CSM – 16/17

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 any **three** of the remaining questions selecting at least **one** from each Section.*

SECTION – A

1. Answer any **four** of the following : 15×4 = 60

   (a) Discuss the mechanism of active transport through membranes.

   (b) What are the characteristic properties of semiconducting materials ? Give a brief account of some important applications of semiconductors.

(c) The octahedral complex ion $[Co(CN)_6]^{3-}$ is known to be diamagnetic whereas $[CoCl_6]^{3-}$ is paramagnetic. Explain this difference on the basis of valence bond theory and from crystal field theory point of view. On the basis of crystal field theory, what can you say about the crystal field splitting strength of CN^- and Cl^-.

(d) Discuss the Main-Smith colour sequence for tripositive lanthanide ions.

(e) Describe the role of cytochrome P-450 in biological systems.

2. (a) The wave function $\psi(r, \theta, \phi)$ for hydrogen atom for 1s state is $\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$, where a_0 is the Bohr radius. Show that the wave function is normalized and find the average distance of the electron from the nucleus in 1s orbital, given that $\int_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}}$. 20

(b) Deduce the expression of the energy for H-atom using the above-mentioned wave function (ψ_{1s}). 20

(c) Give one example for each of the following reactions in liquid sulphur dioxide : 20

(i) Acid-base reaction

(ii) Precipitation reaction

(iii) Complex formation reaction

(iv) Reaction with organic compounds

(v) Redox reaction

3. (a) Write the basic principles of Valence Bond Theory (VBT). How does this theory explain the formation of covalent bond in hydrogen molecule ? 20

(b) Give the electronic configuration of CO and HF molecules. Draw their energy level diagrams and predict whether the molecules are stable or not. 20

(c) Derive, by means of Born-Haber cycle, the expression for lattice energy (U_0) of an ionic oxide crystal such as MO, where M is a divalent metal. 20

4. (a) Describe how the crystal structure of NaCl is established. 20

(b) What are the different kinds of defects that occur in crystals and how they can be controlled ? Can the level of defects be predicted based on thermodynamic principles ? Is it of any advantage to have crystals with defects ? 20

(c) Discuss the mechanism of intake of oxygen by myoglobin and hemoglobin. How would you account for the diamagnetic character of oxygenated myoglobin and oxygenated hemoglobin ? 10

SECTION – B

5. Answer any **three** questions of the following : 20×3 = 60

(a) Using the Maxwell's velocity distribution law, find V_x for which the probability falls to 1/e times its maximum value. Also, deduce expressions for $\bar{V}_x$ and $\bar{V}_x^2$.

(b) Define the term 'partition function' and discuss its physical significance. Establish the relationship between partition function and (i) enerygy and (ii) C_v.

(c) Establish the relationship between equilibrium constant of a gaseous (ideal) chemical reaction and partition functions of the species involved in the reaction.

(d) What is meant by degeneracy of an energy level ? Determine the degree of degeneracy of the evergy level $17h^2 / 8ma^2$ of a particle in a cubical box.

6. (a) How the concept of Entropy was evolved ? Provide the mathematical definition of entropy and discuss its physical significance. Deduce the condition of irreversibility of a process in terms of entropy change. 20

(b) Calculate the entropy change (ΔS) in the following process ;

Benzene (l) $\longrightarrow$ Benzene (g)

(1 mole, 80.2°C, 1 atm) (1 mole, 80.2°C, 0.1 atm)

Given : Enthalpy of vapourization ΔH_v = 7.364k cal mol^{-1}, gas constant R = 1.987 cal K^{-1} mol^{-1}, assume benzene vapour to behave ideally. 20

(c) State and explain Nernst Heat Theorem and mention its limitations. 20

7. (a) Draw and discuss the phase diagram of partially miscible liquids penol-water system. Label the CST on this diagram and mention the corresponding degree of freedom. Illustrate the significance of CST and its utility. How can you determine from the phase diagram the compositions of the conjugate solutions (of phenol in water and water in phenol) coexisting in equilibrium at a given temperature if the starting composition of phenol-water mixture is known ? 20

(b) Explain, with suitable example, the difference between concentration cell with and without

transference. Deduce the expression of the liquid junction potential ($E_{l.j.}$) of the following cell :

$Pt \mid H_2$ (g, 1 atm) | HCl (aq.) ($a \pm (HCl) = a_1$)

| |

| | HCl (aq.) ($a \pm (HCl) = a_2$) | H_2 (g, 1 atm) |

Pt and discuss the inference. 20

(c) What is the basic equation that relates the current density observable at an electrode as a function of over-potential applied at the electrode ? Define the terms involved in this equation. What inferences can be drawn from the limiting forms of this equation under low and high over-potentials ? 20

8. (a) For a consecutive reaction of first order $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, the rate constant $k_2 >> k_1$. Show that $[C] = [A](1 - e^{-k_1 t})$ and justify the statement "the reaction with slower rate is rate determining step". 20

(b) Derive Langmuir's Adsorption Isotherm and discuss its applicability at : 20

(i) Low pressure

(ii) High pressure

(iii) Intermediate pressure

(c) Write BET equation for multi layer adsorption and explain the terms involved. How can this equation be used to determine the surface area of an adsorbent ? 20