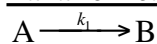


5.60 FINAL REVIEW – KINETICS SUMMARY

Order	Reaction	Rate law	$\tau_{1/2}$	Units of k
0	$A \rightarrow B$	$-\frac{d[A]}{dt} = k$ $[A] = [A]_0 - kt$	$\tau_{1/2} = \frac{[A]_0}{2k}$	$\frac{\text{mol}}{\text{L} \cdot \text{sec}}$
1	$A \rightarrow B$	$-\frac{d[A]}{dt} = k[A]$ $[A] = [A]_0 e^{-kt} \quad \ln[A] = \ln[A]_0 - kt$	$\tau_{1/2} = \frac{\ln 2}{k}$	$\frac{1}{\text{sec}}$
2	$2A \rightarrow B$	$-\frac{d[A]}{dt} = k[A]^2$ $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\tau_{1/2} = \frac{1}{k[A]_0}$	$\frac{\text{L}}{\text{mol} \cdot \text{sec}}$

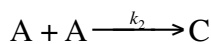
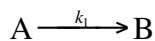
Parallel reactions



C

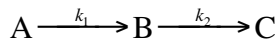
$$[A] = [A]_0 e^{-(k_1 + k_2)t} \quad [B] = \frac{k_1 [A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

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



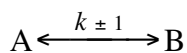
$$[A] = \frac{k_1 [A]_0}{e^{k_1 t} (k_1 + k_2 [A]_0) - k_2 [A]_0}$$

Consecutive reactions



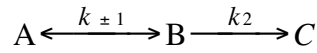
$$[A] = [A]_0 e^{-k_1 t} \quad [B] = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

Reversible reactions



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

Approximations: Steady-State versus Equilibrium



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

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

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

- Approximations only valid after [B] builds to maximum value
- Goal is to rewrite rates in terms of [A] (no intermediates)
- Get limiting behavior, effective rate constant, effective orders

Steady State Approximation	Equilibrium Approximation
<p>[B] forms slowly, gets destroyed quickly</p> <p>$k_2 \gg k_1, k_{-1} \gg k_1$</p>	<p>[B] forms quickly, gets destroyed slowly</p> <p>$k_2 \ll k_1, k_2 \ll k_{-1}$</p>
<p>$A \longrightarrow B$ rate-determining step</p>	<p>$B \longrightarrow C$ rate-determining step</p>
<p>Set $\frac{d[B]}{dt} = 0$, solve for [B]_{ss}</p> <p>Solve for $\frac{d[A]}{dt}$</p> <p>$-\frac{d[A]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [A]$</p>	<p>Set $[B] = \frac{k_1}{k_{-1}} [A]$</p> <p>Solve for $\frac{d[C]}{dt}$</p> <p>$\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}} [A]$</p>

Arrhenius Theory:

$$k = Ae^{-E_a/RT}$$

Small $E_a \rightarrow$ weak T-dependence \rightarrow Fast reaction	Large $E_a \rightarrow$ strong T-dependence \rightarrow Slow reaction
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