CHM202
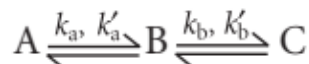
Energetics and dynamics of chemical reactions

Solutions Assignment –IX

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

$$A \underset{\longleftarrow}{\overset{k_a, \ k_a'}{\longrightarrow}} B \underset{\longleftarrow}{\overset{k_b, \ k_b'}{\longrightarrow}} C$$

Show that the mechanism is equivalent to

$$A \underset{\longleftarrow}{\overset{k_{eff}, \ k_{eff}'}{\longrightarrow}} C$$

under specified circumstances.

Sol.:

The rate equations are

$$\frac{d[A]}{dt} = -k_a[A] + k_a'[B]$$

$$\frac{d[B]}{dt} = k_a[A] - k_a'[B] - k_b[B] + k_b'[C]$$

$$\frac{d[C]}{dt} = k_b[B] - k_b'[C]$$

These equations are a set of coupled differential equations and, though it is not immediately apparent, they do admit of an analytical general solution. However, we are looking for specific circumstances under which the mechanism reduces to the second form given. Since the reaction involves an intermediate, let us explore the result of applying the steady-state approximation to it. Then

$$\frac{d[B]}{dt} = k_a[A] - k_a'[B] - k_b[B] + k_b'[C] = 0$$

and $[B] = \dfrac{k_a[A] + k_b'[C]}{k_a' + k_b}$

Therefore, $\dfrac{d[A]}{dt} = -\dfrac{k_a k_b}{k_a' + k_b}[A] + \dfrac{k_a' k_b'}{k_a' + k_b}[C]$

This rate expression may be compared to that given in the text [Section 22.4] for the mechanism

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B \qquad \left[\text{here } A \underset{k_{eff}'}{\overset{k_{eff}}{\rightleftharpoons}} C \right]$$
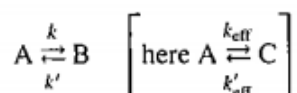
Hence, $k_{eff} = \dfrac{k_a k_b}{k_a' + k_b} \qquad k_{eff}' = \dfrac{k_a' k_b'}{k_a' + k_b}$

The solutions are $[A] = \left(\dfrac{k_{eff}' + k_{eff}e^{-(k_{eff}' + k_{eff})t}}{k_{eff}' + k_{eff}} \right) \times [A]_0 \ [22.23]$

and $[C] = [A]_0 - [A]$

Thus, the conditions under which the first mechanism given reduces to the second are the conditions under which the steady-state approximation holds, namely, when B can be treated as a steady-state intermediate .

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

Sol.:

Let the forward rates be written as

$$r_1 = k_1[A], \quad r_2 = k_2[B], \quad r_3 = k_3[C]$$

and the reverse rates as

$$r_1' = k_1'[B], \quad r_2' = k_2'[C], \quad r_3' = k_3'[D]$$

The net rates are then

$$R_1 = k_1[A] - k_1'[B], \quad R_2 = k_2[B] - k_2'[C], \quad R_3 = k_3[C] - k_3'[D]$$

But $[A] = [A]_0$ and $[D] = 0$, so that the steady-state equations for the net rates of the individual steps are

$$k_1[A]_0 - k_1'[B] = k_2[B] - k_2'[C] = k_3[C]$$

From the second of these equations we find

$$[C] = \frac{k_2[B]}{k_2' + k_3}$$

After inserting this expression for [C] into the first of the steady-state equations we obtain

$$[B] = \frac{k_1[A]_0 + k_2'[C]}{k_1' + k_2} = \frac{k_1[A]_0 + k_2'\left((k_2[B])/(k_2' + k_3)\right)}{k_1' + k_2}$$

which yields, upon isolating [B],

$$[B] = [A]_0 \times \frac{k_1}{k_1' + k_2 - \left(k_2 k_2'/(k_2' + k_3)\right)}$$

Thus, at the steady state

$$R_1 = R_2 = R_3 = [A]_0 k_1 \times \left(1 - \frac{k_1}{k'_1 + k_2 - \left(\frac{k_2 k'_2}{k'_2 + k_3}\right)} \right) = \boxed{\frac{k_1 k_2 k_3 [A]_0}{k'_1 k'_2 + k'_1 k_3 + k_2 k_3}}$$
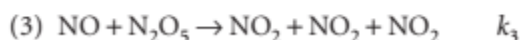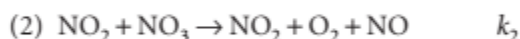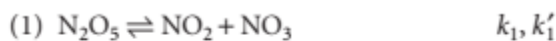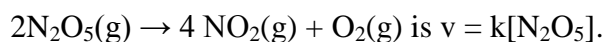
COMMENT. At steady state, not only are the net rates of reactions 1, 2, and 3 steady, but so are the concentrations [B] and [C]. That is,

$$\frac{d[B]}{dt} = k_1[A]_0 - (k'_1 + k_2)[B] + k'_2[C] \approx 0$$

and $\dfrac{d[C]}{dt} = k_2[B] - (k'_2 + k_3)[C] \approx 0$

In fact, another approach to solving the problem is to solve these equations for [B] and [C].

