

Reaction order and reaction mechanism

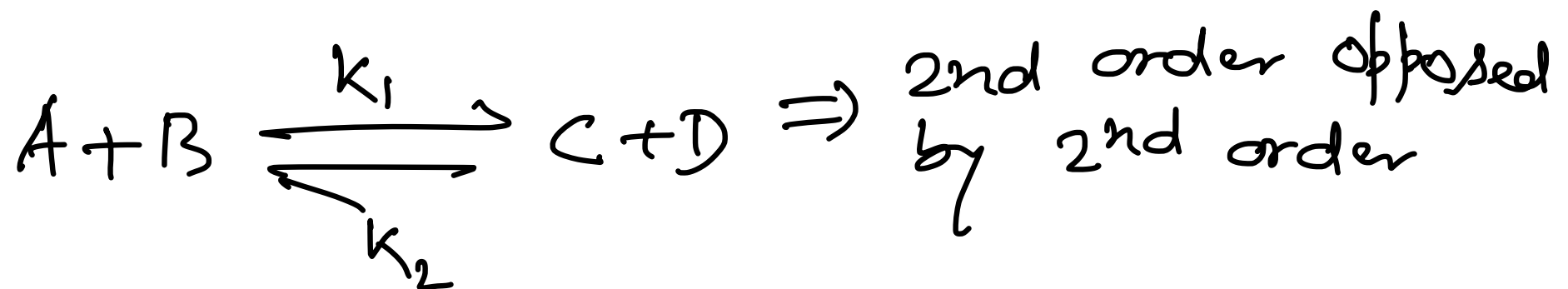
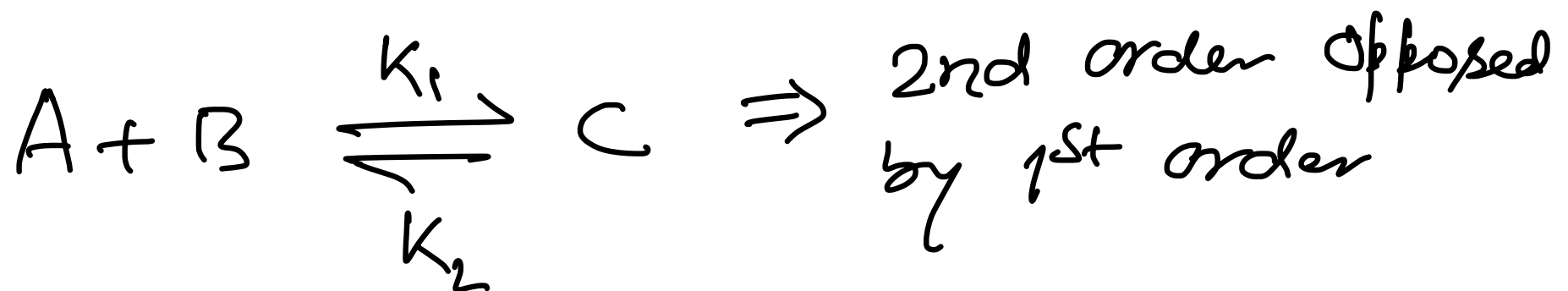
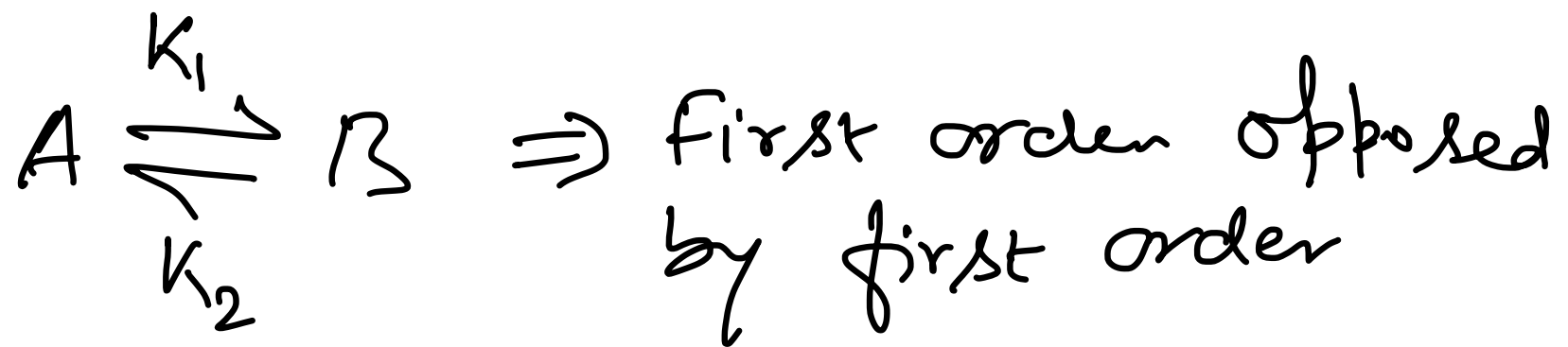
- ① Opposed elementary rxn or reversible "
- ② Side or concurrent elementary rxn
- ③ Consecutive or sequential rxn.

