CSM – 16/18

Chemistry

Paper – I

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 : 20×3 = 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^{st} order reaction is represented by the equation ; $k\ (set^{-1}) = 4.5 \times 10^{13} \exp(-105.0\ kJ\ mole^{-1}/RT)$. The above equation can be carried out in the presence of a catalyst that lowers the entropy of activation by 8.5 kJ $mole^{-1}$ and lowers the activation energy by 20.5 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 :

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

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

Calculate the temperature at which $k_{Cis} = k_{Trans}$.

(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°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 $\frac{1}{2} + \frac{(-1)^K}{n\pi}$ if n is odd where $n = 2K + 1$ and $K = 0, 1, 2, 3, ...$ 20

(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.

$\frac{P}{V} = \frac{1}{K_1 V_m} + \frac{P}{V_m}$, 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 H_3O^+, ClO_3^+ and ICl_4^- using VSPER 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 $[Ni(en)_3]^{+2}$ in aqueous solution shows the spectral bands at 11,000, 18500 and 30,000 cm^{-1}. Using Orgel diagram assign the

transitions. The complex $[Fe(F_6)]^{3-}$ is colourless whereas $[Co(F_6)]^{3-}$ 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 dm^3 per gram of the gel. Calculate the surface area of the gel if each nitrogen molecule occupies 16.2×10^{-20} m^2. 15+5 = 20

(b) Explain, why: 5×4 = 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 : 10×2 = 20

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

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

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

$Ni(CO)_4$, $[Fe(H_2O)_5NO]SO_4$, IF_7, $[Co(NH_3)_6]^{3+}$, $[Ag(NH_3)_2]^+$

(ii) Calculate the free energy for transferring 3 Na^+ from cytosol to exterior of the cell and 2 K^+ from the exterior of the cell to the cytoplasm, where $[Na^+]_{exterior}/[Na^+]_{cytosol}$ = 15 and $[K^+]_{cytosol}/[K^+]_{exterior}$ = 25. 15+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 → vapour and liquid → 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 $ZnSO_4$, (b) Sugar in equilibrium with its solution at 25°C and (c) Solid camphor in equilibrium with its vapor. 14+6 = 20

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

$$A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C$$

and calculate k_1 and k_2 from the following data :

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

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

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

(c) (i) Calculate crystal field stabilization energies for tetrahedral and octahedral complexes of Co(II) and 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 :

$Br_2 \longrightarrow 2Br$; rate constant = k_1

$Br + H_2 \longrightarrow HBr + H$; rate constant = k_2

$H + Br_2 \longrightarrow HBr + Br$; rate constant = k_3

$H + HBr \longrightarrow H_2 + Br$; rate constant = k_4

$Br + Br \longrightarrow Br_2$; rate constant = k_5

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°C, the efficiency increases to 55%. Calculate the two temperatures in the 1st 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 cm^{-1} and fundamental vibrational frequency – 215 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 $[Fe(CN)_6]^{3}$? 20