CSM – 16/16

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) Verify the Heisenberg uncertainty principle for the ground state 1-D simple harmonic oscillator. State the difference between thermodynamic equilibrium and chemical equilibrium. Give appropriate examples.

Calculate the short and long wavelength limits of Lyman series in the spectrum of hydrogen atom ($R_H = 109.677\ cm^{-1}$).

(b) Explain orthogonal wave functions. Show that 1s and 2s wave function of hydrogen atom, given by $\psi_{1s} \equiv \psi_{1,0,0} = \frac{1}{\gamma\pi a_0^{\frac{3}{2}}} e^{-r/a_0}$;

$$\psi_{2s} \equiv \psi_{2,0,0} = \frac{1}{4\gamma\pi a_0^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0},$$

are orthogonal to each other.

(c) Give the structure, hybridization and magnetic moment of cis-platin. Write its action on cancer cells.

(d) What is Yttrium barium copper oxide YBCO ? Mention its use. Suggest why nitrogen is not a suitable atmosphere for the following reaction, $2LnF_3 + 3Ca \longrightarrow Ln + 3CaF_2$.

(e) Define the following terms in chromatographic techniques :

(i) Phase volume ratio (β)

(ii) Retardation factor (R_f)

(iii) Retention factor (k)

(iv) Plate number and Plate height

(f) $Ce^{3+}(4f^1)$ ion is colorless, whereas $Ti^{3+}(3d^1)$ solution is purple ..... State the fact behind such phenomenon. State the correct order of increasing basicity of La^{3+}, Ce^{3+}, Eu^{3+} and Lu^{3+}.

2. (a) Explain why nickel does not form inner orbital octahedral complexes. What are the limitations of VBT theory ? Explain the different magnetic behaviours of $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ using VBT and CFT. 20

(b) Define John-Teller effect with suitable example. Explain why the peak is not symmetrical in case of electronic spectra of $[Ti(H_2O)_6]^{3+}$ and $[Cu(H_2O)_6]^{2+}$ ions. 20

(c) State the effect of temperature on the susceptibility of ferromagnetic substances. Explain the spin-exchange interaction of MnO with the aim to describe its anti-ferromagnetic behaviours. 20

3. (a) Which among, $Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_2(CO)Cl$ will be more reactive towards oxidative addition of H_2? Define Wilkinson catalyst. Write down its structure and application. Ethylene cannot be hydrogenated catalytically using Wilkinson catalyst. Draw the structure of catalytic reaction intermediates and explain. Write down the mechanism of hydroformylation of propene catalyzed by $HRh(CO)(PPh_3)_2$. Mention the major product formed during the reaction. 20

(b) Among $Ti(C_2H_5)_4$, $Ti(CH_2Ph)_4$, $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$ which is unstable and why? Write down the structure of Zeise's salt and interpret its different metal to ligand bond. 20

(c) Arrange the values of CO stretching frequencies of $Ni(CO)_4$, $Ni(CO)_3(PMe_3)_3$, $Ni(CO)_2(PMe_3)_2$ in their increasing order. State and illustrate the quadruple bonding in Re_2Cl_8. 20

4. (a) Explain the role of "Mn" in the formation of Oxygen Evolving Complex (OEC) for photosynthetic process. What are ferritin, apo-ferritin and trans-ferritin ? Explain the role of "ferredoxins" and "rebredoxin" in biological processes with their structural arrangement. 20

(b) What are color centers ? How do they arise ? Derive an expression for the number of Schottky defects in a crystal. Define Meissner effect in superconductivity. 20

(c) Explain High Temperature Superconductivity (HTSC) with suitable example. Calculate the electronic contribution to the internal energy at 25°C in sodium metal, given that the Fermi energy of Na is 5.04×10^{-19} J. 20

SECTION – B

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

(a) Derive the expression of Maxwell distribution of molecular velocities in 3-dimension. State

the effect of temperature on this distribution. Calculate the fraction of oxygen molecules at 1 atm and 27°C; whose kinetic energy lies in the range of ($\varepsilon - 0.005\varepsilon$) and ($\varepsilon + 0.005\varepsilon$).

(b) Joule-Thomson effect is an isenthalpic process. Justify the statement. Derive the equation, $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$ for real gases. Define inversion temperature with suitable examples.