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

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

(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

Sol.:

The intermediates are NO and NO_3 and we apply the steady-state approximation to each of their concentrations

$$k_2\,[NO_2]\,[NO_3] - k_3\,[NO]\,[N_2O_5] = 0$$

$$k_1\,[N_2O_5] - k'_1\,[NO_2]\,[NO_3] - k_2\,[NO_2]\,[NO_3] = 0$$

$$\text{Rate} = -\frac{1}{2}\frac{d\,[N_2O_5]}{dt}$$

$$\frac{d\,[N_2O_5]}{dt} = -k_1\,[N_2O_5] + k'_1\,[NO_2][NO_3] - k_3[NO][N_2O_5]$$

From the steady-state equations

$$k_3 [NO][N_2O_5] = k_2 [NO_2][NO_3]$$

$$[NO_2][NO_3] = \frac{k_1 [N_2O_5]}{k_1' + k_2}$$

Substituting,

$$\frac{d [N_2O_5]}{dt} = -k_1 [N_2O_5] + \frac{k_1' k_1}{k_1' + k_2} [N_2O_5] - \frac{k_2 k_1}{k_1' + k_2} [N_2O_5] = -\frac{2k_1 k_2}{k_1' + k_2} [N_2O_5]$$

$$\text{Rate} = \frac{k_1 k_2}{k_1' + k_2} [N_2O_5] = k [N_2O_5]$$

Q.4 Consider the acid-catalysed reaction

$$(1) \quad HA + H^+ \rightleftharpoons HAH^+ \qquad\qquad k_1 k_1', \text{ both fast}$$
$$(2) \quad HAH^+ + B \rightarrow BH^+ + AH \qquad k_2, \text{ slow}$$
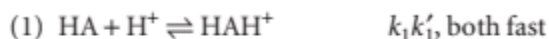
Deduce the rate law and show that it can be made independent of the specific term $[H^+]$.

Sol.:

The rate of production of the product is

$$\frac{d [BH^+]}{dt} = k_2 [HAH^+][B]$$

HAH^+ is an intermediate involved in a rapid pre-equilibrium

$$\frac{[HAH^+]}{[HA][H^+]} = \frac{k_1}{k_1'} \text{ so } [HAH^+] = \frac{k_1 [HA][H^+]}{k_1'}$$

and $\dfrac{d [BH^+]}{dt} = \boxed{\dfrac{k_1 k_2}{k_1'} [HA][H^+][B]}$

This rate law can be made independent of $[H^+]$ if the source of H^+ is the acid HA, for then H^+ is given by another equilibrium

$$\frac{[H^+][A^-]}{[HA]} = K_a = \frac{[H^+]^2}{[HA]} \text{ so } [H^+] = (K_a[HA])^{1/2}$$

and $\dfrac{d[BH^+]}{dt} = \boxed{\dfrac{k_1 k_2 K_a^{1/2}}{k_1'} [HA]^{3/2}[B]}$

Q.5 The half-life period of a first-order decomposition of $N_2O_5(g)$ is expressed as

$t_{1/2} = -30.3 + \dfrac{12581.78}{T}$ 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.

Sol.:

For a first order reaction, $t_{y_2} = \dfrac{0.693}{k_{obs}}$

The reaction is $2N_2O_5 \rightarrow 4NO_2 + O_2$

So, rate $= -\dfrac{1}{2} \dfrac{d[N_2O_5]}{dt} = k[N_2O_5]$

$-\dfrac{d[N_2O_5]}{dt} = 2k[N_2O_5] = k_{obs} = [N_2O_5]$

Here $k_{obs} = 2k$ where $k =$ rate constant

$t_{y_2} = \dfrac{0.693}{A e^{-E/RT}} = \dfrac{0.693}{A} e^{-E/RT}$

Expressing t in secs and A in sec^{-1} and taking logarithm, we have

$\therefore \ln t_{y_2} = \ln \dfrac{0.693}{A} + \dfrac{E}{RT}$

Compairing the equation with the given expression, we have

$$\ln \frac{0.693}{A} = -30.3$$

i.e. $A = 9.997 \times 10^{12}$ and $\frac{E}{R} = 12581.78$

i.e. $E = 12581.78 \times 1.987 \, cal \, mol^{-1} = 25 \, k \, cal \, mol^{-1}$

As time is expressed in sec, frequency factor $= 9.997 \times 10^{12} sec^{-1}$; the unit is same as that of the rate constant.

