

Complex Reactions: Opposite, Consecutive and Parallel Reactions

Opposite or Reversible Reactions

- Reactions having both forward and backward reactions are called as opposite reaction or reversible reaction

- Example of synthesis of Ammonia: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
- Example of transformation of carbon mono-oxide: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$

First-Order Opposite Reactions: Forward and reverse reactions are both first order



$$v = v_A = v_P$$

⇒ Rate of reaction = Rate of consumption of A = Rate of formation of P

Rate of forward reaction: $v_1 = k_1[A]$

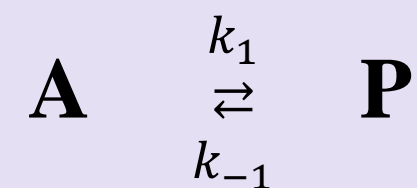
Rate of reverse reaction: $v_{-1} = k_{-1}[P]$

Total (overall) rate of reaction: $v = v_1 - v_{-1}$

At equilibrium, $v_1 = v_{-1}$ and $v = 0$

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Opposite Reactions



Time	Conc. of A	Conc. of P
t=0	$[A]_0$	0
t	$[A]$	$[P]$
At equilibrium	$[A]_{eq}$	$[P]_{eq}$

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

$$\text{Since, } [P] = [A]_0 - [A]$$

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

$$= k_{-1}[A]_0 - (k_1 + k_{-1})[A]$$

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

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

Last step is because at equilibrium (dynamic) i.e. $t \rightarrow \infty$, $v = 0$:

$$\frac{d[A]}{dt} = 0 \Rightarrow \frac{[P]_{eq}}{[A]_{eq}} = \frac{[A]_0 - [A]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}} = K \Rightarrow [A]_{eq} = \frac{k_{-1}}{(k_1 + k_{-1})} [A]_0$$

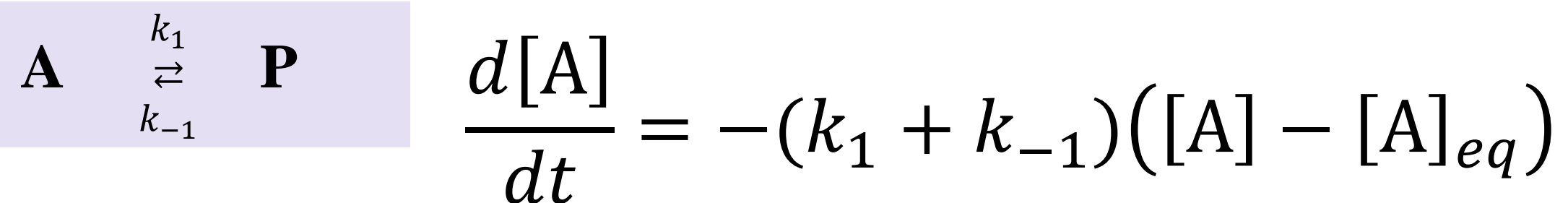
We can use the expression of equilibrium constant (K) to eliminate k_{-1} from Eq. 1.

$$\Rightarrow \frac{d[A]}{dt} = -k_1[A] + \frac{k_1}{K}[P] = -k_1[A] \left(1 - \frac{1}{K} \frac{[P]}{[A]} \right)$$

- It is obvious that initially $\frac{d[A]}{dt} = -k_1[A]$ i.e. the rate is $k_1[A]$ and but the rate slows down as P accumulates
- When $\frac{[P]}{[A]} = K$, the reaction is at equilibrium and rate is zero.

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Integrated Rate Equation of First-Order Opposite Reactions



$$\int_{[A]_0}^{[A]} \frac{d[A]}{([A] - [A]_{eq})} = -(k_1 + k_{-1}) \int_0^t dt$$