(c) Discuss the structure of electrified interfaces with reference to :

(i) The Helmholtz-Perrin model

(ii) The Guoy-Chapman model

(iii) Stern model

Calculate the ionic strength (1), mean activity coefficient ($\gamma\pm$) and activity ($a\pm$) at 298 K for 0.1 (M) $CuCl_2$ solution.

(d) The plot of compressibility factor (z) and pressure for 1 mole of NH_3, CH_4, He and H_2 gases are different. Explain the fact.

6. (a) Illustrate the mechanism of heterogeneous catalysis with suitable example. Define Mercus-Cross relation theory for the mechanism of outer sphere exchange reaction of :

$$[Fe\ (H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+} \longrightarrow [Fe\ (H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+}$$

Derive a relation between $t_{1/2}$ and temperature for nth order reaction (n > 2). 20

(b) Illustrate the effect of temperture on the partial miscibility of phenol-water and tri-ethyl amine-water system with their corresponding phase diagram. Explain the different factors that affect the solubility of gas in liquids. 20

(c) Derive van der Waal's gas equation from virial equation. Deduce the expression $G = N\mu = NKT \ln (\lambda^3 z)$ for grand canonical ensemble, where; G, N, μ, λ, z are assigned their usual meanings. 20

7. (a) What is amperommetry ? How one can estimate the equivalence point by amperommetric titration. Derive Ilkovic equation, $i_d = 708nCD^{1/2}m^{2/3}t^{1/6}$ for the measurement of diffusion current in polarography. 20

(b) What is Gibbs adsorption isotherm ? Explain the related factors. Define Stark-Einstein law of photochemical equivalence. A sample of gaseous HI was irradiated by light of wavelength 253.7 nm, when 307 J of energy was found to decompose 1.30×10^{-3} mol of HI. Calculate the quantum yield for the dissociation of HI. What is photosensitization and quenching ? Illustrate with suitable example. Derive "Stern-Volmer" equation and explain its importance in photochemistry. 20

(c) What do you mean by concentration cell with or without transference ? Write down the

mathematical expression for each. What is liquid junction potential ? How will you eliminate the junction potential ? Calculate the liquid junction potential for the given cell, Ag(s), AgCl(s), HCl(m_1 – 1.0,γ_1 – 0.809) || HCl (m_2 – 0.05,γ_2 – 0.830), AgCl, Ag(s) (Given t_{H+} = 0.83) 20

8. (a) What do you mean by fast reaction ? Give example. Define "relaxation" in fast reaction. How do you estimate the kinetic of a fast reaction by "Temperature Jump Method". The relaxation time for the fast reaction

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

is 10 μs and the equilibrium constant is 1.0×10^{-3}. Calculate the rate constant for forward and backward reaction. 20

(b) Define Kohlrausch's law for electrolytic solution. What is electrophoretic effect and exaplain the importance of Debye-Huckel-Onsager equation in accounting to the

magnitude of asymmetry and electrophoretic effects. At 25°C, the degree of dissociation (α) of pure water is 1.90×10^{-9}. Calculate the molar conductance (λ^{o}_{m}) and specific conductance (k) of water at this temperature. The value of λ^{o}_{H+} and $\lambda^{o}_{OH^-}$ are 349.83×10^{-4} and 198.50×10^{-4} respectively. 20

(c) (i) State the importance of excess thermodynamic function. Calculate the change in entropy accompanying the heating of 1 mol of He (g) (ideal) from temperature 298 K to a temperature of 1000 K at a constant pressure (Given $C_v = 3/2\ R$). 10

(ii) For the dissociation reaction,

$$N_2O_4(g) \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2NO_2(g)$$

the equilibrium constant K_P is 0.120 at a temperature of 298 K and a total pressure of 2 atm. Calculate the degree of dissociation of N_2O_4. 5

(iii) For the dissociation of water,

$$H_2O \underset{K_2}{\overset{K_1}{\rightleftharpoons}} H^+ + OH^-,$$

the relaxation time obtained by the temperature jump method is 40 μs, at 25°C; at which temperature, $K_w = [H^+][OH^+] = 1.0 \times 10^{-14} (mol.dm^{-3})^2$. Calculate the rate constant K_1 and K_2. 5