LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2017**

CH 920 – CHEMICAL KINETICS

Date: 10-11-2017 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. Write the assumptions of conventional transition state theory.
2. Calculate the half-life of the decomposition reaction at 600 K with rate constant 3.72×10^{-5} s^{-1}.
3. What are Skrabal plots?
4. Mention the significance of Hammett acidity function.
5. What is meant by capillary condensation?
6. Why a reaction is exothermic if the adsorption is spontaneous?
7. State the principle of temperature jump technique for studying the kinetics of fast reactions.
8. Distinguish between stationary and non-stationary chain reactions.
9. Determine the enthalpy of activation for a reaction at 298 K having Gibbs energy and entropy of activation of 97.2 kJ mol^{-1} and -151.1 J $K^{-1}mol^{-1}$ respectively.
10. Compare thermal and photochemical reactions.

Part-B

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

11. Derive Bronsted-Bjerrum equation for ionic reactions in solutions.
12. Explain the need for the potential energy surfaces in the reaction kinetics.
13. Describe any two methods of determining order of a reaction.
14. The molecular radius of nitrogen and oxygen are 1.58×10^{-8} cm and 1.46×10^{-8} cm respectively. When 2.45×10^{19} molecules of each are mixed in the reaction vessel at 27ºC, calculate the number collisions per second between nitrogen and oxygen molecules in one cm^3 (Given: molecular masses of N_2 and O_2 are 28 and 32 g mol^{-1} respectively).
15. Discuss the kinetics of consecutive reactions with a relevant graph.
16. At 30ºC in 80% ethanol, the rate constants in $dm^3mol^{-1}s^{-1}$ for the hydrolysis of m-chloroethylbenzoate and p-methoxyethylbenzoate are 0.454 and 0.0114 respectively. Given that σ values of m-Cl and p-OMe are +0.37 and -0.27 respectively. Calculate the reaction constant ρ.
17. Explain the kinetics of bimolecular quenching reaction and hence derive Stern-Volmer equation.

18. Discuss the kinetics of opposing reactions.

19. Derive the expression for Langmuir adsorption isotherm.

20. Explain flash photolysis technique with a neat diagram,

21. Show that Bronsted catalytic law is a form of linear free energy relationship.

22. Compare the rate constant expressions derived by collision and transition state theories for the reaction between atoms.

Part-C

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

23a. 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.

b. At 327℃, the rate constant of a first order reaction is $1.6 \times 10^{-5}\ s^{-1}$. If the temperature is increased by 100℃, the value of rate constant increases to $6.36 \times 10^{-3}\ s^{-1}$. Calculate the activation energy for the reaction. **(7+3)**

24. Differentiate the following: (a) Prototropic and Protolytic mechanisms

(b) True and Time orders (c) Arrhenius and Van't Hoff type intermediates. **(3+4+3)**

25a. Explain the kinetics of bimolecular surface reactions with a specific example. Derive the relevant rate law for each mechanism.

b. Explain the double sphere model for the influence of dielectric constant on the rate of ion-ion reactions in solution. **(5+5)**

26a. How is surface area of a solid determined using BET equation?

b. Explain any one flow technique applied for studying the kinetics of fast reactions. **(5+5)**

27a. Derive Michaelis-Meten equation of an enzymatic reaction.

b. In a typical Lineweaver-Burk plot of 1/rate vs 1/[S], the slope and Y- intercept are 40.0and2.0 respectively. Determine the maximum rate and K_M value if the concentration is in mmol/L and time in seconds. **(7+3)**

28 a. Derive Eyringequation which relates the thermodynamic parameters with the rate constant of the reaction.

b. Discuss the kinetics of hydrogen-bromine thermal chain reaction. **(5+5)**

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