

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:

20 × 3 = 60

- (a) Set up and solve the Schrodinger equation for particle in one-dimensional box.
- (b) Briefly discuss M.O. theory. Explain the formation of H₂ molecule on the basis of this theory.
- (c) Write the electronic configuration of NO molecule. (i) What is its bond-order? (ii) How many unpaired electrons are present? (iii) What will be the bond-order of NO⁺ [?]? (iv) Will the bond-length be shorter or longer than NO⁺?
- (d) What are liquid-crystals? Mention their characteristics. Which substances generally behave as liquid-crystals?

2. (a) (i) Explain Frenkel and Schottky defects in a crystal, with a suitable example (ii) What do the indices of a set of planes passing through the lattice stand for? Draw the sets of planes, viz. 100 and 110, passing through the lattice points of the crystal. **20**

(b) Derive the Van der Waals equation of state for real gases. What are the units of Van der Waals constants? **20**

(c) Define the terms critical temperature, critical pressure and critical volume. How are these constants determined experimentally? **20**

3. (a) The enthalpy of neutralization of NH₄OH and HCl is -51.46 kJ/mole. Calculate the enthalpy of ionisation of NH₄OH. Assume that the enthalpy of neutralization of a strong acid with a strong base is -55.9 kJ/mole. **20**

(b) Discuss the entropy change in reversible and irreversible processes. Comment on the statement: Entropy of the universe is always increasing. **20**

(c) Explain Nernst heat-theorem. How does it lead to the enunciation of the Third Law of Thermodynamics? How can the latter be verified experimentally? **20**

4. (a) The vapour pressure of ice ⇌ water system at 0.0075 °C [?] is 4.58 mm [?] and at 0° C is 759.8 mm of Hg. Calculate the molar heat of fusion of ice. Given that the specific volumes of ice and water at 0° C are 1.0907 cc [?] and 1.0001 cc [?] respectively. Density of Hg at 0°C = 13.6 g per cc [?]. **20**

(b) Explain the terms: upper consolute temperature and lower consolute temperature, conjugate solution and tie-line as applied to the solubility of partially miscible liquids. **20**

(c) Give an account of Debye-Huckel theory of strong electrolytes. Discuss its significance. **20**

English version compiled from published transcriptions and cross-checked across sources; not a facsimile of the official UPSC question paper.

SECTION 'B'

5. Answer any three of the following:

20 × 3 = 60

- (a) Considering the following electrochemical cell: $\text{Fe}, \text{Fe}^{+2} (0.1 \text{ M}) \parallel \text{Cd}^{+2} (0.01 \text{ M}), \text{Cd}$, (i) write the cell reaction, (ii) calculate the EMF of the cell, (iii) determine the direction of the spontaneous reaction and (iv) calculate the equilibrium constant of the reaction.
- (b) Derive the rate equations for the consecutive reaction and parallel reaction.
- (c) Derive the kinetics of the photochemical reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$
- (d) Derive expression for the BET adsorption isotherm. What is the application of this equation?
6. (a) Explain the theories of heterogeneous catalysis. **20**
- (b) Discuss the stability of cyclopentadienyl complexes. Give suitable examples containing carbonyl and nitrosyl ligands. **20**
- (c) The activation energy of a reaction in the absence and in the presence of catalyst are 75.24 kJ/mole and 50.14 kJ/mole respectively. How many times will the rate of the reaction grow in the presence of the catalyst if the reaction proceeds at 25° C? **20**
7. (a) Discuss the chemistry of photosynthetic process in green plants. **20**
- (b) What are actinides? Explain the oxidation state and complex forming tendency of actinides. **20**
- (c) What are the main features of valence-bond theory? Point out its shortcomings. **20**
8. (a) What is meant by stability of a complex ion? On what factors does the stability of a complex ion depend? Explain with suitable examples. **20**
- (b) Discuss any four types of chemical reactions that take place in liquid-ammonia. **20**
- (c) Explain the structures of $\text{Cr}(\text{CO})_6$, $\text{Fe}_2(\text{CO})_9$, $\text{Re}_2(\text{CO})_{10}$ and $\text{Fe}_3(\text{CO})_{12}$. Show that the metal atoms in these carbonyls obey inert gas rule. **20**