have their usual}$$

meaning. Discuss the use of this equation for measuring the surface area of an adsorbent. 20

(b) Discuss the geometry of  $\text{H}_3\text{O}^+$ ,  $\text{ClO}_3^+$  and  $\text{ICl}_4^-$  using VSEPR model for predicting molecular structures. 20

(c) Define and discuss the types of semiconductor. Discuss the types of extrinsic conductors with appropriate diagrams. 20

### SECTION - B

5. Answer any three of the following :

(a) (i) The complex containing  $[\text{Ni}(\text{en})_3]^{+2}$  in aqueous solution shows the spectral bands at 11,000, 18500 and 30,000  $\text{cm}^{-1}$ . Using Orgel diagram assign the

transitions. The complex  $[\text{Fe}(\text{F}_6)]^{3-}$  is colourless whereas  $[\text{Co}(\text{F}_6)]^{3-}$  is coloured with single transition in the visible region, explain.

- (ii) The volume of nitrogen gas at 1 atm pressure and 273 K temperature required to cover a sample silica gel with a monomolecular layer is  $0.129 \text{ dm}^3$  per gram of the gel. Calculate the surface area of the gel if each nitrogen molecule occupies  $16.2 \times 10^{-20} \text{ m}^2$ .  $15+5 = 20$

(b) Explain, why:  $5 \times 4 = 20$

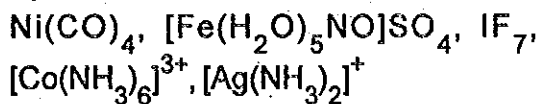
- (i) 'He' has the highest ionization energy.
- (ii) The second ionization energy is always higher than the first ionization energy.
- (iii) The difference between first and second ionization energy of alkali metals are noticeably large.
- (iv) The first ionization energy of 3d and 4d transition elements are almost similar.

(c) Estimate :  $10 \times 2 = 20$

(i) The magnetic moment in BM for  $\text{Pr}^{3+}$  with outer configuration  $4f^2, 6s^0$ .

(ii) The ground state magnetic moment in BM of  $\text{Sm}^{3+}$  at room temperature.

(d) (i) Discuss the hybridization of the following :



(ii) Calculate the free energy for transferring  $3 \text{Na}^+$  from cytosol to exterior of the cell and  $2 \text{K}^+$  from the exterior of the cell to the cytoplasm, where  $[\text{Na}^+]_{\text{exterior}} / [\text{Na}^+]_{\text{cytosol}} = 15$  and  $[\text{K}^+]_{\text{cytosol}} / [\text{K}^+]_{\text{exterior}} = 25$ .  $15 \times 5 = 20$

6. Answer the following :

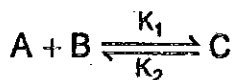
(a) (i) Derive Clapeyron-Clausius equation. How does it help in deciding the slope of the line corresponding to solid  $\rightarrow$  vapour and liquid  $\rightarrow$  vapour transformation at the triple point of water ?

(ii) How many degrees of freedom will be possessed by each of the following systems ?

(a) An aqueous solution of  $\text{ZnSO}_4$ ,

(b) Sugar in equilibrium with its solution at  $25^\circ\text{C}$  and (c) Solid camphor in equilibrium with its vapor.  $14+6 = 20$

(b) Find the relationship between  $k_1$ ,  $k_2$  and  $\tau$  for the fast reaction of type :  $20$



and calculate  $k_1$  and  $k_2$  from the following data :

$$[\text{A}]_e = 2 \times 10^{-3} \text{ dm}^{-3} \text{ mol}$$

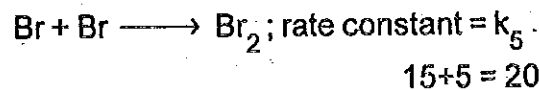
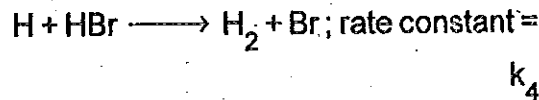
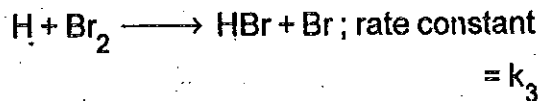
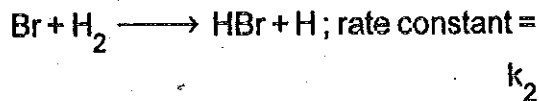
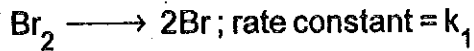
$$[\text{B}]_e = 5 \times 10^{-3} \text{ dm}^{-3} \text{ mol}$$

$$[\text{X}]_e = 1 \times 10^{-3} \text{ dm}^{-3} \text{ mol} \quad \tau = 50 \mu\text{s}$$

(c) (i) Calculate crystal field stabilization energies for tetrahedral and octahedral complexes of  $\text{Co(II)}$  and  $\text{Ni(II)}$ . Give your comments on the stability of these complexes on the basis of CFSE.



- (ii) Derive the rate of the reaction between  $H_2$  and  $Br_2$ , while reaction follows the following chain reaction :



$$15+5 = 20$$

7. Answer the following :

(a) (i) Determine the total work done by a Carnot cycle.

(ii) A Carnot engine working between two temperatures has an efficiency of 40%. When the temperature of the sink is reduced by  $60^\circ C$ , the efficiency increases to 55%. Calculate the two temperatures in the 1<sup>st</sup> case.  $15+5 = 20$

(b) (i) Derive Ostwald's dilution law for a binary electrolyte. Explain the validity of the Ostwald's dilution law.

(ii) Discuss briefly about spin-orbital coupling parameter & inter electronic repulsion parameter.  $10+10 = 20$

(c) (i) Show that  $K = \frac{1}{V^{\Delta n}} \times \frac{(q_M)^m (q_N)^n}{(q_A)^a (q_B)^b}$  for an

equilibrium reaction of type  $aA + bB \leftrightarrow mM + nN$ .

(ii) Estimate molar heat capacity of  $I_2$  at 300 K. The rotational constant  $B = 0.037 \text{ cm}^{-1}$  and fundamental vibrational frequency  $-215 \text{ cm}^{-1}$ .  $10+10 = 20$

8. Answer the following :

(a) Discussing the postulates of valence bond theory and apply the theory to explain the bonding in  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(CN)_6]^{3-}$ ?

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