Reaction Order - Graphical Picture

**Zero order**: $n = 0$

**First order**: $n = 1$

**Second order**: $n = 2$

$A \longrightarrow \text{Products}$
Half-life, $t^{1/2}$

the length of time it takes for the concentration of the reactants to fall to one-half its initial value

depends on the order of the reaction
[A] vs time for a 1st order reaction

Length of half life is constant.

1st half life

2nd half life

3rd half life

Time, sec.

[A], M

0.20

0.15

0.10

0.05

0.00
[A] vs time for a 2nd order reaction

Length of half life increases with decreasing concentration.

1st half life

2nd half life

3rd half life

mol/L

Time, sec.
Chapter 14 - Chemical Kinetics II

Integrated Rate Laws
Reaction Rates and Temperature
Reaction Mechanisms
Catalysis
Integrated Rate Laws
Zero Order Reactions

Rate = \( k[A]_0 = k \) (constant rate reactions)

\([A] = -kt + [A]_0\)

graph of \([A] vs t\) is straight line
(\(slope = -k\) and \(y\) intercept = \([A]_0\))

\(t^{\frac{1}{2}} = \frac{[A]_0}{2k}\)
First Order Reactions

Rate = k[A]
\[ \ln[A] = -kt + \ln[A]_0 \]

Graph of \( \ln[A] \) vs \( t \) is straight line
\( \text{(slope} = -k, \text{y intercept} = \ln[A]_0) \)

\[ t^{1/2} = \ln2/k = (0.693)/k \quad \text{(constant half-life)} \]
Second Order Reactions

Rate = $k[A]^2$

$1/[A] = -kt + 1/[A]_0$

Graph of $1/[A]$ vs $t$ is straight line

(slope = $+k$ and y intercept = $1/[A]_0$)

$t^{1/2} = 1/(k[A]_0)$
<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Units of $k$</th>
<th>Integrated Rate Law</th>
<th>Straight-Line Plot</th>
<th>Half-Life Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$Rate = k[A]^0$</td>
<td>M·s$^{-1}$</td>
<td>$[A]_t = -kt + [A]_0$</td>
<td><img src="image" alt="Graph" /></td>
<td>$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$</td>
</tr>
<tr>
<td>1</td>
<td>$Rate = k[A]^1$</td>
<td>s$^{-1}$</td>
<td>$\ln[A]_t = -kt + \ln[A]_0$</td>
<td><img src="image" alt="Graph" /></td>
<td>$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$</td>
</tr>
<tr>
<td>2</td>
<td>$Rate = k[A]^2$</td>
<td>M$^{-1}$·s$^{-1}$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$</td>
<td><img src="image" alt="Graph" /></td>
<td>$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$</td>
</tr>
</tbody>
</table>
Determining Rate Graphically

Zero Order Reactions

First Order Reactions

Second Order Reactions
Data for

\[ \text{NO}_2 (g) \rightarrow \text{NO} (g) + \text{O}_2 (g) \]

\[ \ln[\text{NO}_2] \text{ vs time} \]

\[ \frac{1}{[\text{NO}_2]} \text{ vs time} \]
Reaction Rates and Temperature
**Temperature:**
Changing the temperature changes the rate constant in the rate law.

These factors are incorporated into rate constant \( k \) by the **Arrhenius equation:**

\[
k = A e^{-E_a/RT}
\]

- \( R \) = universal gas constant \((\text{in J/mol} \cdot \text{K})\)
- \( T \) = temperature \((\text{in kelvin})\)
- \( A \) is a collisional frequency factor.
  
  (Includes frequency of collisions and an orientation factor)

- \( E_a \) = Activation energy, The minimum energy of molecular collisions required to break bonds in reactants, leading to formation of products.
Collision Theory

In order for a chemical reaction to occur, reactant molecules must collide with sufficient energy and in the proper orientation.

Effective collisions involve both of these factors.

When two molecules have an effective collision, a temporary, high-energy (unstable) chemical species, the reactive intermediate*, is formed.

*also referred to as an activated complex or transition state
Arrhenius equation:

\[ k = A e^{-\frac{E_a}{RT}} \]
Reaction Energy Profile

High-energy transition state ("activated complex")

Activation energy ($E_a$)
Reaction Energy Profile

Partially broken and partially formed bonds

The amount of energy necessary to form the “activated complex”
The Reaction of CH₃Br and OH⁻
Reaction Energy Diagram for the Reaction of CH$_3$Br and OH$^-$
The Arrhenius equation can be rearranged:

\[ k = Ae^{-\frac{E_a}{RT}} \]

Or, taking the natural log of both sides…

\[ \ln k = \ln(Ae^{-\frac{E_a}{RT}}) \]

\[ \ln k = \ln A - \frac{Ea}{RT} \]

Which gives us another one of those linear relationships

\[ \ln k = \ln A - \frac{E_a}{RT} \left( \frac{1}{R} \frac{1}{T} \right) \]

\[ y = b + mx \]
\[ \ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A \]

We rewrite one equation:

\[ \ln k_2 + \frac{E_a}{RT_2} = \ln A \]

And substitute this in for \( \ln A \) into the other equation:

\[ \ln k_1 = -\frac{E_a}{RT_1} + \ln k_2 + \frac{E_a}{RT_2} \]

Finally, simplify:

\[ \ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2} \]

\[ \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]
According to the rearranged Arrhenius equation, the activation energy for a reaction can be determined by plotting $k$ vs $1/T$ which yields a line whose slope is $-E_a/R$ and whose intercept is $\ln A$. 

