LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – NOVEMBER 2015

CH 3814 - THERMODYNAMICS & CHEM. KINETICS

Date : 05/11/2015 Dept. No. Max. : 100 Marks

Time : 09:00-12:00

Part-A

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

1. Mention the significance of chemical potential.
2. How do you classify gases in terms of their compressibility factor?
3. Calculate the translational heat capacities for nitrogen gas at 298 K and at 1 atm.
4. Predict the ground state electronic degeneracy for the terms $^2P_{3/2}$ and $^2D_{5/2}$.
5. What are distinguishable and indistinguishable particles? Give an example each.
6. Define collision number of a reaction and write the mathematical expression to calculate it for a reaction between two different molecules.
7. Differentiate time and true order of a reaction.
8. What is the significance of the ratio of partition functions when two non-liner molecules form a non-linear activated complex based on transition state theory?
9. The pK_a values of *p*-chlorobenzoic acid and benzoic acid are 3.98 and 4.19 respectively. Calculate the substituent constant (σ) for *p*-Cl. (Given that, reaction constant = 1)
10. Draw the potential energy diagram for the formation of van't Hoff intermediate in homogeneous catalyzed reactions.

Part-B

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

11. Discuss the variation of fugacity with temperature.
12. A flask has a capacity of 4 dm^3. 3 g of O_2 and 9 g of N_2 at 27ºC are added to it. Calculate a) mole fraction of each gas and b) the partial pressure.
13. Discuss the importance of reduced phase rule to understand the phase diagram of a ternary system.
14. Explain Seebeck and Peltier effects.
15. Define symmetry number and predict the symmetry number of PCl_5 molecule.
16. The difference in energy between the first excited state, $^2P_{1/2}$ of bromine atom and the ground state $^2P_{3/2}$ is 0.19eV. Calculate the electronic partition function of Br atom at 1100K.
17. Using appropriate diagrams discuss the potential energy surfaces in reaction kinetics.
18. Discuss the influence of dielectric constant of the medium on the rate of ionic reactions in solution.
19. Explain Langumuir-Hishelwood mechanism for bimolecular surface reactions with an example.

20a. What are reversible inhibitors?

b. Calculate the degree of inhibition if the rate of the reaction, 2.1×10^{-4} Ms^{-1} is decreased by a factor of 3.2, in the presence of 5×10^{-5} M of competitive inhibitor. **(2+3)**

21. Explain the kinetics of consecutive reactions with relevant graph.
22. Write the principle of flow techniques and explain any one flow method to study the kinetics of fast reactions.

Part-C

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

23a. What is Ellingham's plot? How does it help to understand extraction of metals?

b. Calculate the molar residual entropy of a crystal in which the molecules can adopt seven orientations of equal energy at 0 K. **(6+4)**

24a. Discuss the entropy production in chemical reactions.

b. Calculate the rotaional partition function for hydrogen molecules at 300 K. Moment of inertia of H_2 is 4.59×10^{-47} kgm^2. **(6+4)**

25a. How is rotational energy derived from rotational partition function?

b. Calculate the translational energy and translational enthalpy for oxygen gas at 298 K and at 1 atm. **(6+4)**

26a. Derive Eyring equation which connects rate constant and thermodynamic parameters of a reaction.

b. Calculate the number of collisions per second in one cubic centimeter of oxygen at 298 K and 101.3 k_{Pa} pressure. (The diameter of oxygen molecule = 2.92 Å) **(6+4)**

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

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

28a. Explain the kinetics of hydrogen-chlorine thermal chain reaction.

b. Write a note on first and second explosion limits for H_2-O_2 branched chain reaction. **(6+4)**

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