

Chemical Kinetics

Chem 36
Spring 2002

What is it?

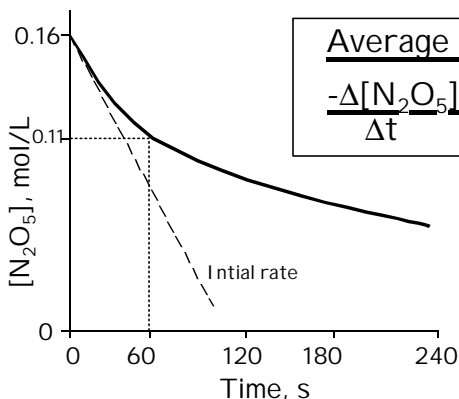
- **Thermo**: *Could the reaction happen?*
- **Kinetics**: *How does the reaction happen?*

Two Goals of Kinetics:

1. Determine the reaction pathway (*Mechanism*)
 - ✓ What steps are involved in the reaction?
2. Control the *Rate* of the reaction
 - **Example:** $\text{CO (g)} + \text{NO (g)} \rightarrow \text{CO}_2 \text{ (g)} + \frac{1}{2}\text{N}_2 \text{ (g)}$
 - ✓ Thermodynamically favored, but is *slow*

Reaction Rates

➤ Let's look at this reaction:



Average Decomposition Rate =

$$\frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{-(0.11 - 0.16)}{60 - 0} = 8.3 \times 10^{-4} \text{ mol/L-s}$$

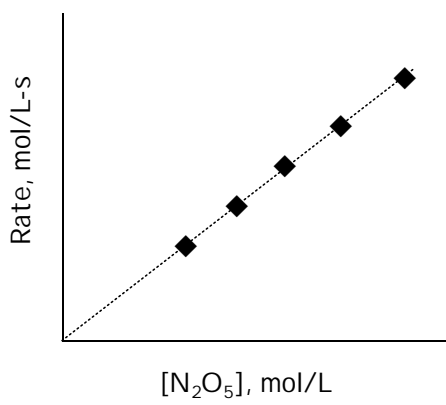
Instantaneous Rate:
As $\Delta t \rightarrow 0$, rate becomes:

$$\frac{-d[\text{N}_2\text{O}_5]}{dt}$$

← Slope at any time t

Rate Laws

➤ Reaction rate varies with $[\text{N}_2\text{O}_5]$:



Linear relationship:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

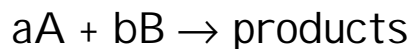
Rate constant (slope of line)

$$k = \frac{\text{rate}}{[\text{N}_2\text{O}_5]} = \frac{0.056 \text{ mol/L-min}}{0.160 \text{ mol/L}}$$

$$k = 0.35 \text{ min}^{-1}$$

Rate Laws - In General

- For any reaction:



We can write:

$$\text{Rate} = k[A]^m[B]^n$$

- ✓ $m + n = \text{overall rxn order}$
- ✓ m and $n \neq a$ and b
- ✓ Products play no role in rate of reaction

$m = \text{order of A in rxn}$

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The Method of Initial Rates

- One way to determine values for m and k
- **Example:** *Decomposition of acetaldehyde*



Rate Law: $\text{Rate} = k[\text{CH}_3\text{CHO}]^m$

Method:

- Measure *initial rate* for reactions having different $[\text{CH}_3\text{CHO}]$

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Data and Data Crunching

[CH ₃ CHO]	0.10	0.20	0.30	0.40	mol/L
Initial Rate	0.18	0.72	1.6	2.9	mol/L-s

Find Order (m)

For any two data points:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{CH}_3\text{CHO}]_1^m}{k[\text{CH}_3\text{CHO}]_2^m} = \frac{([\text{CH}_3\text{CHO}]_1)^m}{([\text{CH}_3\text{CHO}]_2)^m}$$

$$\frac{0.18}{0.72} = \frac{(0.10/0.20)^m}{1} \quad \Rightarrow \quad 1/4 = (1/2)^m \quad \boxed{m = 2}$$

How does one solve for *m*?

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What about *k* ?