So, rate constant,

$$K_{obs} = A \, e^{-E/RT} = (9.997 \times 10^{12} sec^{-1}) \, e^{-\frac{25000 \, cal \, mol^{-1}}{(1.987 \, cal \, mol^{-1} K^{-1})(300K)}}$$
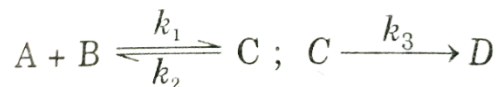
$$= 6.108 \times 10^{-6} sec^{-1}$$

$$t_\theta = \frac{1}{K_{obs}} \ln \frac{1}{1-\theta};$$

$$\ln \frac{1}{1-\theta} = K_{obs} \, t_\theta = (6.108 \times 10^{-6} sec^{-1}) \times (3600 \, sec)$$

$$= 0.022$$

$$\therefore \theta = 0.0217$$

So, 0.0217 fraction of N_2O_5 decomposes at $27°c$ at the end of 1 hr.

Q.6 For the mechanism

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

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

Sol.:

Applying steady-state approximation,

$$\frac{d[c]}{dt} = k_1[A][B] - k_2[c] - k_3[c] = 0 ;$$

$$\therefore [c] = \frac{k_1[A][B]}{k_2 + k_3}$$

Rate of the reaction $= k_3[c] = \frac{k_1 k_3}{k_2 + k_3}[A][B].$

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?

Sol.:

The maximum velocity is $k_b[E]_0$ and the velocity in general is

$$v = k[E]_0 = \frac{k_b[S][E]_0}{K_M + [S]} \quad \text{so } v_{max} = k_b[E]_0 = \frac{K_M + [S]}{[S]}v$$

$$v_{max} = \frac{(0.042 + 0.890)\ \text{mol dm}^{-3}}{0.890\ \text{mol dm}^{-3}}(2.45 \times 10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}) = \boxed{2.57 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}$$

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
v/(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.

Sol.: We draw up the following table:

[S]]/(mmol dm^{-3})	(v)/(mmol dm^{-3} s^{-1})	1/[S]	1/(v)
0.334	0.152	2.994012	6.578947
0.45	0.201	2.222222	4.975124
0.667	0.269	1.49925	3.717472
1	0.417	1	2.398082
1.33	0.505	0.75188	1.980198
1.67	0.667	0.598802	1.49925

INTERCEPT   -0.1673

1/(v)

1/[S]
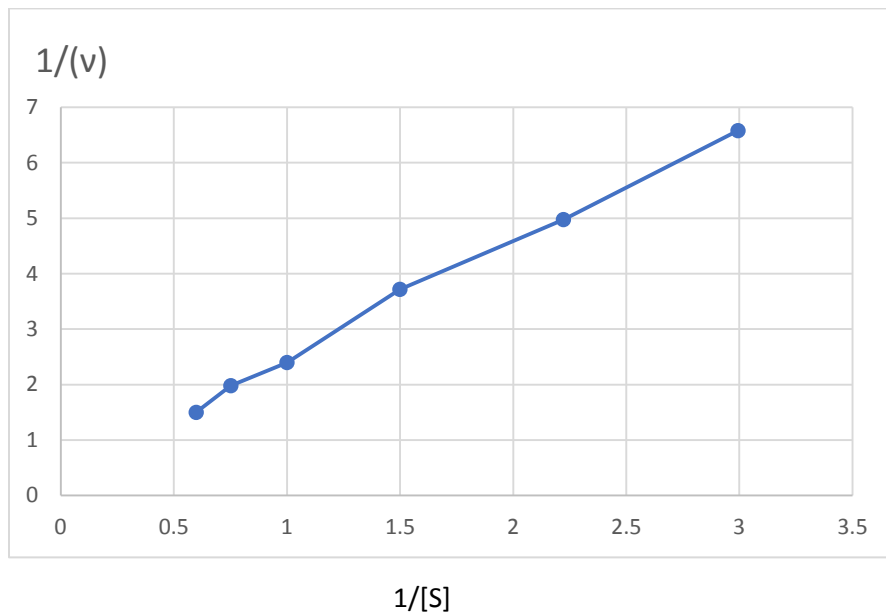
Then we plot Lineweaver-Burk plot using the data. It should gives a straight line with a slope of $\frac{K_M}{v_{max}}$, a y-intercept at $\frac{1}{v_{max}}$ and x-intercept at $-\frac{1}{K_M}$. As we get negative intercept (-0.1673) at x-axis. So,

$$-\frac{1}{K_M} = -0.1673$$

$$K_M = \frac{1}{0.1673} = 5.988 \text{ mmol dm}^{-3}$$

And

$$\text{Slope} = \frac{K_M}{v_{max}} = 0.48$$

$$\frac{5.988}{0.48} = v_{max}$$

$$v_{max} = 12.475 \text{ mmol dm}^{-3} \text{ s}^{-1}$$