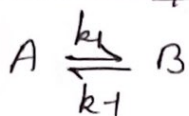


## Reaction Mechanism

(7)

### 1. Opposing reaction/reversible reaction



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

$$\text{or } \frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

If the initial concentration of A is  $[A]_0$  and no B is present in the reaction mixture, then at all times

$$[A] + [B] = [A]_0$$

$$\text{Therefore } \frac{d[A]}{dt} = -k_1[A] + k_{-1}([A]_0 - [A])$$

$$\frac{d[A]}{dt} = -(k_1 + k_{-1})[A] + k_{-1}[A]_0 \quad \text{--- (1)}$$

The solution of this first order differential eq<sup>n</sup> is

$$[A] = \frac{k_{-1}[A]_0}{k_1 + k_{-1}}$$

$$[A] = \frac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}} [A]_0 \quad \text{--- (2)}$$

At  $t \rightarrow \infty$ , the exponential term in eq<sup>n</sup> (2) is zero, and the concentrations reach their equilibrium values.

$$[A]_{eq} = \frac{k_{-1}[A]_0}{k_1 + k_{-1}}$$

$$[B]_{eq} = [A]_0 - [A]_{eq}$$

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

$$= \frac{k_1}{k_1 + k_{-1}} [A]_0$$

Equilibrium constant

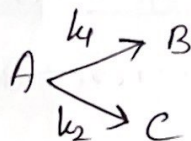
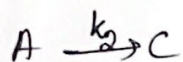
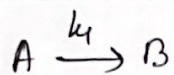
$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}}$$

⊗ At equilibrium the forward and the backward rates must be the same

$$k_1[A]_{eq} = k_{-1}[B]_{eq}$$

## 2. Parallel reactions

(8)



$$\frac{d[A]}{dt} = -k_1[A] - k_2[A] \quad \text{--- (1)}$$

$$\frac{d[B]}{dt} = k_1[A] \quad \text{--- (2)}$$

$$\frac{d[C]}{dt} = k_2[A] \quad \text{--- (3)}$$

The solution of (1) is straight forward

$$[A]_t = [A]_0 \exp \{-(k_1+k_2)t\}$$

Substituting this in eqn (2)

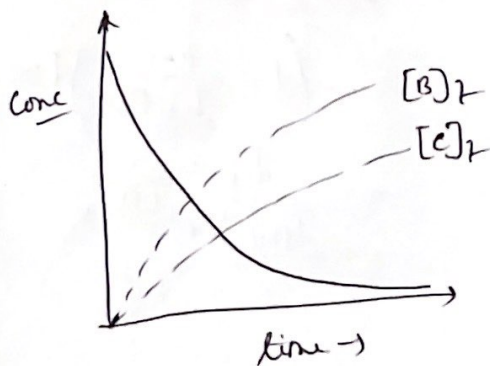
$$\frac{d[B]}{dt} = k_1[A]_0 e^{-(k_1+k_2)t}$$

Integrating  $\int_{[B]_0}^{[B]_t} d[B] = k_1[A]_0 \int_0^t e^{-(k_1+k_2)t} dt$

$$\text{or } [B]_t = \frac{k_1[A]_0}{(k_1+k_2)} \left[ -e^{-(k_1+k_2)t} \right]_0^t$$

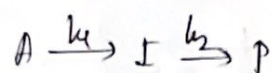
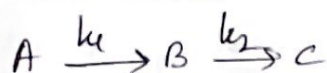
$$\text{or } [B]_t = \frac{k_1[A]_0}{k_1+k_2} \left[ 1 - e^{-(k_1+k_2)t} \right] \quad [B]_0 = 0$$

$$\text{Similarly } [C]_t = \frac{k_2[A]_0}{k_1+k_2} \left[ 1 - e^{-(k_1+k_2)t} \right] \quad [C]_0 = 0$$



### 3. Consecutive reaction

(9)



$$\frac{d[A]}{dt} = -k_1[A] \quad \text{--- (1)}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \text{--- (2)}$$

$$\frac{d[C]}{dt} = k_2[B] \quad \text{--- (3)}$$

Steady-State-Approximation  
(SSA)