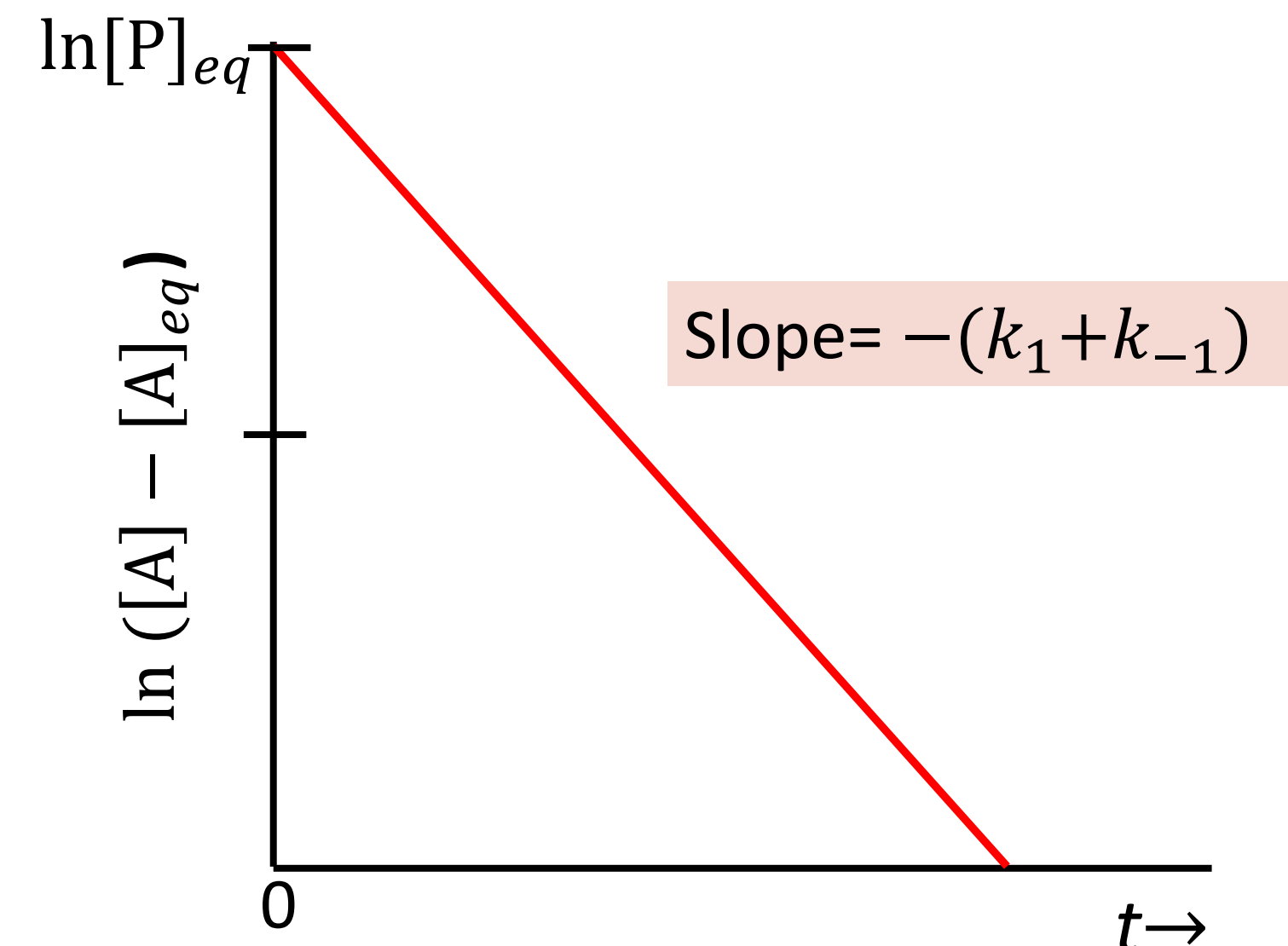
$$\ln \frac{[A] - [A]_{eq}}{[A]_0 - [A]_{eq}} = -(k_1 + k_{-1})t$$

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

Since, $[P] = [A]_0 - [A]$ and $[P]_{eq} = [A]_0 - [A]_{eq}$

$$\ln \frac{\{[A]_0 - [P]\} - [A]_{eq}}{[P]_{eq}} = -(k_1 + k_{-1})t$$

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



The rate at which the reaction will approach to the equilibrium is decided by the sum of the rates constants for the forward and reverse reactions, rather than only by the rate of forward reaction

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Integrated Rate Equation of First-Order Opposite Reactions

In exponential form: $[A] - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k_1+k_{-1})t}$

