

Lecture 20

Thursday, November 21, 2024 10:00

Topic 17 E : Reaction Mechanisms

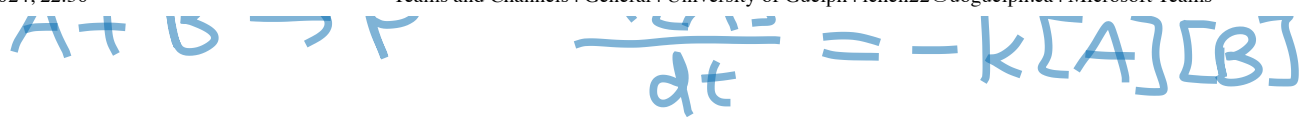
Elementary reactions : a step in the overall mechanism



Molecularity : the number of molecules coming together to react in an elementary reaction
unimolecular, bimolecular, etc.

Need to distinguish from reaction order, which is an empirical quantity obtained from the rate law





Consecutive Elementary Reactions



e.g.



Ignoring reverse reactions (for now),

what is the rate law for the overall process?

$$\frac{d[A]}{dt} = -k_1[A] \quad \textcircled{1}$$

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \quad \textcircled{2}$$

$$\frac{d[P]}{dt} = k_2[I] \quad \textcircled{3}$$

For ①, the integrated rate law, assuming that the initial concentration of $[A]$ is $[A]_0$, is $[A] = [A]_0 e^{-k_1 t}$

Substituting the above expression into ②,

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

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

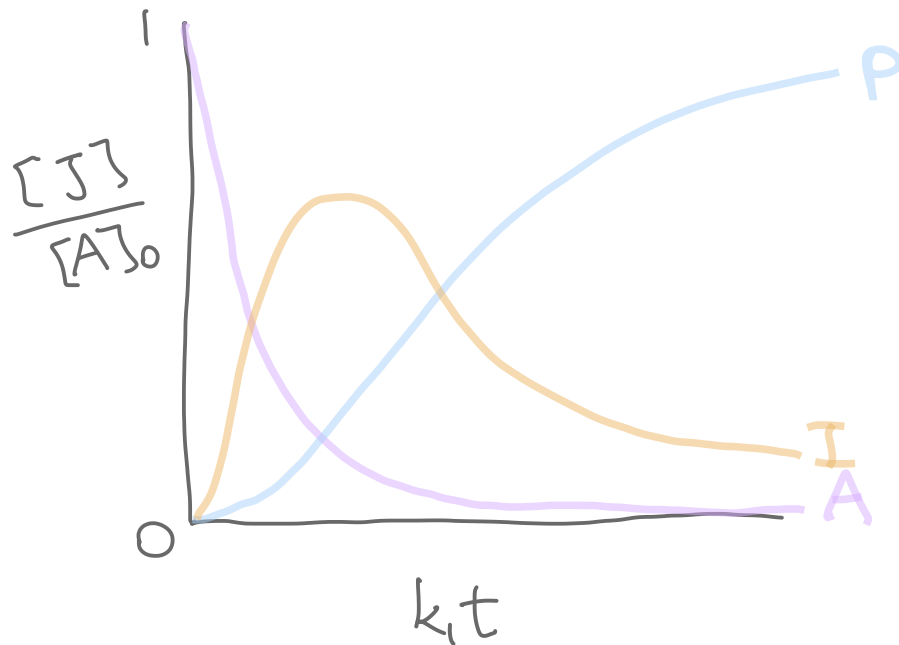
This differential equation has a standard solution:

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

Noting that $[A] + [I] + [P] = [A]_0$,

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

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



Practice Problem: suppose that an industrial batch process produces the desired compound I which goes on to decay to a worthless product P, each step of the reaction being first order. At what time will I be present in the greatest concentration?

Solution:

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

$$\frac{d[I]}{dt} = 0 \text{ when } k_1 e^{-k_1 t} - k_2 e^{-k_2 t} = 0$$

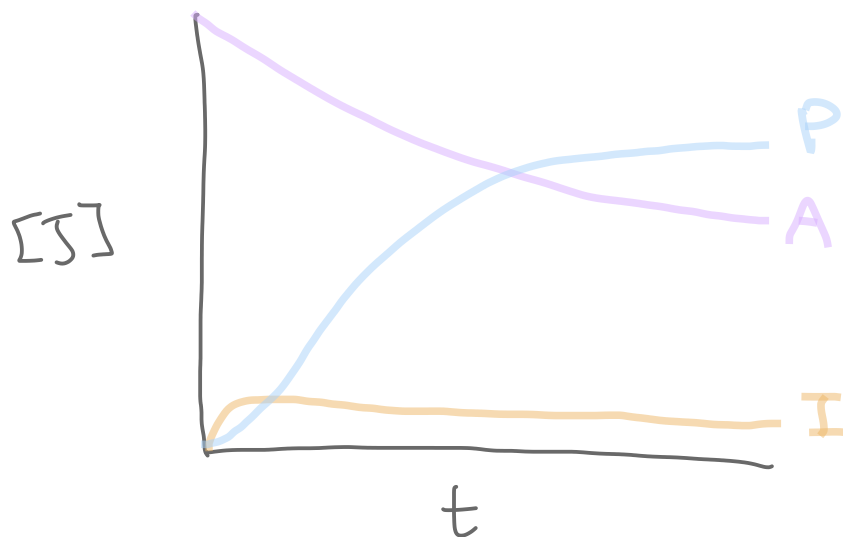
$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$\ln k_1 - k_1 t_{\max} = \ln k_2 - k_2 t_{\max}$$

