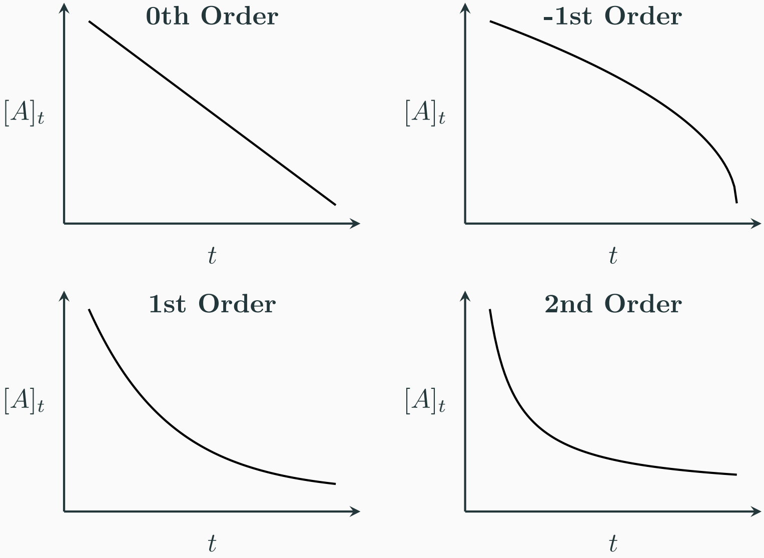
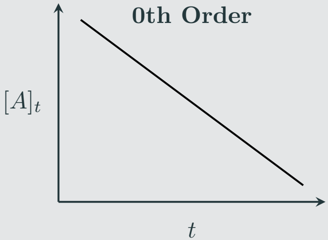
Lecture 34: Reaction Kinetics

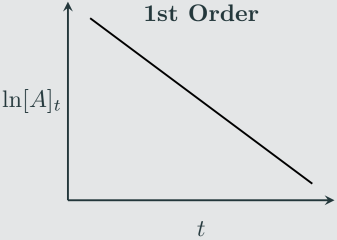
Reaction order meaning, Half Life, Collision Theory, Arrhenius Equation

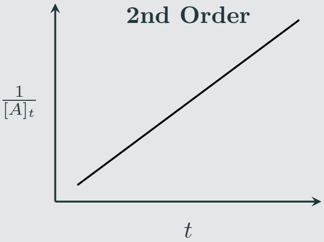
Meaning of Reaction orders



Straight Line Plots and Half Lives







$$[A]_t = -kt + [A]_0$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$t_{1/2} = \frac{\ln 2}{k}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Half life: time to reach $\frac{1}{2}$ of it's initial concentration, include radioactive decay

Half Life for 1st order

Half life: time to reach $\frac{1}{2}$ of it's initial concentration, include radioactive decay

1st Order

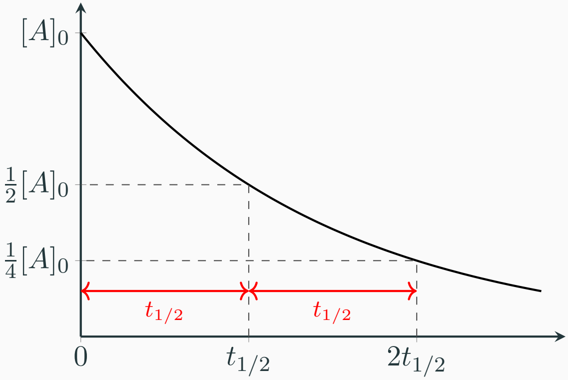
$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

Substitute $[A]_t = \frac{1}{2}[A]_0$:

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$t_{1/2} = \frac{-\ln(\frac{1}{2})}{k}$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$



Half Life - Other orders

0th Order

$$[A]_t = -kt + [A]_0$$

Substitute $[A]_t = \frac{1}{2}[A]_0$:

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0$$
$$\frac{1}{2}[A]_0 = kt_{1/2}$$
$$\boxed{t_{1/2} = \frac{1}{2k}[A]_0}$$

2nd Order

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Substitute $[A]_t = \frac{1}{2}[A]_0$:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$
$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$
$$\frac{1}{[A]_0} = kt_{1/2}$$
$$\boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

Example: Half Life

A 15 kg dog is administered 150 mg of phenobarbital before surgery. Metabolism follows first-order kinetics with $t_{1/2} = 4.5\,\text{h}$. After 2 h, surgical procedure requires more time than anticipated. Determine the mass of phenobarbital required to restore the drug level to its original 150 mg level.