Derive rate law & integrated rate law for such elementary rxns

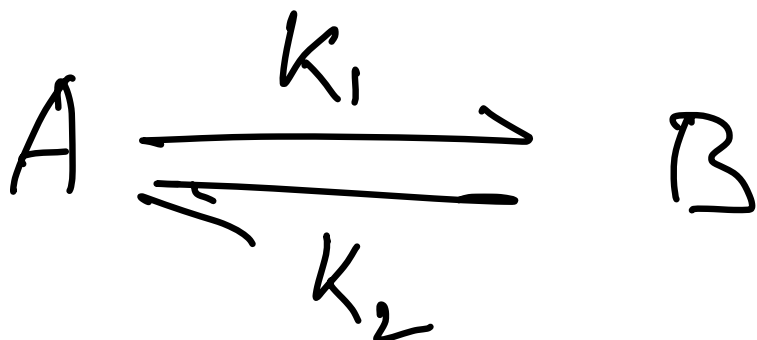
- ① Opposed or reversible elementary rxn.



Elementary \Rightarrow molecularity
= order



① First order opposed by first order.



rate of rxn = rate of forward rxn - rate of backward rxn.

$$\Rightarrow -\frac{d[A]}{dt} = k_1[A] - k_2[B]$$

If x = extent of rxn divided by volume, at any time t

then,

$$[A] = [A]_0 - x$$

$$[B] = x$$

⊗ We assume no B was present at the beginning.

$$\Rightarrow -\frac{d}{dt} \{ [A]_0 - x \} = k_1([A]_0 - x) - k_2x$$

$$\Rightarrow \boxed{\frac{dx}{dt} = k_1[A]_0 - (k_1 + k_2)x}$$

At equilibrium,

rate of forward rxn = rate of backward rxn

$$\Rightarrow k_1([A]_0 - x_{eq}) = k_2 x_{eq}$$

x_{eq} = extent of rxn divided by volume at equilibrium

$$\Rightarrow k_2 = \frac{k_1 [A]_0}{x_{eq}} - k_1$$

$$\text{or } k_1 + k_2 = \frac{k_1 [A]_0}{x_{eq}}$$

$$\frac{dx}{dt} = k_1([A]_0 - x) - \left(\frac{k_1 [A]_0}{x_{eq}} - k_1 \right) \cdot x$$

$$\frac{dx}{dt} = k_1 [A]_0 \left(1 - \frac{x}{x_{eq}} \right)$$

$$\text{or, } \frac{dx}{dt} = \frac{k_1 [A]_0}{x_{eq}} (x_{eq} - x)$$

$$\Rightarrow \int \frac{dx}{x_{eq} - x} = \frac{k_1 [A]_0}{x_{eq}} \int dt$$

$$\Rightarrow -\ln(x_{eq} - x) = \frac{k_1 [A]_0}{x_{eq}} t + C$$

$$\text{at } t=0, x=0$$

$$\Rightarrow -\ln x_{eq} = C$$

$$\Rightarrow \ln \frac{x_{eq}}{x_{eq} - x} = \frac{k_1 [A]_0}{x_{eq}} \cdot t$$

$$\Rightarrow \frac{x_{eq} - x}{x_{eq}} = e^{-\frac{k_1 [A]_0 \cdot t}{x_{eq}}}$$

$$\Rightarrow x = x_{eq} \left[1 - e^{-\frac{k_1 [A]_0 t}{x_{eq}}} \right]$$

Earlier we got

$$k_1 + k_2 = \frac{k_1 [A]_0}{x_{eq}}$$

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

→ Integrated rate law of a reversible rxn $A \rightleftharpoons B$

$$[A] = [A]_0 - x$$

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

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

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

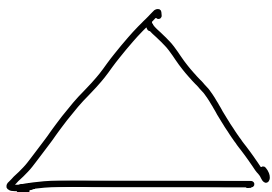
$$\boxed{[A] = [A]_0 \cdot \frac{k_1}{k_1 + k_2} \left[\frac{k_2}{k_1} + e^{-(k_1 + k_2)t} \right]}$$

