LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – APRIL 2010

CH 3812 / 3801 / 4807 - CHEMICAL KINETICS

Date & Time: 28/04/2010 / 1:00 - 4:00 Dept. No. Max. : 100 Marks

PART A

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

1. Explain the observed fact that the reaction between triethylamine and ethyl iodide is more than 2000 times faster in nitrobenzene as solvent as compared to that in n-hexane as solvent.
2. At a certain temperature, the half-life for the decomposition of xenon diflouride,
   $XeF_{2(g)} \longrightarrow Xe\ (g) + Fe\ (g)$,
   is 200 seconds when the initial concentration of XeF_2 is 0.01 M and 66.7 seconds when the initial concentration is 0.03 M. What is the order of the reaction?
3. Show that the collision energy of activation will be less than the energy of activation using Arrhenius equation.
4. A certain reaction exhibits primary isotopic effect ($k_H/k_D = 3.69$). What is your inference?
5. For benzoylation of para nitro aniline, the rate constant is 5.5×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ at 25^0C. What is the rate constant for the bezoylation of aniline given the following data: $\rho = -2.781$, $\sigma_{pNO2} = 0.78$.
6. Write the rate law for a reaction catalysed by both general acid and general base in water.
7. In a typical Lineweaver-Burk plot for a single substrate enzymatic reaction, 1/rate (y-axis) versus $1/[S]_0$ gave a straight line with slope = 3.65×10^{-5} min and y-intercept = 8.25×10^{-3} l min mol^{-1}. Calculate K_M.
8. What are Arrhenius and van't Hoff type intermediates?
9. What is the significance of Stern-Volmer constant?
10. The nuclide Ac-227 undergoes β^- emission (98.6%) and α-emission (1.4%) in two parallel paths. The overall half life is 21.6 year. Determine the rate constants for the two paths.

PART – B

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

11. The data were obtained for the reaction, A + B → Products

Initial rate (mol dm^{-3} s^{-1}) (disappearance of A)	[A] (moles dm^{-3})	[B] (moles dm^{-3})
0.02	0.5	0.5
0.08	1.0	0.5
0.16	1.0	1.0

(a) Deduce the rate expression and the order of the reaction. (b) Calculate the rate constant. (3+2)

12. Discuss the Lindemann Mechanism of unimolecular reactions for the process where the activation of the reactant molecule A takes place only by the collision with a non-reactant molecule M.
13. Explain the influence of hydrostatic pressure on the rate of a reaction in solutions.
14. The rate constants for a reaction are 1.6×10^{-3} s^{-1} and 1.625×10^{-2} s^{-1} at 10^0C and 30^0C respectively. Calculate the activation energy. Determine also $\Delta H^{\#}$ for this reaction at 27^0C.
15. How do the symmetry numbers affect the rate of a reaction?
16. Hydrogen iodide gas has a viscosity of 39.66×10^{-5} poise at 560 K and 101.3 kPa pressure. Calculate the collision diameter of Hydrogen iodide molecules.(M_{HI}=128 g/mol).

17. For the reaction H^+ (aq) + $C_6H_5COO^-$ (aq) ⇔ C_6H_5COOH, $k_1 = 3.5 \times 10^{10}$ l mol^{-1} s^{-1} and k_2 = 2.2×10^6 s^{-1} and $K_a = 6.6\ 10^{-5}$ for C_6H_5COOH (aq). Calculate the relaxation time for a 0.01 M solution of benzoic acid.
18. In a typical BET plot for the adsorption of H_2(g) on Al_2O_3 (s) at 7.3 K, y-intercept = 3.98×10^{-6} mm^{-3} and slope = 1.23×10^{-3} mm^{-3}. Calculate C and V_m for this system.
19. Explain the kinetics of bimolecular quenching reaction and hence derive Stern-Volmer equation.
20. Show that Brosnted catalytic law is a form of linear free energy relation.
21. The effective rate constant for a gaseous reaction that follows Langumir-Hinshelwood mechanism is 2.5×10^{-4} s^{-1} at 1.30 kPa and 2.1×10^{-5} s^{-1} at 12 Pa. Evaluate the rate constant for the activation step in the mechanism.
22. Explain flash photolysis.

PART – C

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

23. a) Compare the rate constants calculated by the ARRT and the Collision Theory for the reaction between two atoms. (8)
    b) A radioactive element gives 4000 counts per minute at a given time and one hour later 1500 counts per time. What is the half life? (2)

24. a) How does the ionic strength of the medium affect the rate of a reaction between ions in solutions? (5)
    b) The pre-exponential term for a bimolecular gas reaction occurring at 300^0C is 7.4×10^{10} dm^3 mol^{-1} s^{-1} and the energy of activation for this reaction at this temperature is 190 kJ per mole. Determine $\Delta S^{\#}$ for this reaction. How much will $\Delta S^{\#}$ change if the standard state is expressed in terms of molecules dm^{-3}. (5)

25. Explain the kinetics of single substrate enzymatic reaction. How are kinetic parameters evaluated for the same?

26. Explain any two of the following: (5+5)
    a) Kinetics of consecutive reactions b) Relaxation techniques
    c) Kinetics of branched chain explosions d) Hammett acidity function

27. Explain the kinetics of bimolecular surface reactions with special reference to $H_2(g) + D_2(g) \rightarrow 2HD(g)$ in the presence of a solid catalyst. Assume each reactant gas is dissociatively chemisorbed. Derive the rate law in each case and explain.

28. For the oxidation of aliphatic alcohols by bis(trifluoroacetoxy) iodobenzene (TFAIB) in aqueous medium, the following data were obtained: 1) The plots of log [TFAIB] vs time were linear. 2). A plot of $1/k_{obs}$ against 1/[alcohol] is linear with an intercept on the ordinate. 3) The rate of oxidation of alcohols by TFAIB was unaffected by the change in ionic strength of the medium. 4) $\Delta S^{\#}$ is negative. 5) The oxidation of alcohols by TFAIB failed to induce the polymerization of acrylonitrile. (5)

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

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