CSM – 16 / 15

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 **five** of the following : 12×5 = 60

   (a) What is the difference between lanthanides and lanthanoids ? Explain why the magnetic moment of trivalent gadolinium (Z = 64) complexes can be obtained by the spin only formula but not for trivalent terbium complexes. What is the principle involved in solvent extraction of lanthanides by using tri-n-butyl phosphate.

   (b) Interpret the physical significance of ψ and $\psi \cdot \psi^*$ (where ψ is a wave function). Describe

the azimuthal and magnetic quantum numbers of 5 degenerate "d" orbitals along with their shapes.

(c) State and deduce the uncertainty relation of time and energy from Heisenberg uncertainty principle.

(d) Explain the magnetic property and the stability of the following compounds N_2, N_2^+, N_2^-, N_2^{2-} from MOT.

(e) In a bomb calorimeter an unknown compound is reacted with excess of oxygen to give CO_2 and H_2O. The temperature of 2 kg water is rose from 12.72°C to 20.72°C. The heat capacity of the calorimeter is 2.02 $KJ.K^{-1}$ and the specific heat of water is 4.184 J/g°C. Calculate the heat given off by this combustion reaction.

(f) Explain the relation between limiting radius ratio and co-ordination number of ionic compound.

2. (a) Explain Chelate effect with regard to stability of complexes. 20

(b) Draw the structure of $Ir_4(CO)_{12}$. Explain the fluxionality of this compound using any of its substituent. Explain the oxidative addition of O_2 to $Ir(CO)Cl(PPh_3)_2$. 20

(c) Giving reasons, arrange the following in increasing order of CFSE : 5×4 = 20

(i) CoF_6^{3-}

(ii) $Co(CNS)_4^{2-}$

(iii) $[Mn(H_2O)_6]^{2+}$

(iv) $Co(NH_3)_6^{3+}$

3. (a) Give the synthesis scheme of Zeise's salt. Distinguish between σ and π bonding interactions (metal-carbonyl bond formation) in $[PtCl_3(C_2H_4)]^-$ using orbital interaction diagrams. 20

(b) Write down the assumption of VSEPR theory. Deduce the structural geometry of the following compounds : 20

(i) ClF_3

(ii) ICl_4^-

(iii) IF_7

(iv) $TeCl_4$

(v) ICl_2^+

(c) Define John-Teller distortion in crystal field theory. In[$Cu(hfacac)_2(bipy)$], there are two short Cu-O bonds and two long Cu-O bonds. Explain the fact. [hfacac=hexafluoroacetylacetone anion, bipy=2,2-bipyridine]. 20

4. (a) Why are d-metals such as Mn, Fe, Co and Cu are present in redox enzymes in preference to Ga and Ca ? What are ionophores ? Mention their role in biology. "Cytochrome C is a redox protein but myoglobin is an oxygen storage protein", Justify the statement. Explain the co-operative binding effect in oxygen transport of hemoglobin. 20

(b) Explain Schottky and Frenkel defects in ionic crystals with suitable examples. ZnO turns yellow upon heating — explain fact. 20

(c) Define the term liquid crystal with suitable examples. Mention its application advanced material field. 20

Section – B

5. Answer any **three** of the following : $20 \times 3 = 60$

(a) Explain the term super critical fluid. At high temp. and low pressure real gases are behaved like deal gases. Explain the fact in terms of the compressibility factor (z). Derive an expression of fugacity for real gases at high pressure and low pressure.

(b) Explain Trouton's rule. Boiling point of Bromine is 59.2°C. Find out the standard molar enthalpy. What is residual entropy ? Discuss with suitable examples. Does it violate the third law of thermodynamics ?

(c) Discuss Carnot Cycles. Complete conversion of heat into work is possible — Explain the fact.

(d) Differentiate the Helmholtz electrical double layer and Gouy electrical double layer. Explain the origin of charge in colloidal particles with suitable example of positively charged and negatively charged colloidal particles.

6. (a) Deduce $\theta = Ka[A] / 1 + Ka[A]$ for Langmuir adsorption isotherm, where θ is fraction of surface covered, [A] concentration of the gas, Ka is equilibrium constant for adsorption

process. What will be the final expression if the concentration of A is high/low. If the gas molecules are being dissociated during adsorption what will be the changes in the final expression ? 20

(b) Draw and discuss the phase diagram of sulphur. What do you mean by "Critical Solution Temperature (CST)" and explain this temperature in a binary liquid system. Calculate the final pressure of a sample of argon (Y = 5/3) which was at 100 KPa and then expands reversibly and adiabatically to twice its initial volume. 20

(c) What do you mean by canonical and micro-canonical ensembles ? Deduce expression for rotational and vibrational partition function. Deduce S = KlnZ in canonical system. 20

7. (a) Deduce the expressions of partial molar quantities in a mixture of ideal gases. Describe the general behaviour of free energy (G) as a function of ξ, the advancement of reaction for a simple reaction $A \leftrightarrow B$. A two component gas mixture obeys the equation of state $P(V - n_1b_1 - n_2b_2) = (n_1 + n_2)RT$, where b_1 and b_2 are constants.

Find the value of partial molar volume V_1 and V_2. 20

(b) At high concentration of electrolyte the Debye-Huckel limiting law fails. Explain the fact with appropriate reasons. Deduce an expression for μ_{solute} of [m] molar solution of $ZnBr_2$, assuming complete dissociation. Assuming complete dissociation of $AlCl_3$, calculate I, Y± and a ± at 298 K temperature. 20

(c) What do you mean by liquid junction potential of a cell, involve electrolytic solution of different composition ? What are the ways of eliminating liquid junction potential ? In a transport number experiment, a solution of $AgNO_3$ containing 0.0074 gm/gm of water used. During experiment 0.0875 gm Ag was deposited in Ag voltameter placed in series with the transport apparatus. After the experiment 25 gm of the anode solution contained 0.2553 gm $AgNO_3$. Find the transport number of Ag+ and NO_3^-. 20

8. (a) What is hydrodynamic voltammetry ? Explain why an excess of supporting electrolyte is added to electroactive species in

polarographic analysis ? A substance undegoes a two electron reversible reduction at dropping mercury electrode and gives a diffusion current of 7.5 mμ. Calculate $E_{1/2}$ when the potential at the dropping mercury electrode is – 0.615 V, the current is 1.5 mμ. For a redox reaction Cd2 + 2e – ↔ Cd, the observed anodic potential is – 650 mV in cyclic voltammetry at hanging mercury drop electrode. Calculate the cathodic potential. 20

(b) Explain fluorescence and phosphorescence in terms of Jabonski diagram. Define vibrational relaxation. What is photo isomerism ? Give suitble example. Deduce the mathematical expression of fluorescence intensity in terms of fluorescence quantum yield. 20

(c) What do you mean by Fast Reactions ? Describe stop-flow and relaxation methods for the study of fast reaction. Molecularity of a reaction can never be in fraction but reaction order can be in fraction. Explain the fact. 20