

CHEMISTRY

(Paper I)

Time Allowed : Three Hours
Maximum Marks : 300

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.

Candidate has to attempt FIVE questions in all.

Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.

The number of marks carried by a question/part is indicated against it.

Wherever any assumptions are made for answering a question, they must be clearly indicated.

Word limit in questions, wherever specified, should be adhered to.

SECTION 'A'

1. Answer any three of the following:
 - (a)(i) State and explain Heisenberg's uncertainty principle. Why is it not applicable to large particles. 10
 - (a)(ii) When an electron was accelerated through a potential difference of 1.00 ± 0.01 kilovolt, what is the uncertainty of position of the electron along its line of projection? 10
 - (b) How does the principle of 'maximum overlap' explain the stability of a chemical bond? Enumerate the essential condition. 20
 - (c) What is atomic radius of a cubic lattice? Find the atomic packing factor in simple cubic system, body- centered cubic system and face-centered cubic system. 20
 - (d) A perfect monatomic gas is expanded reversibly and adiabatically at 300 K from a pressure of 10^6 Pa to 10 Pa. What is the final temperature? How much work can be done? 20
2. (a) What is meant by electron probability function? Draw the radial distribution curves for 1s, 2s, 2p, 3s, 3p and 3d electrons, and explain radial nodes, radius of maximum probability and penetrating power of electrons. 20
 - (b)(i) What is the essential difference between ionic bond and covalent bond? Explain why water molecule is non-linear while methane molecule is tetrahedral. 10
 - (b)(ii) What is lattice energy? Describe how lattice energy of an ionic solid is evaluated by Born Haber cycle. 10
 - (c) State and explain Maxwells law of distribution of velocities of molecules of a gas at a definite temperature. What is meant by most probable velocity? 20
3. (a) What are semiconductors? Explain n - type and p-type semiconductors. Discuss the effect of temperature on semiconductors. 20
 - (b)(i) Derive the Kelvin equation for the vapour pressure of droplets and bubbles. 10
 - (b)(ii) What are nucleation centres? Indicate their importance. 10
 - (c) Explain the criteria of equilibrium and spontaneity in terms of U, S, A and G. 20
4. (a)(i) "The third law of thermodynamics states an impossibility." Justify this statement. 10
 - (a)(ii) Explain why the molar entropy of ice crystals approaches $3.35 \text{ J K}^{-1}\text{mol}^{-1}$ [?], as the temperature approaches zero kelvin. 10

- (b) Define chemical potential. Explain its significance. Deduce equations for the variation of chemical potential with temperature and pressure. **20**
- (c)(i) What is the maximum number of phases that can be in equilibrium at constant pressure and temperature in two- and three- component systems? **10**
- (c)(ii) For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $K_p = 1.64 \times 10^{-4}$ at 670 K. Calculate ΔG . **10**

SECTION 'B'

5. Answer any three of the following:
- (a) Define activity, activity coefficient and mean activity coefficient of ions in solution. Derive and use the Debye-Huckel limiting law for mean activity coefficient, and indicate how it can be extended to more concentrated solution. **20**
- (b) Derive an equation to relate temperature on rate of reaction and calculate the energy of activation. **20**
- (c)(i) "Tetrahedral complexes of 3d transition metals are always of high spin." Justify the statement. **10**
- (c)(ii) Calculate the crystal field stabilisation energy and spin-only magnetic moment of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$. **10**
- (d)(i) "Actinides are more prone to complex formation than lanthanides." Justify the statement. **10**
- (d)(ii) Explain why zirconium and hafnium occur together in nature. **10**
6. (a) What is first-order reaction? Deduce an equation for first-order reaction and show that its half-life period is independent of the initial concentration of the reactant. **20**
- (b) With neat diagram, describe – (i) lead acid battery with discharge and charging reactions; (ii) H_2 - O_2 fuel cell with anodic and cathodic reactions. **20**
- (c) State and explain the law of photochemical equivalence. How are the discrepancies of this law explained? **20**
7. (a) What are heterogeneous catalysts? Discuss the characteristics and mechanism of reaction on heterogeneous catalysts. **20**
- (b)(i) Identify one significant role in biological processes for each of the following elements: Fe, Mg, K, Zn, I **10**
- (b)(ii) How is iron stored and transported in mammals? What is the oxidation state of iron for storage and transfer? **10**
- (c)(i) "The complex $[\text{NiCl}_4]^{2-}$ is paramagnetic whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic." Justify the observations. **10**
- (c)(ii) Explain the origin of pale pink colour of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. **10**
8. (a)(i) Explain the possible isomerism in the following complexes: $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ **10**
- (a)(ii) "The trans-effect series has proved very useful in rationalising known synthetic procedures and in devising new ones." Justify the statement with suitable examples. **10**
- (b) Explain with the aid of suitable diagrams how CO forms sigma and pi bonds in $[\text{Ni}(\text{CO})_4]$. Apply EAN rule to $[\text{Ni}(\text{CO})_4]$. **20**
- (c) Explain the structure and bonding in (i) iodine pentafluoride and (ii) polythiazyl. **20**