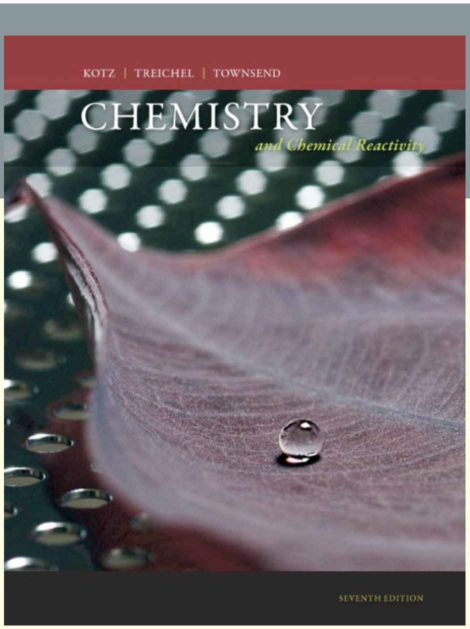

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Chapter 15
Principles of Reactivity: Chemical Kinetics

John C. Kotz • State University of New York, College at Oneonta

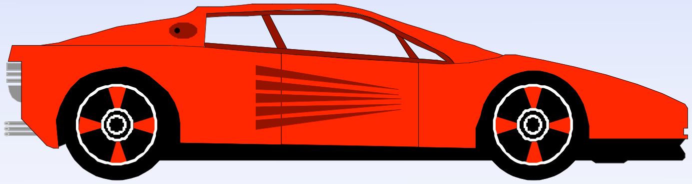
Chemical Kinetics

- We can use thermodynamics to tell if a reaction is product- or reactant-favored.
- But this gives us no info on HOW FAST reaction goes from reactants to products.
- **KINETICS** — the study of REACTION RATES and their relation to the way the reaction proceeds, i.e., its MECHANISM.
- The reaction mechanism is our goal!

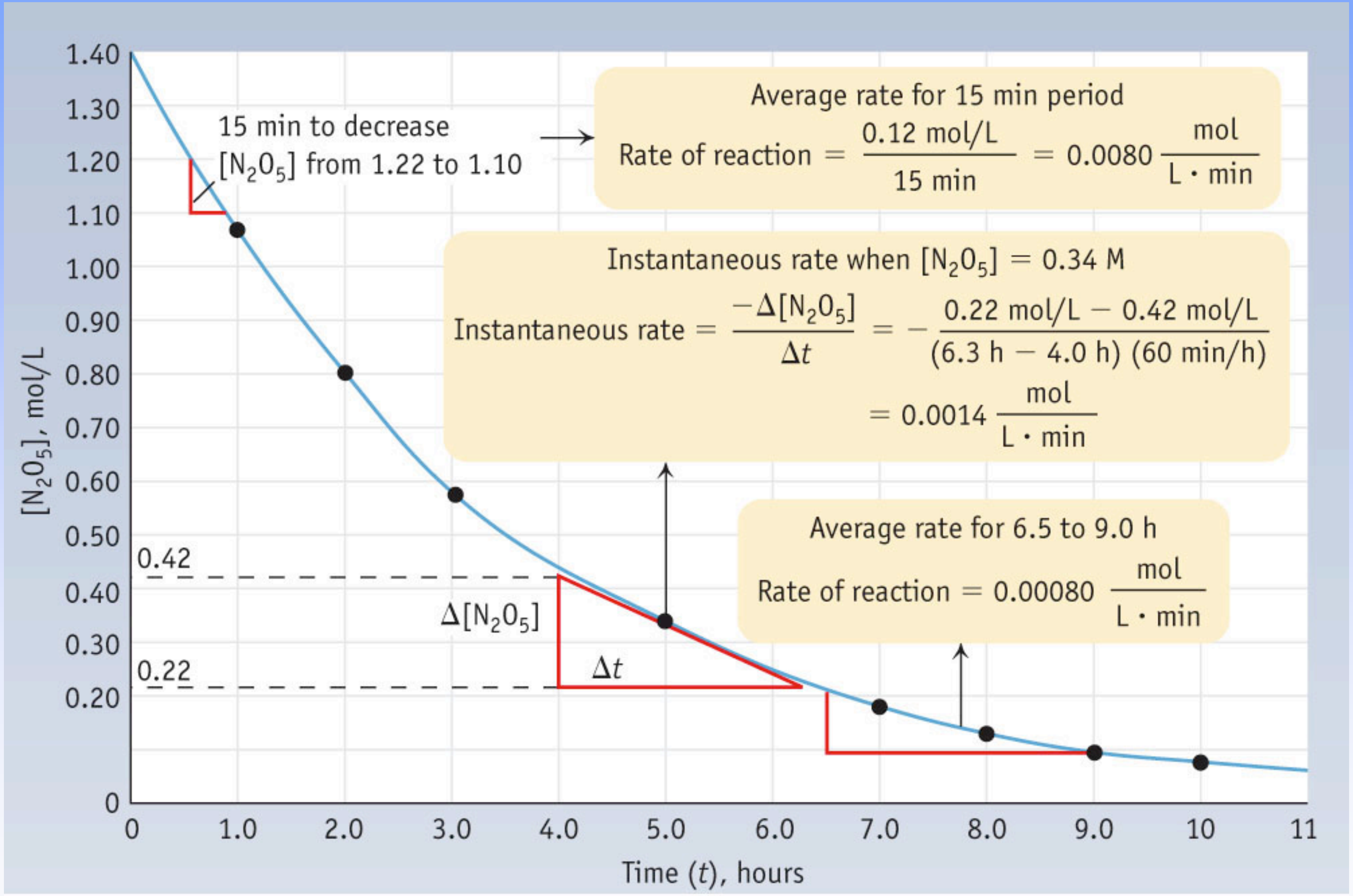
Reaction Rates

Section 15.1

- **Reaction rate = change in concentration of a reactant or product with time.**
- **Three "types" of rates**
  - **initial rate**
  - **average rate**
  - **instantaneous rate**



Determining a Reaction Rate



15 min to decrease $[N_2O_5]$ from 1.22 to 1.10 →

Average rate for 15 min period

$$\text{Rate of reaction} = \frac{0.12\ \text{mol/L}}{15\ \text{min}} = 0.0080\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Instantaneous rate when $[N_2O_5] = 0.34$ M

$$\text{Instantaneous rate} = \frac{-\Delta[N_2O_5]}{\Delta t} = -\frac{0.22\ \text{mol/L} - 0.42\ \text{mol/L}}{(6.3\ \text{h} - 4.0\ \text{h})\ (60\ \text{min/h})}$$

$$= 0.0014\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

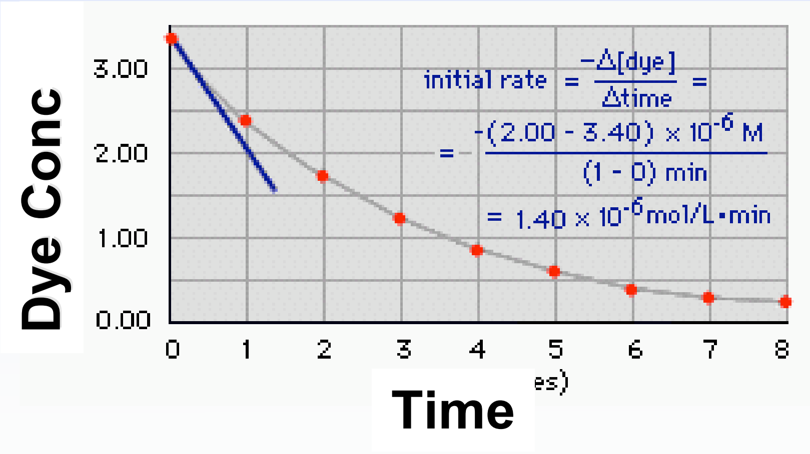
Average rate for 6.5 to 9.0 h

$$\text{Rate of reaction} = 0.00080\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

See Active Figure 15.2

Determining a Reaction Rate

PLAY MOVIE



Blue dye is oxidized with bleach.

Its concentration decreases with time.

The rate — the change in dye conc with time — can be determined from the plot.

See Chemistry Now , Chapter 15

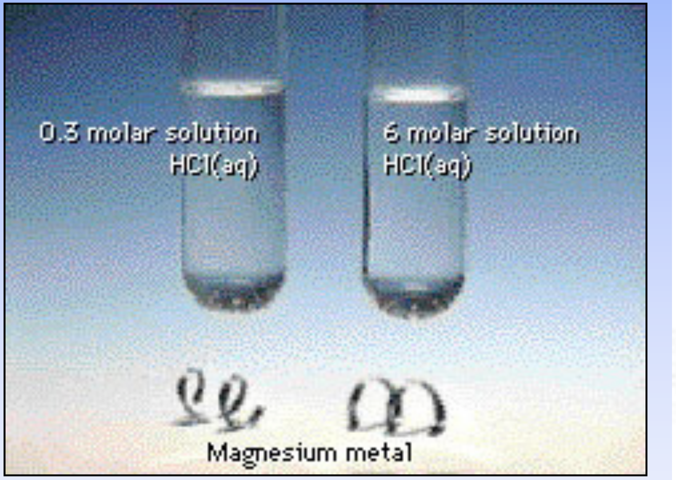
Factors Affecting Rates

- Concentrations
- and physical state of reactants and products
- Temperature
- Catalysts

Concentrations & Rates

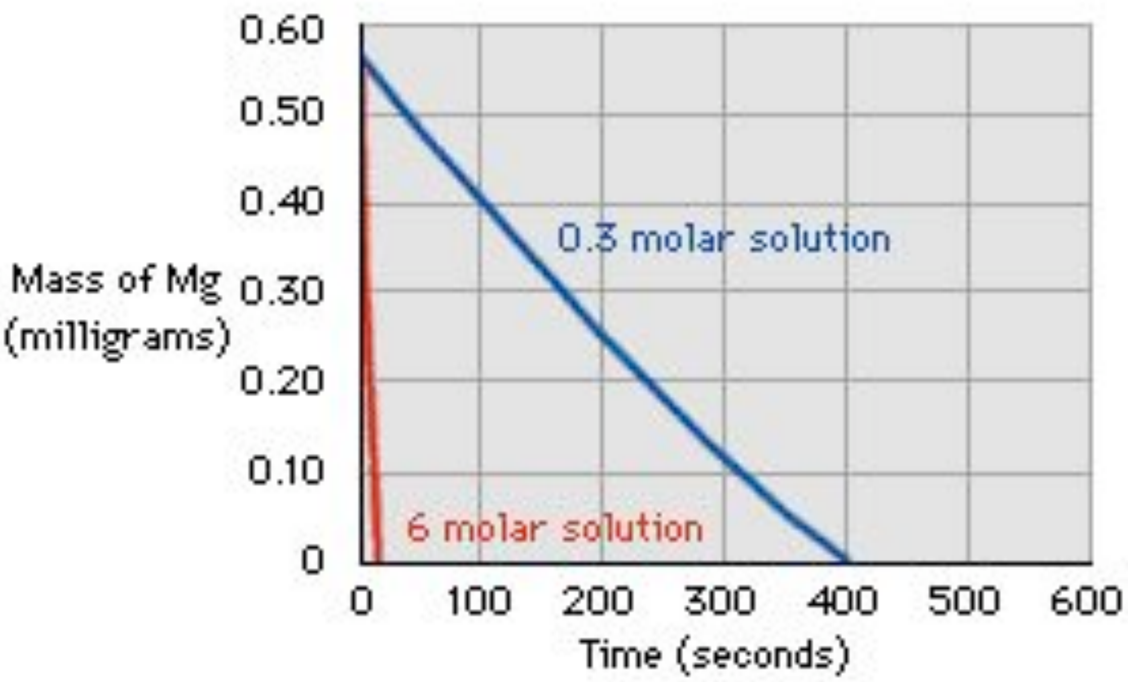
Section 15.3

$$Mg(s) + 2\ HCl(aq)\ f\ MgCl_2(aq) + H_2(g)$$



0.3 M HCl **6 M HCl**

PLAY MOVIE



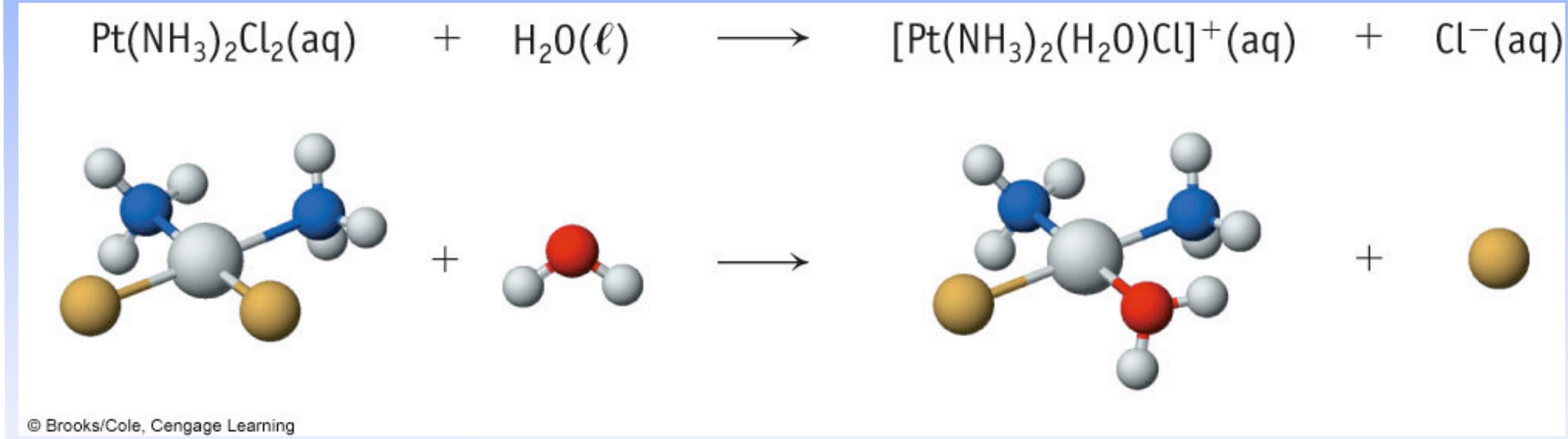
Concentrations and Rates

To postulate a reaction mechanism, we study

- reaction rate and
- its concentration dependence

Concentrations and Rates

Take reaction where Cl^- in cisplatin $[Pt(NH_3)_2Cl_3]$ is replaced by H_2O



$$Pt(NH_3)_2Cl_2(aq) + H_2O(\ell) \longrightarrow [Pt(NH_3)_2(H_2O)Cl]^+(aq) + Cl^-(aq)$$