➤ Solve for *k*:

For any data point:

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^2$$

$$k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^2} = \frac{0.18 \text{ mol/L-s}}{(0.10 \text{ mol/L})^2} = \underline{\underline{18. \text{ L/mol-s}}}$$

✓ Knowing *m* and *k*, Rate at *any concentration* can be predicted

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How does Reactant Concentration vary with Time?

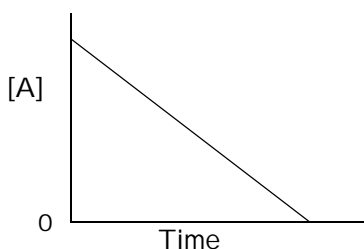
Depends on the reaction *order*:

Integrated Rate Laws

➤ **Zero-th Order Reactions**

- Rate is *independent* of concentration:

$$\text{Rate} = k[A]^0 = k$$



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

slope y-intercept

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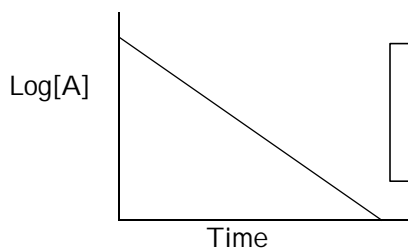
First-Order Reactions

For the reaction: $A \rightarrow \text{products}$

$$\text{Rate} = k[A]^1$$

Using a bit of calculus:

$$\text{Log}[A]_t = -(k/2.303)t + \text{Log}[A]_0$$

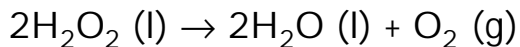


NOTE: Reaction rate *decreases* with time, so that [A] never reaches zero at any finite time t.

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1st-Order Reaction Example

➤ Decomposition of hydrogen peroxide:



$$m=1 \quad k=0.0410 \text{ min}^{-1}$$

If we start with 0.500 mol/L H_2O_2 , what will $[\text{H}_2\text{O}_2]$ be after 10.0 min?

Plug into 1st-order integrated rate equation:

$$\text{Log}[\text{H}_2\text{O}_2]_{10 \text{ min}} = -(0.0410 \text{ min}^{-1}/2.303)(10.0 \text{ min}) + \text{Log}(0.500 \text{ M})$$

$$\text{Log}[\text{H}_2\text{O}_2]_{10 \text{ min}} = -0.479$$

$$[\text{H}_2\text{O}_2]_{10 \text{ min}} = \underline{\underline{0.332 \text{ mol/L}}}$$

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More 1st-Order

How long will it take for $[\text{H}_2\text{O}_2]$ to drop to 0.100 M?

Solve integrated rate law for t :

$$t = (2.303/k)\text{Log}([\text{A}]_0/[\text{A}]_t)$$

Substituting and solving:

$$t = (2.303/0.0410 \text{ min}^{-1}) \text{Log} (0.500/0.100)$$

$$t = \underline{\underline{39.3 \text{ minutes}}}$$

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Special Case

How long will it take for *half* of the H_2O_2 to react?

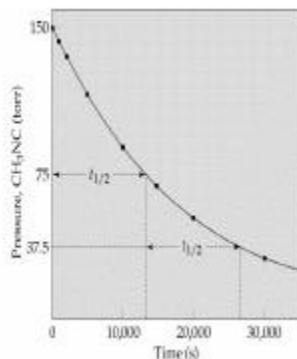
$$t = (2.303/k) \text{Log} (2.00) = \underline{\underline{16.9 \text{ min}}}$$

For *any 1st-order reaction*:

$$t_{1/2} = 0.693/k$$

Half-Life

Time to *halve* the concentration is a *constant!*



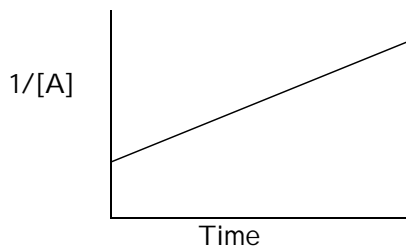
2nd-Order Reactions

For the reaction: $A \rightarrow \text{products}$

$$\text{Rate} = k[A]^2$$

Again, with the help of a bit of calculus:

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



Determining m and k

➤ Finding m

Which plot is linear?

