

(p) Define the ensemble averaging and give its postulate.

8

(q) Calculate the translational P.F. of the H_2 molecule confined to a 1000 cm^3 vessel at room temp. ($T = 25^\circ\text{C}$).

4

(r) For a homonuclear diatomic and symmetrical linear polyatomic molecules derive rotational partition function.

$$Z_r = \frac{T}{\sigma \theta_r}$$

Where θ_r = Characteristic rotation temperature,
 σ = Symmetry number.

4

M.Sc. (Part-I) Semester-II (CBCS Scheme) Examination
CHEMISTRY
(Physical Chemistry)-II
Paper-VII

Time : Three Hours]

[Maximum Marks : 80

N.B. :- (1) **ALL** questions are compulsory and carry equal marks.

(2) Use of log table and calculator is permitted.

1. (a) Discuss the kinetics of branched chain reactions. Explain the terms first explosion limit and second explosion limit. 6
- (b) What are oscillating reactions ? Explain in detail w.r. to Belousov-Zhabotinsky reaction. 6
- (c) Describe the stopped flow method for studying kinetics of fast reactions. 4

OR

- (p) Explain the kinetics and mechanism of thermal reaction between H_2 and Br_2 . 8
- (q) Discuss the flash photolysis technique for the study of fast reactions. 4
- (r) Discuss the relaxation methods for study of kinetics of fast reactions. 4

2. (a) Apply LCAO-MO method to H_2 molecule and obtain expressions for bonding and antibonding energy levels. 8
- (b) Construct Sp^2 hybrid orbitals by combining one 2S and two 2p atomic orbitals and establish the value of angle between the hybrid orbitals so obtained. 4
- (c) Apply Hückel Molecular Orbital (HMO) theory to ethylene molecule and find out HMO energies. 4

OR

- (p) Explain the criteria for forming M.O. and A.O. 8
- (q) Discuss bond order and change density calculation with suitable example. 4
- (r) By applying H. M. O. theory to cyclo-butadiene system, derive an expression for delocalization energy. 4
3. (a) Discuss mechanism of polymerization. 8
- (b) Explain light scattering method to determine molar mass of a polymer. 4
- (c) Define number average and mass average molecular mass of polymer. When M_n and M_w are equal. 4

OR

(p) Write notes on :

(i) Electrophoresis

(ii) Polymer liquid crystals. 8

- (q) A protein sample consists of an equimolar mixture of ribonuclease ($M = 13.7 \text{ kg mol}^{-1}$) hemoglobin ($M = 15.5 \text{ kg mol}^{-1}$). Calculate number average and mass average molecular mass of sample. 4
- (r) Explain the stability of biological polymers. 4
4. (a) Discuss Debye-Hückel-Onsager treatment and its extension. 6
- (b) Give advantages and applications of voltametry. 4
- (c) What are different methods used for monitoring and prevention of corrosion ? 6

OR

- (p) Describe various theories of ion-solvent interactions. 6
- (q) Give applications of Butler-Volmer equation. 5
- (r) What is corrosion ? Explain different types of corrosion. 5
5. (a) Compare Microcanonical, Canonical and Grand Canonical ensemble based on their thermodynamic environment. 6
- (b) Derive expression for translational partition function for a lightest molecule H_2 at room temperature. 6
- (c) Calculate the value of molecular rotational partition function for $N_{2(g)}$ at 298 K. The moment of inertia is $1.407 \times 10^{-46} \text{ kg m}^2$ and the symmetry number is 2 for N_2 (g). Given $K = 1.381 \times 10^{-23} \text{ JK}^{-1}$
 $h = 6.626 \times 10^{-34} \text{ JS}$. 4

OR