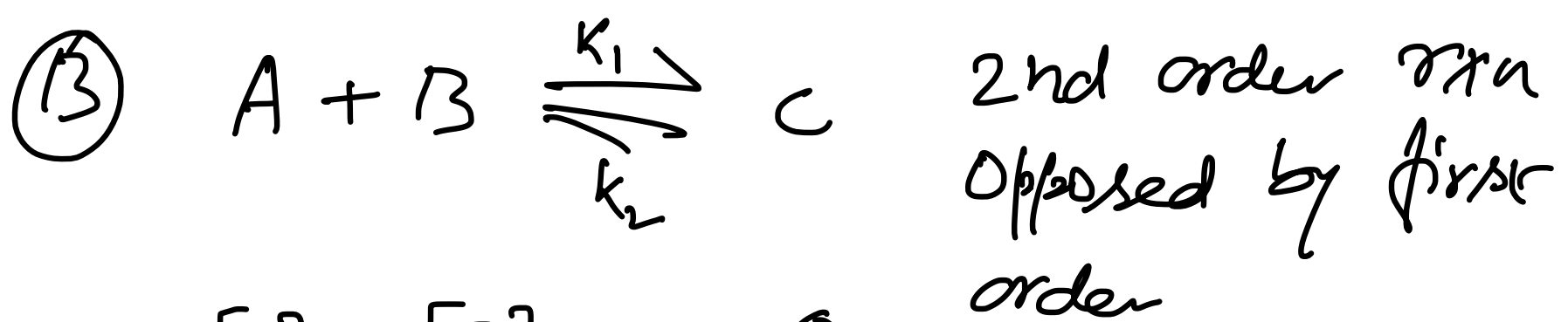
$$\therefore \frac{k_2}{k_1} = K_{eq}$$

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

Example:

isomerization of cyclopropane into propene





$t=0$ $[A]_0$ $[B]_0$ 0

$t=t$ $[A]_0 - x$ $[B]_0 - x$ x

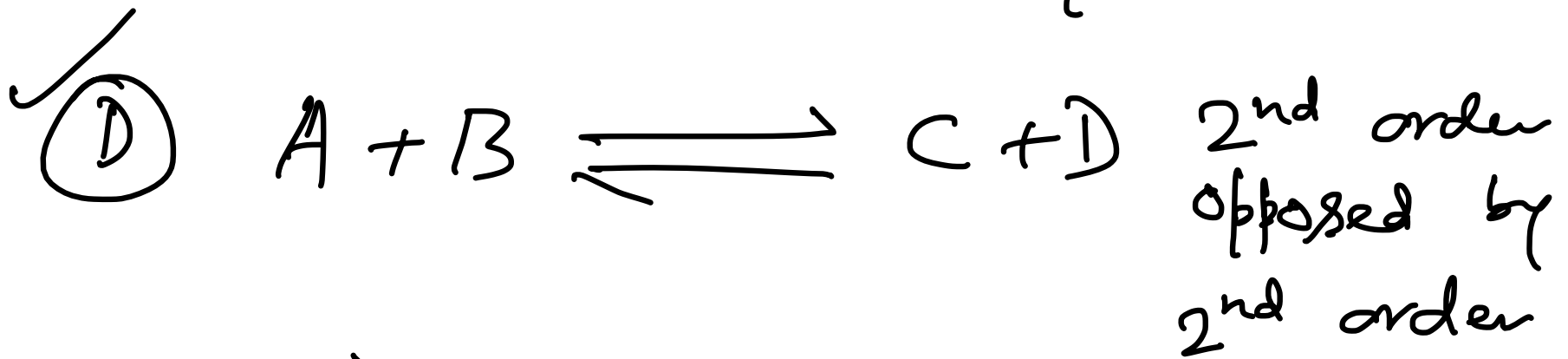
rate law, $\frac{dx}{dt} = k_1 ([A]_0 - x) ([B]_0 - x) - k_2 x$

∴

$$\ln \left[\frac{x_{eq} ([A]_0^2 - x x_{eq})}{[A]_0^2 (x_{eq} - x)} \right] = k_1 \frac{[A]_0^2 - x_{eq}^2}{x_{eq}} t$$

