

Chemical Kinetics

Syllabus Learning Outcomes : 5, 7, 9

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Kinetics: study reaction rates and relate to the mechanism

- **Mechanism:** the chemical steps that a reaction takes to get from reactants to products.
- **Thermodynamics** tells if a reaction is product or reactant favored.
- **Kinetics** tells how fast (reaction rate) a reaction goes to products.

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Reaction Mechanism:

sequence of events that control the speed and outcome of a reaction.

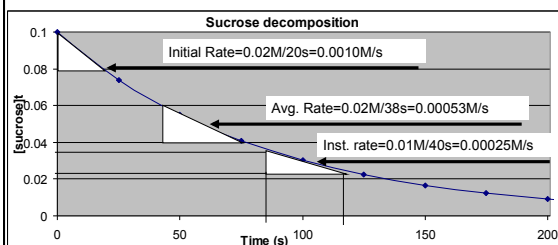
Reaction rate depends on the slow step

Reaction rate: change in concentration of a reactant or product with time.

- Three “types” of rates
 - initial rate
 - average rate
 - instantaneous rate

Measure reaction rate
Bleach oxidizes blue dye
Plot [dye] vs. time
Rate is the slope of the plot,
 $-\Delta[\text{dye}]/\Delta t$

Measure reaction rate:



Reaction rate= slope = $\Delta Y / \Delta X$

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These affect reaction rate:

- **[Reactants]**
- **Physical state of reactants**
- **Temperature**
- **Catalysts**

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[] ↑, rate ↑

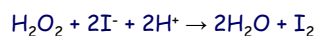
T ↑, rate ↑

Surface area ↑, rate ↑

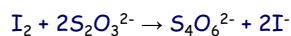
Add catalyst, rate ↑

Lab: iodine clock reaction

1. Peroxide oxidizes iodide to iodine (slow)



2. Thiosulfate reduces iodine to iodide (fast)



3. Iodine gives a blue starch complex after thiosulfate is gone.

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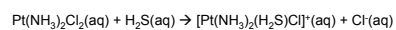
To determine a reaction mechanism from experiments:

Vary the initial concentration of reactant

Measure the effect on rate

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For example: H_2S replaces Cl^- in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



Experiments find that reaction rate increases linearly with increasing concentration of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, and it increases linearly with increasing concentration of H_2S

Write rate law based on data:

[] ↑, rate ↑

Rate law: rate = k [Pt(NH₃)₂Cl₂][H₂S]

$$\frac{-\Delta[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]}{\Delta t} = k [\text{Pt}(\text{NH}_3)_2\text{Cl}_2][\text{H}_2\text{S}]$$

k is the rate constant which is independent of concentration, but increases with increasing temperature.

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Write rate law based on data

For a general reaction: $aA + bB \xrightarrow{C} dD + eE$

$$\text{Rate} = -1/a(d[A]/dt) = -1/b(d[B]/dt) = 1/d(d[D]/dt) = 1/e(d[E]/dt)$$

$$\text{Rate law: rate} = k[A]^p[B]^q[C]^r$$

p , q , and r are the order of reaction for A , B , and catalyst C from experiment, respectively.

Order	Effect of concentration on rate
0	rate unaffected by []
1	rate increases linearly with []
2	rate increases with [] ²
$\frac{1}{2}$	rate increases with [] ^{1/2}

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Example: rate law

For rate = $k[A]^p$

if p is _____ When $[A]$ doubles, rate ? _____

0

1

2

$\frac{1}{2}$

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Example: rate law

For rate = $k[A]^p$

if p is _____ When $[A]$ doubles, rate ? _____

0 rate stays constant, $2^0 = 1$

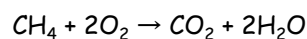
1 rate doubles, $2^1 = 2$

2 rate quadruples, $2^2 = 4$

$\frac{1}{2}$ rate increases 1.4x, $2^{1/2} = 1.4$

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Example: Determine m , n , k , and then rate from rate law.



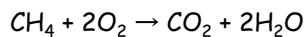
$$\text{rate} = k[\text{CH}_4]^m[\text{O}_2]^n$$



$[\text{CH}_4]$	$[\text{O}_2]$	rate (M/s) T=25°C
1.0	1.0	2.0
1.0	2.0	4.0
2.0	1.0	8.0
2.0	2.0	?

