# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – NOVEMBER 2011

**CH 3812/4807 - CHEMICAL KINETICS**

Date : 08-11-2011 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

Part A

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

1. For a reaction when the initial concentration of the reactant was 0.0135 M, the half-life was 267.2 seconds and when the initial concentration was 0.054 M, the half-life was 133.4 seconds. Determine the order of the reaction.
2. The rate constant ($k_2$) of a second order reaction is given as $k_2$ ($dm^3$ $mol^{-1}$ $s^{-1}$) = 2.05 x $10^{13}$ exp (-8681/T). Evaluate the activation energy of the reaction at $327^0$C.
3. Hydrolysis of benzoyl chloride has a positive ρ (reaction constant) value. What is your inference about the mechanism of this reaction?
4. Explain the influence of dielectric constant on the rate of the following reaction $Et_3N + EtI \rightarrow Et_4N^+I^-$.
5. If the rate constant at high pressure for the isomerization of cyclopropane is 1.52 x $10^{-4}$ $s^{-1}$ and that at low pressure is 3.14 x $10^{-6}$ $torr^{-1}$ $s^{-1}$, below what pressure will the isomerization be for all practical purposes a second order reaction?
6. What are van't Hoff type intermediates?
7. The observed rate of the gas phase reaction $2NO + O_2 \rightarrow 2NO_2$ was found to decrease with increase of temperature. Explain.
8. The adsorption of a gas is described by the Langmuir isotherm with b =0.85 $kPa^{-1}$ at $25^0$C. Calculate the pressure at which the fractional surface coverage is 0.15.
9. What are Skrabal plots?
10. "Conventional methods of analyzing the kinetics of ultrafast reactions fail." Why?

PART – B

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

11. Derive an equation that shows that increase of temperature decreases the half-life of a reaction
12. Draw and explain the potential energy diagrams for the reaction, $H_A + H_BH_C \rightarrow H_AH_B + H_C$
13. Write a note on Okamato-Brown Equation.
14. For the first order isomerization of an organic compound at $130^0$C, the activation energy is 108.4 kJ $mol^{-1}$ and the rate constant is 9.12 x $10^{-4}$ $s^{-1}$. Determine $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ for this reaction .
15. Calculate the translational partition function for $NH_3$ in 1 $cm^3$ at 300 K
16. For the reaction, $A^x + B^- \rightarrow$ Products, the rate constant (k) varies with ionic strength (μ) as follows:

| μ x $10^3$/mol $dm^{-3}$ | 2.35 | 3.65 | 4.45 |
|---|---|---|---|
| k/$dm^3$ $mol^{-1}$ $s^{-1}$ | 1.05 | 1.12 | 1.16 |

Determine the charge on ion A.

17. Explain the significance of acidity functions.
18. Pencillinase (an enzyme) with molecular mass 3 x $10^5$ g/mol, catalyses the decomposition of an antibiotic. The turnover number of the enzyme is 2000 $s^{-1}$ at $28^0$C. If 6.4 μg of Pencillinase catalyses the destruction of 3.11 mg of an antibiotic (molecular mass 364 g/mol) in 20 seconds at $28^0$C how many active sites does the enzyme have?
19. Derive Stern-Volmer equation for bimolecular quenching.

$$\text{U-238} \xrightarrow[t_1]{} \text{Th-234} \xrightarrow[t_2]{} \text{Pa-234} \xrightarrow[t_3]{} \text{U-234}$$

20. The first three steps in the decay of U-238 are

The half life periods $t_1$,$t_2$ $t_3$ are 4.5 x$10^9$ y, 24.1 days, 1.14 min respectively. If we start with 100 g of pure U-238, what percentage will be Th-234 after 10 days?

21. Deduce the expression for relaxation time for the reaction of the type $A + B \rightleftharpoons C$ second order forward and first order backward.

22. How is surface area of a solid determined using BET equation?

**PART – C**

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

23. a) The following data were obtained for the reaction $C_6H_5COCl + 2C_6H_5NH_2 \rightarrow C_6H_5CONHC_6H_5 + C_6H_5NH_2HCl$ in aqueous medium at $27^0$C. The initial concentration of $C_6H_5COCl$ as 5 x $10^{-3}$ mol $dm^{-3}$ and that of aniline was 1 x $10^{-2}$ mol $dm^{-3}$. Calculate the rate constant in units of $dm^3$ $mol^{-1}$ $s^{-1}$

| Time/second | 0 | 150 | 312 | 576 | 876 | 1290 |
|---|---|---|---|---|---|---|
| $[C_6H_5COCl]x10^3$/mol $dm^{-3}$ 5.0 | 4.5 | 4.0 | 3.5 | 3.0 | 2.5 | (8) |

b) Estimate the sign of $\Delta S^{\#}$ in the following reaction. Substantiate your answer. $[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow$ Products (2)

24. a) Explain the effect of internal pressure on the rate of a reaction between two molecules. (6)

b) What is the probability that at $500^0$C, the energy of a collision is (a) 41 kJ $mol^{-1}$ and (b) 246.0 kJ $mol^{-1}$ in excess of the average energy? What is your inference? (4)

25. a) Explain the kinetics of single substrate enzymatic reaction and derive the rate law.
b) How are the kinetic parameters evaluated for an enzymatic reaction?

26. Explain any two of the following (5+5) a) Kinetics of $H_2$-$Br_2$ chain reaction (thermal)
b) Determination of rate constants for a reaction catalyzed by both general acid and general base
c) Flash photolysis- Principle and methodology
d) Langmuir-Hinshelwood mechanism for a bimolecular surface reaction and its salient features.

27. a) The decomposition of ozone to form $O_2$(g) proceeds through the following mechanism

i) $O_3(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g)$

(ii) $O_3 + O \xrightarrow{k_3} 2O_2(g)$ (rds)

Deduce the rate law for $-d[O_3]/dt$ using 1) fast equilibrium for step (i) 2) using steady state approximation for O(g). Under what conditions the two rate expressions become identical.
(3+4)

b) Deduce an expression for overall activation energy of the above reaction in terms of $E_1$, $E_2$ and $E_3$ using fast equilibrium approach. (3)

28. For the oxidation of diols by butyltriphenylphosphonium dichromate (BTPPD), the following data were obtained: (i) The plot of log [BTPPD] vs time was found to be linear. (ii). The pseudo-first order rate constants ($k_{obs}$) were obtained at different [diol] but at constant [BTPPD], $[H^+]$ and temperature. The values of $k_{obs}/[diol]^2$ were nearly constant and Van't Hoff differential method gave a slope equal to two with respect to diols. (iii) The magnitude of slope of a plot of log $k_{obs}$ vs log$[H^+]$ was found to be two (iv) The oxidation of diols by BTPPD in an atmosphere of nitrogen failed to induce polymerization of acrylonitrile (v) $\Delta S^{\#}$ is negative for this oxidation (vi) The isokinetic temperature was 1976 K. Explain the data.
(6)

Propose a suitable mechanism to account for the above data and write the rate expression. (4)

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