$[A]$ vs. t ? → $m = 0$

$\text{Log}[A]$ vs. t ? → $m = 1$

$1/[A]$ vs. t ? → $m = 2$

➤ Finding k

$m = 0$ → $k = -\text{slope}$ ($[A]$ vs. t plot)

$m = 1$ → $k = -2.303 \times \text{slope}$ ($\text{Log}[A]$ vs. t plot)

$m = 2$ → $k = \text{slope}$ ($1/[A]$ vs. t plot)

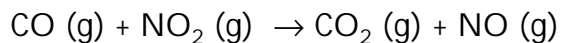
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How do reactions happen?

➤ Collision Theory

Reactions take place as a result of *collisions* between reactants

Example:



$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$

✓ Doubling $[\text{CO}]$ or $[\text{NO}_2]$ will double reaction rate

✓ WHY?

Doubling number of reactant species will double *collision frequency*

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Not All Collisions Result in a Reaction

➤ Must Be Above a Threshold Energy

- ✓ Kinetic Energy of reactants must exceed the *Activation Energy* (E_a)
 - For our example reaction: $E_a = 132 \text{ kJ/mol}$
- ✓ E_a is:
 - Independent of temperature
 - Independent of concentration
 - Always a *positive* value
- ✓ Fraction of reactants with K.E. $> E_a$ is often small

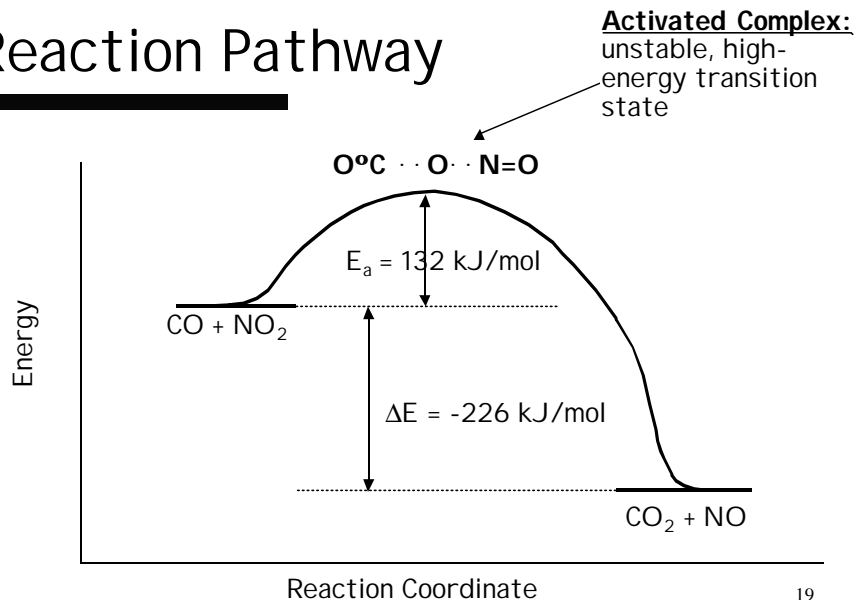
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Sufficient Energy is Not Enough

- Colliding reactants must have *proper orientation* in order to react
 - ✓ Must be oriented so as to form an *activated complex* that will breakup into products
- ❖ Reaction Rate depends on:
 1. Collision Frequency
 2. Fraction of *activated* species
 3. Geometric Probability

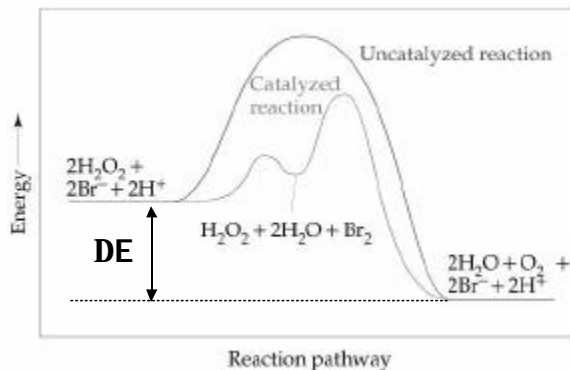
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Reaction Pathway