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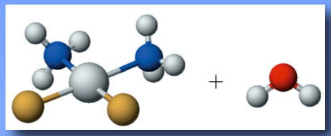
Rate of change of conc of Pt compd

$$= \frac{\text{Am't of cisplatin reacting (mol/L)}}{\text{elapsed time (t)}}$$



Concentrations & Rates

Rate of change of conc of Pt compd

$$= \frac{\text{Am't of cisplatin reacting (mol/L)}}{\text{elapsed time (t)}}$$

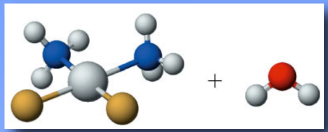
Rate of reaction is proportional to $[Pt(NH_3)_2Cl_2]$

We express this as a RATE LAW

Rate of reaction = k $[Pt(NH_3)_2Cl_2]$

where k = rate constant

k is independent of conc. but increases with T



Concentrations, Rates, & Rate Laws

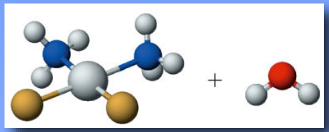
In general, for

a A + b B f x X with a catalyst *C*

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

The exponents m, n, and p

- are the reaction order
- can be 0, 1, 2 or fractions
- must be determined by experiment!



Interpreting Rate Laws

Rate = k $[A]^m[B]^n[C]^p$

- If m = 1, rxn. is 1st order in A

  Rate = k $[A]^1$

  If [A] doubles, then rate goes up by factor of __

- If m = 2, rxn. is 2nd order in A.

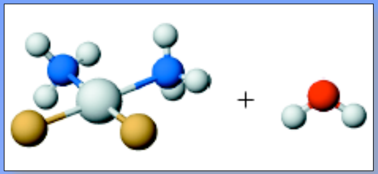
  Rate = k $[A]^2$

  Doubling [A] increases rate by ________

- If m = 0, rxn. is zero order.

  Rate = k $[A]^0$

  If [A] doubles, rate ________



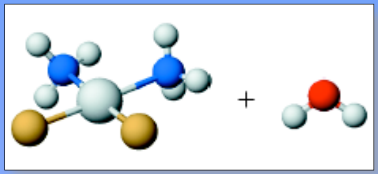
Deriving Rate Laws

Derive rate law and k for

$CH_3CHO(g)$ f $CH_4(g)$ + $CO(g)$

from experimental data for rate of disappearance of CH_3CHO

Expt.	$[CH_3CHO]$ (mol/L)	Disappear of CH_3CHO (mol/L•sec)
1	0.10	0.020
2	0.20	0.081
3	0.30	0.182
4	0.40	0.318



Deriving Rate Laws

Rate of rxn = k $[CH_3CHO]^2$

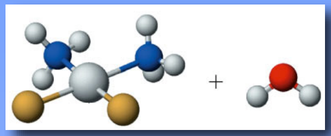
Here the rate goes up by ________ when initial conc. doubles. Therefore, we say this reaction is ______________________ order.

Now determine the value of k. Use expt. #3 data—

0.182 mol/L•s = k $(0.30 \text{ mol/L})^2$

k = 2.0 (L / mol•s)

Using k you can calc. rate at other values of $[CH_3CHO]$ at same T.



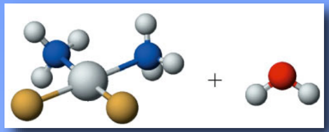
Concentration/Time Relations

What is concentration of reactant as function of time?

Consider **FIRST ORDER REACTIONS**

The rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta \text{time}} = k\,[A]$$



Concentration/Time Relations

Integrating - (Δ [A] / Δ time) = k [A], we get

ln is natural logarithm

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

$[A]_0$ at time = 0

$[A] / [A]_0$ =fraction remaining after time t has elapsed.

Called the *integrated first-order rate law*.

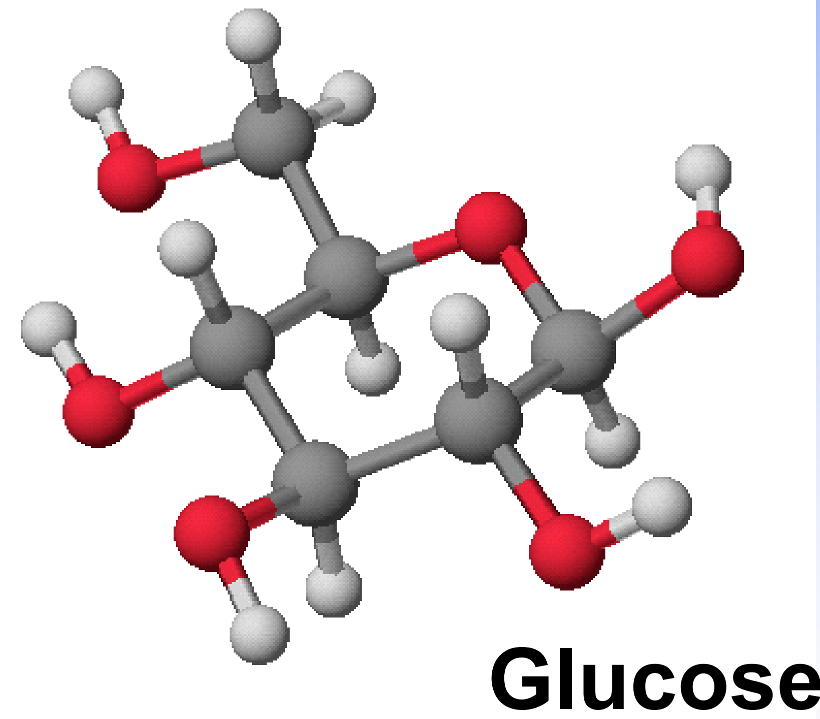
Concentration/Time Relations

Sucrose decomposes to simpler sugars

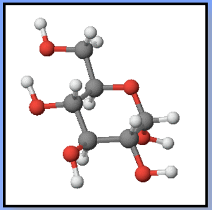
Rate of disappearance of sucrose = k [sucrose]

If $k = 0.21\ \text{hr}^{-1}$
and [sucrose] = 0.010 M

How long to drop 90%
(to 0.0010 M)?



Glucose



Concentration/Time Relations

Rate of disappear of sucrose = k [sucrose], k = 0.21 hr^{-1}. If initial [sucrose] = 0.010 M, how long to drop 90% or to 0.0010 M?

Use the first order integrated rate law

$$\ln\left(\frac{0.0010}{0.010}\right) = -\,(0.21\ \mathrm{h}^{-1})\ t$$

ln (0.100) = - 2.3 = - (0.21 hr^{-1})(time)

time = 11 hours

Integrated 1st order rate law

- Use to find either time to reach a particular concentration or to find a concentration after a certain time, t
- Zero order and 2nd order have different equations

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

Using the Integrated Rate Law

The integrated rate law suggests a way to tell the order based on experiment.

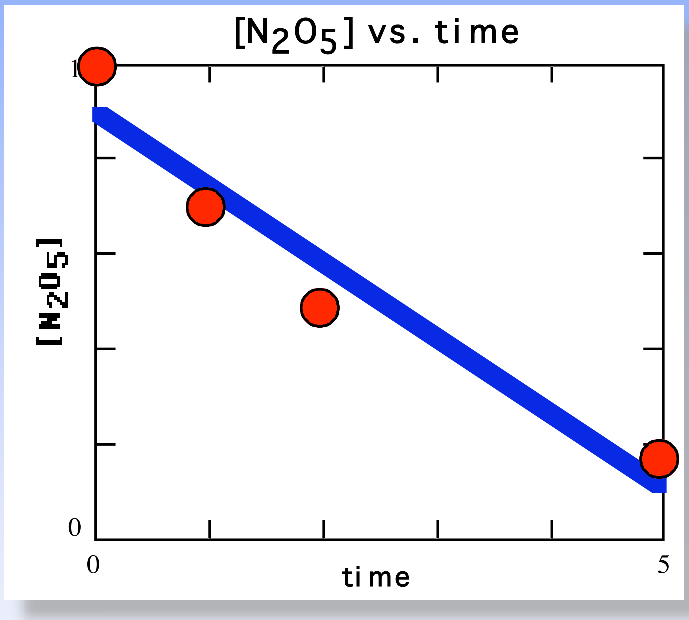
$$2\ N_2O_5(g)\ \ f\ \ 4\ NO_2(g)\ +\ O_2(g)$$

Time (min)	$[N_2O_5]_0$ (M)	ln $[N_2O_5]_0$
0	1.00	0
1.0	0.705	-0.35
2.0	0.497	-0.70
5.0	0.173	-1.75

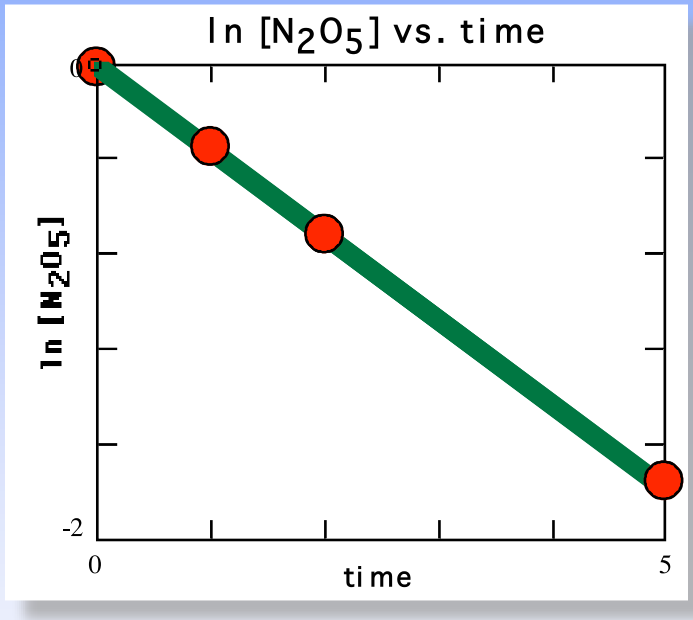
$$\text{Rate} = k\,[N_2O_5]$$

Using the Integrated Rate Law

$2\ N_2O_5(g)$ f $4\ NO_2(g)\ +\ O_2(g)$ Rate = k $[N_2O_5]$

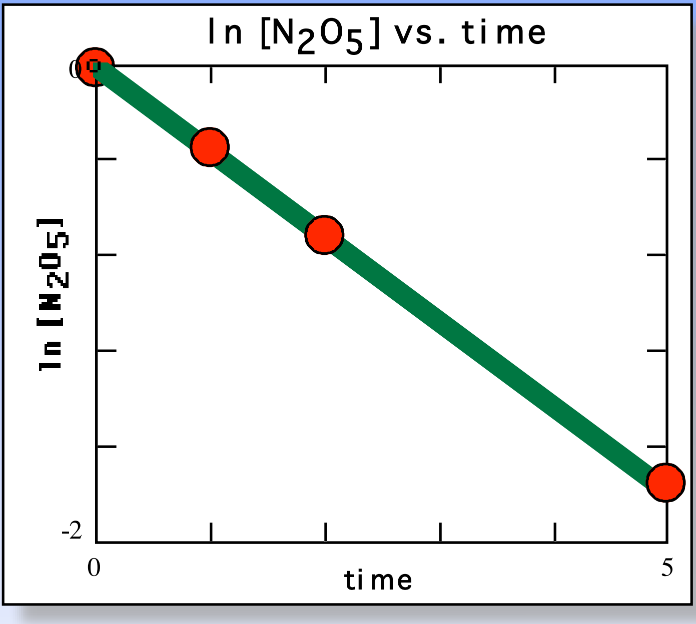


Data of conc. vs. time plot do not fit straight line.



