LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2017**

16PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 03-11-2017 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. Calculate the ionic strength of 0.01M K_2SO_4.
2. Show that $\left(\frac{\partial}{\partial}\right)_{T, n1,n2,} = \bar{V}_i$
3. Mention the importance of phenomenological coefficients.
4. Write the rotational partition function for *ortho* hydrogen.
5. Indicate the relationship between pressure and partition function.
6. What are true and time orders of a reaction?
7. How does electrostriction affect the entropy of activation for the reactions in solution?
8. The presence of 2.24 mM $L^{-1}$of a competitive inhibitor decreases the initial rate of a reaction catalyzed by a factor of 1.8. Calculate the degree of inhibition if the initial rate is 3.26×10^{-5} M s^{-1}.
9. State the principle of temperature jump technique for studying the kinetics of fast reactions.
10. Distinguish between thermal and branched chain explosions.

Part-B

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

11a. Discuss the physical significance of chemical potential.

b. The van der Waals constants for CO_2 gas are a = 3.59 X 10^6 m^3 atm mol^{-2} and b = 42.7 m^3 mol^{-1}. Find out the fugacity of the gas at 100 atm pressure and 50^{o}C.

12. Sketch the phase diagram and arrive at the degrees of freedom for all the regions of a ternary system leading to the formation of hydrates.
13. Show that Seebeck and Peltier effects are coupled phenomena.
14. Calculate the entropy change of one mole of helium when it is heated from 300 K to 600 K at constant pressure.
15. Explain the Onsager theory in the light of phenomenological reciprocal relationship.
16. How do you calculate the equilibrium constants using partition functions?
17. Explain the Langmuir-Hinshelwood mechanism of bimolecular surface reactions.
18. Calculate the frequency factor and rate constant at 700 K and one atmosphere for the decomposition of HI if its collision diameter is 0.36 nm and the activation energy is 220.0 kJ mol^{-1}. (Molecular mass of HI is 128 g mol^{-1})
19. Describe the influence of ionic strength on the rate of ionic reactions in solution.
20. Discuss the kinetics of free radical polymerization reaction.
21. Show that the pyrolysis of acetaldehyde follows fractional order kinetics.
22. Explain the stopped flow technique to study the kinetics of fast reactions. Mention its advantages over continuous flow method.

Part-C

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

23a. Explain the uses of Ellingham diagram with suitable examples.

b. Discuss any two methods of determination of activity and activity coefficients of non-electrolytes. (5+5)

24a. Discuss the entropy production and entropy flow in open systems.

b. Obtain the phenomenological equations and their cross coefficients for electrokinetic phenomenon. (5+5)

25a. What are Fermions? Obtain the most probable distribution of indistinguishable particles using Fermi-Dirac statistics.

b. Calculate the molecular rotational partition function for nitrogen gas at 27^0C. The moment of inertia of nitrogen is 13.9×10^{-47} kg m^2. (6+4)

26a. Compare the rate constants for the reaction between atoms and the reaction between complex non-linear molecules calculated by transition state theory.

b. Calculate the entropy of activation for a bimolecular gaseous reaction having the pre- exponential factor of 111.0 kJ mol^{-1} at 500 K. (7+3)

27a. Discuss the effect of substrate concentration on enzymatic reaction.

b. The Wolff plot for an enzyme catalyzed reaction has a straight line with the y-intercept of 41.25 min and the slope equal to 4020 L mol^{-1} min. Evaluate v_{max} and K_M for the reaction. (7+3)

28 a. Derive the expressions for the concentrations of A, B and C at any instant for a first order consecutive reaction $A \rightarrow B \rightarrow C$.

b. State Lindemann-Christiansen hypothesis of unimolecular reactions. (8+2)

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