The simplest consecutive mechanism is

$$A \xrightarrow{k_1} X \xrightarrow{k_2} Z$$

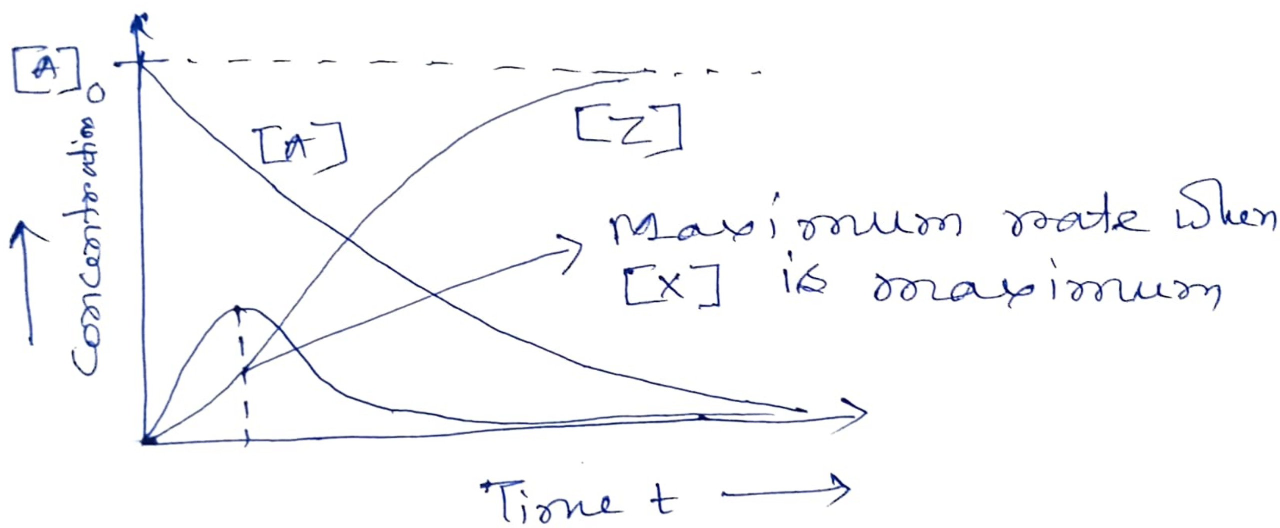
Concentrations of A, X and Z are given below

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

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

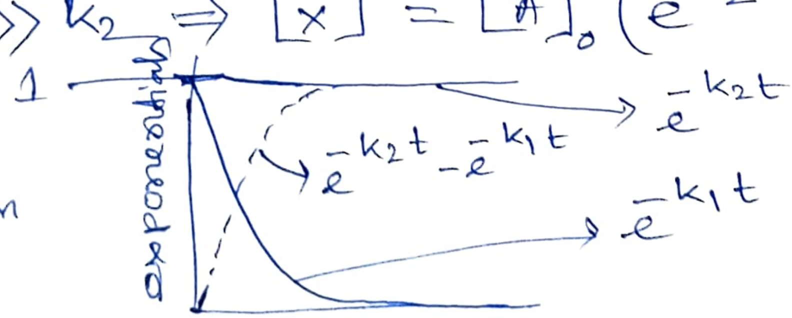
$$[Z] = \frac{[A]_0}{k_2 - k_1} \left[k_2 \left(1 - e^{-k_1 t} \right) - k_1 \left(1 - e^{-k_2 t} \right) \right]$$

$[A]_0$ is the initial concentration of the reactant A.



Limiting cases:

Case I: $k_1 \gg k_2 \Rightarrow [X] = [A]_0 \left(e^{-k_2 t} - e^{-k_1 t} \right)$



After induction period,

$[X] = [A]_0$

Case II: Steady state approximation:

$k_2 \gg k_1$. $A \xrightarrow{k_1} X \xrightarrow{k_2} Z$

$$[X] = [A_0]\frac{k_1}{k_2}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

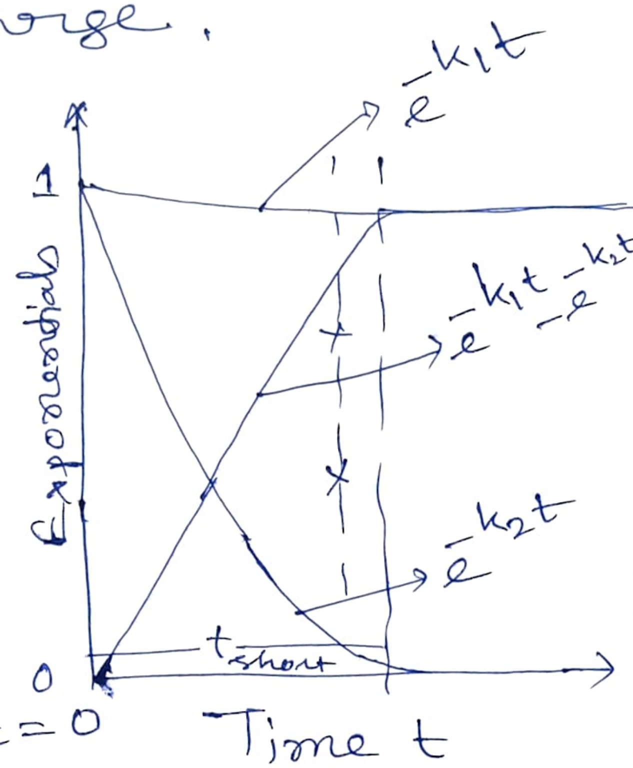
When k_1 is ~~very very~~ infinitesimally small and k_2 is very large.

At $t = 0$, $e^{-k_1 t} = e^{-k_2 t} = 1$

$\therefore [X] = 0$

After a very short time (t_{short}), relative to the duration of the reaction,

$e^{-k_1 t} - e^{-k_2 t} \simeq 1$



Suppose $k_1 = 0.0001\,s^{-1}$ & $k_2 = 100\,s^{-1}$

then $e^{-k_1 t} \approx 0.999$ & $e^{-k_2 t} \approx 0.00\ldots$

$\therefore e^{-k_1 t} - e^{-k_2 t} = 0.999 - 0.00 \approx 0.99 = 1$

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

less than one

Therefore $[X] \ll [A]_0$.

As $[A]_0$, k_1 and k_2 are constants, after the very short time,

$\frac{d[X]}{dt} = 0 \Rightarrow$ This is the basis of steady state approx.

* The steady-state treatment is of great importance in the analysis of composite mechanism.

consider the mechanism,

① $A + B \rightleftharpoons X$

② $X \longrightarrow Z$

The differential rate equations for the set of rxns are

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

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

$$\frac{d[Z]}{dt} = k_2[X]$$

Applying steady-state approximation

$\frac{d[X]}{dt} = 0$, we get

$$k_1[A][B] - k_{-1}[X] - k_2[X] = 0$$

$$[X] = \frac{k_1[A][B]}{k_{-1} + k_2}$$

Therefore, $v = v_2 = \frac{d[Z]}{dt} = k_2[X] = \frac{k_1 k_2}{k_{-1} + k_2}[A][B]$