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

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

Steady-State Approximation: assumes that the intermediate I is in a low, constant concentration.



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

Suppose that we could apply the steady-state approximation to the previous reaction. Then,

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

$$[I] = \frac{k_1}{k_2} [A]$$

$$d[P] \quad , \quad [A]$$

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

$$\frac{d[P]}{dt} \approx k_1 [A]$$

$$\int_0^t d[P] = \int_0^t k_1 [A] dt$$

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

Practice Problem: Using the Steady-State

Approximation





Solution: note that both NO_3 and NO are intermediates.

$$\begin{aligned} \frac{d[\text{NO}_3]}{dt} &= k_{1f} [\text{N}_2\text{O}_5] - k_{1r} [\text{NO}_2][\text{NO}_3] \\ &\quad - k_2 [\text{NO}_2][\text{NO}_3] = 0 \quad (4) \end{aligned}$$

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{N}_2\text{O}_5] \\ &= 0 \quad (5) \end{aligned}$$

From equation 4,

$$k_{1f} [\text{N}_2\text{O}_5] = (k_{1r} + k_2) [\text{NO}_2][\text{NO}_3]$$

$$[\text{NO}_3] = \frac{k_{1f} [\text{N}_2\text{O}_5]}{k_{1r} + k_2}$$

$$[NO_3] = \frac{(k_{1r} + k_2) [NO_2]}{k_3 [N_2O_5]}$$

From equation 5,

$$[NO] = \frac{k_2 [NO_2]}{k_3 [N_2O_5]} [NO_3]$$

$$[NO] = \frac{k_2 \cancel{[NO_2]}}{k_3 \cancel{[N_2O_5]}} \cdot \frac{k_{1f} \cancel{[N_2O_5]}}{(k_{1r} + k_2) \cancel{[NO_2]}}$$

$$[NO] = \frac{k_2 k_f}{k_{1r} k_3 + k_2 k_3}$$

$$\frac{d[N_2O_5]}{dt} = -k_{1f} [N_2O_5] + k_{1r} [NO_2] [NO]$$

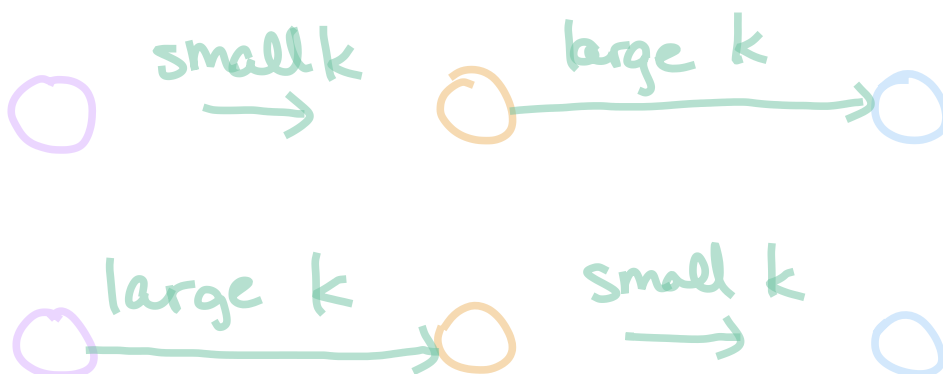
$$- k_3 [NO] [N_2O_5]$$

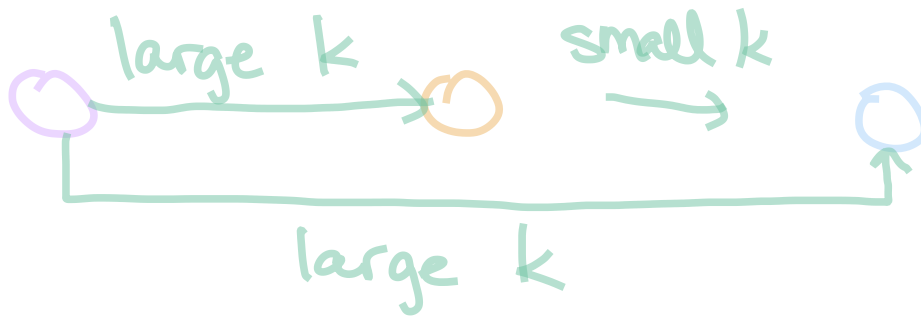
$$= -k_{1f} [N_2O_5] + k_{1r} \frac{k_f [N_2O_5]}{(k_{1r} + k_2) [N_2O_5]}$$

