 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

THIRD SEMESTER – **NOVEMBER 2012**

# CH 3812 / 4807 - CHEMICAL KINETICS

Date : 08/11/2012 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

Part A

Answer ALL the questions. (10 x 2 = 20 Marks)

1. In the reaction 2NO + 2H2🡪 N2 + 2H2O, mixture of reactant gases at an initial pressure of 336 mm of Hg, was half changed in 108 sec and when the initial pressure was 288 mm of Hg, it was half changed in 147 sec. Determine the order of reaction.
2. Show that the energy of activation according to the collision theory is less than the energy of activation given by Arrhenius theory.
3. If the rate constant at high pressure for the isomerization of cyclopropane is 1.2 x 10-4 s-1 and that at low pressure is 5.14 x 10-6 torr-1 s-1, below what pressure will the isomerization be for all practical purposes a second order reaction?
4. Explain electrostriction.
5. Addition of acetonitrile in an atmosphere of N2, has no effect on the oxidation of thioacids by benzyl trimethyl ammonium chlorobromate. What is your inference regarding the mechanism of this reaction?
6. What is meant by turn over number? What is its significance?
7. The observed activation energy for the gas phase recombination of iodine atoms in the presence of argon is negative. Explain.
8. Draw the concentration-time profile for the consecutive reaction, A 🡪 B 🡪 C, with proper labeling.
9. What is Hammett acidity function?
10. In water the fluorescence quantum yield and the observed fluorescence life time of tryptophan are 0.2 and 2.6 ns respectively. Calculate the fluorescence rate constant.

PART – B

Answer ANY EIGHT questions (8 x 5 = 40 Marks)

1. Explain Guggenheim’s method for first order reactions
2. Hydrogen iodide gas has a viscosity of 39.66 x 10-5 poise at 560 K and 101.3 kPapressure. Calculate the collision diameter of hydrogen iodide molecule.
3. Explain the need for activation energy based on potential energy surfaces. Illustrate your answer by taking the following reaction as example:

Hα+ Hβ - Hγ -🡪 Hα - Hβ + Hγ

1. The pre-exponential term for a unimolecular gas reaction occurring at 2000C is 2.75 x 1015 s-1. Calculate the entropy of activation. How does the result depend upon the standard state used?
2. Using double sphere model explain the effect of dielectric constant of the medium on the rate of the reaction between ions in solutions.
3. The pKa for the dissociation of phenol in water at 250C is 9.85. The ρ value for the dissociation H2O + X-C6H4OH 🡪 X-C6H4O- + H3O+ is 2.00. The σ-p values of –NO2 and – COOH are + 1.27 and + 0.73 respectively and the σ+p values of - CH3 and – Cl- are –0.31 and + 0.11 respectively. Arrange the substituted phenols in the order of increasing acid strength.
4. What are Skrabalplots?Explain.
5. The rate of the reaction HA + H2O H3O+ + A- is studied using T-jump method. Calculate the expected relaxation time if a 0.1 M solution has a pH of 4 and k-1 is 1010 M-1 s-1.
6. The rate law for the reaction between 2- bromo butane and OH-1 in 75% ethanol (aq) at 300C is given by rate = 3.2 x 10-5  [RBr][OH-1] + 1.5 x 10-6 [RBr]. What percentage of reaction will take place by an SN2 path way if a) [OH-1] = 1 M b) [OH-1] = 10-3 M.
7. Discuss the salient features of the kinetics of H2-Br2 chain reaction (No derivation is needed).
8. Explain the kinetic scheme for a bimolecular quenching process and hence derive Stern-Volmer equation.
9. How are kinetic parameters evaluated for a single substrate enzymatic reaction?

## PART – C

Answer ANY FOUR questions (4 x 10 = 40 Marks)

1. a) The isotope 90Sr emits β--radiation and has a half life of 28 years. If 2 micro gram of90Sr is absorbed by a newly born child, how much of it is left behind after (a) 18 years (b) 70 years. (5)

b) Derive the expression for the number of collisions between two different gas molecules A and B.(5)

24. a) The rate constant k for the reaction between persulphate ions and iodide ions in aqueous solution at 250C varies with ionic strength ( as follows. Estimate ZAZB.

x 10-3/ mol dm-3 2.45 4.45 8.45

k/ 10-4 dm3 mol-1 s-1 1.05 1.16 1.26 (6)

b) How are the reactions classified on the basis of the volume of activation? (4)

25. a) Explain how the catalytic constants for a reaction catalyzed by both general acid and general base are evaluated. (6)

b) Show that Bronsted catalytic law is a form of LFER. (4

26. Explain any two of the following: (5+5)a) Kinetics of H2-O2 explosive reaction b) van’t Hoff type and Arrhenius type intermediates.

c) Surface area measurement using BET equation d) Kinetics of reversible reactions

27. a) Discuss the Rideal-Eley mechanism for a bimolecular surface reaction with a specific example. (6)

## b) The decomposition of O3, 2O3🡪 3 O2 is observed to obey the rate law – d[O3]/dt = 2 k [O3]2/[O2], suggest a suitable mechanism and explain. (4)

* 1. For the oxidation of hexacyano ferrate (II) by peroxodisulphate in aqueous perchloric acid medium, the following data were obtained: (i) Plots of log [Fe(CN)64-] vs time were linear at constant ionic strength and [H+] (ii) The pseudo first order rare constants (kobs) vary linearly with peroxodisulphate concentration at constant ionic strength and [H+] (iii) At constant [Fe(CN)64-] [S2O82-] and ionic strength, increasing [perchloric acid] increased the rate. Plots of [S2O82-] /kobsvs 1/[H+] were linear (iv) Increasing the ionic strength of the medium, increased the rate (v) ΔS# is negative. Explain the data. (5)

Propose a suitable mechanism to account for the above data and write the rate expression. (5)

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