

FS – 9 / 15-16

Chemistry

Paper – I

Time : 3 hours

Full Marks : 200

The figures in the right-hand margin indicate marks.

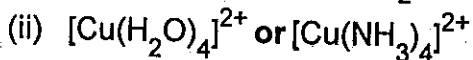
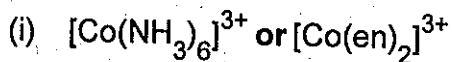
*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and any **three** of the remaining questions, selecting at least **one** from each Section.*

SECTION – A

1. Answer any **five** of the following : $8 \times 5 = 40$
- (a) Arrange the octahedral complexes $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{CrF}_6]^{3-}$ in increasing order of their crystal field splitting and give the supporting argument for the same.
- (b) How many geometrical isomers could $[\text{Rh}(\text{py})\text{Cl}_3]$ have ? (py is an abbreviation for the ligand pyridine).

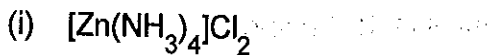
- (c) Explain why the square planar complexes are seldom optically active.
- (d) The formula $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{Cl}$ could represent a carbonate or a chloride. Write the two possible structures and name them.
- (e) State "Pauli's Exclusion Principle" and explain its usefulness in calculating the maximum number of electrons in each principal level.
- (f) Discuss the mechanism of oxygen transport by haemoglobin in human body.
2. (a) Describe the various factors, which apparently affect the stability of a complex ion. Which complex ion in each of the following pairs should exhibit greater stability?

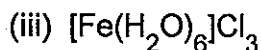
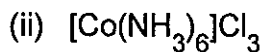
14



- (b) Draw orbital diagram to show hybridization in the following complexes for central metal ion:

14





- (c) Explain the colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ with the help of crystal field theory. 12

3. (a) Discuss the limitations of valence bond theory. In what way crystal field theory is superior to valence bond theory? 14

- (b) What is Lanthanide Contraction? What are its important consequences? 14

- (c) What are the problems in the separation of lanthanides from one another? Discuss the ion exchange method for the separation of lanthanides. 12

4. Answer any **two** of the following : $20 \times 2 = 40$

- (a) Discuss the kinetics of substitution reactions in square planar complexes.

- (b) What is a Fluxional Molecule? Discuss the structure of one such molecule.

- (c) Explain the following giving reasons :
- (i) Solutions of alkali metals in liquid ammonia are coloured.
 - (ii) The structure of ferredoxins.

SECTION – B

5. Answer any **two** of the following : $20 \times 2 = 40$

- (a) What is the 'First Law of Thermodynamics' ? Write down the mathematical form of this law and explain the terms involved. How can this relation be justified ?
- (b) What are the questions regarding the processes which cannot be answered by the 'First Law of Thermodynamics' ? Illustrate how the 'Second Law of Thermodynamics' provides the answers to these questions.
- (c) Write down the Maxwell's equation for the distribution of speed of gaseous molecules and based on this equation show the effect of temperature change on the distribution of speed. What are the important applications of the knowledge of such distribution ?

6. (a) What is meant by 'macro' and 'micro' states ?

Defining the partition function, derive the equation in terms of partition function for the equilibrium constant of a reaction involving ideal gases. 14

(b) Depict a suitable 'concentration cell with transference', which can be used to determine the transport numbers of H^+ and Cl^- ion in aqueous HCl solution. Write down the equation for the **emf** of this cell and illustrate its application for the determination of the desired transport numbers. 13

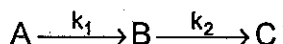
(c) What are the Fuel Cells ? Name the various types of fuel cells and give a schematic diagram of the most advanced H_2-O_2 fuel cell labelling all its components. Illustrate the method of calculating the efficiency of

this cell. What are the advantages of using such fuel cells for obtaining electricity? 13

7. (a) Draw the phase diagram of Sulphur and discuss its salient aspects in the light of Gibbs Phase rule. Can all the possible phases of sulphur co-exist in equilibrium?

20

- (b) Derive the rate expressions for a consecutive reaction (involving first order reactions):



Illustrate the methods to determine k_1 and k_2 . How can it be confirmed that the reaction is a 'consecutive' one and not a 'parallel' one (giving B and C from A sidewise)? 20

8. (a) What is LCAO-MO approach? How is this approach used to determine the energy of H_2^+ molecular ion? Comment on the electron probability density between the nuclei. 20

(b) The total wave function of a molecule is written as $\psi = \psi_{\text{cov.}} + \lambda\psi_{\text{ionic}}$. What is the significance of λ in it? Calculate the fraction of ionic wave function in HBr molecule if the ionic character is 11%. 12

(c) What kind of orbitals are the following? 8

(i) $\psi = \frac{1}{\sqrt{2}}(\psi_{2s} + \psi_{2px})$

(ii) $\psi = \frac{1}{\sqrt{2}}(\psi_{2s} - \psi_{2px})$