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

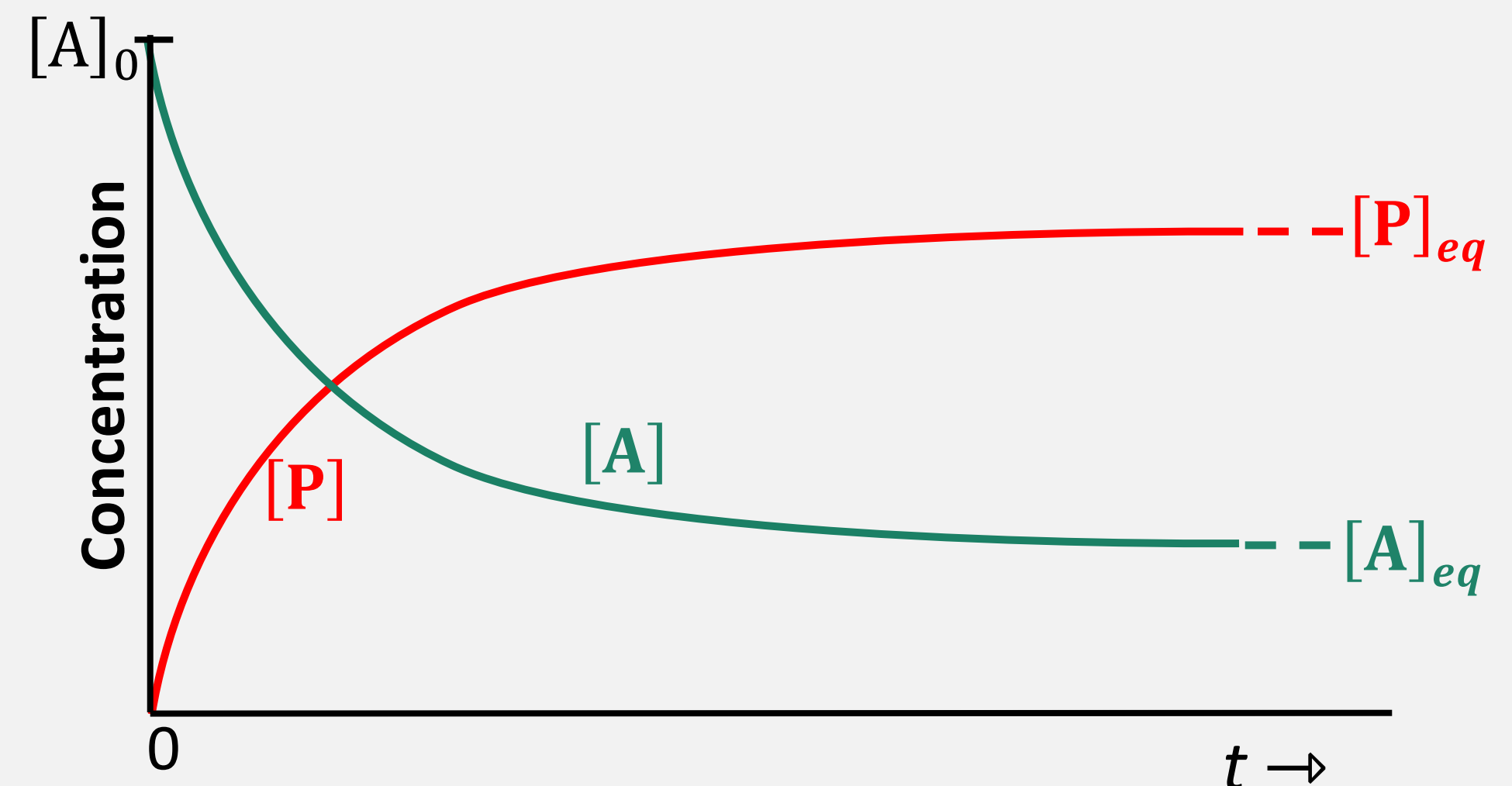
$$[A] - \frac{k_{-1}}{(k_1+k_{-1})} [A]_0 = [A]_0 \left(\frac{k_1 + k_{-1} - k_{-1}}{(k_1+k_{-1})} \right) e^{-(k_1+k_{-1})t}$$