Plot of ln $[N_2O_5]$ vs. time is a straight line!

Using the Integrated Rate Law



Plot of ln $[N_2O_5]$ vs. time is a straight line!

Eqn. for straight line:

$$y = mx + b$$

$$\ln [N_2O_5] = -kt + \ln [N_2O_5]_o$$

conc at time t

rate const = slope

conc at time = 0

All 1st order reactions have straight line plot for ln [A] vs. time.

(2nd order gives straight line for plot of 1/[A] vs. time)

Properties of Reactions

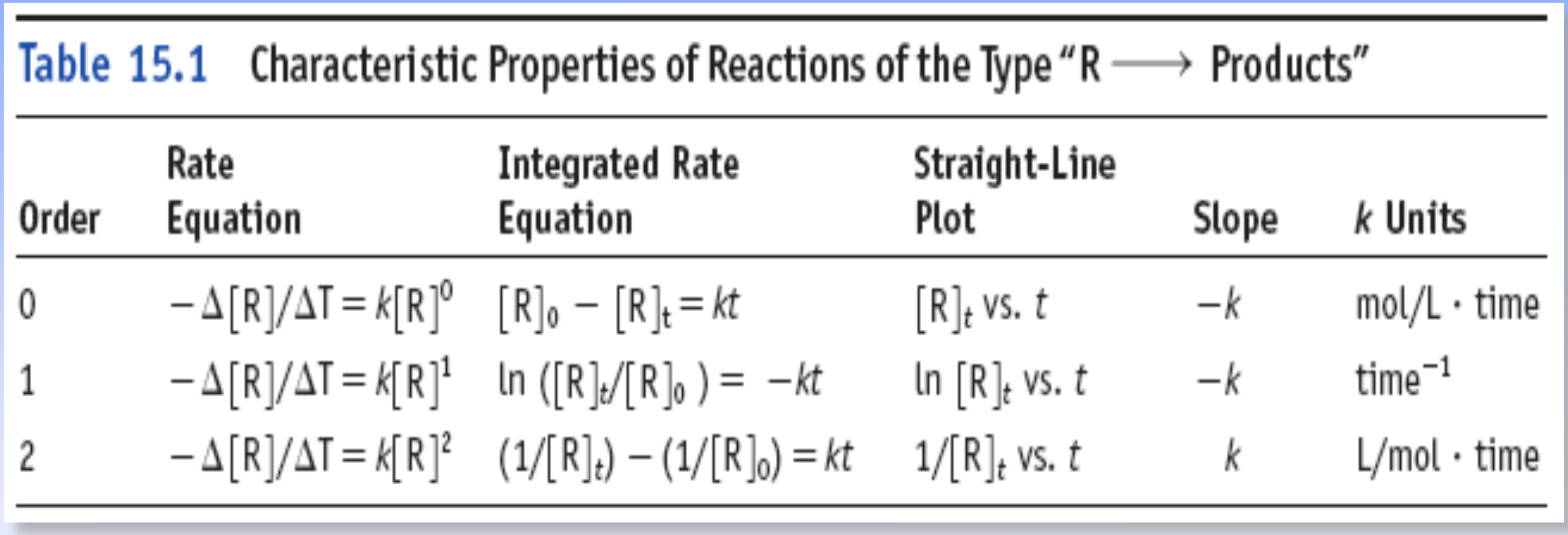


Table 15.1 Characteristic Properties of Reactions of the Type "$R \longrightarrow$ Products"

Order	Rate Equation	Integrated Rate Equation	Straight-Line Plot	Slope	k Units
0	$-\Delta[R]/\Delta T = k[R]^0$	$[R]_0 - [R]_t = kt$	$[R]_t$ vs. t	$-k$	mol/L · time
1	$-\Delta[R]/\Delta T = k[R]^1$	$\ln([R]_t/[R]_0) = -kt$	$\ln [R]_t$ vs. t	$-k$	time^{-1}
2	$-\Delta[R]/\Delta T = k[R]^2$	$(1/[R]_t) - (1/[R]_0) = kt$	$1/[R]_t$ vs. t	k	L/mol · time

Factors Affecting Rates

- Concentrations
- and physical state of reactants and products
- Temperature
- Catalysts

Factors Affecting Rates

- Physical state of reactants

Factors Affecting Rates

Catalysts: catalyzed decomp of H_2O_2

$$2\ H_2O_2\ f\ \ 2\ H_2O\ +\ O_2$$

PLAY MOVIE

Catalysts

(a) $t = 0$ (b) $t = 3$ sec (c) $t = 15$ sec (d) $t = 17$ sec (e) $t = 21$ sec

See Page 702

1. CO_2(g) e CO_2 (aq)
2. CO_2 (aq) + H_2O(liq) e H_2CO_3(aq)
3. H_2CO_3(aq) e H^+(aq) + HCO_3^-(aq)

- Adding trace of NaOH uses up H^+. Equilibrium shifts to produce more H_2CO_3.
- Enzyme in blood (above) speeds up reactions 1 and 2

Factors Affecting Rates

- **Temperature**

Bleach at 54 ˚C

PLAY MOVIE

Bleach at 22 ˚C

Iodine Clock Reaction

1. Iodide is oxidized to iodine

$H_2O_2 + 2\,I^- + 2\,H^+ \text{ f } 2\,H_2O + I_2$

2. I_2 reduced to I^- with vitamin C

$I_2 + C_6H_8O_6 \text{ f } C_6H_6O_6 + 2\,H^+ + 2\,I^-$

When all vitamin C is depleted, the I_2 interacts with starch to give a blue complex.

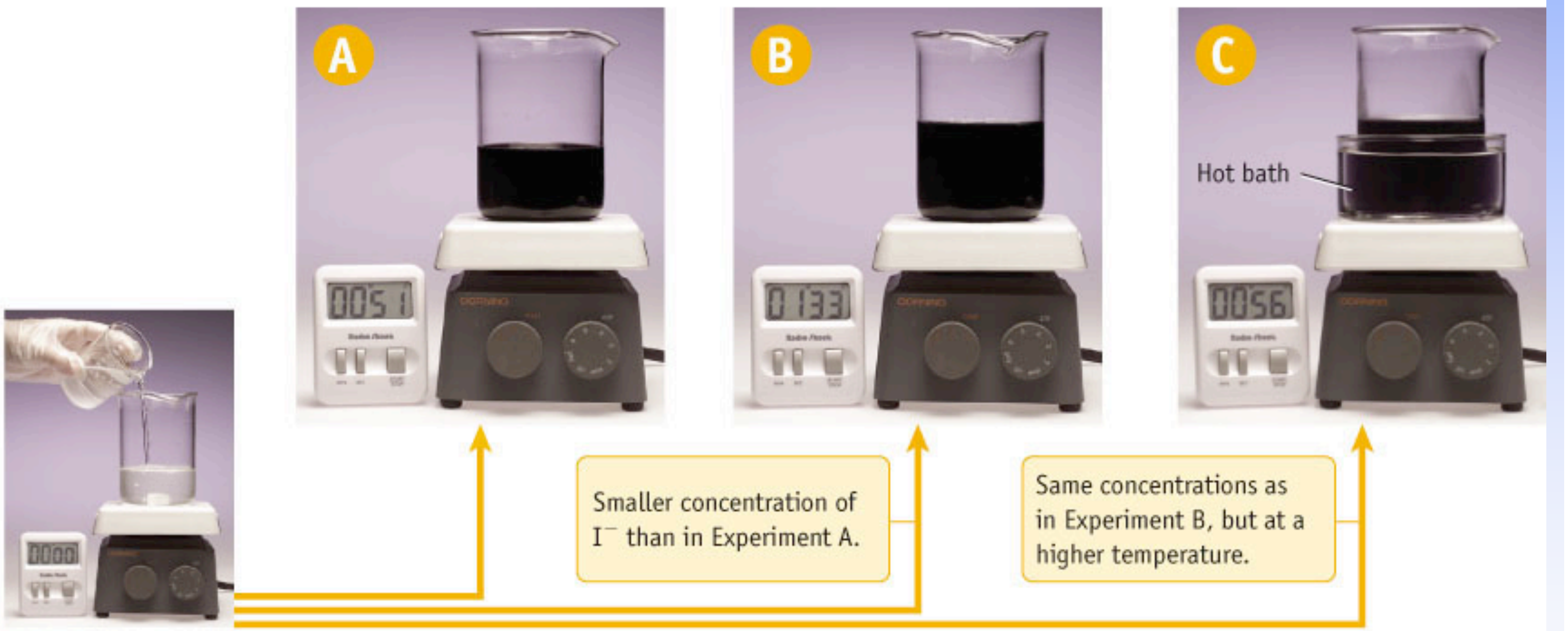
(a) Initial Experiment.
The blue color of the starch–iodine complex develops in 51 seconds.

Iodine Clock Reaction

(a) Initial Experiment. The blue color of the starch–iodine complex develops in 51 seconds.

(b) Change Concentration. The blue color of starch–iodine complex develops in 1 minute, 33 seconds when the solution is less concentrated than A.

(c) Change Temperature. The blue color of the starch–iodine complex develops in 56 seconds when the solution is the same concentration as in B but at a higher temperature.

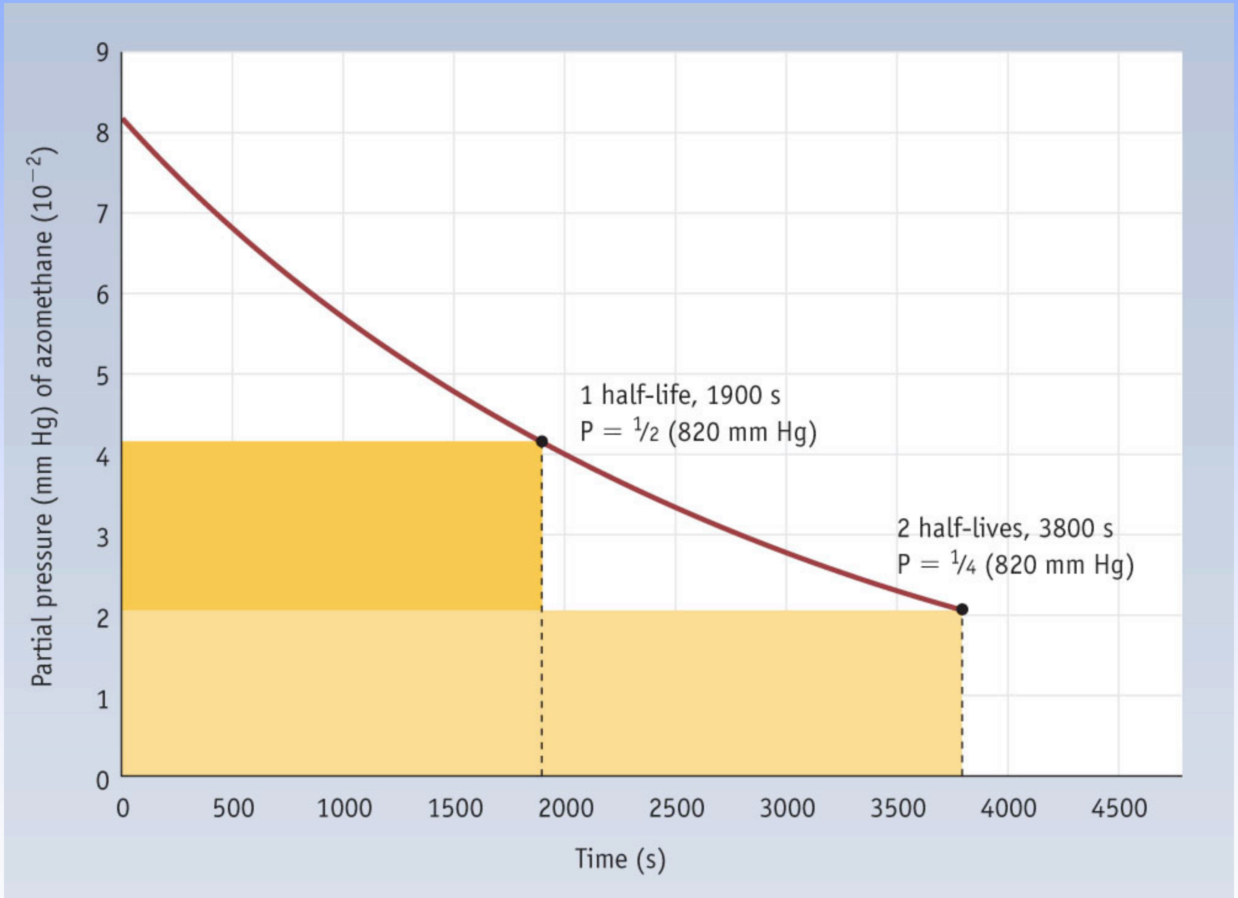


Smaller concentration of I^- than in Experiment A.

Same concentrations as in Experiment B, but at a higher temperature.

Solutions containing vitamin C, H_2O_2, I^-, and starch are mixed.

