

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:

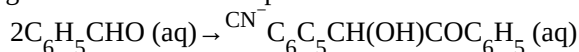
20×3=60

- (a) What do you understand by orthogonal wave function? Normalise the wave function, $\psi_n(x) = A \sin n\pi x/a$ for a particle in a one-dimensional box of size 'a'.
- (b) Explain why CO₂ has a linear structure whereas SO₂ is a bent molecule.
- (c) Mention the temperature and pressure at which water has a triple point where it can exist as solid ice, liquid and vapour. Apply phase rule to this triple point.
- (d) Half life of a first order may be determined from its rate constant. If rate constant of a first order reaction is $4.5 \times 10^{-5} \text{ min}^{-1}$ then calculate its half life.

2. (a) Explain following: (i) Ion selective electrodes (ii) Quantum yield (iii) Nernst heat theorem (iv) Fuel cells (v) Langmuir isotherm

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(b) Benzaldehyde undergoes transformation in presence of CN⁻ as:



where following kinetic data were obtained:

$\text{C}_6\text{H}_5\text{CHO (aq)}$ initial concn. (mol dm ⁻³)	CN^- (aq) initial concn. (mol dm ⁻³)	Initial reaction rate (mol dm ⁻³ s ⁻¹)
0.50	0.50	1.00×10^{-4}
1.00	0.50	4.01×10^{-4}
1.00	1.00	7.96×10^{-4}

Calculate overall order of reaction and its rate constant.

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(c) Prove that entropy is a state function.

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3. (a) Justify that s-orbitals are non-directional whereas p- and d-orbitals have directional character. Derive wave functions of sp³ hybridized orbitals.

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(b) What are seven crystal systems and 14 Bravais lattices? Discuss the structures of CsCl and ZnS.

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(c) What are the factors that decide the percent ionic character in polar compounds?

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4. (a) Explain crystal fields stabilization energy (CFSE). What are the various factors which affect its magnitude? Calculate CFSE and magnetic moments (μ_{eff}) in cases of FeCl₃·6H₂O and K₄Fe(CN)₆.

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(b) Derive Clausius-Clapeyron equation for the variation of vapour pressure with temperature. Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C

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assuming their densities to be 2.25 and 3.51 g cm^{-3} and $\Delta G = 2900 \text{ J mol}^{-1}$.

- (c) Explain the role of metal ions in biological systems and their role in ion transport across the cell membrane. 10

SECTION 'B'

5. Answer any three of the following:

20×3=60

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|--------|--|----|
| (a) | Define Frenkel and Schottky defects in a crystal with a suitable example for each. | |
| (b) | Explain the intense blue colour of aqueous permanganate solution. What happens to it when the solution is left in sunlight for a day? | |
| (c) | Heme acts as carrier of O_2 in the system whereas toxic effects of CO can be explained by replacement reaction. Explain. | |
| (d) | Draw the nature of a typical polarogram and explain diffusion current, limiting current and residual current. Show that $E_{1/2}$ is independent of concentration. | |
| 6. (a) | Name all the lanthanides and show how its common oxidation state is +3 though some of these exhibit other oxidation states as well. Explain why ionic radii decreases from La^{3+} to Lu^{3+} even though atomic number increases by 14. | 30 |
| (b) | Explain the nature of metal-carbonyl bond in carbonyls. Draw the structures of $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, $\text{Mn}_2(\text{CO})_{10}$ and $\text{Ni}(\text{CO})_4$. In what respects terminal CO group is different than bridging CO in such complexes? | 20 |
| (c) | Discuss the role of photosynthesis in ferredoxin molecule and describe its structural features. | 10 |
| 7. (a) | What are metallocenes and their characteristic structural features? Discuss the structure of ferrocene with MO diagram. | 20 |
| (b) | Explain 'trans effect' and discuss its theories. Describe substitution in square planar complexes with suitable examples. | 20 |
| (c) | Describe the construction and functioning of lithium batteries and its advantages over conventional batteries. | 20 |
| 8. (a) | Define molecular partition function and explain its importance. Show that heat capacity of an ideal gas is $3/2R$. | 20 |
| (b) | Derive an expression for the entropy of mixing of two ideal gases at the same temperature and pressure. | 20 |
| (c) | Explain homogenous and heterogeneous catalysis with a suitable example for each. Derive and expression for the rate of a surface catalyzed reaction. | 20 |