

CSM – 16/20
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 **three** of the following : $20 \times 3 = 60$
- (a) What are atomic orbitals ? Write the shapes of s, p and d orbitals. The first, second and third shells in an atom contain, respectively, upto 2, 8 and 18 electrons. Discuss the distribution of electrons in terms of quantum numbers.

- (b) State third law of thermodynamics. How can it be verified experimentally ?
- (c) Write the postulates of Langmuir theory of adsorption. When a diatomic gas adsorbs as atoms on the surface of solids, derive the expression for Langmuir adsorption isotherm.
- (d) On the basis of molecular orbital theory explain why the bond order in O_2^{2-} is less than that in O_2^- .

2. Answer the following : 20×3 = 60

- (a) Derive the relation between Bragg angle and Miller indices for a tetragonal crystal system. KNO_3 crystalizes in orthorhombic system with the unit cell dimensions $a = 542$ pm, $b = 917$ pm and $c = 645$ pm. Calculate the diffraction angles for first order X-ray reflections from (100), (010) and (111) places using radiation of wave length 154.1 pm.
- (b) What is congruent melting point ? Write the phase rule and discuss its application for two

component system of solids forming compound with congruent melting point.

- (c) Using the Rice-Herzfeld mechanism for the reaction, $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ and employing steady state approximation for $[\text{H}]$ and $[\text{Br}]$, derive the rate law expression for the formation of HBr .

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

- (a) What is meant by excluded volume ? Show that the excluded volume, designated as b , is four times the actual volume of the gas molecule.
- (b) How relaxation and electrophoretic effects retard the free mobility of ions ? Explain.
- (c) Calculate the mean ionic activity coefficient of 0.002 M aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ complex at 25°C (Given $A = 0.51$).

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

- (a) Differentiate between electrode-concentration cells and electrolyte-

concentration cells. Give examples. Write the cell reactions and expression for electrode potential of hydrogen electrode concentration cell.

- (b) What is over voltage ? Discuss the theory of hydrogen over voltage by considering proton transfer as slow process.
- (c) At 378.3°C the half-life period for the first-order thermal decomposition of ethylene oxide is 363 min, and the energy of activation of the reaction is 52,000 cal/mol. From these data estimate the time required for ethylene oxide to be 75% decomposed at 450°C .

SECTION – B

5. Answer any three of the following : $20 \times 3 = 60$
- (a) What is the cause of Schottky defects ? Derive an expression for number of Schottky defects in a crystal.
 - (b) Outline the postulates of activated complex theory. Give the statistical formulation of activated complex theory of reaction rates.

- (c) What is coordination number ? Discuss the geometries adopted by $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{SbF}_5]^{2-}$ complexes.
- (d) Discuss entropy changes in reversible and irreversible processes. Comment on the statement "Entropy of the universe always increasing".

6. Answer the following : 20×3 = 60

- (a) Explain "Half-wave potential" and its application in qualitative and qualitative analysis.
- (b) Write the Jablonsky diagram and explain the following physicochemical processes :
- (i) Intersystem crossing
 - (ii) Internal conversion
 - (iii) Fluorescence
 - (iv) Phosphoresce
- (c) What are polar and non-polar covalent bonds ? Explain the structures of BH_3 and NH_3 based on their dipole moments.

7. Answer the following : 20×3 = 60

- (a) At 0°C and 1 atm. pressure, the volume of N_2 gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be $130 \text{ cm}^3 \text{ g}^{-1}$ of the gel. Calculate the surface area per gram of silica gel (Given that the area occupied by a N_2 molecule is 0.162 nm^2).
- (b) Which of following is the most stable complex and why ? $[Ag(NH_3)_2]^+$ and $[Cd(NH_3)_4]^{2+}$. Discuss the factors affecting the stability of complexes.
- (c) Why separation of lanthanides so difficult ? Discuss the following methods of their separation in pure form :
- (i) Solvent extraction
 - (ii) By precipitation

8. Answer the following : 20×3 = 60

- (a) Discuss the chemistry of liquid ammonia as a solvent. What are the advantages and disadvantages of liquid ammonia as solvent ?

(b) Describe the bonding in $[\text{Fe}(\text{CH})_6]^{3-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ from VBT.

(c) The rotational constants for H_2O molecules are $A = 27.878 \text{ cm}^{-1}$, $B = 14.509 \text{ cm}^{-1}$ and $C = 9.287 \text{ cm}^{-1}$. Calculate the rotational partition function at 298 K.