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Example: Determine m , n , k , and then rate from rate law.



$$\text{rate} = k[\text{CH}_4]^2[\text{O}_2]^1$$

$$k = 2.0 \text{ s}^{-1}\text{M}^{-2}$$

order \neq stoichiometry

$[\text{CH}_4]$	$[\text{O}_2]$	rate (M/s) T=25°C
1.0	1.0	2.0
1.0	2.0	4.0
2.0	1.0	8.0
2.0	2.0	16

Run experiment at another temperature to get effect of T on k

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To determine [] at time, t , integrate the rate laws

For zero order, $\int -d[A]/dt = \int k[A]^0$ gives:

$$[A]_t = [A]_0 - k \cdot t$$

Given: integrated zero-order rate law

For first order, $\int -d[A]/dt = \int k[A]^1$ gives:

$$\ln([A]_0/[A]_t) = k \cdot t$$

Given: integrated first-order rate law

For second order, $\int -d[A]/dt = \int k[A]^2$ gives:

$$1/[A]_t - 1/[A]_0 = k \cdot t$$

Given: integrated second-order rate law

Know the result, not the diff. eqs.

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Example: integrated rate law

If the rate law for the reaction of sucrose is $\text{rate} = k[\text{sucrose}]$, and $k = 0.012\text{s}^{-1}$, how long does it take for the concentration of 0.10M sucrose to drop by 90%?

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Example: integrated rate law

If the rate law for the reaction of sucrose is $\text{rate} = k[\text{sucrose}]$, and $k = 0.012\text{s}^{-1}$, how long does it take for the concentration of 0.10M sucrose to drop by 90%?

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = k \cdot t \quad (\text{use first order})$$

$$k = 0.012\text{s}^{-1}, [A]_0 = 0.10\text{M}, [A]_t = 0.10 \cdot (1 - 0.9)$$

$$\ln(0.10/0.01) = 0.012\text{s}^{-1} \cdot t$$

$$t = 190\text{s}$$

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Integrated rate laws and straight-line plots of data

First order: $\ln\left(\frac{[A]_0}{[A]_t}\right) = k \cdot t$
A plot of $\ln(1/[A]_t)$ vs. t is a line with slope= k , or $\ln([A]_t)$ vs. t has slope= $-k$.

Zero order: $[A]_t = [A]_0 - k \cdot t$
A plot of $[A]_t$ vs. t is a line with slope= $-k$.

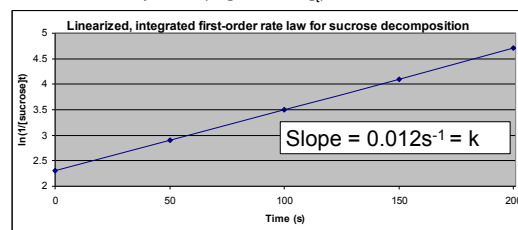
Second order: $1/[A]_t - 1/[A]_0 = k \cdot t$
A plot of $1/[A]_t$ vs. t is a line with slope= k .

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Integrated first-order rate law for sucrose using experimental data

t	$[\text{suc.}]_t$	$\ln(1/[\text{suc.}]_t)$
0	0.100	2.30
50	0.055	2.90
100	0.030	3.50
150	0.016	4.10
200	0.009	4.70

plot $\ln(1/[\text{sucrose}]_t)$ vs. t .



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Half Life: time for $\frac{1}{2}$ of initial sample to react

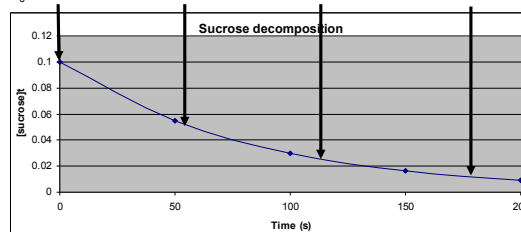
- For first-order reactions, each half-life takes the same time (not true for other reaction orders).
- Half life can be calculated with $\ln\left(\frac{[A]_0}{[A]_t}\right) = k \cdot t$ using k and $[A]_t = \frac{1}{2}[A]_0$, which gives $t = t_{\frac{1}{2}} = 0.693/k$.
- $t_{\frac{1}{2}} = 0.693/k$ for first-order reactions.

