BE - sem - VII (old) chemi — Reaction Kinetics 15/12/16
Reaction Kinetics.

Q.P. Code : 615701

(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) **20**
   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 : **10**

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3^*$$

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

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

$$NO^* + NO_3^* \xrightarrow{k_4} 2NO_2$$

   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. **10**

3. a) From the following half-life data for thermal decomposition of N_2O gas phase at 650° C. Determine the rate equation which fits this data. **10**

P_0 (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. **10**

[TURN OVER]

7-1

4. An aqueous phase reversible reaction R $\leftrightarrow$ S is carried out between 0° C and 100° C. Free energy and heat of reaction at 25° C is ΔG^0 = - 3 510 cal/ mol and ΔH^0 = -20000 cal/ mol. **10**
Calculate:
i) The variation of equilibrium constant with temperature and
ii) The variation of equilibrium conversion with temperature.

5. a) Derive the Langmuir- Hinshelwood type rate equation for A + B $\leftrightarrow$ C + D, where rate of desorption of C controls the rate equation. **10**
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. **10**

6. a) Sample of silica-alumina cracking catalyst of particle densities of 1.26 and 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 m^2/gm. Surface area of sample two is 3.72 m^2/ gm, Determine by mercury displacement method which sample has larger pore radius? **10**
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. **10**

7. 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.

7-2