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

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

Since $[P] = [A]_0 - [A]$

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

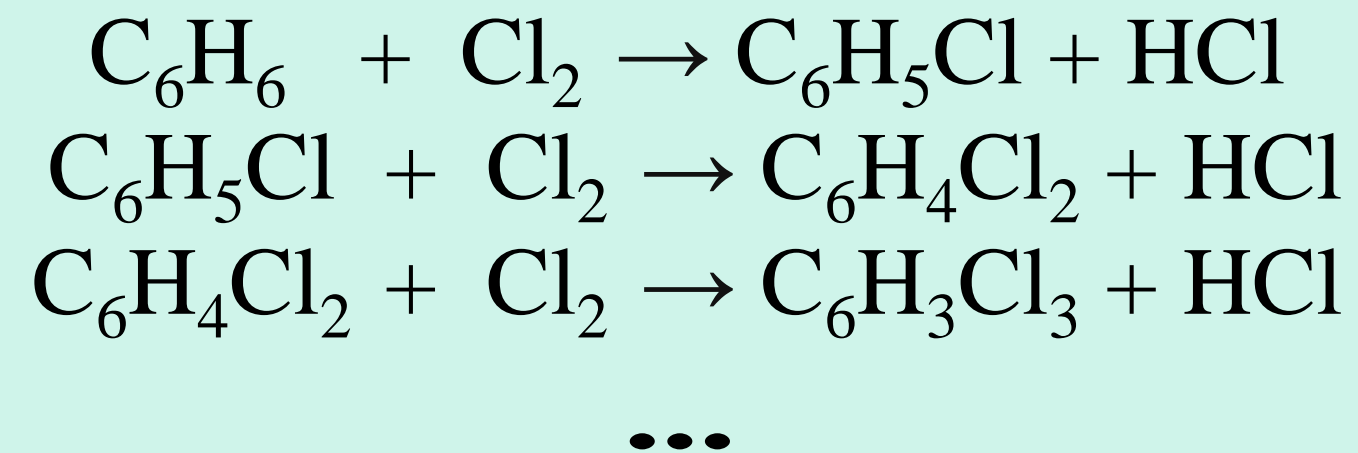


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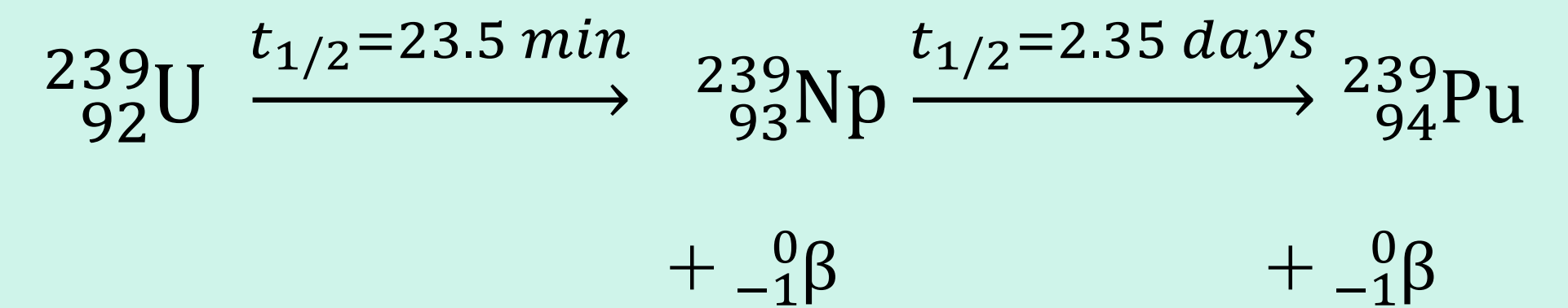
Consecutive Reactions

- When certain product of a reaction is a reactant of another reaction (other than reverse reaction), the combination of these reactions is called a consecutive reaction

Example of chlorination of benzene in liquid phase:



Example of radioactive elements:



Complex Reactions: Opposite, Consecutive and Parallel Reactions

Consecutive Irreversible First-Order Reactions:

- All the reactions involved (1 and 2) are of first order



Time	Conc. of A	Conc. of I	Conc. of P
$t = 0$	$[A]_0$	0	0
t	$[A]$	$[I]$	$[P]$

For the three species, we can write:

$$v_A = -\frac{d[A]}{dt} = k_1[A]$$

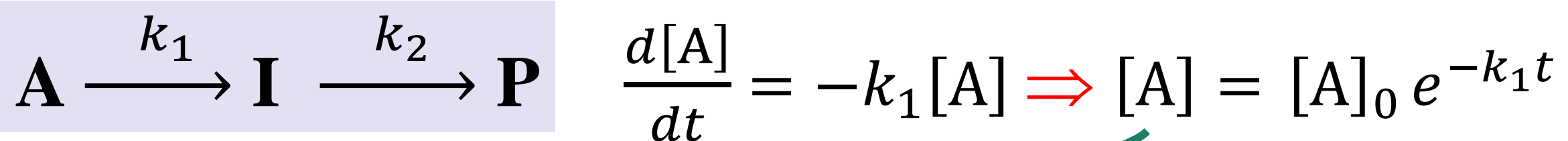
$$v_I = \frac{d[I]}{dt} = k_1[A] - k_2[I]$$

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

Only two of these simultaneous differential equations are independent because $v_I = v_A - v_P$

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Integrated Rate Equation of First-Order Consecutive Reactions



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

First order differential equation of the form

$$\frac{df(x)}{dx} + af(x) = b \quad (a \text{ and } b \text{ are functions of } x \text{ or constants})$$