Given

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For the sucrose reaction, $k = 0.012\text{s}^{-1}$, giving $t_{\frac{1}{2}} = 58\text{s}$

$[\text{sucrose}]_0 = 0.1\text{M}$	1st half life, $\frac{1}{2}$ or 0.05M sucrose remains at 58s	2nd half life, $\frac{1}{4}$ or 0.025M sucrose remains at 116s	3rd half life, $\frac{1}{8}$ or 0.0125M sucrose remains at 174s
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Example: Half-Life

Rate = $k[\text{H}_2\text{O}_2]$ and $k = 3.3 \times 10^{-4} \text{ sec}^{-1}$. Half-life is 35 min. Start with 5.00 g H_2O_2 . What mass remains after 2 hr and 20 min (140 min)?

Solution:

2 hr and 20 min = 4 half-lives

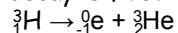
Half-life	Time Elapsed	Mass	Fraction
1st	35 min	2.50 g	1/2
2nd	70	1.25 g	1/4
3rd	105	0.625 g	1/8
4th	140	0.313 g	1/16

Or calculate from integrated first-order expression

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Example: half Life, integrated rate

- Radioactive decay is first-order



How much of a 2.00g sample of tritium is left after 36.9 years if the half life is 12.3 years?

Solution

- $k = 0.693/t_{1/2} = 0.056 \text{ yr}^{-1}$.
- $\ln(2.00/[A]_t) = 0.056 \text{ yr}^{-1} \cdot 36.9 \text{ yr}$
- $[A]_t = 0.25 \text{ g}$ (or use 3 half lives, $\frac{1}{8} \cdot {}^3\text{H}$)

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Half-Lives of Radioactive Elements

