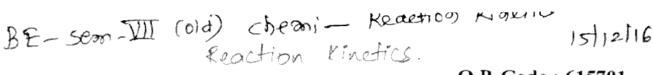
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(3 Hours)

[Total Marks: 100

N.B.: (1) Question No 1 is compulsory.

- (2) Answer any four questions from rest.
- (3) Assume suitable data wherever necessary.
- 1. Solve any Four (5 Marks each)

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- a) Differentiate between elementary and non-elementary reactions.
- b) What is a Shifting Order reaction?
- c) Explain half-life time method of finding order & rate constant.
- d) Define true density, apparent density and bulk density of catalyst in a bed.
- e) Significance of HATTA number in fluid-fluid reactions.
- 2. a) Show that the following equations are consistent and can explain the observed first order decomposition of N_2O_5 :

$$N_2O_3 \xrightarrow{k_1} NO_2 + NO_3 *$$

$$NO_2 + NO_3 * \xrightarrow{k_2} N_2O_5$$

$$NO_2 + NO_3 * \xrightarrow{k_3} NO_2 + NO * + O_2$$

$$NO * + NO_3 * \xrightarrow{k_4} 2NO_3$$

- b) An aqueous solution of ethyl acetate is to be saponified with sodium hydroxide. The initial concentration of ethyl acetate is 5 gm/lit and that of caustic is 0.1N. The values of second order rate constant at 0° C and 20° C are k=0.235 and 0.924 lit/ (mol. min) respectively. The reaction is irreversible. Calculate the time required to saponify 95% of ester at 40° C.
- a) From the following half-life data for thermal decomposition of N₂O gas phase at 650° C. Determine the rate equation which fits this data.

P _o (mm Hg)	52.5	140	280	360	_
t _½ (sec)	860	470	250	210	

b) Calculate the first order rate constant for the disappearance of A in the gas reaction A → 1.6R, if the volume of reaction mixture starting with pure A increases by 50% in 4 minutes. The total pressure within the system stays constant at 1.2 atm, and the temperature is 25°C.

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4. An aqueous phase reversible reaction $R \leftrightarrow S$ is carried out between 0° C 10 and 100° C. Free energy and heat of reaction at 25° C is $\Delta G^{\circ} = -3510$ cal/mol and $\Delta H^{\circ} = -20000$ cal/ mol.

Calculate:

- i) The variation of equilibrium constant with temperature and
- ii) The variation of equilibrium conversion with temperature.
- a) Derive the Langmuir-Hinshelwood type rate equation for A + B ↔ C + D, 10 where rate of desorption of C controls the rate equation.
 - b) On doubling the particle size from R to 2R, the time required for complete conversion triples. What mechanism controls the overall rate of reaction for a heterogeneous non-catalytic solid-fluid reaction? In 5 hrs the conversion of the solid spherical particle is 70%, find the time required for complete conversion of the particle.
- 6. a) Sample of silica-alumina cracking catalyst of particle densities of 1.26 and 10 0.962 gm/cc respectively. The true density of solid particles in each case is 2.7 gm/cc. Surface area of sample one is 1.67 m²/gm. Surface area of sample two is 3.72 m²/gm, Determine by mercury displacement method which sample has larger pore radius?
 - b) Derive an expression when the diffusion through gas film controls the overall mechanism by unreacted core model for spherical particle of unchanging size in fluid particle reaction.
- Solve any Four (5 Marks each)

20

- a) Differentiate between physical and chemical adsorption
- b) Effectiveness factor for isothermal first order irreversible reaction.
- c) Explain models for non-catalytic reactions of solid with surrounding fluid.
- d) What is optimum temperature progression?
- e) Rate controlling step for fluid-solid non-catalytic reaction.

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