LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2009

CH 3812 / 4807- CHEMICAL KINETICS

Date & Time: 10/11/2009 / 9:00 - 12:00 Dept. No. Max. : 100 Marks

PART A

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

1. Differentiate between time order and concentration order with special reference to the thermal decomposition of CH_3CHO.
2. The experimentally determined energy of activation for the decomposition of N_2O_5 to give NO_2 and O_2 is 104.2 kJ mol^{-1}. Calculate the energy of activation at 400^0C according to collision theory expression
3. Write down the expression for the rate constant of a reaction between two non linear molecules forming a linear transition state on the basis of ARRT.
4. The rate of a reaction between X and Y^{2-} has been investigated in aqueous solution at 298 K and the second order rate constant (k_2^0) at zero ionic strength is found to be 0.745 M^{-1} s^{-1}. When ionic strength of the medium (μ) is 1.60 x 10^{-3} M, the second order rate constant (k_2) is 0.901 M^{-1} s^{-1}. Predict the charge on X.
5. Oxidation of aliphatic alcohols by bis(trifuoroacetoxy) iodobenzene exhibited excellent isokinetic relationship. What is your inference about the mechanism of this reaction?
6. What are Skrabal plots?
7. For a single substrate enzyme catalysed reaction with a single active site, K_M = 25 x 10^{-3} M^{-1} and a turn over number of 4 x 10^7 s^{-1}. Calculate the initial rate with $[E]_0$ = 16 x 10^{-8} M and $[S]_0$ = 4.32 x 10^{-6} M.
8. What is capillary condensation?
9. For the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ the observed rate constant was found to decrease with increase in temperature. Explain
10. For a parallel I order reaction, k_1 = 3.74 s^{-1} and k_2 = 4.65 s^{-1}. What is the maximum percentage of 'C' obtainable at this temperature, if the reactions are A→B and A→C?

PART – B

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

11. Calculate the translational partition function for CO in the standard state of 10^3 mol m^{-3} at 27^0C for the purpose of calculation of free energy.
12. If the rate constant at high pressures for the isomerization of cyclopropane is 1.2 x 10^{-2} s^{-1} and that at low pressures is 3.46 x 10^{-6} $torr^{-1}$ s^{-1}, below what pressure will the isomerization be for all practical purposes a second order reaction?
13. Give the significance of Taft Equation
14. Describe the need for the energy of activation from the potential energy curves of the following reaction. $H_AH_B + H_C <=> H_BH_C + H_A$
15. The rate constant for a certain unimolecular reaction is 2.5 x 10^{-2} s^{-1} at 500^0C and the energy of activation for this reaction at this temperature is 68 kJ per mole. Determine $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ for this reaction at this temperature.
16. Determine the general expression for the k_n and $t_{1/2}$ for n^{th} order reaction, when n>1
17. Derive an expression for the relaxation time for a reaction of the type A,=> C+B which is first order (forward) and second order (backward).
18. Write BET equation. Mention the terms involved. How is the equation verified? (2+3)

19. Explain the potential energy diagrams for a reaction proceeding through i) Arrhenius type intermediate ii) van't Hoff type intermediate.
20. The first three steps in the decay of U-238 are U-238 → Th-234 → Pa-234 → U-234 with half lives 4.5 $x10^9$ y, 24.1 days and 1.14 min respectively. If we start with pure U-238, what fraction will be Th-234 after 80 days?
21. 2:2' bipyridine forms a complex with Ru^{2+} that has a strong MLCT transition at 450 nm. The quenching of the complex excited state by $[Fe(H_2O)_6]^{3+}$ was monitored by measuring emission life time at 600 nm. In a typical plot of $1/\tau$ vs [Q] a straight line was got with slope = 3 x 10^9. What conclusion can you draw? Evaluate K_{SV}.
22. For a weak organic base (B) in 2 $x10^{-2}$ M $HClO_4$, $[BH^+]/[B] = 0.01$. Calculate i) pK_{BH+} for the conjugate acid of the base ii) the ratio of [BH+]/[B] in a solution of $[H_3O^+] = 0.05$ M using the same Hammett base. Also calculate H_0 value.

PART – C

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

23. a) ^{90}Sr generated during nuclear explosions is a health hazard, since it gets incorporated in place of Ca^{2+} in bones. It decays by beta emission. The half life of ^{90}Sr is 28 years. If 2 µg of ^{90}Sr is absorbed by a newly born child, how much of it is left behind after 75 years.
    b) Describe how the internal pressure will affect the rate of a reaction between neutral molecules.
24. a) Calculate the number of collisions per second between nitrogen molecules and oxygen molecules in 1 cm^3 of an equimolecular mixture of gases at 27^0C and at a total pressure 101.3 kPa pressure, given the molecular radius of oxygen to be 1.46 $x10^{-8}$ cm and that of nitrogen is 1.58 $x10^{-8}$ cm. (5)
    b) Using double sphere model for a reaction between two ions derive the relation connecting the rate constant and dielectric constant of the medium and explain. (5)
25. a) Explain how the catalytic constants be evaluated for a reaction catalysed both by general acid and general base in water (6)
    b) What is Bronsted catalytic law? How is it verified? (4)
26. Deduce the rate law for the reaction, $2O_3 \rightarrow 3O_2$ if it follows the mechanistic scheme:

    (i) $O_3 \underset{k_2}{\overset{k_1}{\Leftrightarrow}} O_2 + O$ (ii) $O_3 + O \xrightarrow{k_3} 2O_2$ (slow)

    Using 1) fast equilibrium step (i) 2) steady state approximation for 'O' and explain. How is E_a for the reaction obtained using fast equilibrium step (i)
27. Explain any two of the following:
    a) Rideal-Eley mechanism for a bimolecular surface reaction with an example.
    b) Evaluation of kinetic parameters for an enzymatic reaction
    c) Flash phtolysis d) Kinetics of $2H_2 + O_2 \rightarrow 2H_2O$ in the presence of electric spark
28. For the oxidation of thiosulphate ion by hexacyano ferrate (III) in aqueous perchloric acid, the following data were obtained: i) The plots of log $[Fe(CN)_6^{3-}]$ vs time were linear. ii) The rate increased linearly with $[S_2O_3^{2-}]$ and the plots of pseudo first order rate constants (k_{obs}) vs $[S_2O_3^{2-}]$ at constant ionic strength and at constant $[H^+]$ passed through the origin. iii) At constant $[Fe(CN)_6^{3-}]$, $[S_2O_3^{2-}]$ and ionic strength, increasing $[HClO_4]$ increased the rate. The order with respect to $[H^+]$ was less than unity. Plots of $[S_2O_3^{2-}]/k_{obs}$ vs $1/[H^+]$ were linear. iv) The rate was found to increase with increasing ionic strength of the medium. v) $\Delta S^{\#}$ is negative. (5)

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

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