Example

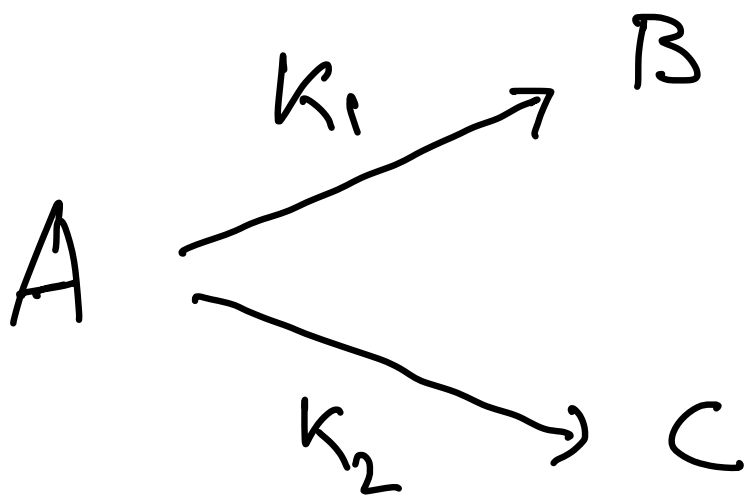




⋮

Try yourself, integrated rate for (C) & (D)

(2) Side or concurrent elementary rxn.



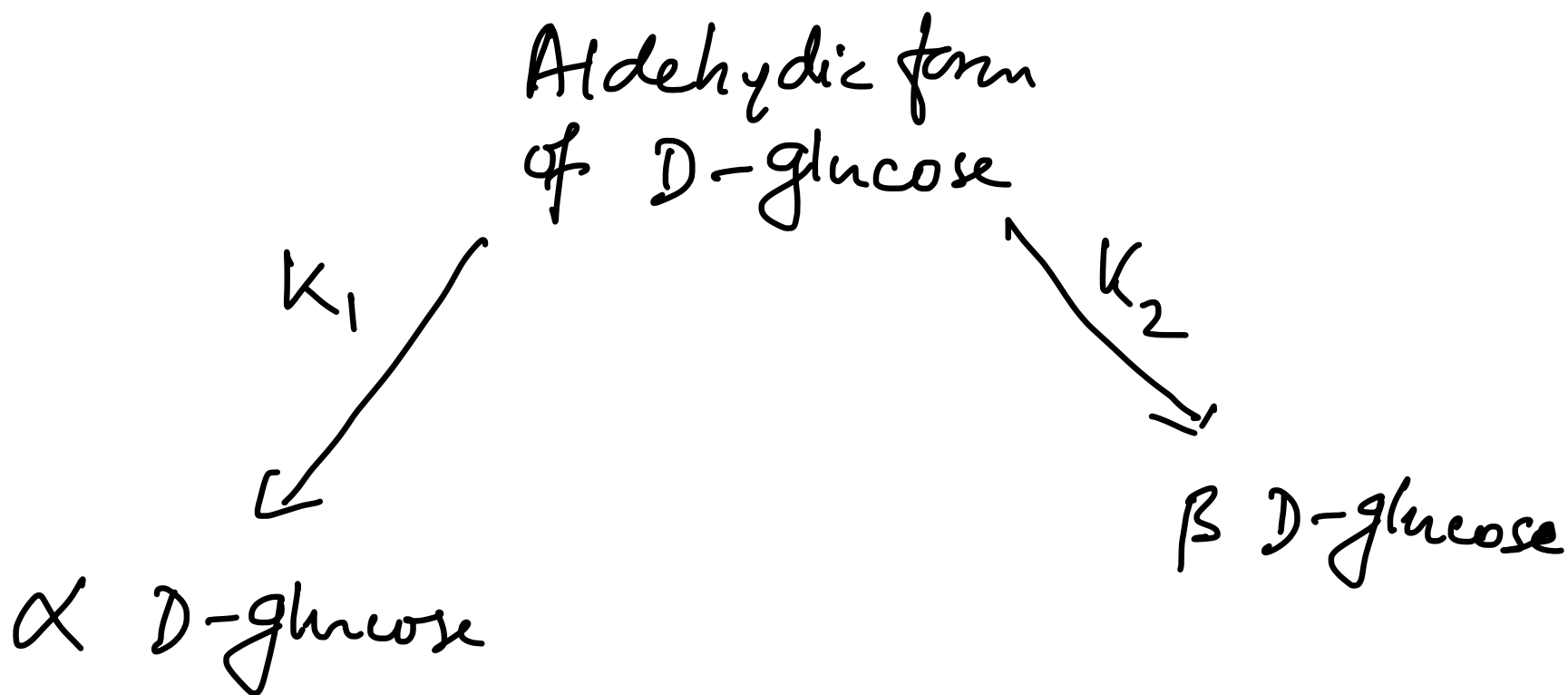
Rate of disappearance of A.

$$\Rightarrow -\frac{d[A]}{dt} = k_1[A] + k_2[A]$$
$$= (k_1 + k_2)[A]$$

⋮

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

Example:



③ consecutive or sequential rxn:



$$[A]_0 = [A] + [B] + [C] \text{ at any time } t$$

$\searrow \text{①}$

$$-\frac{d[A]}{dt} = k_1[A] \longrightarrow \text{②}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \longrightarrow \text{③}$$

$$\frac{d[C]}{dt} = k_2[B] \longrightarrow \text{④}$$

$$\text{From ①, } [A] = [A]_0 \cdot e^{-k_1 t} \longrightarrow \text{⑤}$$

$$\text{From ②, } \frac{d[B]}{dt} + k_2[B] = k_1[A]$$

$$\begin{aligned}\therefore \frac{d}{dt} \{ [B] \cdot e^{k_2 t} \} &= e^{k_2 t} \cdot \frac{d[B]}{dt} \\ &\quad + [B] \cdot k_2 \cdot e^{k_2 t} \\ &= e^{k_2 t} \left\{ \frac{d[B]}{dt} + k_2 [B] \right\}\end{aligned}$$

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

$$\therefore [A] = [A]_0 \cdot e^{-k_1 t}$$

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

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

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

$$\text{at } t=0 \quad [B]=0$$

$$\Rightarrow C = -\frac{k_1}{k_2 - k_1} \cdot [A]_0$$

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

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

$$\therefore [A]_0 = [A] + [B] + [C]$$

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

$$\begin{aligned} \Rightarrow [C] &= [A]_0 - [A]_0 \cdot e^{-k_1 t} \\ &\quad - \frac{k_1}{k_2 - k_1} [A]_0 \left(e^{-k_1 t} - e^{-k_2 t} \right) \end{aligned}$$

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

$$\Rightarrow [C] = \frac{[A]_0}{k_2 - k_1} \left[k_2 - k_1 - k_2 e^{-k_1 t} + \cancel{k_1 e^{-k_1 t}} - \cancel{k_1 e^{-k_1 t}} + k_1 \cdot e^{-k_2 t} \right]$$

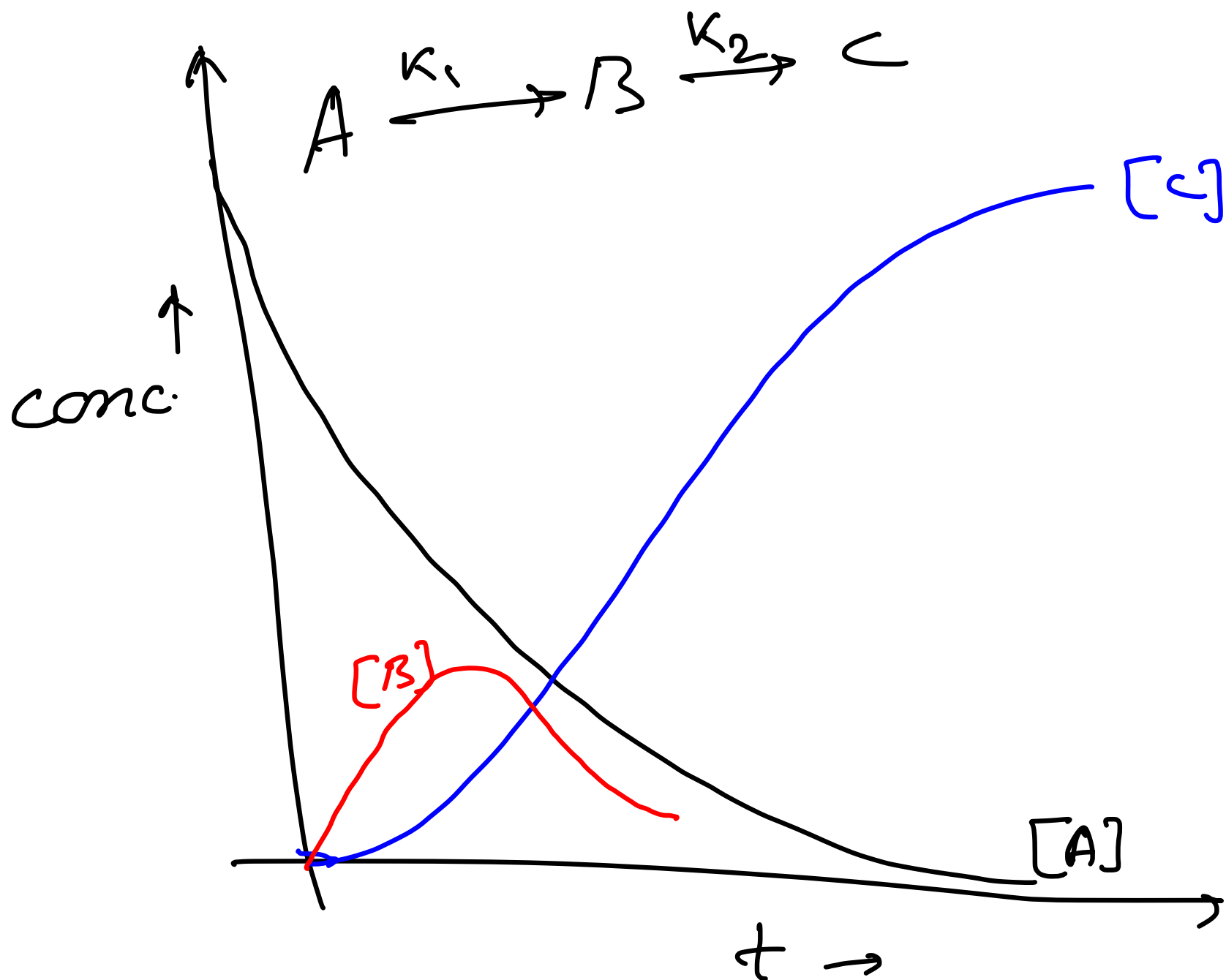
$$\Rightarrow [C] = [A]_0 \left[1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right]$$

