CHEMICAL KINETICS

L1 1) Stoichiometric Coefficient (ν) is -ve for reactants and positive for products.

2) For time-independent stoichiometry,

$$aA + bB + \dots \rightarrow \dots yY + zZ$$

$$\frac{n_A - n_A^\circ}{-a} = \frac{n_B - n_B^\circ}{-b} = \dots = \frac{n_Y - n_Y^\circ}{y} = \frac{n_Z - n_Z^\circ}{z}$$

3) Extent of the reaction, $\xi = \frac{n - n^\circ}{\nu}$.

4) Rate of reaction : $= \frac{1}{V}\frac{d\xi}{dt} = \frac{\dot{\xi}}{V}$

$$= \frac{1}{\nu_i}\frac{d[P]}{dt}$$

(if volume does not change)

L2 1) When volume is not constant,

$$\text{rate} = \frac{1}{\nu_i}\frac{dc_i}{dt} + \frac{c_i}{\nu_i V}\frac{dV}{dt}.$$

2) <u>zero order</u> : $aA \rightarrow P \Rightarrow [A] = -akt + [A_0]$

$$t_{1/2} = \frac{[A_0]}{2ak}$$

3) <u>First order</u> : $[A] = [A_0]e^{-akt}$; $t_{1/2} = \frac{\ln 2}{ak}$

4) <u>Second order</u> : $\frac{1}{[A]} = akt + \frac{1}{[A_0]}$; $\frac{1}{ak[A_0]}$

5) For n^{th} order reaction :

$$\frac{1}{[A]^{n-1}} = \frac{1}{[A_0]^{n-1}} + (n-1)kt$$

where $n = \frac{1}{2}, \frac{3}{2}, 2, 3 \ldots$ and $n \neq 1$.

$$t_{1/2} = \frac{2^{(n-1)} - 1}{ak(n-1)[A_0]^{(n-1)}}$$

L3 1) ⇒ <u>First order opposite reactions :</u>

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$$

(a) Rate of reaction = Rate of consumption of A = R formed

(b) Rate of frwd reaction $v_1 = k_1[A]$

" " bkwd " $v_{-1} = k_{-1}[P]$

Total rate of reaction $= v_1 - v_{-1}$

(c) $[P] = [A_0] - [A]$

(d) $$\frac{d[A]}{dt} = -k_1[A] + k_{-1}([A_0] - [A])$$

$$[A_{eq}] = \frac{k_{-1}}{k_1 + k_{-1}} [A_0]$$

When $\frac{[P]}{[A]} = K = \frac{k_1}{k_{-1}}$, the reaction is at equilibrium and rate is zero.

Integrated rate equation :

$$\frac{d[A]}{dt} = -(k_1 + k_{-1})([A] - [A]_{eq})$$

gives

$$\rightarrow \ln([A] - [A]_{eq}) = -(k_1 + k_{-1})t + \ln[P]_{eq}$$

$$\rightarrow \ln \frac{[P]_{eq} - [P]}{[P_{eq}]} = -(k_1 + k_{-1})t$$

$$\rightarrow [A] = \frac{k_{-1}[A]_0}{(k_1 + k_{-1})}\left(1 + \left(\frac{k_1}{k_{-1}}\right) e^{-(k_1 + k_{-1})t}\right)$$

$$\rightarrow [P] = \frac{k_1[A]_0}{(k_1 + k_{-1})}\left(1 - e^{-(k_1 + k_{-1})t}\right)$$

Consecutive first order reactions (Irreversible) :

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

(constant volume

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P \quad \text{(constant volume)}$$

(L4) 1) ⇒

(a) $[A] = [A_0]\, e^{-k_1 t}$

(b) $[I] = [A]_0 \dfrac{k_1}{(k_2 - k_1)} \left(e^{-k_1 t} - e^{-k_2 t}\right)$

(c) $[P] = [A_0] \left\{ 1 - \dfrac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right\}$

(d) At all times, $[A] + [I] + [P] = [A_0]$

(e) $[I]_{max.} = [A]_0 \left(\dfrac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)}$

at time $t_{max.} = \dfrac{\ln(k_2/k_1)}{(k_2 - k_1)}$

2) When $\dfrac{k_1}{k_2} << 1$, I acts as an unstable intermediate and $\dfrac{d[I]}{dt} \approx 0$

$$\Rightarrow k_1 [A] - k_2 [I] = 0$$

$$\Rightarrow [I]_{ss} = \frac{k_1}{k_2} A = \frac{k_1}{k_2} [A_0] e^{-k_1 t}$$

3) When the concentrations of intermediates (I) remain small and hardly change during most of the course of the reaction, then we can write $\dfrac{d[I]}{dt} \approx 0$ (The steady state approximation