$$
\begin{aligned}
A_0 &= 150\,\text{mg} \\
t_{1/2} &= 4.5\,\text{h} = \frac{\ln 2}{k} \\
k &= 0.15\,\tfrac{1}{\text{h}} \\
A_t &= A_0 e^{-kt} \\
A_t &= (150\,\text{mg}) e^{-(0.15\,\frac{1}{\text{h}})(2\,\text{h})} = 110.2\,\text{mg} \\
\text{Amount to add} &= 39.8\,\text{mg}
\end{aligned}
$$

Collision Theory

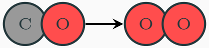
Collision frequency in gas $\sim 1 \times 10^{33}$ collisions/cm^3/s

Collision Theory Criteria

1. Collision: Molecules must physically collide
2. Sufficient Energy: Kinetic energy exceeds activation energy
3. Correct Orientation: Geometry must be correct

$$CO\,(g) + O_2(g) \longrightarrow CO_2(g) + O\,(g)$$

Incorrect Orientation

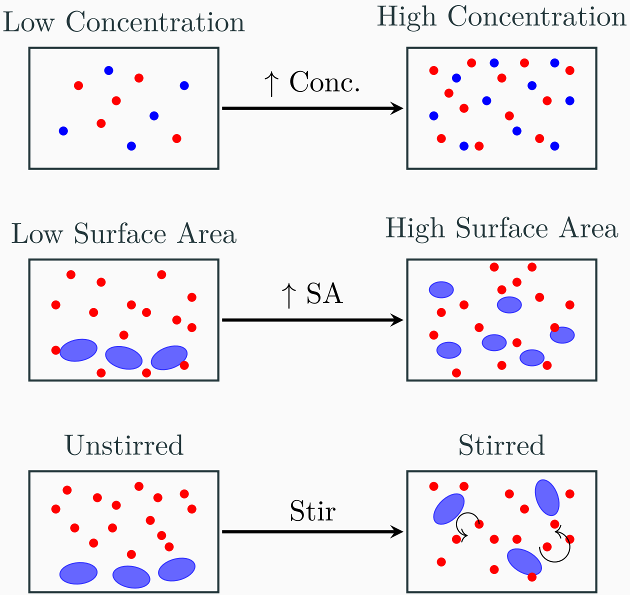


No Reaction

Correct Orientation

Success!

How to increase collisions?



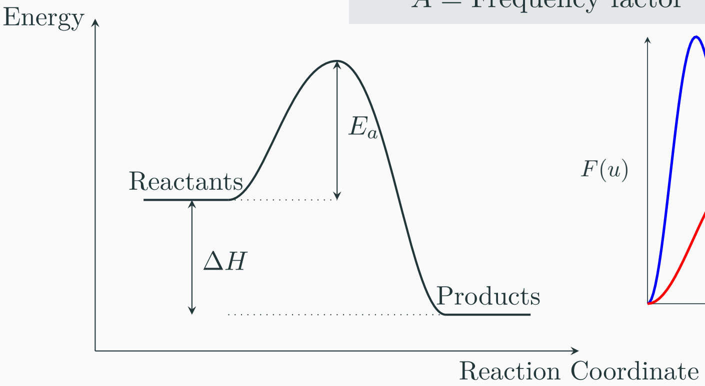
Arrhenius Equation

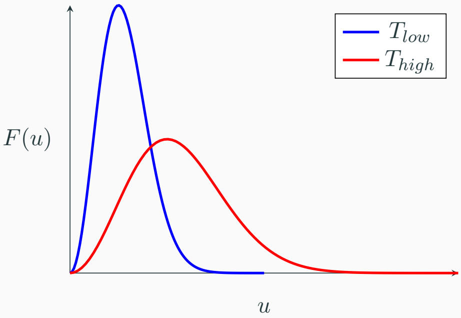
Arrhenius Equation

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

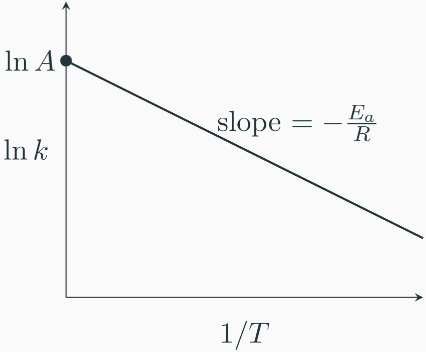
k = rate constant

A = Frequency factor





Rate constant changes with temperature



More Arrhenius

Straight Line form:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

Rate constant different T:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$