Catalysts

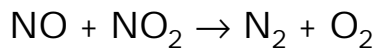
- Substances which increase reaction rate but are not changed/consumed by the reaction
- How? Provide a reaction pathway with a *lower* E_a :



Note: ΔE is *unaffected* by the catalyst

Catalysts: Example

■ Catalytic Converters

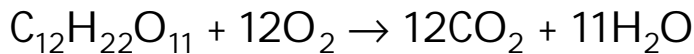


- ✓ Use Pt and Rh (deposited onto Al_2O_3 honeycomb) as catalysts
- ✓ *Heterogeneous Catalysis*
- ✓ Pb "poisons" catalyst (must use unleaded gasoline)

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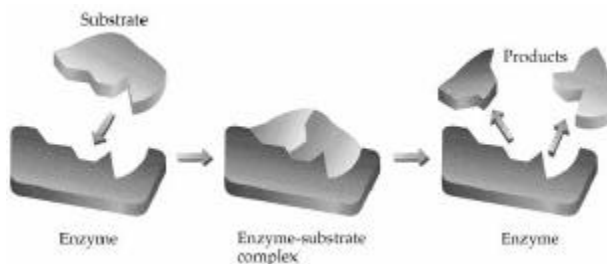
Catalysts: Another Example

➤ Combustion:



✓ Very slow reaction at body temperature (37 °C)

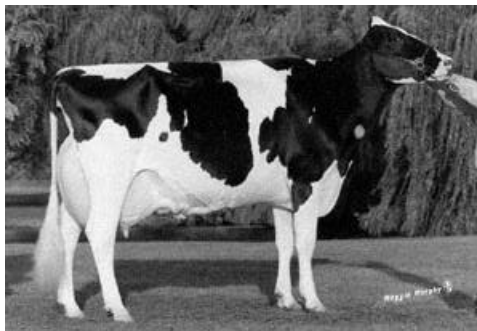
✓ *Enzymes* act as catalysts and speed up reaction:



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What's This?

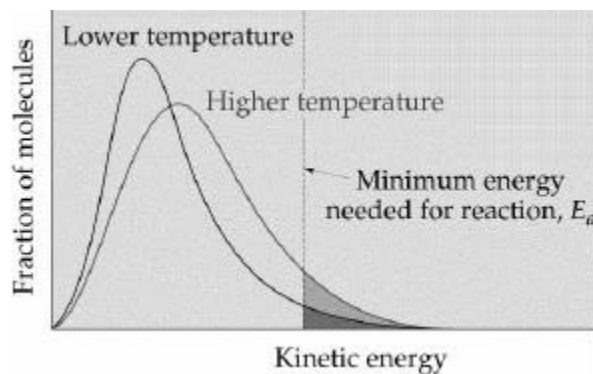
- Jersey
- Guernsey
- Angus
- Brahman
- Texas Longhorn
- Brown Swiss
- Holstein



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Effect of Temperature

- Increasing temperature, increases fraction of reactants with $K.E. > E_a$



Rule of Thumb: Rxn rate *doubles* for every $10\text{ }^\circ\text{C}$ increase

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The Arrhenius Equation

- Allows us to *quantify* the effect of temperature on rate constant:

$$\text{Ln}k = -(E_a/R)(1/T) + \text{Ln}A$$

Rate constant

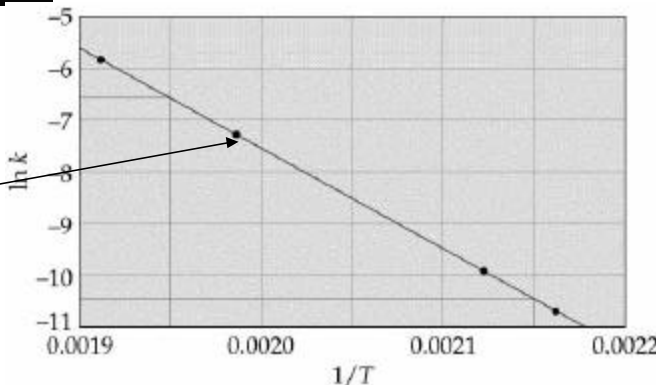
Arrhenius Constant
(function of collision frequency and steric factors)