L4 1) ⇒ **First order parallel reactions :**

$$A \xrightarrow{k_1} P$$
$$A \xrightarrow{k_2} Q$$

(a) $[A] = [A]_0 e^{-(k_1+k_2)t}$

(b) $[P] = \dfrac{k_1 [A_0]_0}{(k_1+k_2)} \left(1 - e^{-(k_1+k_2)t}\right)$

(c) $\dfrac{[P]}{[Q]} = \dfrac{k_1}{k_2}$

This means the composite reaction involves a pre-equilibria.

2) ⇒ **Pre-equilibria**

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P$$

Case I : $k_{-1} >> k_2$.

$$K = \frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]}$$

$$\frac{d[P]}{dt} = k_2 [I] = \frac{k_2 k_1}{k_{-1}} [A][B]$$

∴ 2nd order.

Case II: What if "I" to "P" conversion is not too slow

$$\frac{d[P]}{dt} = k_2[I]$$

$$\frac{d[I]}{dt} = k_1[A][B] - k_{-1}[I] - k_2[I]$$

$$SSA \Rightarrow [I] \approx \frac{k_1[A][B]}{k_2 + k_{-1}}$$

~~2nd order~~

$$\Rightarrow \frac{d[P]}{dt} = k_2[I] = \frac{k_1 k_2}{k_2 + k_{-1}}[A][B].$$

$\therefore$ 2nd order.

(5) 1) $k = A e^{-E_a/RT} = pZ e^{-E_a/RT}$

A: Pre-exponential factor or frequency factor

p: Orientation factor

Z: collision frequency

2) A → Number of times the reactants approach the activation barrier per unit time.

3) $e^{-E_a/RT}$ → represents the fraction of molecules th enough energy to make it over the activation barrier on a given approach.

4) $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

5) Catalyst does not modify the standard Gibb's free energy change for the reaction : $\Delta G^\circ = -RT\ln K$

6) $k_{catalyzed} = k_{uncatalyzed}\, e^{-\Delta E_a/RT}$

7) Degree of inhibition : $\varepsilon_i = \frac{v_0 - v}{v_0} = 1 - \frac{v}{v_0}$

($v_0 \rightarrow$ rate without inhibitor
$v \rightarrow$ rate with inhibitor)

L6 1) Step 1 : $Cl + O_3 \rightarrow ClO + O_2$ (with E_a^1) [Catalytic destruc of ozone]

Step 2 : $ClO + O \rightarrow Cl + O_2$ (with E_a^2)

$O_3 + O \longrightarrow 2O_2$

2) Catalytic converter :

$2NO(g) + 2CO(g) \xrightarrow{\text{Catalysts (Pt, Pd or Rh)}} N_2 + 2CO_2$

3) Hydrogenation of double bonds is a four-step process
(a) Adsorption (b) Diffusion (c) Reaction (d) Desorpti

4) Sucrase enzyme catalyzes breaking up of sucrose (table sugar) into glucose and fructose within the during digestion.

5) Unimolecular Reaction Mechanism : The Lindemann-Hinshelwood mechanism

Step 1 : $A + A \xrightarrow{k_1} A^* + A$ $\quad \frac{d[A^*]}{dt} = k_1[A]^2$

Step 2a : $A + A^* \xrightarrow{k_2} A + A$ $\quad \frac{d[A^*]}{dt} = -k_2[A][A^*]$

Step 2b : $A^* \xrightarrow{k_3} P$ $\quad \frac{d[A^*]}{dt} = -k_3[A^*]$

Case 1 : If step 2b is slow enough, it is overall 1st order kinetics i.e.

$$\frac{d[P]}{dt} = k[A] = \frac{k_1 k_3}{k_2}[A]$$

Case 2 : When [A] is reduced to low pressure i.e $k_2[A] << k_3$

$$\frac{d[P]}{dt} = k_1[A]^2$$ i.e. second order.

Full rate law : $\frac{d[P]}{dt} = k[A]$ where

$$\frac{1}{k} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1[A]}$$