Graphical Determination of $E_a$ (Arrhenius Plot)
Mathematical Determination of $E_a$

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

Consider determination of $k$ two different $T$'s:

\[
\ln k_1 = \frac{-E_a}{R} \left( \frac{1}{T_1} \right) + \ln A \quad \ln k_2 = \frac{-E_a}{R} \left( \frac{1}{T_2} \right) + \ln A
\]

By subtraction,

\[
\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
The Exponential Factor

\[ k = (A)(e^{-\frac{E_a}{RT}}) \]

A number between 0 and 1, representing the fraction of reactant molecules with sufficient energy to make it over the energy barrier.
The Effect of $E_a$ on the Fraction of Collisions with Sufficient Energy to Allow Reaction

$$k = (A)(e^{-\frac{E_a}{RT}})$$

The higher the energy barrier, the fewer molecules that have sufficient energy to overcome the energy barrier.
The Effect of $E_a$ on the Fraction of Collisions with Sufficient Energy to Allow Reaction

![Graph showing the effect of activation energy on reaction rate. The top graph indicates that only molecules with kinetic energy above a certain threshold will react. The bottom graph shows that lowering the threshold energy allows more molecules to react even at lower temperatures.](image-url)
The **Effect of Temperature** on the Fraction of Collisions with Sufficient Energy to Allow Reaction

\[ k = (A)(e^{-\frac{E_a}{RT}}) \]

The **extra kinetic energy of the reactants is converted into potential energy when molecules collide.**
The Effect of Temperature on the Fraction of Collisions with Sufficient Energy to Allow Reaction

Increased temperature increases kinetic energy of molecules and molecular collisions.

Fraction of molecules in sample with sufficient energy to react at $T_1$

Increase in number of molecules in sample with sufficient energy to react at $T_2$; $T_2 > T_1$
Frequency Factor

\[ k = (A)(e^{-\frac{E_a}{RT}}) \]

A number representing the number of reactant molecules which can approach each other with sufficient energy to make it over the energy barrier.
Frequency Factor

\[ A = (p)(z) \]

- **p**: Orientation Factor
- **Z**: Collision Frequency Factor

*for reactions of single atoms, p=1*
*for most molecules p<<1*
Effective Collisions-Orientation Effect

\[ \text{NOCl}(g) + \text{NOCl}(g) \rightarrow 2 \text{NO}(g) + \text{Cl}_2(g) \]
Reaction Mechanisms
Unimolecular Reaction

\[
\text{CH}_3\text{N}≡\text{C} \quad \rightarrow \quad \text{CH}_3\text{C}≡\text{N}
\]
Unimolecular Reaction

Energy

H₃C — N≡C

 Activation energy (Eₐ)

ΔH_rxn

H₃C — C≡N

Activated complex (transition state)

Reactant

Product

Reaction progress
Bimolecular Reaction

2H₂(g) + O₂(g) ⇌ 2H₂O(g)

 Activation Energy

Energy of reactants

Energy of products

Reaction progress
Catalysts

Catalysts are substances that affect the rate of a reaction without being consumed.

Catalysts work by providing an alternative mechanism for the reaction with a lower activation energy.

Catalysts remain unchanged at the end of the chemical process.
Catalysts work by providing an alternative mechanism for the reaction with a lower activation energy.
Types of Catalysts

Homogeneous catalysis
- Catalyst in same phase as reactants
- Reactant
- Product

Heterogeneous catalysis
- Catalyst in different phase from reactants
Catalytic Hydrogenation
(Heterogeneous catalysis)

\[ \text{H-H} + \text{H}_2\text{C} = \text{C-H} \xrightarrow{\text{Ni}} \text{H}_2\text{C} - \text{C-H} \]

- Adsorption
- Diffusion
- Reaction
- Desorption
Reaction Profile for Surface-Catalyzed Reaction
Enzymes

Transformations of most biological molecules require a catalyst in order to proceed at a reasonable rate.

Enzymes are protein molecules that catalyze biological reactions.

Enzymes adsorb the substrate reactant(s) onto an active site that orients the reactant(s) for reaction.
Enzyme-Substrate Binding

Substrate
Active site
Enzyme
Enzyme-substrate complex
Products
Enzymatic Hydrolysis of Sucrose

C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6

Glucose part of molecule
Fructose part of molecule
Bond to be broken
Binding of Glucose to Glucokinase

Glucokinase (an enzyme) + Glucose (the substrate)