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# ST JOSEPH'S UNIVERSITY, BENGALURU -27

## M.Sc (CHEMISTRY) – II SEMESTER

### SEMESTER EXAMINATION: APRIL 2024

**(Examination conducted in May/June 2024)**

**CH 8322 – PHYSICAL CHEMISTRY II**

**(For current batch students only)**

**Time: 2 Hours** **Max. Marks: 50**

**NOTE: This paper contains 2 printed pages, 3 parts, and 16 questions.**

Data: Physical constants h= $6.626 \times 10^{-34}$ J s, $k_b = 1.38 \times 10^{-23}$ J $K^{-1}$.

## PART-A

**Answer any EIGHT of the following questions** **[2 x 8 = 16]**

1. Write any two examples for fluxes and the corresponding forces.
2. What happens to the reaction rate when the internal pressure of both reactants and the solvent is the same, but the internal pressure of the activated complex is higher? Explain it by applying the relevant expression.
3. Distinguish between RRK and RRKM theories.
4. The rate constant of the termination reaction reduces the rate of polymerization of $CH_2$=CHR; explain this with a relevant expression.
5. Write a general mechanism of free radical polymerization.
6. List two postulates of statistical thermodynamics.
7. State the law of equipartition of energy.
8. Write an expression for characteristic vibrational temperature. Explain the terms.
9. What is a thermodynamic excess function? Write an expression for excess thermodynamic volume.
10. Plot the graph showing the variation of the reciprocal density with the weight of the solution. Mark the partial specific volumes on the graph.

## PART-B

**Answer any TWO of the following questions** **[12 x 2 = 24]**

11. a) For the hydrolysis of an acid, the velocity constant observed was $1.16 \times 10^{-3}$ $dm^3$ $mol^{-1}$ $s^{-1}$, while activation energy is 130 kJ $mol^{-1}$. Calculate $\Delta^{\#}G$, $\Delta^{\#}H$, and $\Delta^{\#}S$, of the reaction at 363 K.
    b) Derive an expression for entropy production and its rate in matter flow.
    c) The rate constant of ionic reactions is higher in solvent A than in solvent B. Which one has a higher dielectric constant? Explain. (4+6+2)

12. a) Derive an expression for the thermodynamic formulation of conventional transition state theory.
    b) Calculate the rotational partition function of $H_2$ molecule at 1000 K (B=60 $cm^{-1}$).
    c) A gas is confined to a volume of 1 L at 27 °C. The thermal wavelength of this gas is $1.60 \times 10^{-11}$ m. Solve to obtain the translational partition function for this gas. (6+3+3)

13. a) How does chemical potential help deriving the following: i) Henry's law for gases dissolved in a liquid and ii) Raoult's law for a non-volatile solute in a liquid?
    b) Obtain an expression for the number of particles in the case of Maxwell-Boltzmann statistics for the molecules present in a system of non-degenerate energy levels. (Evaluation of β not required). (6+6)

## PART-C

**Answer any TWO of the following questions** **[ 5 x 2 = 10]**

14. Organic compound A doesn't undergo photolysis in the visible region. However, it undergoes pyrolysis under certain conditions and was found to follow an overall first-order kinetics. Chain initiation was first-order, and the termination was a combination of the two active species involved in the chain propagation steps.
    i) Identify A.
    ii) Write the mechanism using the data given above.
    iii) Write a steady-state equation for this reaction. (1+2+2)

15. The final volume of a solution is 980.0 $cm^3$ at 25 °C by adding 0.32 mole fraction of methanol to water. The partial molar volumes of water and methanol are 15.69 $cm^3$/mol and 40.49 $cm^3$/mol, respectively. The densities of methanol and water are 0.790 g/$cm^3$ and 0.997 g/$cm^3$, respectively, at 25 °C. Evaluate the total volume of methanol and water to be mixed at 25°C.

16. a) Justify the statement, 'if two states are equally degenerate, then both states are equally populated'.
    b) Write the mechanism for the anionic polymerization of butadiene in the presence of a metal alkyl, MR. ( 2+3)