Thus,

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

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

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



What would be the maximum conc. of B. i.e., $[B]_{\max} = ?$

$$\Rightarrow \frac{d[B]}{dt} = 0 \quad \& \quad \frac{d^2[B]}{dt} < 0$$

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

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

$$= 0$$

$$\Rightarrow \frac{k_1}{k_2} = e^{(k_1 - k_2)t_{\max}}$$

$$\Rightarrow \boxed{t_{\max} = \frac{1}{k_1 - k_2} \ln\left(\frac{k_1}{k_2}\right)}$$

$$\frac{d^2[B]}{dt^2} = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (k_1^2 e^{-k_1 t} - k_2^2 e^{-k_2 t})$$

$$\text{For } \frac{d^2[B]}{dt^2} < 0$$

$$\textcircled{1} \quad k_2 - k_1 < 0 \quad \& \quad k_1^2 e^{k_1 t} > k_2^2 e^{-k_2 t}$$



$$k_2 < k_1$$



$$k_1 > k_2$$

$$\Rightarrow k_1^2 e^{-k_1 t} > k_2^2 e^{-k_2 t}$$

True

$$\textcircled{\text{or}} \quad \textcircled{2} \quad k_2 - k_1 > 0 \quad \& \quad k_1^2 e^{-k_1 t} < k_2^2 e^{-k_2 t}$$



$$k_2 > k_1$$



$$k_1 < k_2 \Rightarrow k_1^2 e^{-k_1 t} < k_2^2 e^{-k_2 t}$$

$$\Rightarrow [B]_{\max} = [A]_0 \cdot \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t_{\max}} - e^{-k_2 t_{\max}} \right)$$

Simplify:

$$[B] = [A]_0 \cdot \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{k_1 - k_2}}$$

① Rate determining step

② Steady-state approximation.

Rate-determining Step:

Who is controlling $[C]$, k_1 or k_2 ?

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

Case 1: When $k_2 \gg k_1$

$$\Rightarrow e^{k_2 t} \gg e^{k_1 t}$$

$$\Rightarrow e^{-k_2 t} \ll e^{-k_1 t}$$

$$\Rightarrow k_2 \cdot e^{-k_1 t} \gg k_1 \cdot e^{-k_2 t}$$

$$\Rightarrow k_2 - k_1 \simeq k_2$$

$$\& \quad k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t} \simeq k_2 \cdot e^{-k_1 t}$$

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

$$\Rightarrow [C] \simeq [A]_0 (1 - e^{-k_1 t})$$

So, $[C]$ is controlled by k_1

i.e., rate constant of slowest step

$$\text{as } k_2 \gg k_1$$

Case 2: When $k_1 \gg k_2$

$$\Rightarrow e^{k_1 t} \gg e^{k_2 t}$$

$$\Rightarrow e^{-k_1 t} \ll e^{-k_2 t}$$

$$\Rightarrow k_1 e^{-k_2 t} \gg k_2 e^{-k_1 t}$$

$$\Rightarrow k_2 - k_1 \simeq -k_1$$

$$\& \quad k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \simeq -k_1 e^{-k_2 t}$$

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

$$\Rightarrow [C] = [A]_0 (1 - e^{k_2 t})$$

Again, $[C]$ is controlled by the rate constant of the slowest step as

$$k_1 \gg k_2$$

Thus the production of C depends upon the rate constant of the slowest step. \Rightarrow The slowest step is the rate-determining step.

