

CSM – 16/21
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 the following : 20×3 = 60
 - (a) What is trans effect ? How are three isomers of $[\text{PtBr}(\text{NH}_3)(\text{Cl})\text{py}]$ prepared from $[\text{PtCl}_4]^{2-}$? Discuss the different theories proposed for explaining the trans effect.
 - (b) Discuss in detail thermodynamic and kinetic stability of coordination compounds and

illustrate the determination of stability constant by spectrophotometric method for the formation of $[\text{Fe}(\text{NCS})]^{2+}$.

- (c) What are the postulates of CFT ? Describe the splitting of d-orbital in octahedral and tetrahedral complexes.

2. Answer the following : $20 \times 3 = 60$

- (a) Set up a Born Haber cycle for ionic bond formation. Discuss the application and drawbacks in the concept of Born-Haber cycle.

- (b) Construct MO energy level diagram for the formation of O_2 molecule. Use the diagram to explain the bond dissociation energies of O_2 (494 kJ/mol); O_2^+ (626 kJ/mol) and O_2^{2-} (138 kJ/mol).

- (c) Discuss the chemistry of liquid H_2SO_4 as solvent.

3. Answer the following : $20 \times 3 = 60$

- (a) Discuss briefly on Cytochrome P-450 and its application in body detoxification.

(b) What do you mean by eversion in the activity of $\text{Na}^+ - \text{K}^+$ pump ? Comment on the role of Mg^{2+} in the activity of $\text{Na}^+ - \text{K}^+$ pump. How does Vanadate interfere with the activity of $\text{Na}^+ - \text{K}^+$ pump ?

(c) Discuss consequences and causes of lanthanides contraction. How extraction of mixture of lanthanide salts from monazite sand done ?

4. Answer the following : $20 \times 3 = 60$

(a) Depict photochemical rate law and write the kinetics of photochemical reaction of Hydrogen-chlorine. Calculate the number of moles of $\text{HCl}(\text{g})$ produced by the absorption of one Joule of radiant energy of wave length 480 nm in the reaction. $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}(\text{g})$ if the quantum yield of the photochemical reaction is 1.0×10^6 .

(b) Discuss the mechanism and kinetics of enzyme catalyzed reactions. Calculate k_1/k_{-1} assuming that $k_2 \gg k_{-1}$ for an enzyme substrate system obeying the simple

Michaelis-Menten mechanism, the rate of product formation when the substrate concentration is very large, has the limiting value 0.02 mol dm^{-3} at a substrate concentration of 250 mg dm^{-3} , the rate is half this value.

- (c) Derive thermodynamically the Gibbs adsorption isotherm for the adsorption of a solute on the surface of a liquid.

SECTION – B

5. Answer the following : 20×3 = 60

- (a) Draw and discuss the cooling curves for a Two-component system in which the two components are not miscible in solid state and form a eutectic mixture.
- (b) Describe Lindemann theory and Hinshelwood theory of unimolecular gaseous reaction and mention their limitations.
- (c) Derive integration of rate expression for second order reaction.

6. Answer the following : 20×3 = 60

- (a) State and explain Kohlrausch's law. Illustrate how this law is used for calculating molar ionic conductance at infinite dilution for weak electrolytes and determining transport numbers.
- (b) Give an account of the Debye-Huckel theory of strong electrolytes. Explain clearly what is mean by the asymmetry effect and electrophoretic effect.
- (c) Derive an expression for vibrational partition function. For H_2 gas at 3000 K Calculate the characteristic vibrational temperature θ_{vib} and vibrational partition function q_{vib} given that fundamental vibrational frequency of H_2 molecule obtained from its Raman spectrum is 4405.3cm^{-1} .

7. Answer the following : 20×3 = 60

- (a) Derive an expression for the entropy change accompanying variation of

- (i) Temperature and volume
 - (ii) Temperature and pressure
- (b) Derive an expression for critical pressure, critical temperature of a van der Waals gas. At what pressure will ice-melt at -1.0°C assuming that ΔH_f is independent of pressure and is equal to $6.0095 \text{ kJmol}^{-1}$.

Given that the density of water is 0.9998 g cm^{-3} and that of ice is 0.917 g cm^{-3} .

- (c) Find the points of maximum probability density of the electron in the $2p_x$, $2p_y$ and $2p_z$ states of H atom and 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 $\frac{1}{2} + (-1)^k/n\pi$ if n is odd ($=2k+1$, where $k=0,1,2,\dots$).

8. Answer the following : $20 \times 3 = 60$

- (a) Explain the characteristics of Schottky defect and derive an expression for calculating the number of Schottky defect in a crystal.

- (b) Explain the Nernst heat theorem. How does it lead to the enunciation of the third law of thermodynamics.
- (c) Depict the ethylene-metal bonding and give the synthesis of metal-olefin complexes.

