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 [PtBr(NH_3)(Cl)py] prepared from $[PtCl_4]^{2-}$? 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 $[Fe(NCS)]^{2+}$.

(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 (494kJ/mol); O_2^+ (626kJ/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 Na^+-K^+ pump ? Comment on the role of Mg^{2+} in the activity of Na^+-K^+ pump. How does Vanadate interfere with the activity of Na^+-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 HCl(g) produced by the absorption of one Joule of radiant energy of wave length 480 nm in the reaction. $H_2 + Cl_2 \rightarrow 2HCl(g)$ 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 $k_2 >> k_{-1}$ for an enzyme substrate system obeying the simple

Michaels-Menten mechanism, the rate of product formation when the substrate concentration is very large, has the limiting value 0.02 md 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 : $20 \times 3 = 60$

(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 θviband vibrational partition function q_{vib} given that fundamental vibrational frequency of H_2 molecule obtained from its Raman spectrum is $4405.3 cm^{-1}$.

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 -1.0^0C assuming that ΔH_f is independent of pressure and is equal to 6.0095 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,.,........).

8. Answer the following : 20×3 = 60

(a) Explain the characteristics of Schotty defect and derive an expression for calculating the number of shorty 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.

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