Half-Life

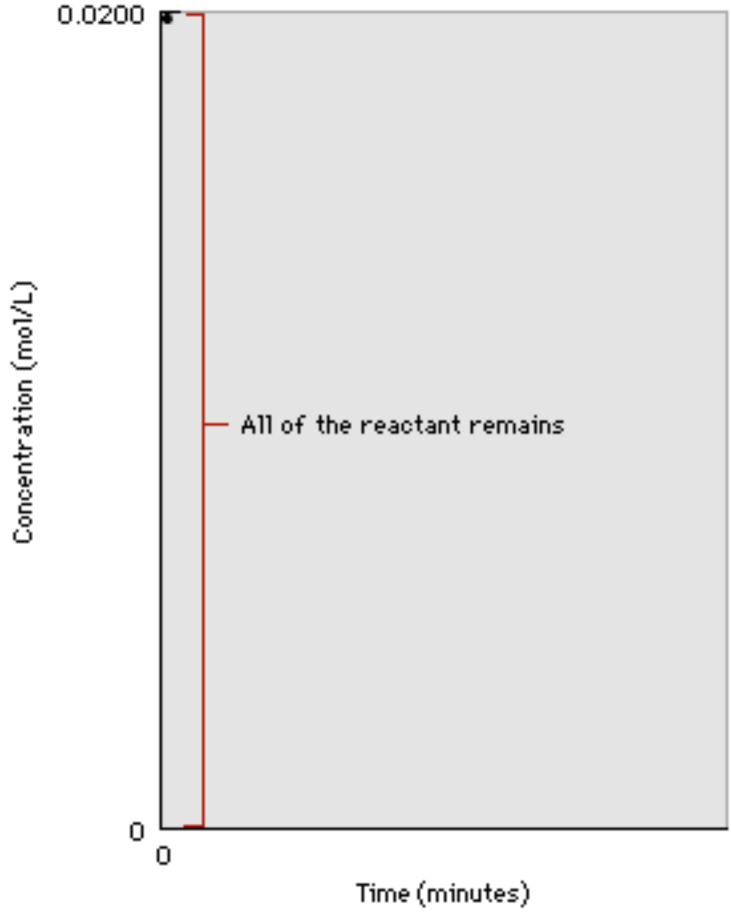


See Active Figure 15.9

HALF-LIFE is the time it takes for 1/2 a sample to disappear.

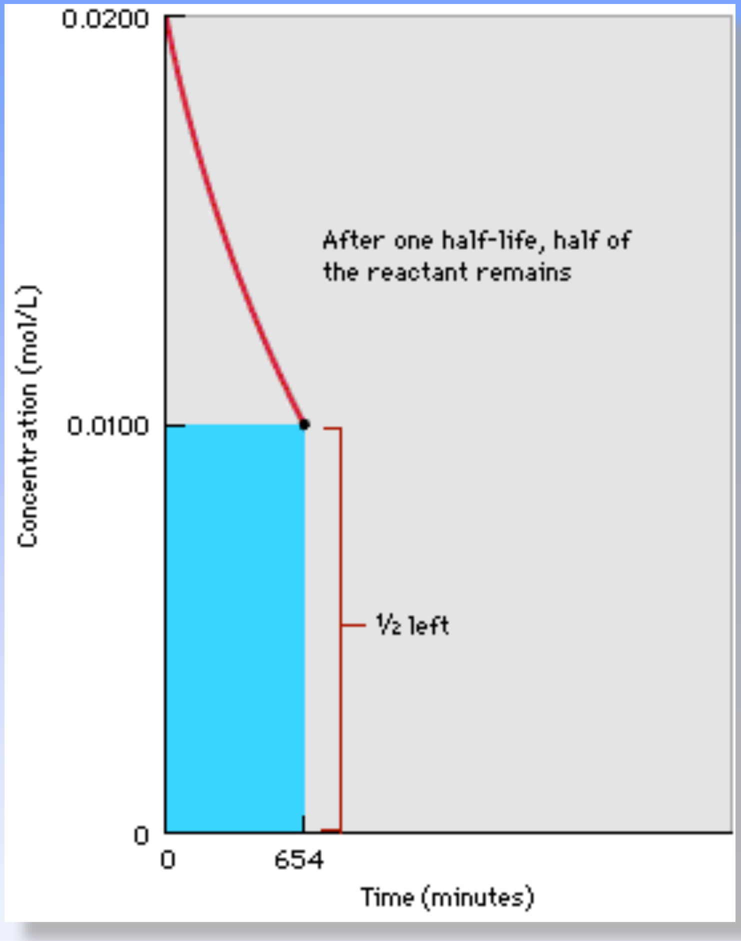
For 1st order reactions, the concept of HALF-LIFE is especially useful.

Half-Life



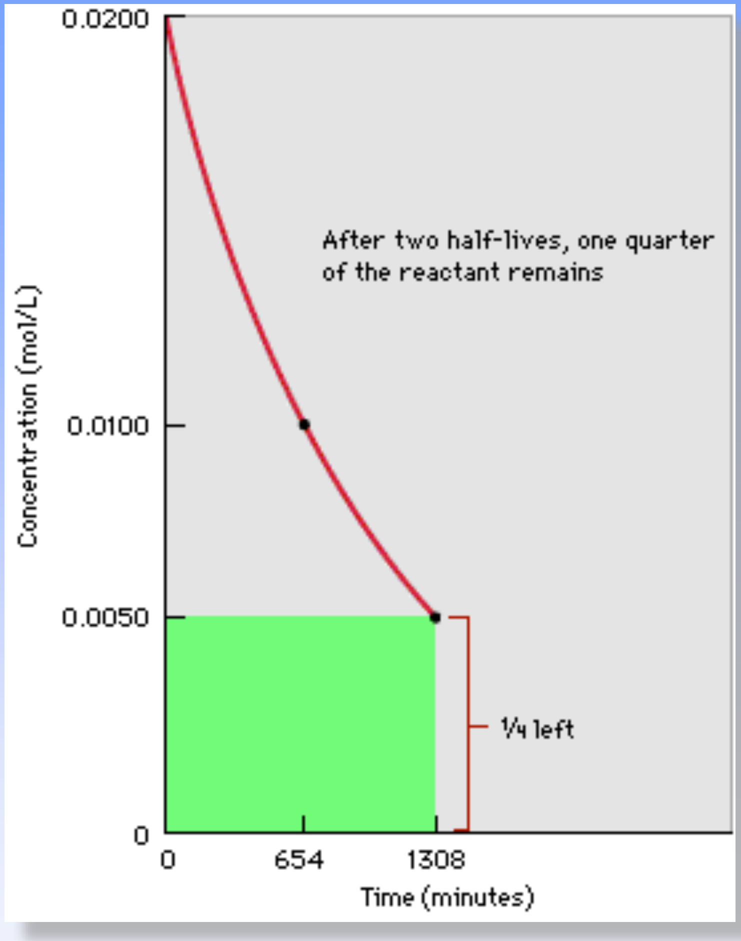
- Reaction is 1st order decomposition of H_2O_2.

Half-Life



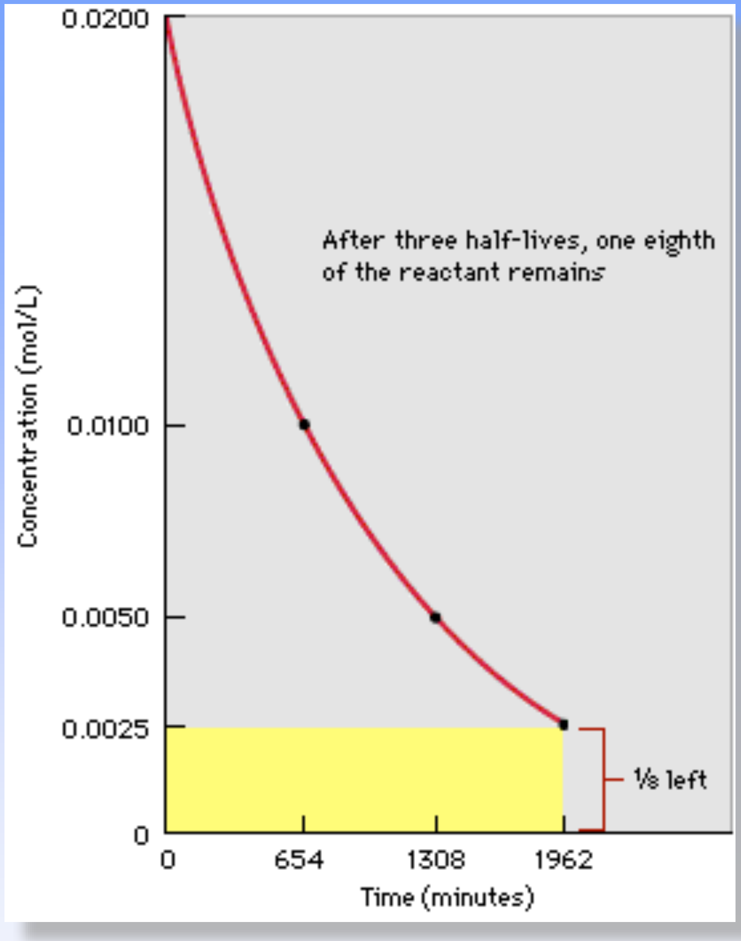
- **Reaction after 1 half-life.**
- **1/2 of the reactant has been consumed and 1/2 remains.**

Half-Life

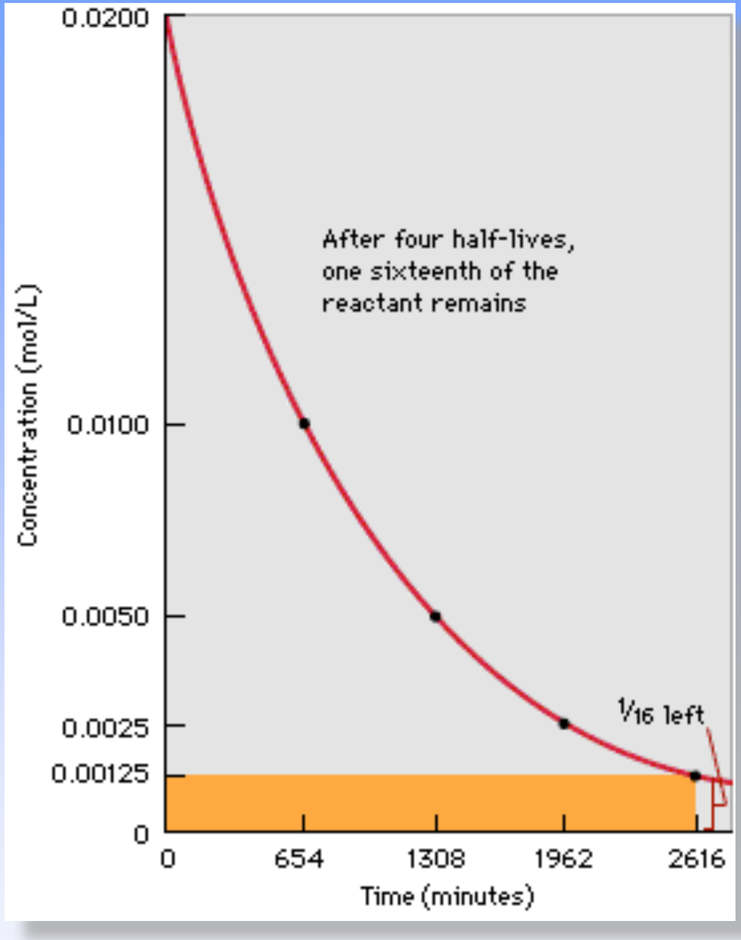


- After 2 half-lives 1/4 of the reactant remains.

Half-Life



- **A 3 half-lives 1/8 of the reactant remains.**



Half-Life

- **After 4 half-lives 1/16 of the reactant remains.**

Half-Life

Sugar is fermented in a 1st order process (using an enzyme as a catalyst).

sugar + enzyme f products

Rate of disappear of sugar = k[sugar]

$$k = 3.3 \times 10^{-4}\ sec^{-1}$$

What is the half-life of this reaction?

Half-Life

Rate = k[sugar] and k = 3.3×10^{-4} sec^{-1}. What is the half-life of this reaction?

Solution

$[A] / [A]_0$ = fraction remaining

when $t = t_{1/2}$ then fraction remaining = __________

Therefore, $\ln (1/2) = - k \cdot t_{1/2}$

$$- 0.693 = - k \cdot t_{1/2}$$

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

So, for sugar,

$t_{1/2} = 0.693 / k = 2100$ sec = 35 min

Half-Life

Rate = k[sugar] and k = 3.3 x 10^{-4} sec^{-1}. Half-life is 35 min. Start with 5.00 g sugar. How much is left after 2 hr and 20 min (140 min)?

Solution

2 hr and 20 min = 4 half-lives

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

Half-Life

Radioactive decay is a first order process.

Tritium f electron + helium

^{3}H $^{0}_{-1}e$ ^{3}He

$t_{1/2}$ = 12.3 years

If you have 1.50 mg of tritium, how much is left after 49.2 years?

