CML103

Minor 1, 2021

Marks: 25

(Prof. Shashank Deep & Prof. Kuntal Manna)

(Important Note: There will be step wise marking. Make sure that every step is written in answer sheet. Skipping of any step will result into deduction of mark. Answersheet will be checked strictly for plagiarism.)

Q1. Consider the overall balanced reaction between molecules A and B to give molecules C and D:

$2A + B \rightarrow C + D$

Rate of reaction is given by: $\vartheta = \frac{k[A]^2[B]}{k'[B]+k''[D]}$

Propose the mechanism of the above reaction. Also write the rules used for deriving the mechanism (6)

Q2. Isomerization of A to B follow competing unimolecular and bimolecular reaction:

$A \rightleftharpoons B$ (First order from both side, k_1 and k_{-1} are rate constants for forward and reverse reaction)

$2A \rightleftharpoons 2B$ (second order from both side, k_2 and k_{-2} are rate constants for forward and reverse reaction)

Find the expression for $ln([A] - [A]_{eq})$ in terms of rate constants, initial concentration of A and time. Take initial concentration of B as zero. (6)

Q3. A reaction $A + 2B \rightleftharpoons C + 2D$ proceeds through the mechanism:

$A + B \rightleftharpoons I + D$ (k_1 and k_{-1} are rate constants for forward and reverse reaction)

$I + B \rightleftharpoons C + D$ (k_2 and k_{-2} are rate constants for forward and reverse reaction)

Applying steady state approximation to I, express $-\frac{d[A]}{dt}$ in terms of rate constant and concentration of reactant and product. (5)

Q4. Show that the kinetic scheme with stationary intermediate AB

$A + B \rightleftharpoons AB$ (k_1 and k_{-1} are rate constants for forward and reverse reaction)

$AB \rightleftharpoons C$ (k_2 and k_{-2} are rate constants for forward and reverse reaction)

Correspond to single relaxation time

$$\frac{1}{\tau} = k_1 p\left([A]_{eq} + [B]_{eq}\right) + k_{-2}(p - 1)$$

Where $p = \frac{k_2}{k_{-1}+k_2}$ (8)