Initial concentration  $[A]_0$ ,  $[B]_0 = [C]_0 = 0$

from eq<sup>n</sup> (1)  $[A]_t = [A]_0 e^{-k_1 t} \quad \text{--- (4)}$

Putting this in eq<sup>n</sup> (2) we obtain,

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [B]$$

The solution to this differential eq<sup>n</sup> provides

$$[B]_t = \frac{k_1}{k_2 - k_1} [A]_0 [e^{-k_1 t} - e^{-k_2 t}] \quad \text{--- (5)}$$

Finally, from the mass balance,  $[A]_0 = [A] + [B] + [C]$

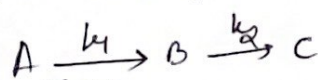
$$[C] = [A]_0 - [B] - [A]$$

$$= [A]_0 - \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] - [A]_0 e^{-k_1 t}$$

$$[C] = [A]_0 \left[ 1 - \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) - e^{-k_1 t} \right]$$

--- (6)

Case I:  $k_1 \gg k_2$



A gets converted  
very quickly to B

$$[B]_t \approx \frac{k_1}{-k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$$

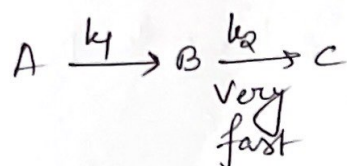
$$\approx (e^{-k_2 t} - e^{-k_1 t}) [A]_0$$

$$\approx e^{-k_2 t} [A]_0$$

The appearance of B will be dominated.



case II:  $k_2 \gg k_1$



$$[B]_t = \frac{k_1}{k_2} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

$$\approx \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$$

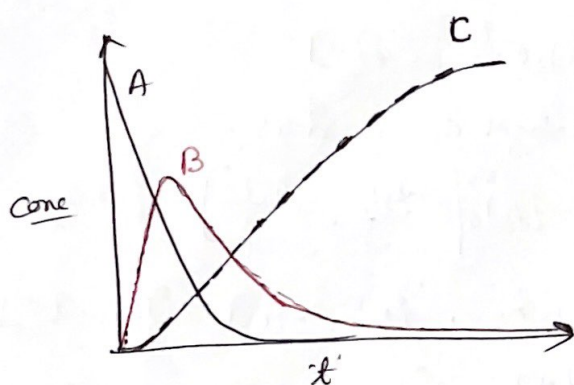
$$\approx k' [A]_0 e^{-k_1 t}$$

— (7)

$$[B]_t \approx \text{const.} \left( \text{unity} - \text{zero} \right)_{t \rightarrow 0}$$

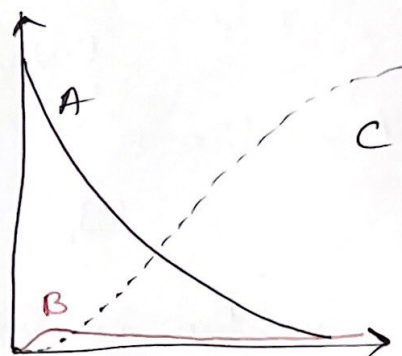
$$[B]_t \approx \frac{k_1}{k_2} [A]_0 \text{ for small } t$$

$$[B]_t \approx \frac{k_1}{k_2} [A]_0 e^{-k_1 t} \text{ for large } t$$



$$k_1 \gg k_2$$

$$k_1 = 10 k_2$$



$$k_2 \gg k_1$$

$$k_2 = 10 k_1$$

"Steady-state Approximation"

From eq (7)  $[B] \approx \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$

or  $[B] \approx \frac{k_1}{k_2} [A]$

or  $k_2 [B] \approx k_1 [A]$

Putting this condition in eq (2) we get

$$\boxed{\frac{d[B]}{dt} = 0}$$

Induction period  $\rightarrow$  the time it takes to produce  $[B]_t$ .

$[B]$  can be calculated by using  $\frac{d[B]}{dt} = 0$