Half-Life

Start with 1.50 mg of tritium, how much is left after 49.2 years? $t_{1/2}$ = 12.3 years

Solution

$\ln [A] / [A]_0 = -kt$

$[A] = ?$ $[A]_0 = 1.50$ mg $t = 49.2$ y

Need k, so we calc k from: $k = 0.693 / t_{1/2}$

Obtain $k = 0.0564\ y^{-1}$

Now $\ln [A] / [A]_0 = -kt = -(0.0564\ y^{-1})(49.2\ y)$

$= -2.77$

Take antilog: $[A] / [A]_0 = e^{-2.77} = 0.0627$

0.0627 = fraction remaining

Half-Life

Start with 1.50 mg of tritium, how much is left after 49.2 years? $t_{1/2}$ = 12.3 years

Solution

$[A] / [A]_0 = 0.0627$

0.0627 is the fraction remaining!

Because $[A]_0$ = 1.50 mg, [A] = 0.094 mg

But notice that 49.2 y = 4.00 half-lives

1.50 mg f 0.750 mg after 1 half-life

f 0.375 mg after 2

f 0.188 mg after 3

f 0.094 mg after 4

Half-Lives of Radioactive Elements

Rate of decay of radioactive isotopes given in terms of 1/2-life.

^{238}U f ^{234}Th + He 4.5 x 10^9 y

^{14}C f ^{14}N + beta 5730 y

^{131}I f ^{131}Xe + beta 8.05 d

Element 106 - seaborgium - ^{263}Sg

0.9 s

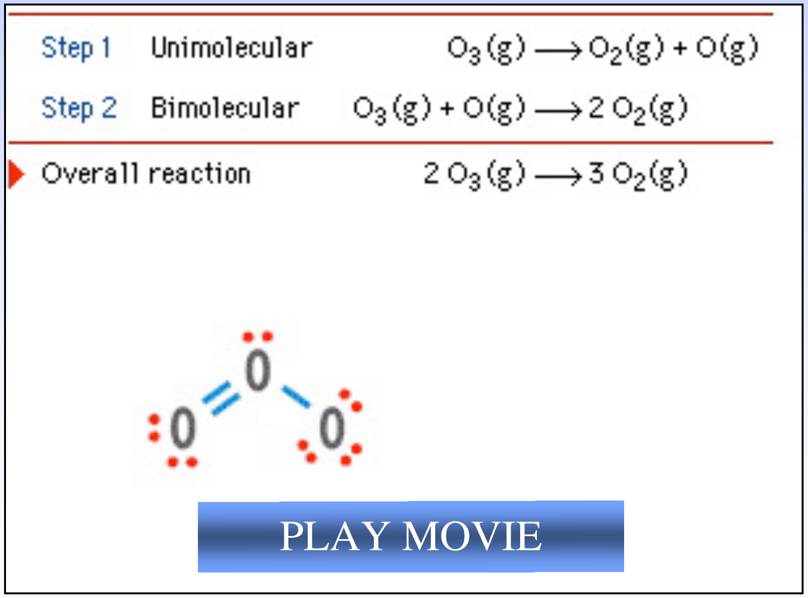
MECHANISMS

A Microscopic View of Reactions

Mechanism: how reactants are converted to products at the molecular level.

RATE LAW f MECHANISM

experiment f theory



Step 1 Unimolecular $O_3(g) \longrightarrow O_2(g) + O(g)$

Step 2 Bimolecular $O_3(g) + O(g) \longrightarrow 2\,O_2(g)$

Overall reaction $2\,O_3(g) \longrightarrow 3\,O_2(g)$

Reaction Mechanisms

The sequence of events at the molecular level that control the speed and outcome of a reaction.

Br from biomass burning destroys stratospheric ozone.

(See R.J. Cicerone, *Science*, volume 263, page 1243, 1994.)

Step 1: $Br + O_3$ f $BrO + O_2$

Step 2: $Cl + O_3$ f $ClO + O_2$

Step 3: $BrO + ClO$ + light f $Br + Cl + O_2$

NET: $2\ O_3$ f $3\ O_2$

Activation Energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier - activation energy, E_a.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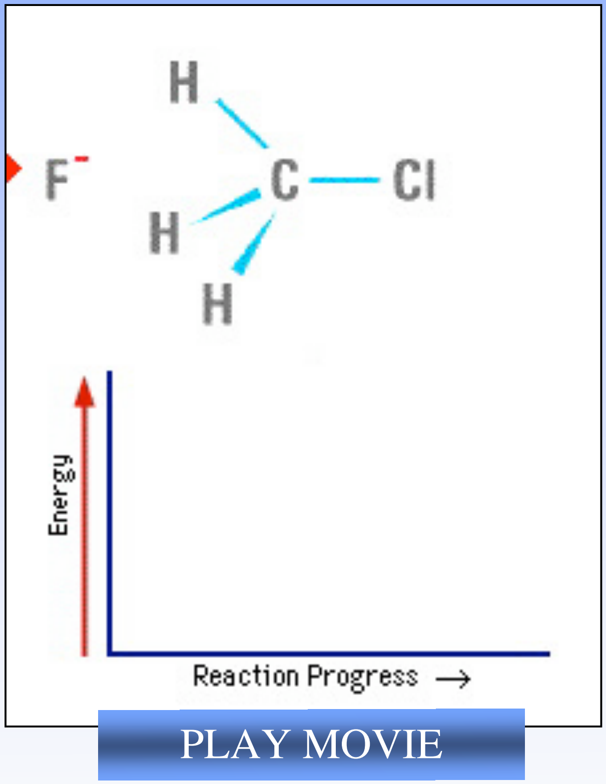
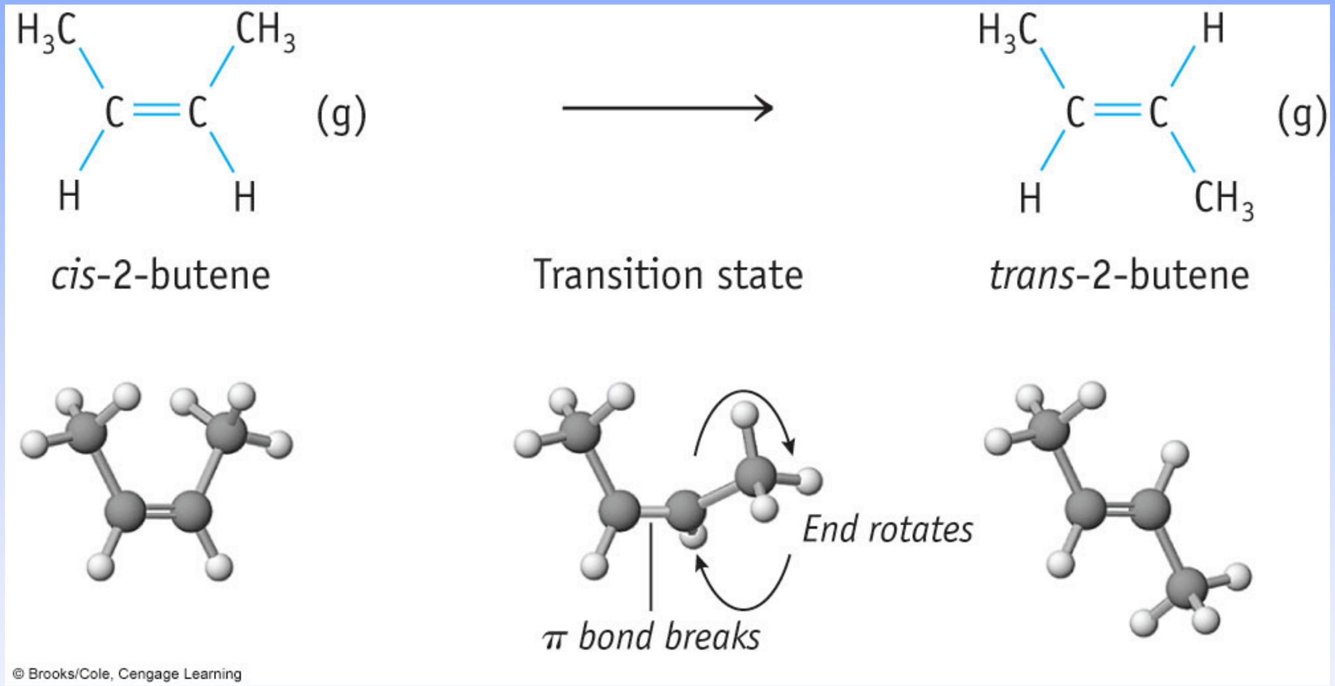


Reaction coordinate diagram

MECHANISMS & Activation Energy

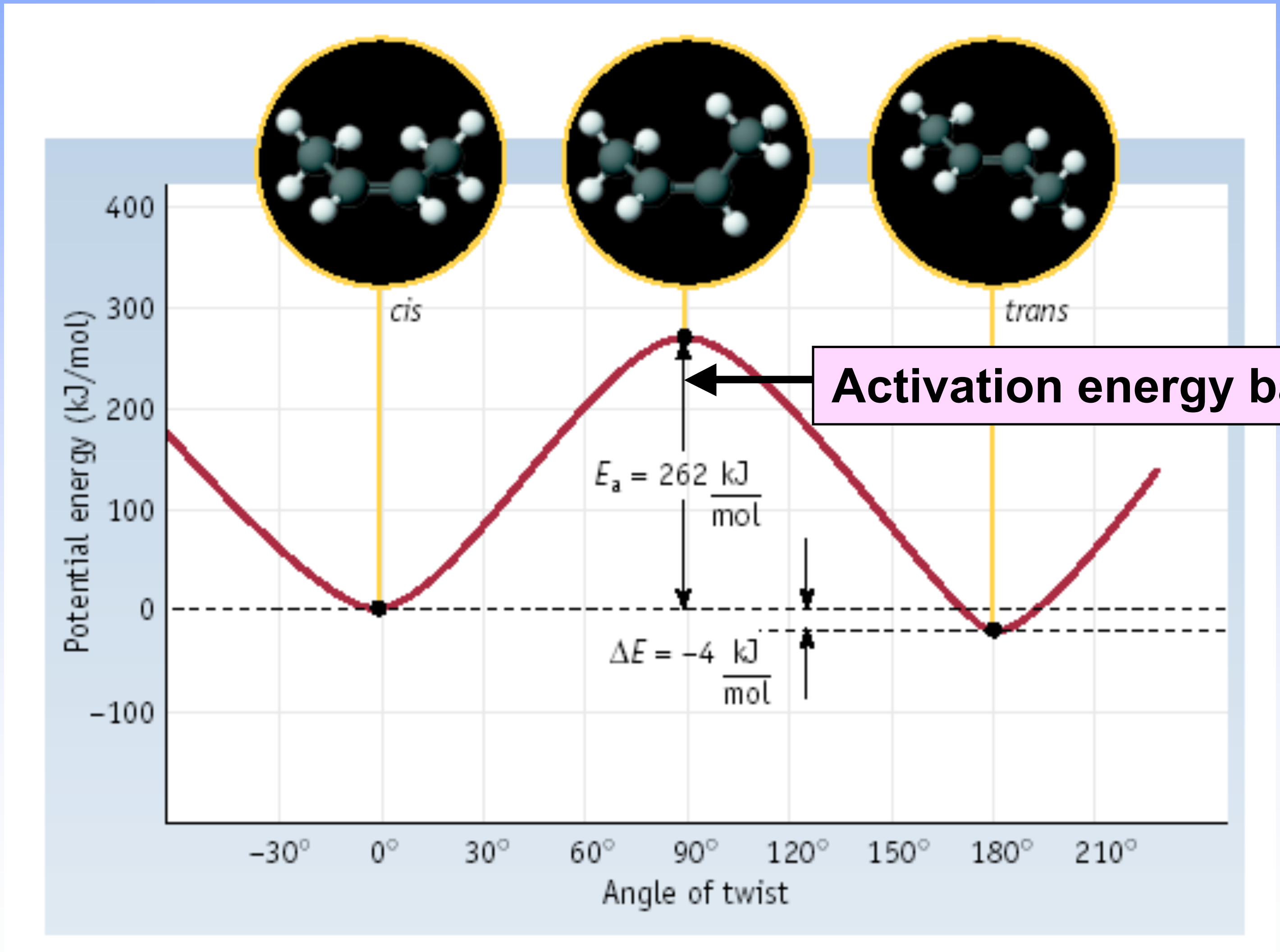


Conversion of cis to trans-2-butene requires twisting around the C=C bond.