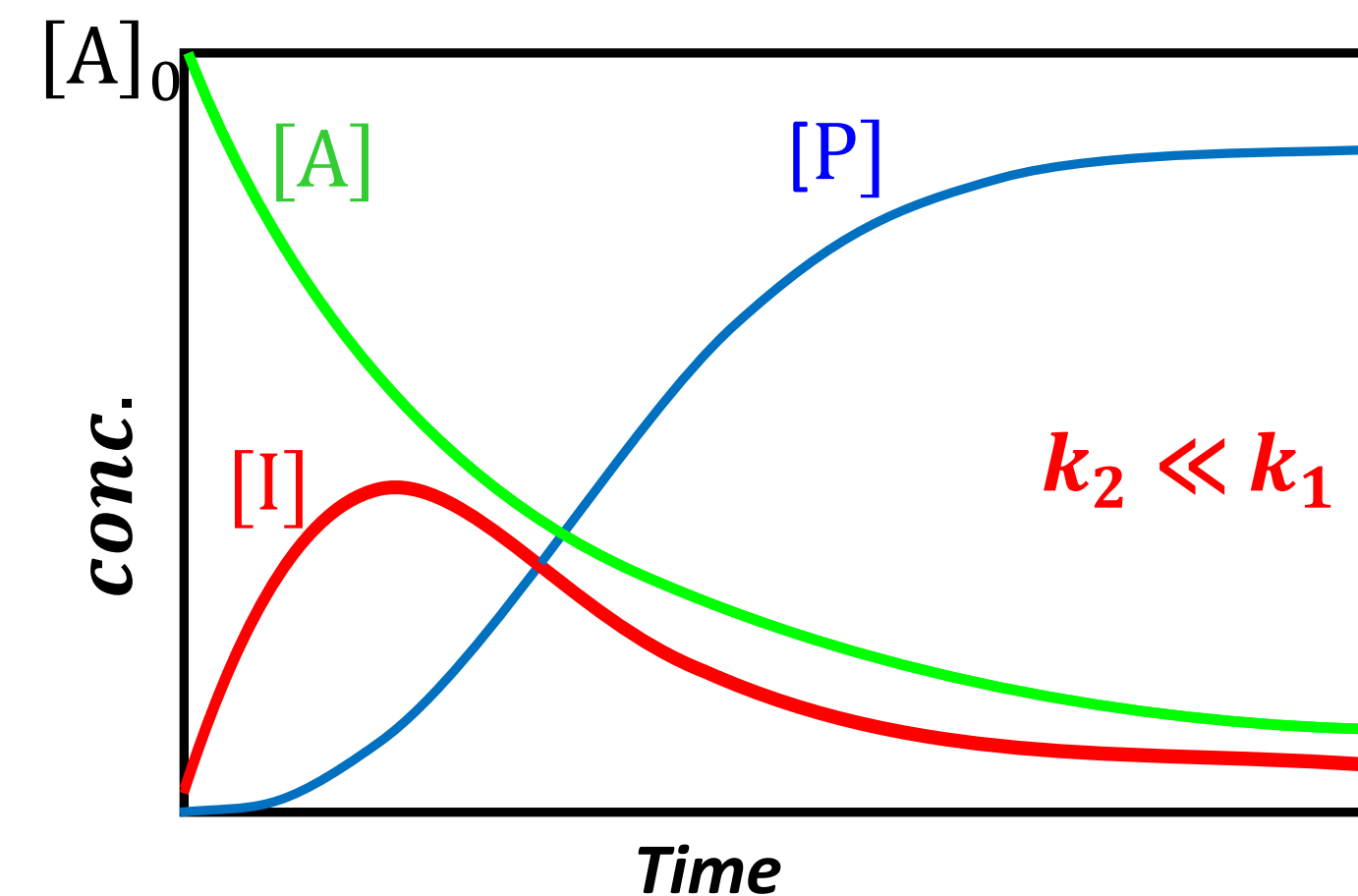
$$f(x)e^{\int a dx} = \int e^{\int a dx} b dx + \text{Const.}$$

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

At all the time: $[A] + [I] + [P] = [A]_0$

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

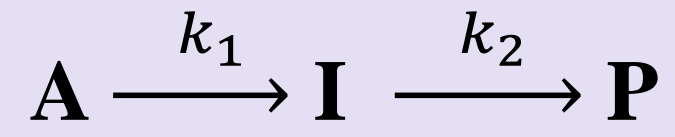
- The concentration of the intermediate **I** rises to a maximum and then fall to zero
- The concentration of **P** rises from zero to towards $[A]_0$, when all **A** has been converted to **P**



- When k_1/k_2 is larger ($k_2 \ll k_1$), **I** acts as a stable intermediate; as **I** maintains higher conc. over a broad time interval

