



Roll No. : -

Post Graduate Teaching Department of Chemistry

(An Autonomous Department)

Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur

End Semester Examination Winter-2021

M.Sc. (Chemistry)- Physical Chemistry (1T3)

Semester – I

Course Name: M.Sc. Chemistry (Physical Chemistry) (1T3)

Time: - 3 Hours

Maximum Marks: 60

Instructions: -

- 1) Solve either 'EITHER' part or 'OR' part.
- 2) Draw neat well labelled diagram wherever necessary.
- 3) All questions from Q. 1 to Q. 5 are compulsory.

Q. 1 a) Give the Kelvin-Planck and Clausius Statements of the second law of Thermodynamics and derive their equivalence with the Carathéodory's Principle. 6M

b) What is integrating factor? Prove that $1/T$ is an integrating factor for $dq = \frac{3}{2}nR dT + \frac{nRT}{V} dV$ for ideal gas. 6M

OR

c) If $U=f(T, V)$ and dU is an exact differential then using the combined statement of the first and second law show that: 6M

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

d) State Nernst Heat Theorem. How entropy of a substance can be determined experimentally from a series of thermal measurements. Give its graphical interpretation. 6M

Q. 2 a) Discuss the variation of Gibbs free energy (G) and entropy (S) with temperature graphically and explain the first order and second order transitions. 6M

b) Derive Gibbs-Duhem-Mergules Equation. 6M

OR

c) State the degree of freedom in the light of the phase rule in each of the following systems. Justify your answer. 6M

- i. An azeotrope in a binary system.
- ii. A pure substance at its critical point.
- iii. A eutectic mixture in a binary system.

d) Define partial molar quantities and explain the concept of chemical potential as partial molar free energy. 6M

Q. 3 a) What is surface excess concentration? Derive the expression for surface excess concentration using Gibbs adsorption isotherm. 6M

b) What is surface catalysis? Taking the example of unimolecular surface reaction $A + S \xrightleftharpoons[k_{-1}]{k_1} AS \xrightarrow{k_2} \text{Product}$, 6M

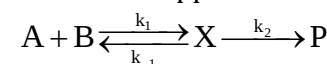
discuss the evaluation of reaction rate under different conditions.

OR

c) Write short notes on: 1. Surface films; 2. Catalytic activity at the surfaces 6M

d) What is Physisorption? Discuss the various characteristics of Physisorption including energy profile diagram. 6M

Q. 4 a) 4. (E) What is Bodeinstein steady state approximation? Discuss its application in consecutive reactions of the type 6M



b) Discuss the Lindeman-Hinshelwood mechanism for unimolecular reactions. 6M

OR

c) Based on kinetic theory of collisions derive the expression for the rate constant in terms of collision frequency. 6M

d) Derive an expression based on transition state theory for the rate constant of a bimolecular reaction. 6M

Q. 5 a) Derive any two Maxwell's relations. 3M

b) Discuss the Sulphur system with well labelled phase diagram. 3M

c) Discuss the variation of Surface tension, Osmotic Pressure, Molar conductivity and turbidity with the concentration of a surfactant in a solution using a graphical representation. 3M

d) The rate constant for a reaction at 30 °C is exactly twice the value at 20 °C. Calculate the activation energy. 3M