Lecture 20

Tuesday, November 21, 2023 11:33

Topic 17E: Reaction Mechanisms cont'd

Last time: break down overall reaction into elementary reactions

"molecularity": inferred from equation

An example: bimolecular

$$\boxed{\overset{1}{H} + \overset{2}{Br_2} \rightarrow HBr + Br}$$

elementary reaction; no phases indicated, no coefficients

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

overall reaction

order: first order

↳ empirically determined

can generally write rate law by inspection

$$r = k[H][Br_2]$$

Consecutive Elementary Reactions

$$\boxed{A \xrightarrow{k_1} I \xrightarrow{k_2} P}$$

overall : $A \rightarrow P$

example

$$^{239}U \xrightarrow{23.5\,min} {}^{239}Np \xrightarrow{2.35\,days} {}^{239}Pu$$

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

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

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

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

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

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

standard differential equation, has tabulated solution

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

Assuming only [A] present initially,

$$[A] + [I] + [P] = [A]_0$$

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

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

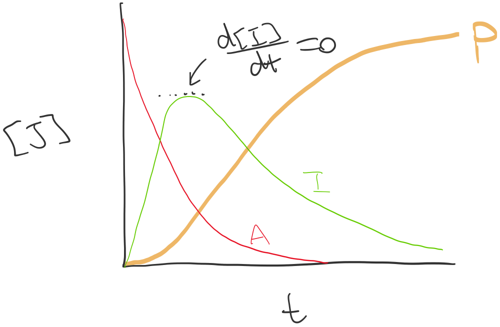
$$- \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[A]_0$$

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

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

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

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



Analyzing Consecutive Reactions

Industrial process:

not valuable

$$A \rightarrow I \rightarrow P$$

valuable

When will "I" have the greatest concentration?

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

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

$$\frac{d[I]}{dt} = 0, \quad k_1 e^{-k_1 t_{max}} = k_2 e^{-k_2 t_{max}}$$

$$\ln k_1 + \ln e^{-k_1 t_{max}} = \ln k_2 + \ln e^{-k_2 t_{max}}$$

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

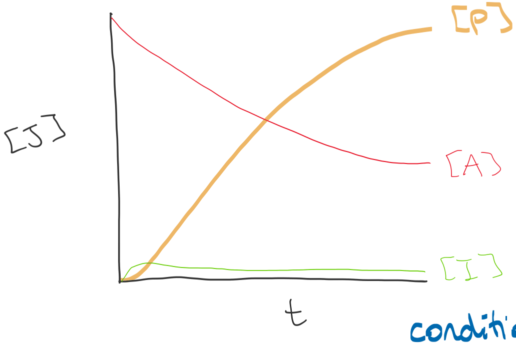
$$\ln k_1 - \ln k_2 = k_1 t_{max} - k_2 t_{max}$$

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

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

The Steady-State Approximation

- assume [I] is low, nearly constant



condition:

$k_1 \ll k_2$

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

① low [I]; as soon as I is made, it is

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

consumed

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

$$0 = k_1[A] - k_2[I]$$

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

② $\frac{k_1}{k_2}$ is small ; [I] changes very little as [A] changes

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

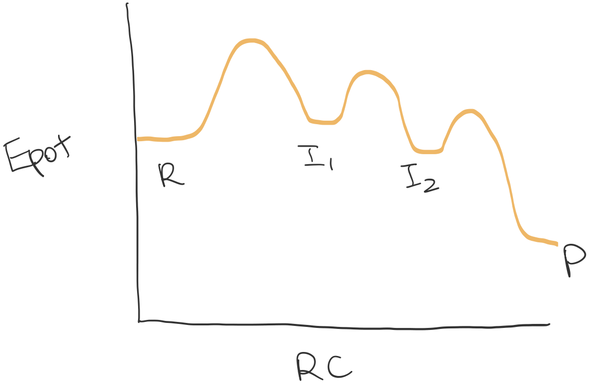
$$\boxed{\frac{d[P]}{dt} \approx k_1[A]}$$

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

$$= k_1 [A]_0 \int_0^t e^{-k_1 t}\,dt$$

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

The Rate-Determining Step

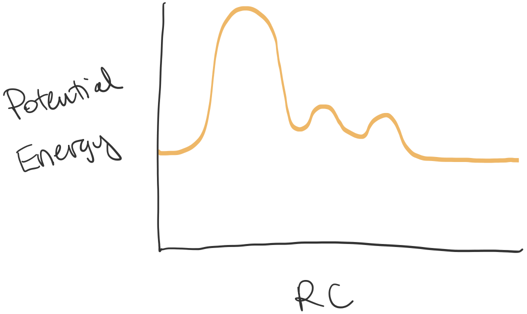


$$R \xrightarrow[\text{small } k]{RDS} I_1 \xRightarrow[\text{large } k]{} I_2 \xRightarrow[\text{large } k]{} P$$

rate-determining step must be a crucial step that leads to products

$$\begin{tikzcd} R \arrow[r, "\xcancel{\text{RDS}}"] \arrow[rr, bend right, "\text{fast}"'] & I \arrow[r, Rightarrow, "\text{fast}"] & P \end{tikzcd}$$

if a different mechanism circumvents the RDS, it is irrelevant



$r_{overall} \approx r_{RDS}$

Pre-Equilibria

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

$$A + B \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} I \xrightarrow{k_2} P$$

standard concentration term to balance units

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

$$[I] = \frac{K}{c^{\ominus}}[A][B] = \frac{k_{1f}}{k_{1r}}[A][B]$$

$$\frac{d[P]}{dt} = k_2[I] = k_2\frac{k_{1f}}{k_{1r}}[A][B]$$

$$\boxed{\frac{d[P]}{dt} = k[A][B]}$$