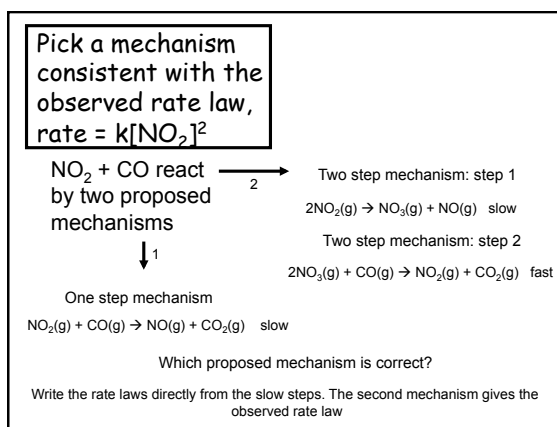
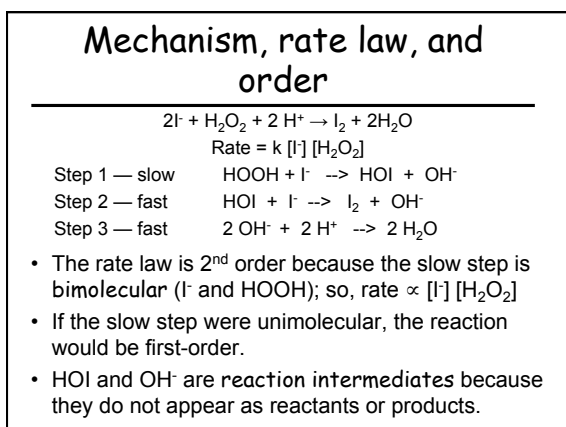
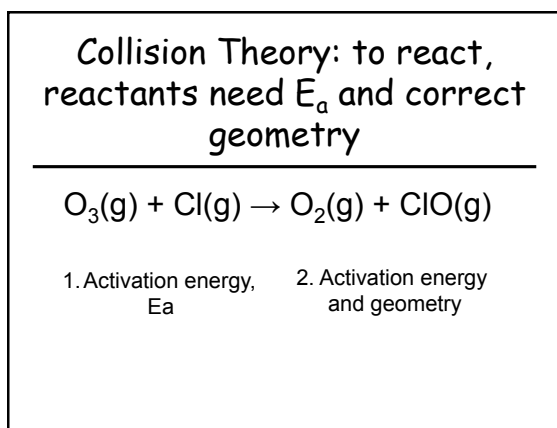
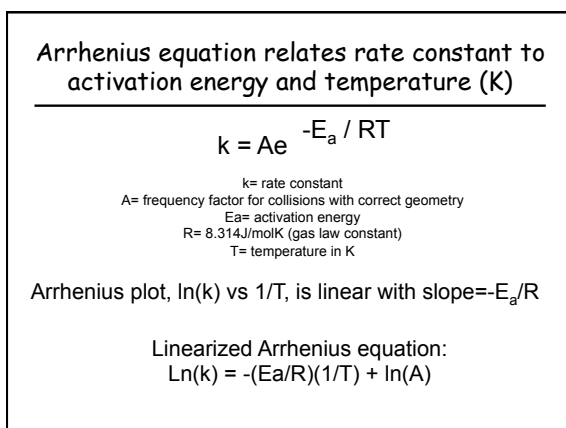
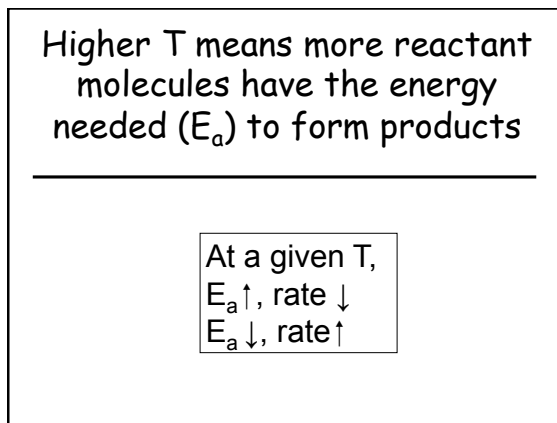
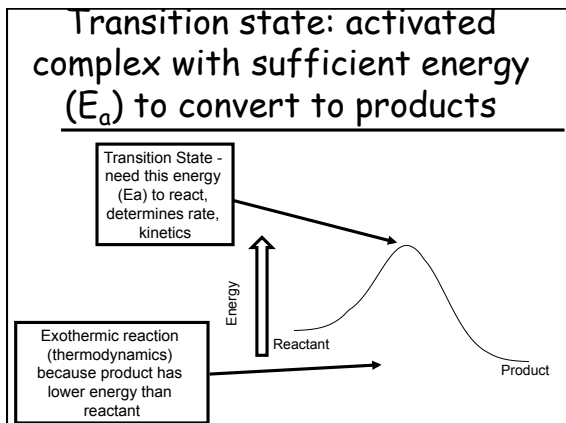
Radioactive decay	Half Life
${}^{99\text{m}}\text{Tc} \rightarrow {}^{99}\text{Tc} + \gamma$	6 hr
${}^{14}\text{C} \rightarrow {}^{14}\text{N} + \beta$	5730 y
${}^{238}\text{U} \rightarrow {}^{234}\text{Th} + \alpha$	$4.468 \times 10^9 \text{ y}$

Mechanisms: how reactants are converted to products

Rate law \rightarrow Mechanism
 experiment \rightarrow theory

Activation energy, E_a :
 energy needed for reactant
 molecules to react.

Molecules must get E_a to react
 for the slow step in the
 mechanism



Catalysts lower E_a , and rate \uparrow

MnO_2 catalyzes decomposition
of H_2O_2 : $2H_2O_2 \rightarrow 2H_2O + O_2$

Decomposition of H_2O_2 is faster
with a catalyst because the
activation energy, E_a , of reaction
is lower

Summary: How do I tell if a reaction is 1st order?

- Rate law has 1 species to the 1st power.
- Reaction rate data increases directly (linearly) with concentration (slope= k).
- $\ln([A]_t)$ data decreases linearly with time (slope= $-k$).
- The slow step in the reaction mechanism has a single chemical reactant (such as a decomposition reaction)
- The half life is constant with time