LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **APRIL 2024**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 04-04-2024 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

Part-A

Answer ALL questions. **(10 × 2 = 20)**

1. Define chemical potential.
2. Calculate the ionic strength of 0.05 M $CaSO_4$ solution.
3. What are forces and flux?
4. Write the expression for vibrational partition function.
5. What are fermions? Cite an example.
6. Differentiate time and true order of a reaction with the relevant graphs.
7. Mention the limitations of collision theory.
8. What is the effect of temperature on enzymatic reactions?
9. The reaction from cis-butene to trans-butene is first order in both directions. At 25^{o}C, the equilibrium constant is 0.406 and forward rate constant is 4.21 $\times 10^{-4} s^{-1}$. Find the rate constant of the reverse reaction.
10. Distinguish between stationary and non-stationary chain reactions.

Part-B

Answer any FOUR questions. **(4 × 10 = 40)**

11. (a) Explain the salient features of Ellingham diagram and its significances.
    (b) Obtain the expression for variation of fugacity with respect to temperature. (5+5)
12. (a) Write the phenomenological equations for electrokinetic phenomenon and deduce their corresponding cross-coefficients.
    (b) State the principle of microscopic reversibility. (6+4)
13. (a) Sketch the phase diagram and arrive at the degrees of freedom for all the regions of a ternary system leading to the hydrate formation.
    (b) Write the expression for electronic partition function. Calculate the molecular rotational partition function (q_{rot}) of N_2 gas at 400 K whose moment of inertia is I = 13.9 x10^{-47} Kg m^2. (6+4)
14. (a) Obtain the most probable distribution of distinguishable particles using Maxwell-Boltzmann statistics.
    (b) Obtain the expression for relationship between enthalpy and partition function.(7+3)
15. (a) Discuss the construction of potential energy surface for a reacting system with an example.
    (b) Describe any one mechanism for the bimolecular surface reactions. (5+5)
16. (a) Write the various types of reversible enzyme inhibition mechanisms.
    (b) A bimolecular gas phase reaction has activation energy of 42.8 kJ mol^{-1}. Calculate the enthalpy of activation at 45 ^{o}C. (6+4)
17. (a) Explain flash photolysis technique for the study of kinetics of fast reactions.
    (b) Discuss the kinetics of free radical polymerization reactions. (5+5)
18. (a) Compare Collision and transition state theories in studying the kinetics of bimolecular reactions.
    (b) Mention the significance of electrostriction in studying the kinetics of ionic reactions. (7+3)

Part-C

Answer any TWO questions. **(2 × 20 = 40)**

19. (a) Discuss any three methods of determining the activity and activity coefficient of non-electrolytes.
    (b) State and explain phenomenological laws leading to the Onsager's reciprocal relations.
    (c) Derive Gibbs-Duhem equation. (10+5+5)

20. (a) Explain the salient features of Debye theory of heat capacities.
    (b) Derive Sackur-Tetrode equation.
    (c) Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm^3. (7+8+5)

21. (a) Discuss Lindeman theory of unimolecular reactions.
    (b) Derive Michaelis-Menten equation. How can it be verified?
    (c) The protein catalase with single active site catalyzes the reaction,
    $2H_2O_2 \rightarrow 2\ H_2O + O_2$ and has a Michaelis constant (K_M) of 25×10^{-3} mol dm^{-3} and a turnover number (k_2) of $4.0 \times 10^7\ s^{-1}$. Calculate the rate of this reaction if the total enzyme concentration is 0.016×10^{-6} mol dm^{-3} and initial substrate concentration is 4.32×10^{-6} mol dm^{-3}. Also calculate ν_{max} for this enzyme. (8+7+5)

22. (a) Explain the kinetics of hydrogen-bromine thermal chain reaction.
    (b) Obtain the rate expression for the reversible reaction A $\rightleftharpoons$ B that follows first order in both the directions and prove that the rate expression is similar to an irreversible first order reaction. (10+10)
