



RAN-1803080201030001

M.Sc. (Sem. - I) Examination November - 2025

Chemistry Paper - III (Physical Chemistry)

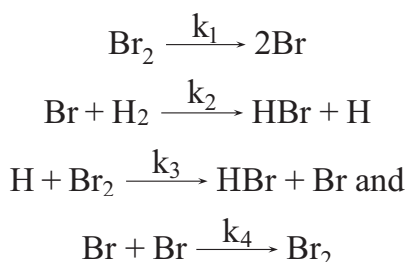
Time: 3 Hours]

[Total Marks: 70

સૂચના : / Instructions (1) ઉપરોક્ત દર્શાવેલ વિગતો ઉત્તરવહી પર અવશ્ય લખવી. Fill up strictly the above details on your answer book (2) All questions are compulsory (3) Figures to the right indicate full marks of the questions.	Seat No.: <table border="1" style="width: 100%;"> <tr> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> </tr> </table> Student's Signature						

Q. 1 Answers any three of the following. 18

- (a) Let us assume that thermal gas phase reaction between H_2 and Br_2 has the following four step mechanism.



Derive the rate expression for the rate of formation of HBr, applying the steady state principle to reactive intermediate.

- (b) Explain primary and secondary salt effect for influence of ionic strength.
 (c) Discuss kinetics and mechanism of thermal decomposition of acetaldehyde.
 (d) For the consecutive first order reaction:



Determine the concentration of A, B & C at $t = 50$ second with $k_1 = 0.02\text{sec}^{-1}$ and $k_2 = 0.16\text{sec}^{-1}$. The initial concentration is 0.5 mol.lit^{-1} .

Q. 2 Answers any three of the following. 18

- (a) Define partial molar enthalpies, partial molar free energies and partial molar volume. Describe a method to determine the partial molar volume.
 (b) What is the limitation of thermodynamics? State all the laws of thermodynamics.
 (c) Derive the equation for excess functions for non ideal solutions.
 (d) The variation of the density of aqueous salt solutions with the molarity (c) at 30°C is given by,

$$\rho = 0.9971 + 3.26 \times 10^{-2}c - 9.63 \times 10^{-4} C^{3/2} - 4.54 \times 10^{-5} C^2 \text{g.cm}^{-3}$$
 Determine the PMV of the salt in a 0.1 molar solution.

- Q. 3** **Answers any three of the following.** **18**
- (a) Evaluate rotational partition function for diatomic molecule.
 - (b) Derive an expression for the Boltzmann Distribution Law.
 - (c) Define the term: Assembly, Canonical ensemble, Statistical weight factor and Probability.
 - (d) Calculate the vibrational partition function for water at 300K. The vibrational frequency is 1654 cm^{-1} .
[$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$, $h = 6.62 \times 10^{-34} \text{ Js}$, $C = 3.0 \times 10^{10} \text{ m/s}$]

- Q. 4** **Answers any three of the following.** **16**
- (a) What is step polymerization? How does it basically differ from addition polymerization?
 - (b) Give the name of phase techniques to produce polymer. Discuss any one homogeneous technique with advantages, disadvantages and uses.
 - (c) What do you understand by static and dynamic osmometer? Describe membrane osmometry method to determine molecular weight of polymer sample.
 - (d) What do you mean by number average and weight average molecular weight of polymer?
A polymer consists of 40% by weight of macromolecule of molecular weight 10,000 and 60% by weight of macromolecule of molecular weight 75000. Calculate PDI.
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