LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2023**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 01-11-2023 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

PART-A

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

1. Define activity and activity coefficient.
2. Sketch the phase diagram for the formation of two pairs of partially miscible liquids.
3. What is meant by Seeback effect?
4. Prove that partition function is a dimensionless quantity.
5. Write the relationship between partition function and pressure.
6. Evaluate $\ln 10^{20}!$ using Stirling's approximation.
7. What is electrostriction?
8. Calculate the limiting rate of an enzyme catalyzed reaction. Given: $[E] = 3.89\times10^{-7}$ M and $k = 2.58\times10^{3}$ s^{-1}.
9. Mention the importance of Turn over number.
10. Define chain length of a reaction.

PART-B

*Answer any **EIGHT** questions.* (8 x 5 = 40)

11. Derive Gibbs- Duhem equation.
12. Obtain an expression for the variation of chemical potential with temperature.
13. Draw and explain the phase diagram of a ternary system consisting of two solids and water with the formation of a double salt.
14. Write the phenomenological equations for electro kinetic effects and deduce their cross coefficients.
15. Discuss the conservation of mass and energy in an open system.
16. Obtain the relationship between partition function and entropy.
17. Calculate the molecular rotational partition function for hydrogen gas at 27 ^{0}C. The moment of inertia of nitrogen is 4.59×10^{-47} Kg m^2.
18. Bring out the differences between Lindemann and Hinshelwood treatments of unimolecular reaction.
19. The decomposition of ozone, $2O_3 \rightleftharpoons 3O_2$ is observed to obey the following rate law, rate $= k_1k_3[O_3]^2 / k_2[O_2] + k_3[O_3]$. Provide a mechanism that agrees with the rate law given.
20. Obtain a rate expression for the decomposition of ammonia on tungsten surface and explain the variation of order with respect to concentration.
21. Distinguish between straight chain and branched chain propagation steps with suitable examples.
22. Explain the salient features of relaxation methods to study the kinetics of fast reactions.

PART-C

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

23. a) How is the fugacity of real gases determined by graphical method?
    b) The fugacity coefficient of a gas at 200 K and 50 atm is 0.72. Calculate the difference in chemical potential of the real gas and an ideal gas. (7+3)

24. What is Onsager reciprocal relation? How is it verified by the principle of microscopic reversibility?
25. What are Bosons? Obtain the most probable distribution of indistinguishable particles using Bose-Einstein statistics.
26. a) Obtain an expression for the rate constant of the reaction, AB + CD → Products in the light of transition state theory, when it forms a linear product.
    b) Energy of activation of a first order reaction is 85 kJ and rate constant at 25°C is 1.8×10^{-3} s^{1}. Calculate $\Delta H^{\neq}$ and $\Delta G^{\neq}$. (5+5)
27. a) Explain the mechanism of anionic polymerization reaction.
    b) A consecutive first order reaction of the type A → B → C has rate constants k_1 and k_2. Given that $[A_\circ] = 2M$, $k_1 = 0.19\ s^{-1}$ and $k_2 = 0.1\ s^{-1}$. Calculate the time for the concentration of B to be maximum and $[B]_{max}$. (6+4)
28. How are the kinetic features of the thermal decomposition of acetaldehyde discussed using Rice – Herzfeld mechanism?

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