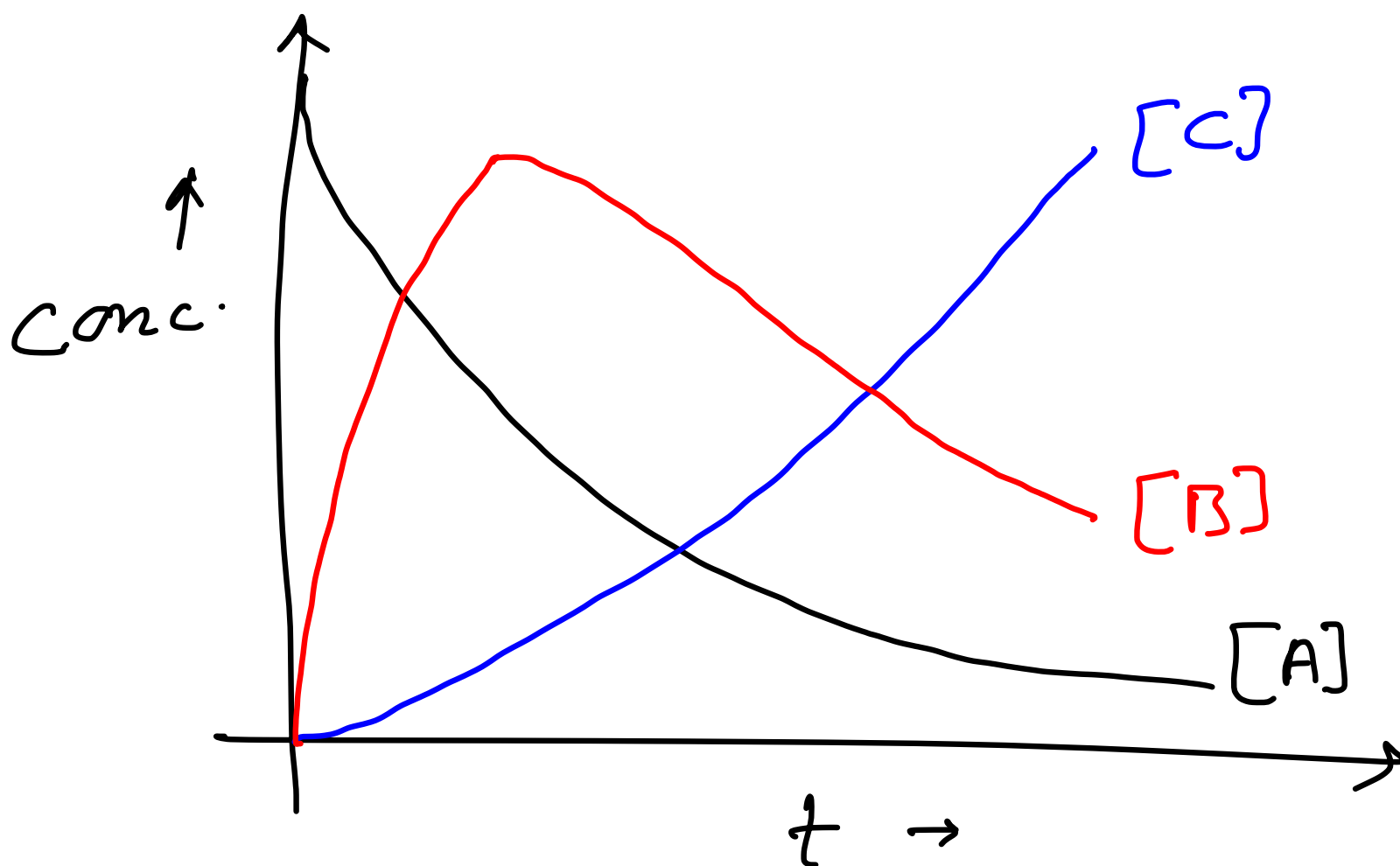
Steady-state approximation: \rightarrow

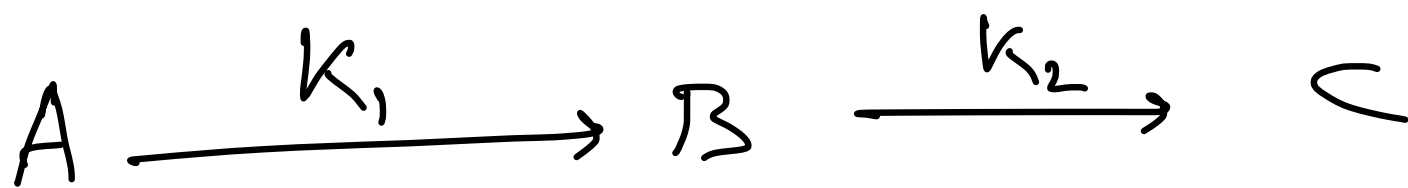


if $k_1 \gg k_2$

\Rightarrow Rate of formation of B is much larger than its decomposition

\Rightarrow B will accumulate in the reaction mixture.