$$\begin{aligned}
 & - \cancel{k_3} \frac{k_2 k_1 f}{(k_{1r} + k_2) \cancel{k_3}} [\text{N}_2\text{O}_5] \\
 & = \left(-k_{1f} + \frac{k_{1f} k_{1r}}{k_{1r} + k_2} - \frac{k_{1f} k_2}{k_{1r} + k_2} \right) [\text{N}_2\text{O}_5] \\
 & = \frac{-\cancel{k_{1f} k_{1r}} - k_{1f} k_2 + \cancel{k_{1f} k_{1r}}}{k_{1r} + k_2} [\text{N}_2\text{O}_5]
 \end{aligned}$$

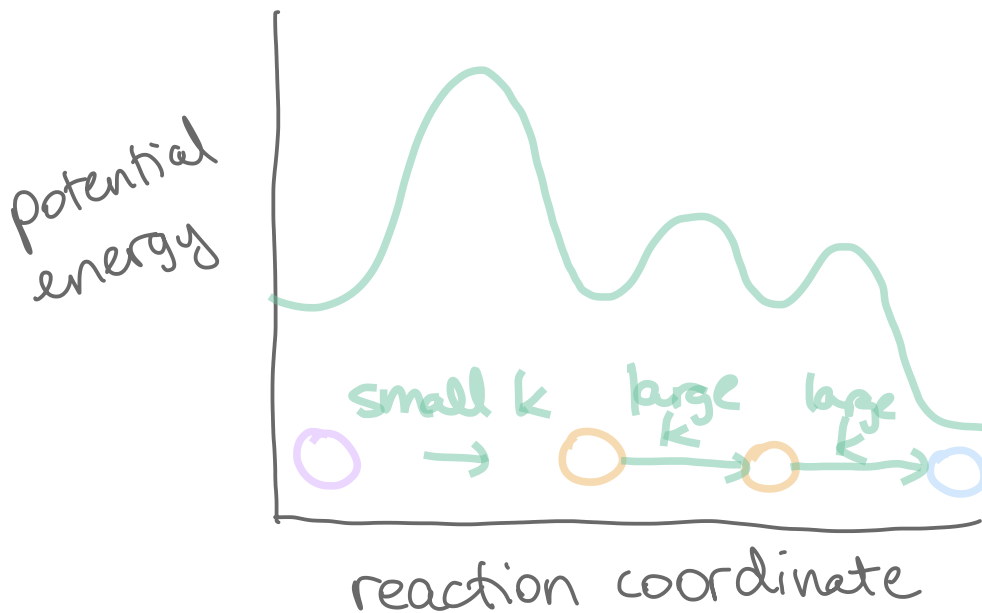
$$\frac{d[\text{N}_2\text{O}_5]}{dt} = - \frac{2k_{1f}k_2}{k_{1r} + k_2} [\text{N}_2\text{O}_5]$$

The Rate-Determining Step

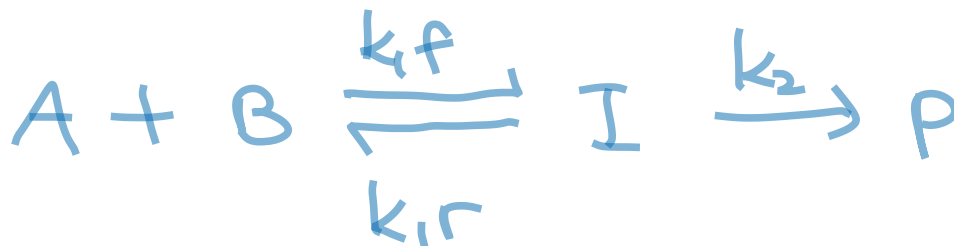




The rate-determining step (RDS) is the step in a mechanism that controls the overall rate of the reaction.



Pre-Equilibria



Pre-equilibrium

In this case, the rate of decay of the intermediate back into the reactants is much faster than the rate at which it forms products.

$$k_{1r} \gg k_2$$

$$K = \frac{[I] c^0}{[A][B]}$$

$$[I] = \frac{K}{c^0} [A][B]$$

$$[I] = \frac{k_f}{k_{1r}} [A][B]$$

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

$$d[P] \quad k_f k_2$$

$$\frac{d[A]}{dt} = -k_r [A][B]$$