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Integrated Rate Equation of First-Order Consecutive Reactions



At the maximum, $[I] = [I]_{max}$

$$\frac{d[I]}{dt} = 0 \text{ at } t = t_{max}$$

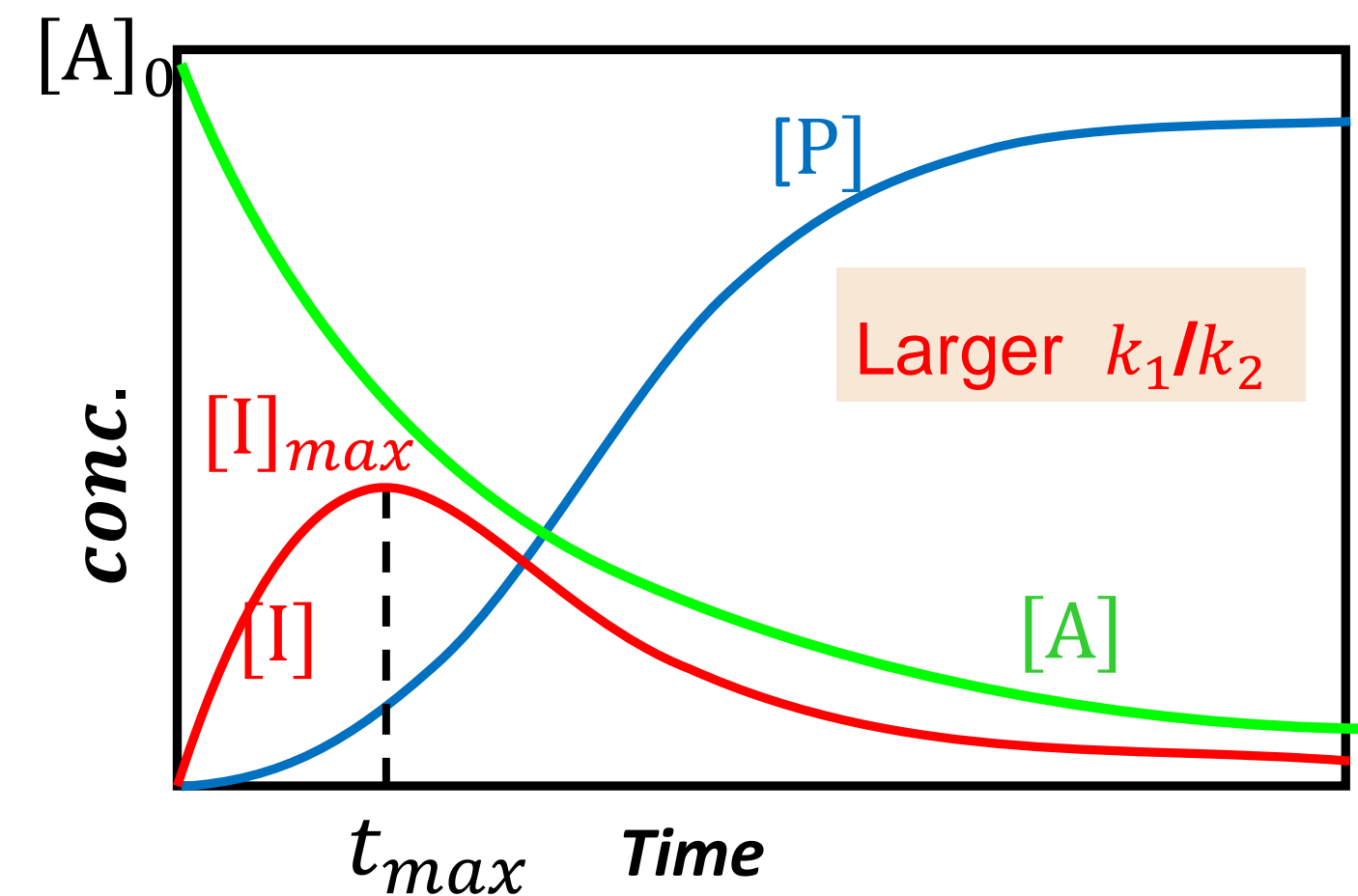
$$\Rightarrow \frac{d[I]}{dt} = [A]_0 \frac{k_1}{(k_2 - k_1)} ((-k_1)e^{-k_1 t} - (-k_2)e^{-k_2 t})$$

$$\frac{d[I]}{dt} = [A]_0 \frac{k_1}{(k_2 - k_1)} (k_2 e^{-k_2 t_{max}} - k_1 e^{-k_1 t_{max}}) = 0$$

$$\Rightarrow t_{max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

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

- k_1 and k_2 can be obtained from t_{max} and $[I]_{max}$ at maximum of c_I



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Integrated Rate Equation of First-Order Consecutive Reactions

