# 5.60 Final Review – Kinetics Summary

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

**Parallel reactions**

$$A \xrightarrow{k_1} B, \quad A \xrightarrow{k_2} C$$

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

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

$$A \xrightarrow{k_1} B$$
$$A + A \xrightarrow{k_2} C$$

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

**Consecutive reactions**

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad [A] = [A]_\circ e^{-k_1 t} \qquad [B] = \frac{k_1[A]_\circ}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

**Reversible reactions**

$$A \xrightleftharpoons{k_{\pm 1}} B \qquad [A] - [A]_{eq} = \left([A]_\circ - [A]_{eq}\right) e^{-(k_1 + k_{-1})t}$$

## **Approximations: *Steady-State versus Equilibrium***

$$A \xrightleftharpoons{k_{\pm 1}} B \xrightarrow{k_2} C$$

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

*-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 |
|---|---|
| $[B]$ forms slowly, gets destroyed quickly<br><br>$k_2 >> k_1,\ k_{-1} >> k_1$ | $[B]$ forms quickly, gets destroyed slowly<br><br>$k_2 << k_1,\ k_2 << k_{-1}$ |
| $A \longrightarrow B$<br>rate-determining step | $B \longrightarrow C$<br>rate-determining step |
| Set $\frac{d[B]}{dt} = 0$, solve for $[B]_{ss}$<br>Solve for $\frac{d[A]}{dt}$<br><br>$-\frac{d[A]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[A]$ | Set $[B] = \frac{k_1}{k_{-1}}[A]$<br>Solve for $\frac{d[C]}{dt}$<br><br>$\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}}[A]$ |

## **Arrhenius Theory:**

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

| | |
|---|---|
| Small $E_a$ → weak T-dependence → Fast reaction | Large $E_a$ → strong T-dependence → Slow reaction |