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Graphical Analysis

- Plot $\text{Ln}k$ versus $1/T$:

Slope = $-E_a/R$



Alternately
(for 2 values):

$$\text{Ln}(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$$

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Reaction Mechanisms

➤ 3-Step Process

1. Propose a Mechanism

- Sequence of *elementary reactions* which sum to the total reaction

2. Determine Rate Law from Mechanism

- Rate Law for any *elementary reaction*:

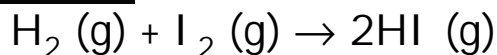


3. Compare Rate Law with Experiment

- Assess *plausibility* of the mechanism

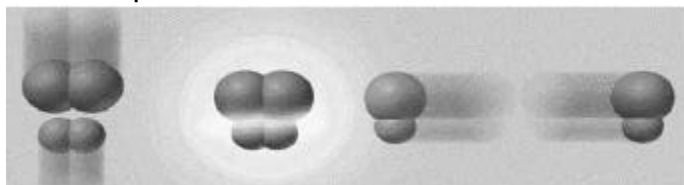
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An Example



Proposed Mechanism: *Single-Step*

- ✓ Reaction proceeds as written: **bimolecular**



- ✓ Rate = $k[\text{H}_2][\text{I}_2]$

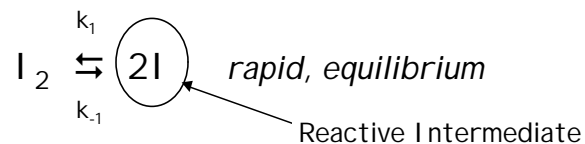
- ✓ Rate Law agrees with experiment

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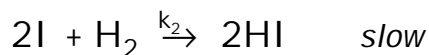
Another Mechanism

➤ A 2-Step Mechanism:

1. Iodine Dissociates (unimolecular process)



2. Iodine atoms combine with H₂ (termolecular)



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Rate Law from Mechanism

➤ *Slow Step* determines the rate:

$$\text{Rate} = k_2[H_2][I]^2$$

From Step 1: *Fwd Rate = Rev Rate* (equilibrium)

$$k_1[I_2] = k_{-1}[I]^2$$

Solve for [I]²: $[I]^2 = (k_1/k_{-1})[I_2]$

Substitute: $\text{Rate} = \frac{k_2 k_1}{k_{-1}} [H_2][I_2]$

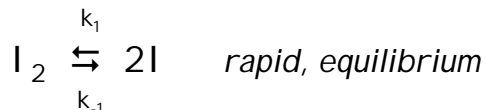
Finally: **Rate = k[H₂][I₂]** agrees with expt.

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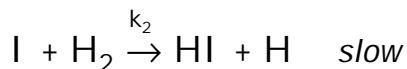
YAM (yet another mechanism)

➤ A 3-Step Mechanism:

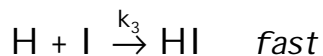
1. Iodine Dissociates (unimolecular process)



2. Displacement



3. Combine Remaining Atoms



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On to the Rate Law

- From the *slow* displacement step:

$$\text{Rate} = k_2[\text{I}][\text{H}_2]$$

From Step 1:
(equilibrium)

$$\text{Fwd Rate} = \text{Rev Rate}$$

$$k_1[\text{I}_2] = k_{-1}[\text{I}]^2$$

Solve for [I]:

$$[\text{I}] = \{(k_1/k_{-1})[\text{I}_2]\}^{1/2}$$

Substitute:

$$\text{Rate} = k_2(k_1/k_{-1})^{1/2}[\text{I}_2]^{1/2}[\text{H}_2]$$

Finally:

$$\text{Rate} = k[\text{H}_2][\text{I}_2]^{1/2}$$

Does NOT agree with experiment!
MECHANISM 3 is not plausible.

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Which Mechanism is Correct?

- Mechanisms I and II are both *plausible*
(rate laws are consistent with experiment)
 - ✓ Do additional experiments:
look for the *reactive intermediate*
(evidence for the existence of **I**?)
 - ✓ Results?
⇒ Evidence favors ***Mechanism II***

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