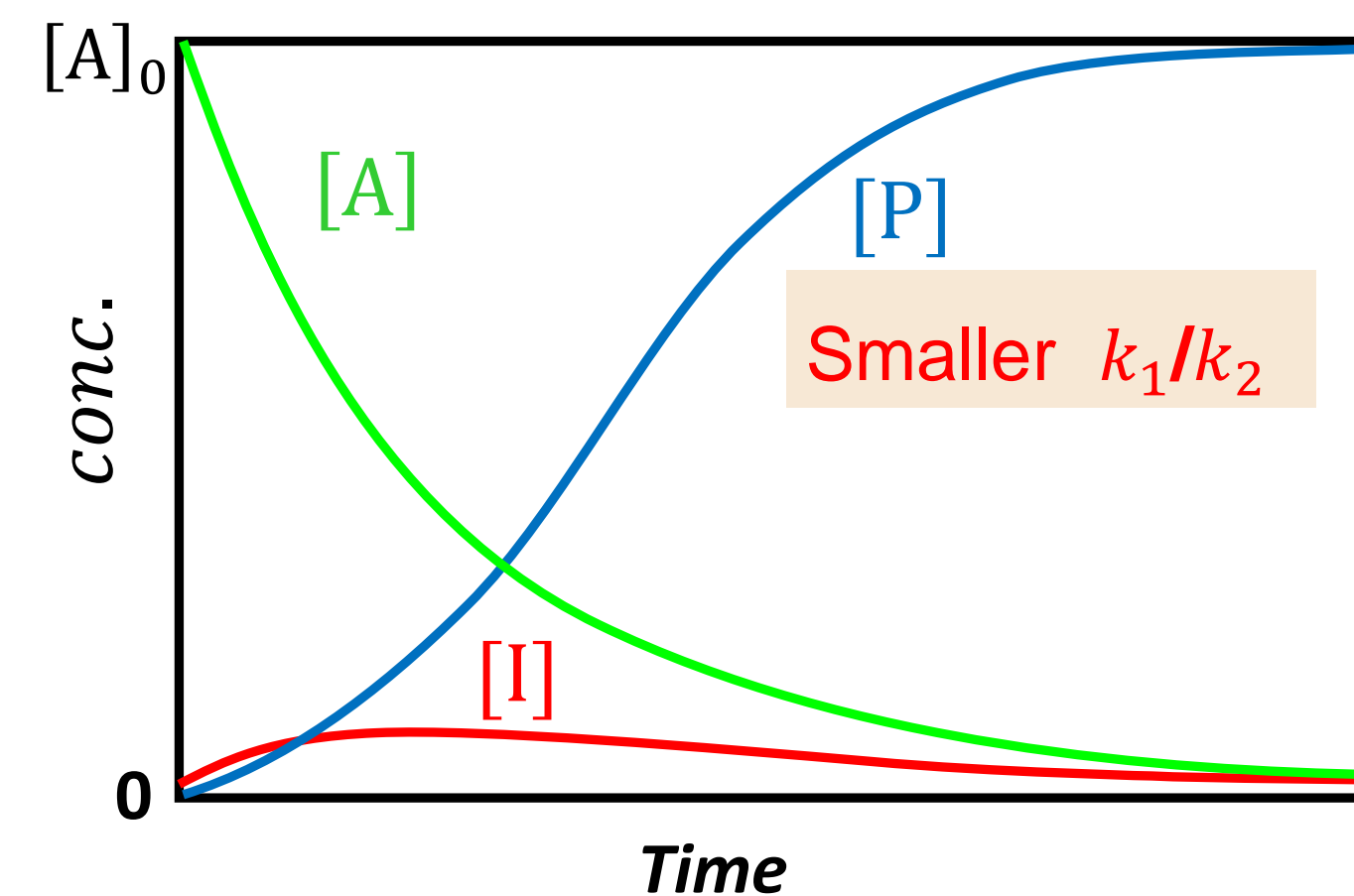
When k_1/k_2 is smaller ($k_2 \gg k_1$), **I** acts as unstable intermediate; as **[I]** is too low over a broad time interval

In this case, **[I]** can be assumed approximately constant with time

$$\frac{d[I]}{dt} \approx 0$$

$$\Rightarrow \frac{d[I]}{dt} = k_1[A] - k_2[I] = 0 \Rightarrow k_1[A] = k_2[I]_{ss}$$

- This equation indicates that **I** is at steady state, which means its rate of consumption is counterbalanced by its rate of formation. This condition is termed as “**Steady State Approximation**”.