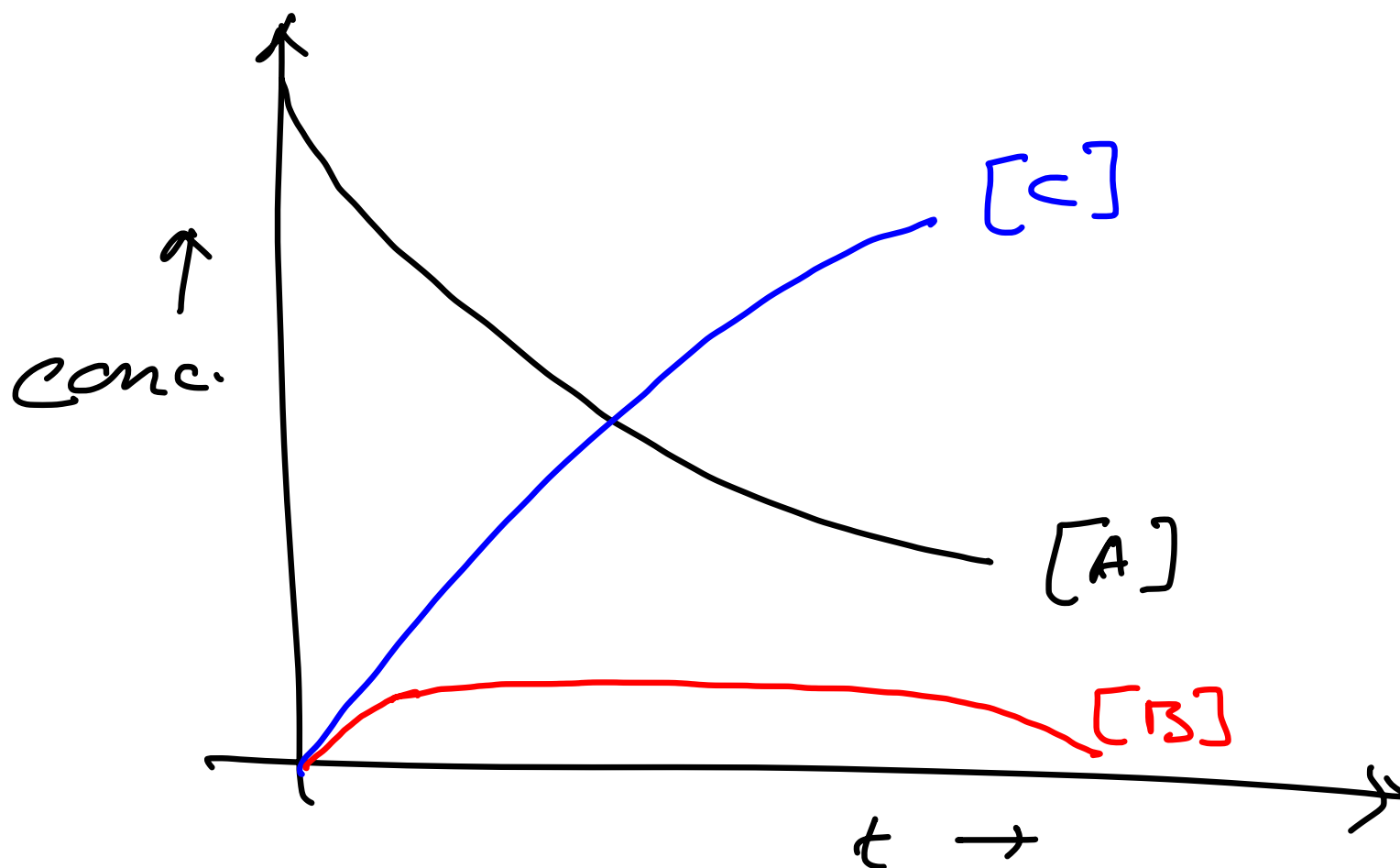


if $k_2 \gg k_1$

\Rightarrow Decomposition of B is much faster than its formation.

\Rightarrow As soon as B is formed, it is decomposed to C.

\Rightarrow B will not accumulate in rxn mixture.



Thus, if $k_2 \gg k_1$, $[B]$ is almost fixed for appreciable amount of time. \Rightarrow Steady-State approximation

$$\frac{d[B]}{dt} = 0 \quad ; \quad B \text{ is a reactive intermediate}$$