Rate = k [cis-2-butene]

MECHANISMS

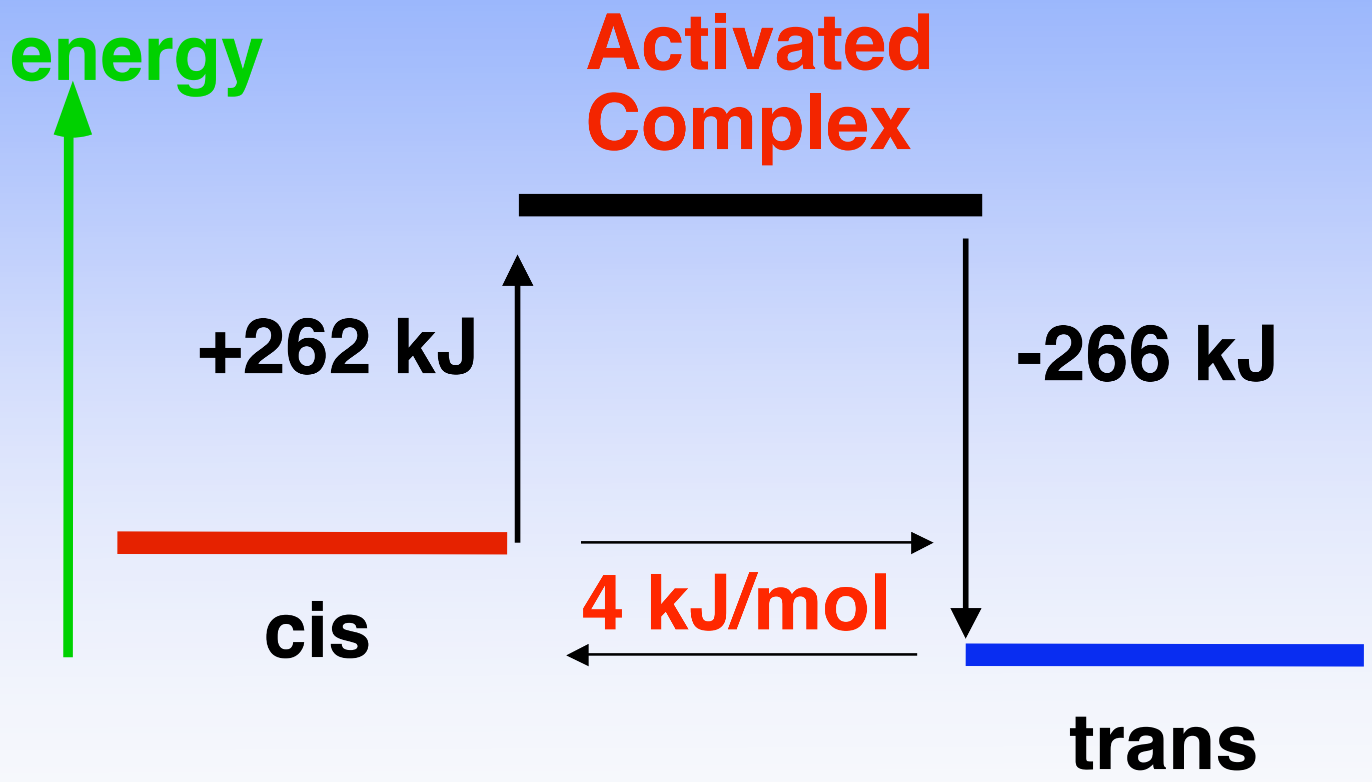
Cis Transition state **Trans**



Activation energy barrier

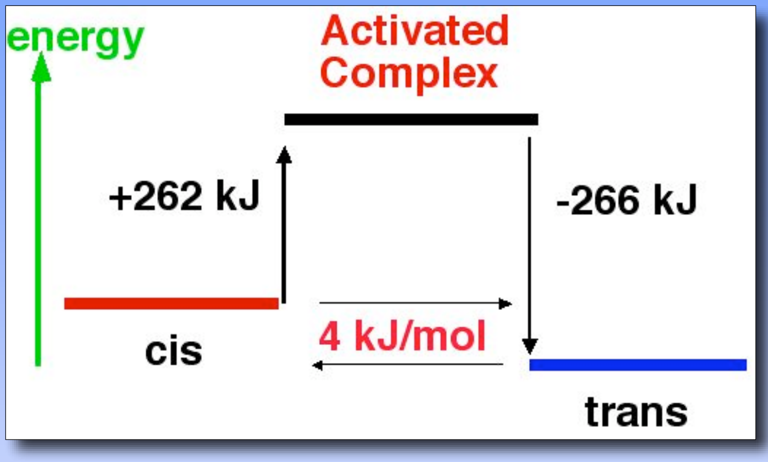
MECHANISMS

Energy involved in conversion of cis to trans butene



Mechanisms

- Reaction passes thru a **TRANSITION STATE** where there is an **activated complex** that has sufficient energy to become a product.



ACTIVATION ENERGY, E_a

= energy req'd to form activated complex.

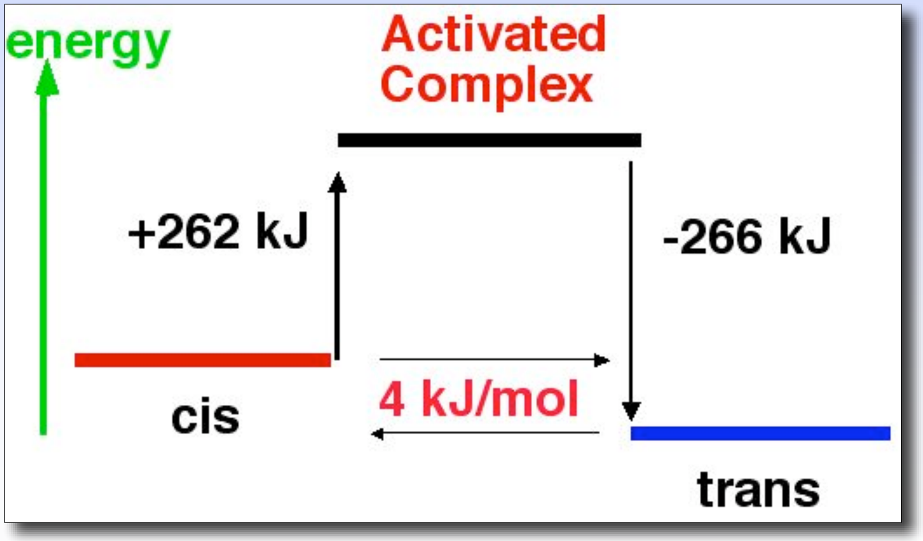
Here E_a = 262 kJ/mol

MECHANISMS

Also note that trans-butene is MORE STABLE than cis-butene by about 4 kJ/mol.

Therefore, cis f trans is EXOTHERMIC

This is the connection between thermodynamics and kinetics.



Collision Theory

- Molecules must collide in order to react
- Must collide with sufficient energy to break bonds (E_a)
- Must collide in the proper orientation

Collision Theory

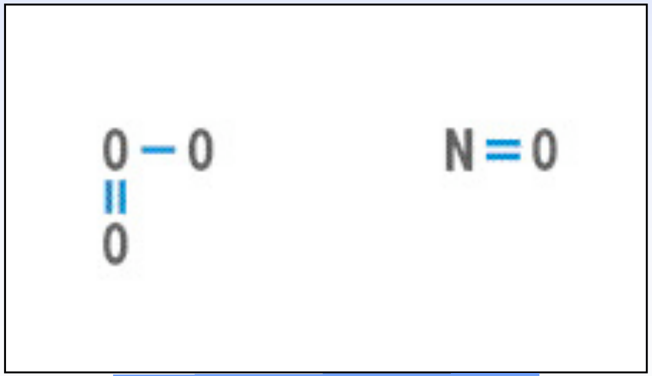
Reactions require

(a) activation energy and

(b) correct geometry.

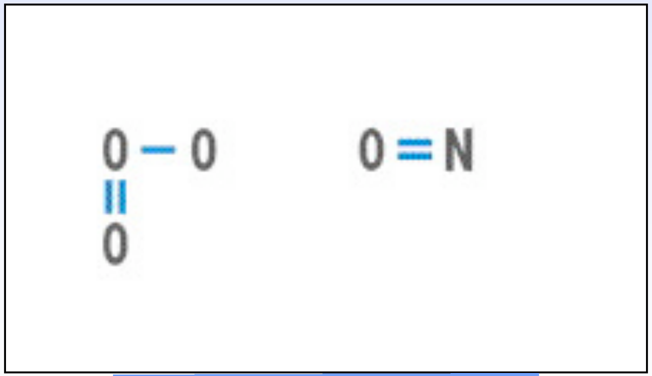
$O_3(g)\ +\ NO(g)\ f\ O_2(g)\ +\ NO_2(g)$

1. Activation energy



PLAY MOVIE

2. Activation energy and geometry



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Effect of Temperature

- **Reactions generally occur slower at lower T.**

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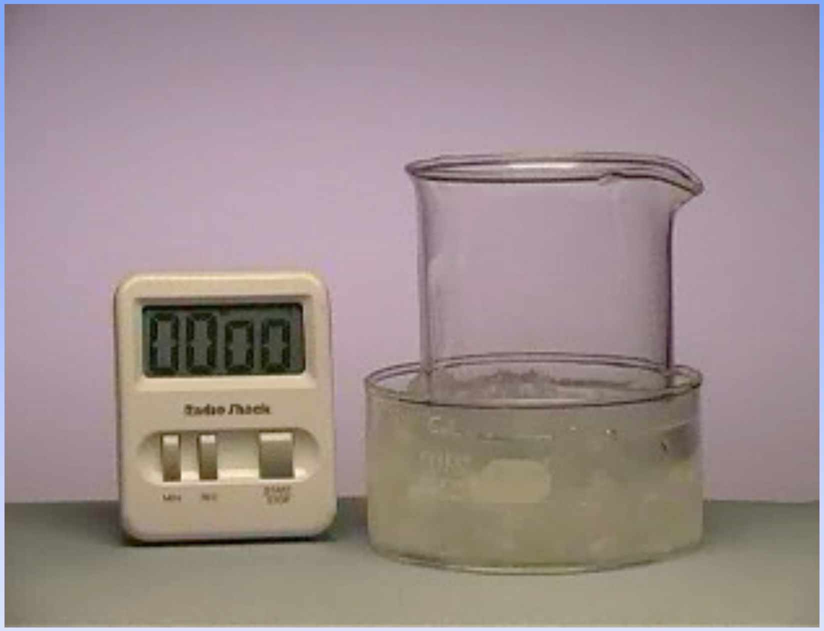

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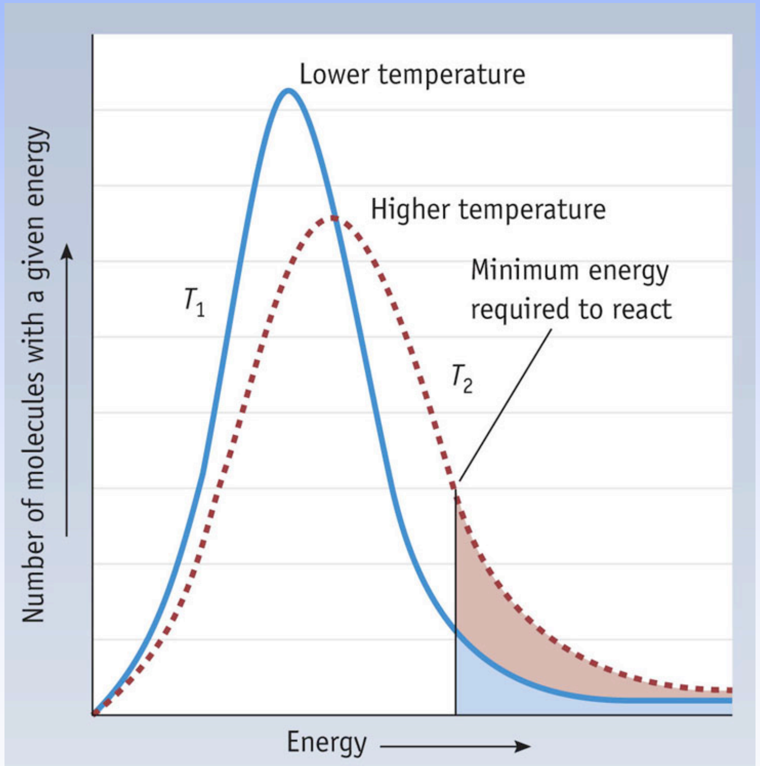
Iodine clock reaction. See Chemistry Now, Ch. 15

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow 2\,H_2O + I_2$$

Activation Energy and Temperature

Reactions are faster at higher T because a larger fraction of reactant molecules have enough energy to convert to product molecules.



© Brooks/Cole, Cengage Learning

In general, **differences in activation energy** cause reactions to vary from fast to slow.