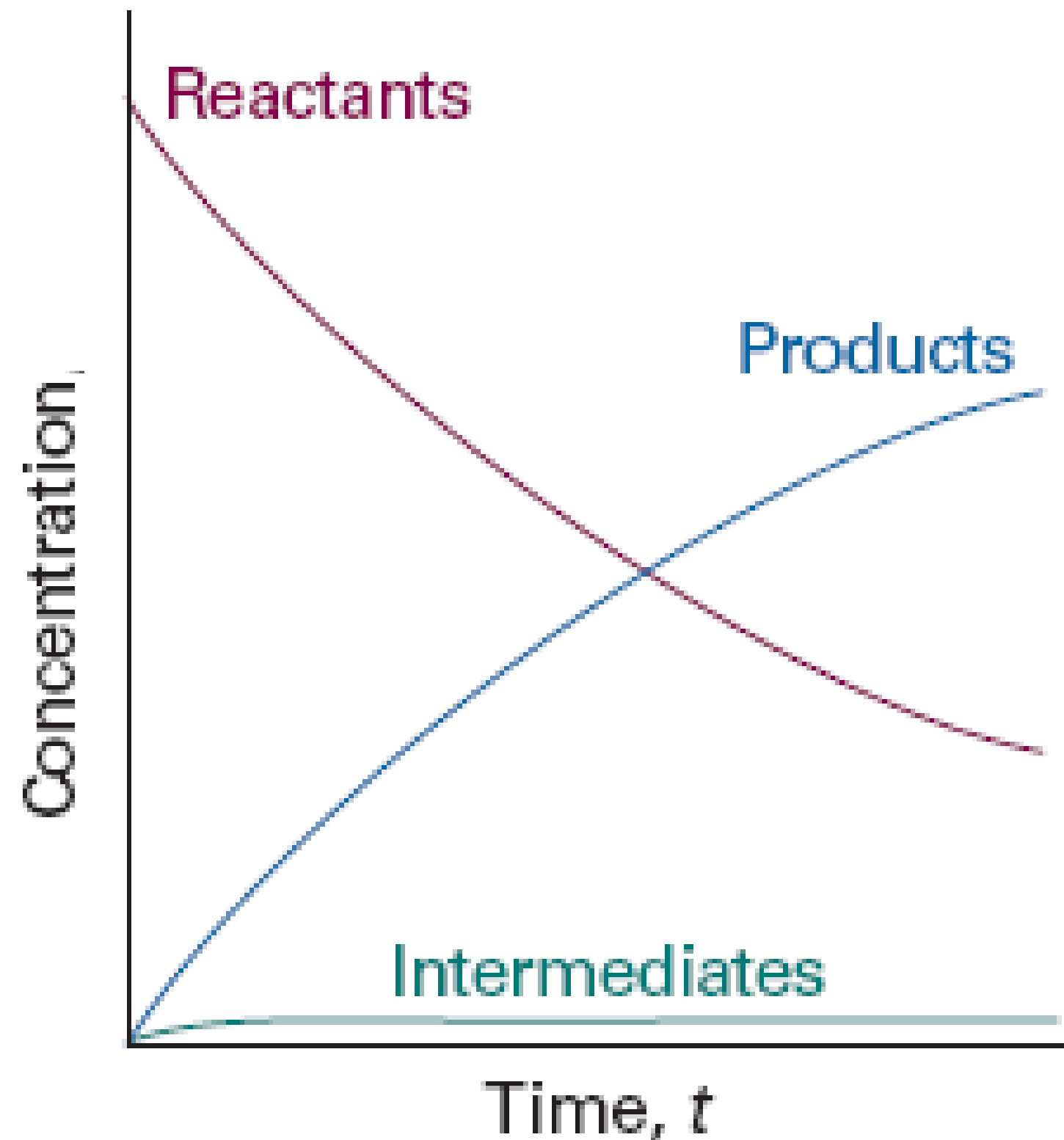


The **steady-state concentration** of intermediate **I** is given by: $[I]_{ss} = \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$

The **steady-state concentration** of the product **P** is given by: $[P]_{ss} = [A]_0 - [A] - [I]_{ss} = \left[1 - \left(1 + \frac{k_1}{k_2} \right) e^{-k_1 t} \right]$

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Steady-state Approximation



When the concentrations of intermediates (I) remain small and hardly change during most of the course of the reaction, then we can write

$$\frac{d[I]}{dt} \approx 0$$

The steady-state Approximation

- This approximation greatly simplifies the discussion of reaction schemes