SECTION—B

5. Answer any *three* of the following : 20×3=60

(a) Set up molecular orbital diagram for nitric oxide molecule and comment on bond order and magnetic property of it.

(b) Describe the structure of ferredoxin and discuss its role in biological system.

(c) Show that if two pure liquids are mixed together in any proportion to give an ideal solution there is no change of volume and enthalpy.

(d) What do you mean by metallocenes? Write the method of preparation of metallocenes. Mention four important properties of it.

6. *(a)* What do you mean by crystal-field splitting and crystal-field stabilisation energy? Discuss the structure of $[Co(NH_3)_6]^{3+}$ and $[Cu(NH_3)_4]^{2+}$ ions on the basis of crystal-field theory. 20

(b) *(i)* Discuss the limitations of valence-bond theory. 10

(ii) Explain on the basis of crystal-field theory that $[Ni(CN)_6]^{2-}$ is diamagnetic but $[NiCl_4]^{2-}$ is paramagnetic. 10

(c) What do you mean by nitrogen fixation? Discuss the role of nitrogenase reductase in biological nitrogen fixation. 20

7. *(a)* Explain the separation of lanthanide elements by change in oxidation state method with examples. Write the consequences of lanthanide contraction. 20

(b) Draw the structure of all the possible isomers of the following : 20

$$[Cr(NH_3)_2(H_2O)_2Br_2]^+, \quad [Cr(en)_2Cl_2]Cl$$

(c) What do you mean by metal carbonyl? Write with examples three methods of preparation of metal carbonyls. Explain with diagrams the structures of $Fe_3(CO)_{12}$ and $Os_2(CO)_9$. 20

8. *(a)* Define quantum yield of a photochemical reaction. Explain why photosynthesis of HCl has very high quantum yield while that of photosynthesis of HBr is very low. What happens to the quantum yield of photosynthesis of HCl if the vessel contains small traces of oxygen? Explain with reasons. 20

(b) *(i)* Explain the different types of ensembles used in statistical mechanics and give the schematic representations of these. 10

(ii) Define partition function. Why is it so called? Obtain the expression for electronic and vibrational partition function. 10

(c) *(i)* Derive an expression for entropy change when n_1 mole of an ideal gas 1 are mixed with n_2 moles of an ideal gas 2. 10

(ii) What do you mean by the EMF of a cell? How can it be measured experimentally? 10

* * *

20

CHEMISTRY

PAPER—I

Time Allowed : Three hours | *Maximum Marks* : 300

The figures in the margin indicate full marks for the questions

Candidates should answer Question Nos. **1** and **5** which are compulsory and other **three** of the remaining questions, selecting at least **one** from each Section

Assume suitable data if considered necessary and indicate the same clearly

SECTION—A

1. Answer any *three* of the following : 20×3=60

(a) Write the Schrödinger equation for a particle of mass m confined to move in an one-dimensional box of length a having infinitely high walls and solve it to obtain the energy of the particle.

(b) Derive the relationship between the relaxation time τ and the rate constants k_1 and k_2 for the fast reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C$$

(c) Using Maxwell's distribution of molecular speed, calculate the average speed, most probable speed and the root-mean-square speed at temperature T.

(d) Deduce Bragg's law of X-ray diffraction.

2. *(a)* Explain the following : 30

(i) Lattice energy

(ii) Langmuir isotherm

(iii) Fuel cells

(iv) Critical solution temperature

(v) Canonical ensemble

(b) Discuss the collision theory of bimolecular gaseous reaction to calculate the rate constant of the reaction. Find the expression for the Arrhenius pre-exponential factor. 10

(c) At a certain temperature, ethyl acetate on saponification gave the following results :

t (min)	:	0	5	25	55	120	∞
ml. of 0·1 N acetic acid used to titrate 10 ml of unreacted alkali	:	16	10·2	4·3	2·3	1·1	0

Show that it is a second-order reaction. How much fraction of the ester will be decomposed in 40 minutes? 20

3. (a) Discuss the reactions in liquid NH_3. 20

(b) Compare valence-bond theory with those of molecular-orbital theory. 20

(c) What do you mean by liquid crystals? State the different classifications of it. Describe the characteristic of one of them. 20

4. (a) Discuss the processes by which a photoactivated molecule return to the ground state by dissipating energy. 20

(b) Explain the Debye-Hückel theory of strong electrolytes. State the Debye-Hückel law and discuss its validity. 20

(c) (i) Deduce the relation

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)}$$

where q is the heat exchanged reversibly per mole of the substance during the phase transformation at temperature T. V_A and V_B are the molar volumes of the pure substance in the phases A and B respectively. dP and dT has the usual meaning. 10

(ii) Calculate the value of dT/dP for the water = ice at 0 °C. ΔH_f for water is 6007·8 J mol^{-1} (1 J = 9·87 × 10^{-3} dm^3 atm); molar volume of water = 18 cm^3 and of ice is 19·63 cm^3. 10