Course: CHM202

Energetics and dynamics of chemical reactions

Assignment –IX

Q.1 Set up the rate equations for the reaction mechanism:

$$A \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} B \underset{k'_b}{\overset{k_b}{\rightleftharpoons}} C$$

Show that the mechanism is equivalent to

$$A \underset{k'_{eff}}{\overset{k_{eff}}{\rightleftharpoons}} C$$

under specified circumstances.

Q.2 Derive an equation for the steady-state rate of the sequence of reactions A ⇌ B⇌ C ⇌ D, with [A] maintained at a fixed value and the product D removed as soon as it is formed.

Q.3 On the basis of the following proposed mechanism, account for the experimental fact that the rate law for the decomposition

$2N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ is $v = k[N_2O_5]$.

(1) $N_2O_5 \rightleftharpoons NO_2 + NO_3$	k_1, k'_1
(2) $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$	k_2
(3) $NO + N_2O_5 \rightarrow NO_2 + NO_2 + NO_2$	k_3

Q.4 Consider the acid-catalysed reaction

(1) $HA + H^+ \rightleftharpoons HAH^+$	$k_1 k'_1$, both fast
(2) $HAH^+ + B \rightarrow BH^+ + AH$	k_2, slow

Deduce the rate law and show that it can be made independent of the specific term $[H^+]$.

Q.5 The half-life period of a first-order decomposition of $N_2O_5(g)$ is expressed as $t_{1/2} = -30.3 + \frac{12581.78}{T}$ when time is expressed in sec. Find out (i) Frequency factor A, (ii) Energy of activation and (iii) fraction of the reactant undergoing the reaction in 1 hour at 300 K.

Q.6 For the mechanism

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C\ ;\ C \xrightarrow{k_3} D$$

Derive the rate law using the steady state approximation to eliminate the concentration of C.

Q.7 The enzyme-catalysed conversion of a substrate at 298 K has a Michaelis constant of 0.042 mol dm^{-3}. The rate of the reaction is 2.45×10^{-4} mol dm^{-3} s^{-1} when the substrate concentration is 0.890 mol dm^{-3}. What is the maximum velocity of this enzymolysis?

Q.8 The enzyme α-chymotrypsin is secreted in the pancreas of mammals and cleaves peptide bonds made between certain amino acids. Several solutions containing the small peptide N-glutaryl-l-phenylalanine-p-nitroanilide at different concentrations were prepared and the same small amount of α-chymotrypsin was added to each one. The following data were obtained on the initial rates of the formation of product:

[S]/(mmol dm^{-3})	0.334	0.450	0.667	1.00	1.33	1.67
ν/(mmol dm^{-3} s^{-1})	0.152	0.201	0.269	0.417	0.505	0.667

Determine the maximum velocity and the Michaelis constant for the reaction.