Mechanisms

1. **Why is *cis-butene* e trans-*butene* reaction observed to be 1st order?**

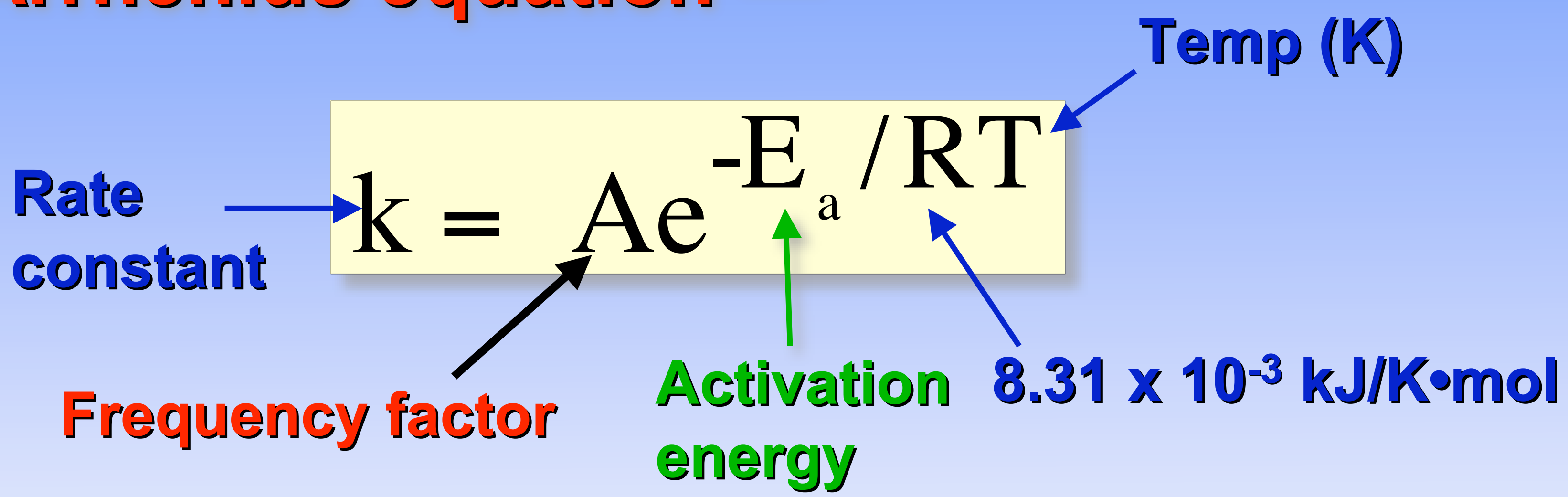
   As [cis] doubles, number of molecules with enough E also doubles.

2. **Why is the *cis* e trans reaction faster at higher temperature?**

   Fraction of molecules with sufficient activation energy increases with T.

More About Activation Energy

Arrhenius equation —



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

Frequency factor related to frequency of collisions with correct geometry.

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

Plot ln k vs. 1/T f
straight line.
slope = $-E_a/R$

Arrhenius equation

- Find k at different temp, then:
- Plot ln k vs 1/T—slope = -Ea/R
- To det’n slope, use “rise over run” (y/x)
- R = 8.314 X 10^{-3} kJ/mol-K or
  8.314 J/mol-K.   See overhead
  y-intercept = ln A

CATALYSIS

Catalysts speed up reactions by altering the mechanism to lower the activation energy barrier.

Dr. James Cusumano, Catalytica Inc.

What is a catalyst?

See Chemistry Now, Ch 15

Catalysts and the environment

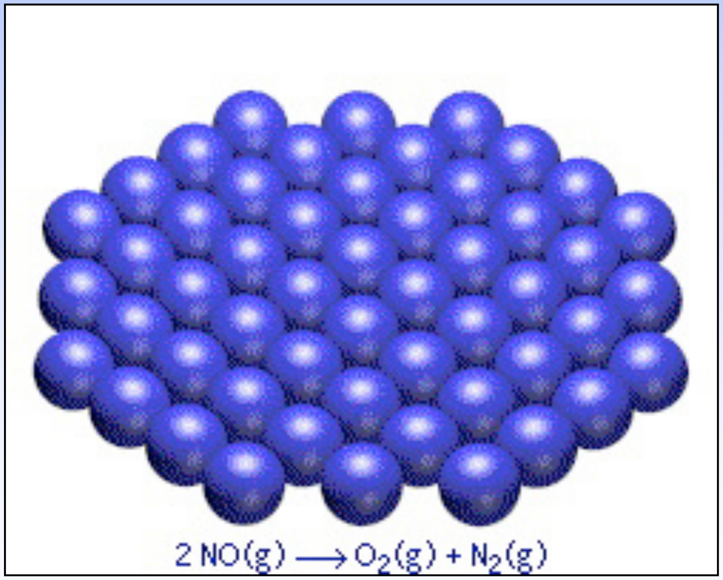
Catalysts and society

CATALYSIS

In auto exhaust systems — Pt, NiO

$2\,CO + O_2 \rightarrow 2\,CO_2$

$2\,NO \rightarrow N_2 + O_2$



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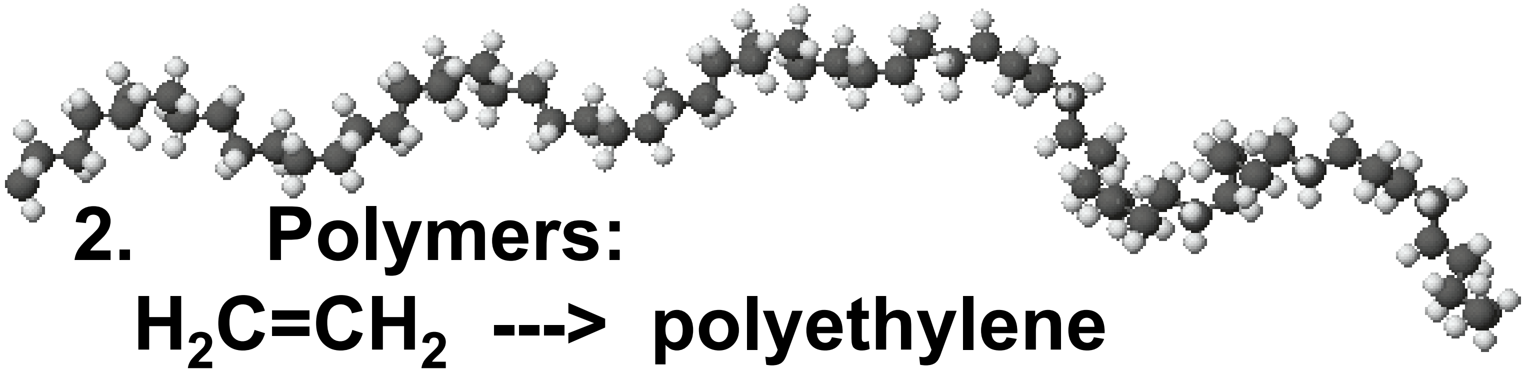
CATALYSIS



2. **Polymers:**

$H_2C{=}CH_2$ ---> polyethylene

3. **Acetic acid:**

$CH_3OH + CO$ f CH_3CO_2H

4. **Enzymes — biological catalysts**

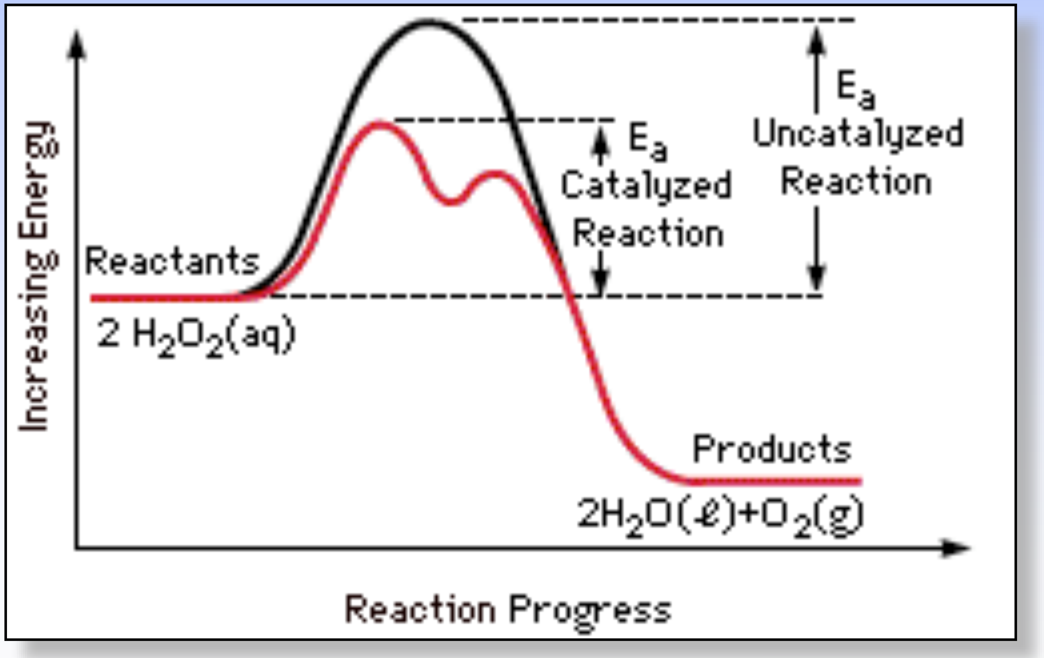
CATALYSIS

Catalysis and activation energy

PLAY MOVIE

MnO_2 catalyzes decomposition of H_2O_2

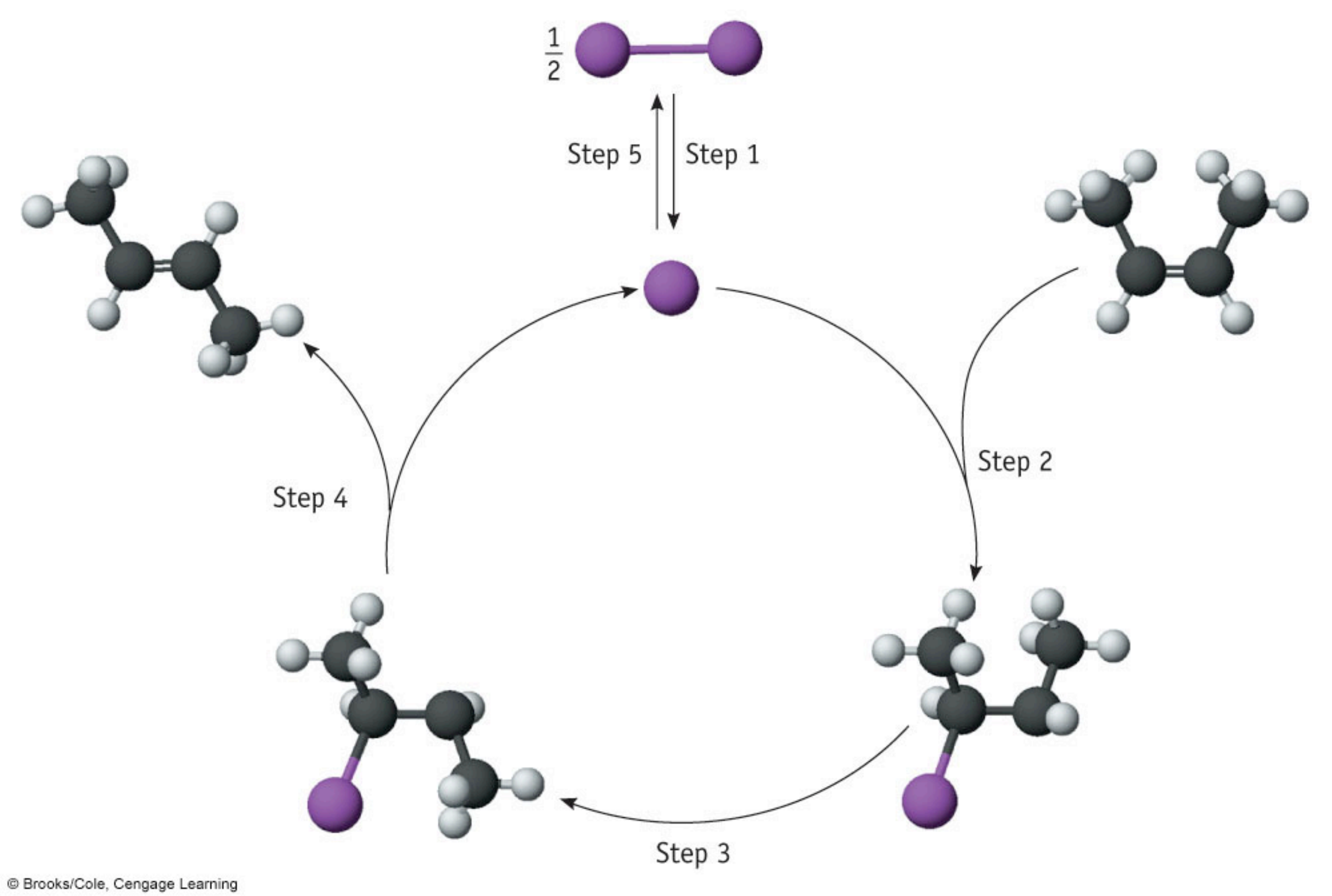
$2\ H_2O_2$ f $2\ H_2O + O_2$



— **Uncatalyzed reaction**

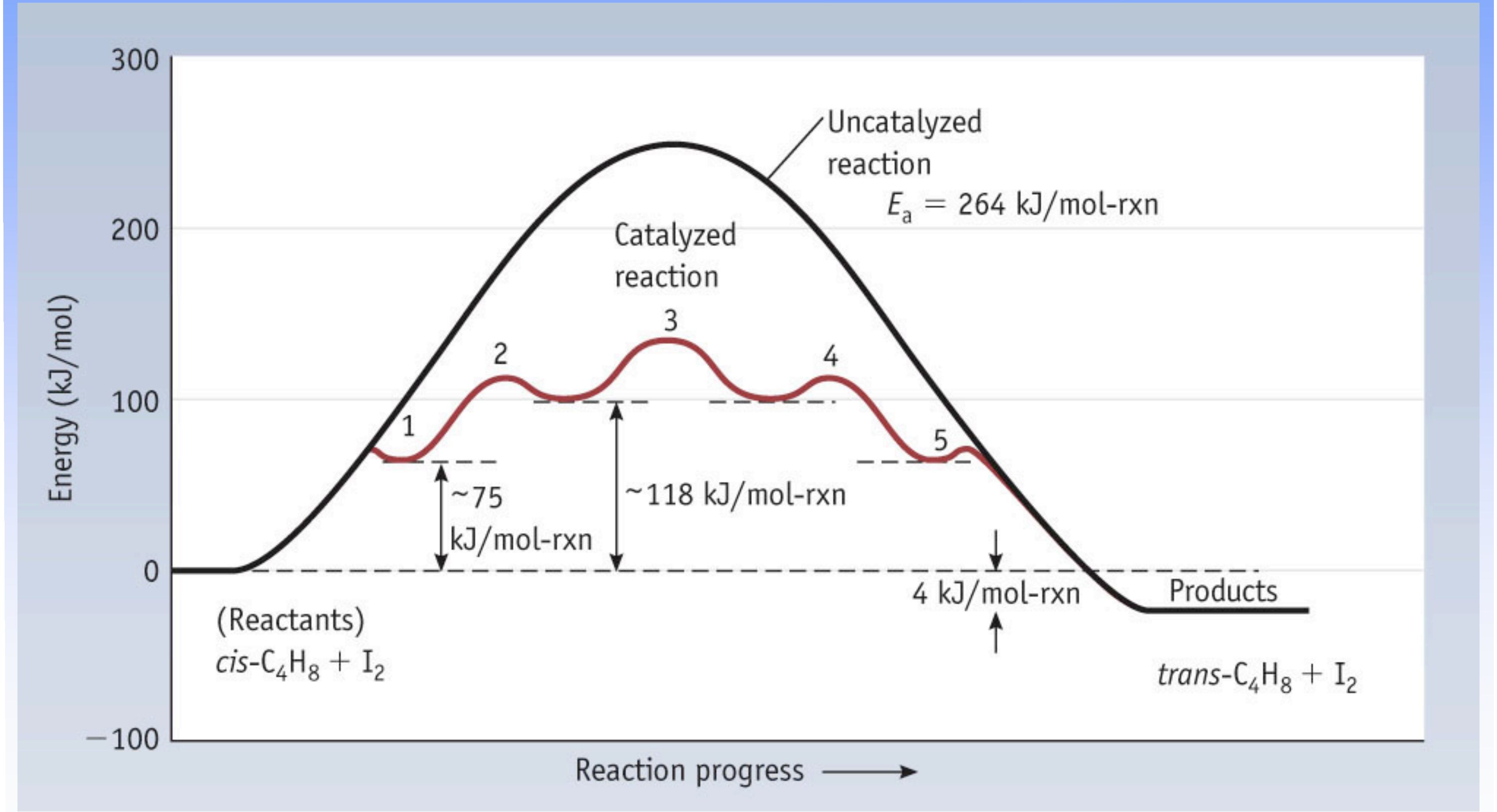
— **Catalyzed reaction**

Iodine-Catalyzed Isomerization of cis-2-Butene



See Figure 15.15

Iodine-Catalyzed Isomerization of cis-2-Butene



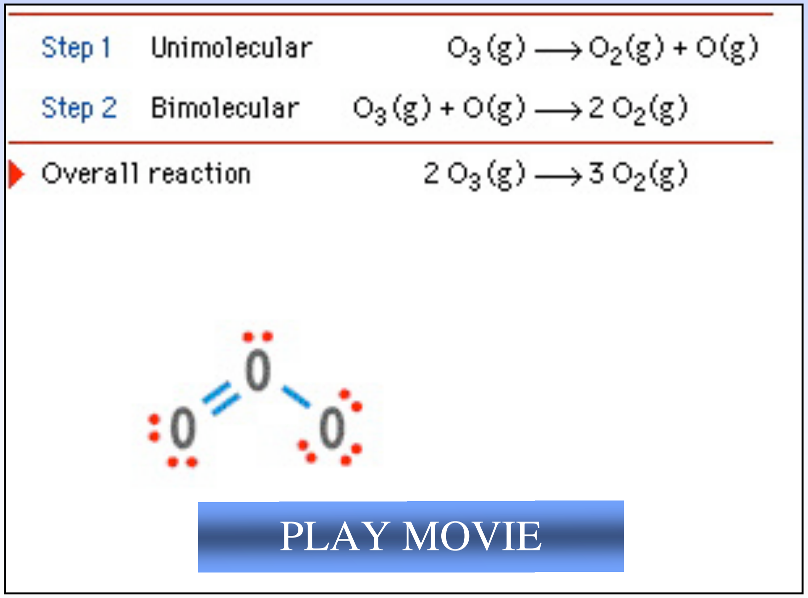
MECHANISMS

A Microscopic View of Reactions

Mechanism: how reactants are converted to products at the molecular level.

RATE LAW f MECHANISM

experiment f theory



Step 1 Unimolecular $O_3(g) \longrightarrow O_2(g) + O(g)$

Step 2 Bimolecular $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$

Overall reaction $2\ O_3(g) \longrightarrow 3\ O_2(g)$

Reaction Mechanisms

The sequence of events at the molecular level that control the speed and outcome of a reaction.

Br from biomass burning destroys stratospheric ozone.

(See R.J. Cicerone, *Science*, volume 263, page 1243, 1994.)

Step 1: $Br + O_3$ f $BrO + O_2$

Step 2: $Cl + O_3$ f $ClO + O_2$

Step 3: $BrO + ClO$ + light f $Br + Cl + O_2$

NET: $2\ O_3$ f $3\ O_2$

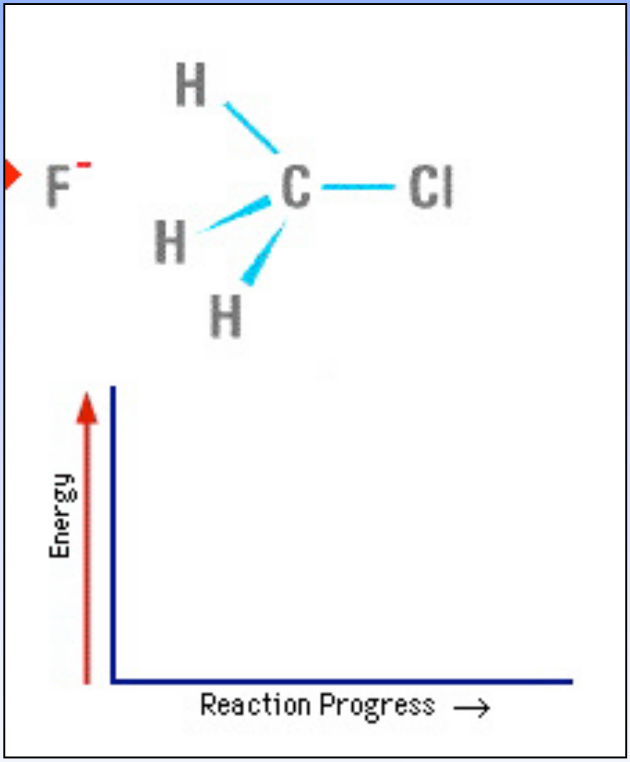
More on Mechanisms

Reaction of

cis-butene f trans-butene is **UNIMOLECULAR** - only one reactant is involved.

BIMOLECULAR — two different molecules must collide f products

A bimolecular reaction



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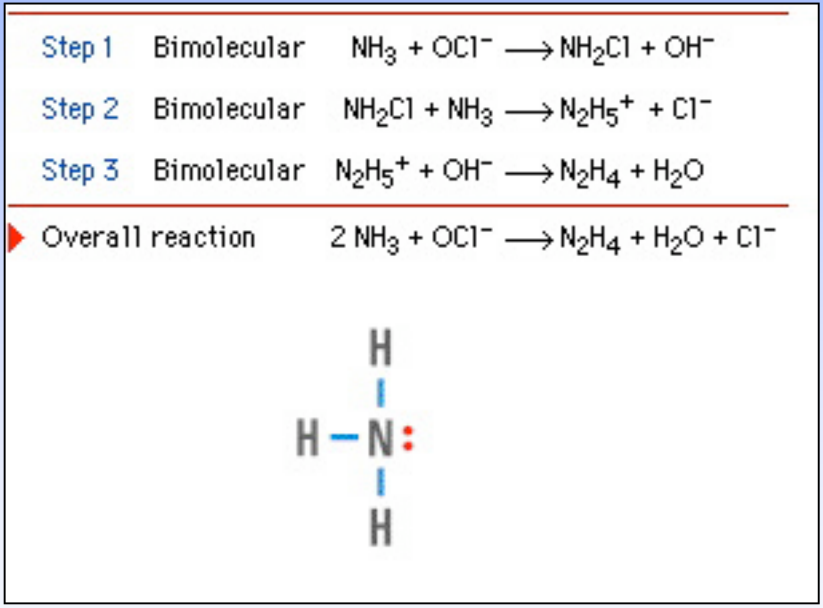
Exo- or endothermic?

Mechanisms

Some reactions occur in a single ELEMENTARY step. Most rxns involve a sequence of elementary steps.

Adding elementary steps gives NET reaction.



Step 1	Bimolecular	$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$
Step 2	Bimolecular	$NH_2Cl + NH_3 \longrightarrow N_2H_5^+ + Cl^-$
Step 3	Bimolecular	$N_2H_5^+ + OH^- \longrightarrow N_2H_4 + H_2O$
▶ Overall reaction		$2\,NH_3 + OCl^- \longrightarrow N_2H_4 + H_2O + Cl^-$

PLAY MOVIE

Elementary steps
(Steps in a mechanism)

• $A \rightarrow$ Products	Uni	Rate = $k[A]$
• $A + B \rightarrow$ Prod	Bi	Rate = $k[A][B]$
• $A + A \rightarrow$ Prod	Bi	Rate = $k[A]^2$
• $2A + B \rightarrow$ Prod	Ter	Rate = $k[A]^2[B]$

- Note: add “molecular” to each prefix in middle column

Mechanisms

Most rxns. involve a sequence of elementary steps.

$$2\,I^- \; + \; H_2O_2 \; + \; 2\,H^+ \;\; f \;\; I_2 \; + \; 2\,H_2O$$

$$\text{Rate} = k\,[I^-]\,[H_2O_2]$$

NOTE

1. **Rate law comes from experiment**
2. **Order and stoichiometric coefficients not necessarily the same!**
3. **Rate law reflects all chemistry down to and including the slowest step in multistep reaction.**

Mechanisms

Most rxns. involve a sequence of elementary steps.

$2\ I^- + H_2O_2 + 2\ H^+$ f $I_2 + 2\ H_2O$

Rate = k $[I^-]\ [H_2O_2]$

Proposed Mechanism

Step 1 — slow HOOH + I^- f HOI + OH^-

Step 2 — fast HOI + I^- f I_2 + OH^-

Step 3 — fast $2\ OH^- + 2\ H^+$ f $2\ H_2O$

Rate of the reaction controlled by slow step —

RATE DETERMINING STEP, rds.

Rate can be no faster than rds!

Mechanisms

$2\ I^- + H_2O_2 + 2\ H^+\ f\ I_2 + 2\ H_2O$

Rate = k $[I^-][H_2O_2]$

Step 1 — slow $HOOH + I^-\ f\ HOI + OH^-$**Step**
2 — fast $HOI + I^-\ f\ I_2 + OH^-$

Step 3 — fast $2\ OH^- + 2\ H^+\ f\ 2\ H_2O$

Elementary Step 1 is **bimolecular** and involves I^- and HOOH. Therefore, this predicts the rate law should be

Rate $\propto [I^-][H_2O_2]$ — as observed!!

The species HOI and OH^- are **reaction intermediates.**

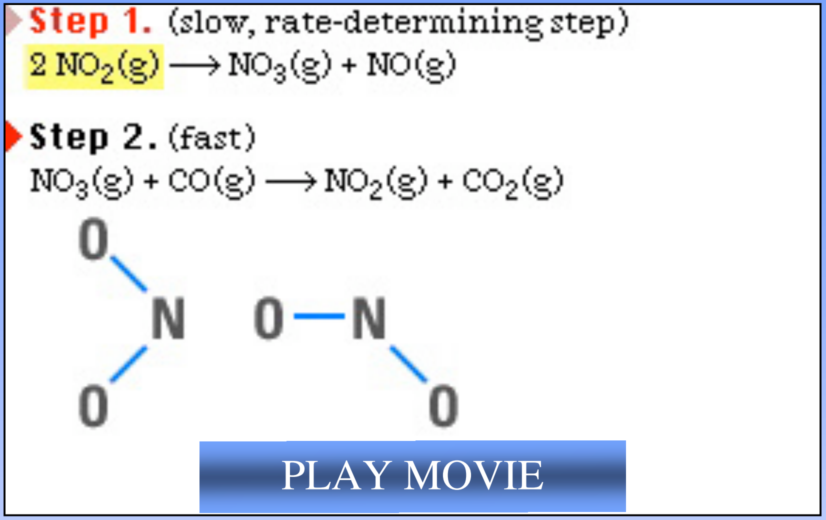
Rate law written in terms of reactants.

Rate Laws and Mechanisms

NO_2 + CO reaction:

Rate = $k[NO_2]^2$

Two possible mechanisms



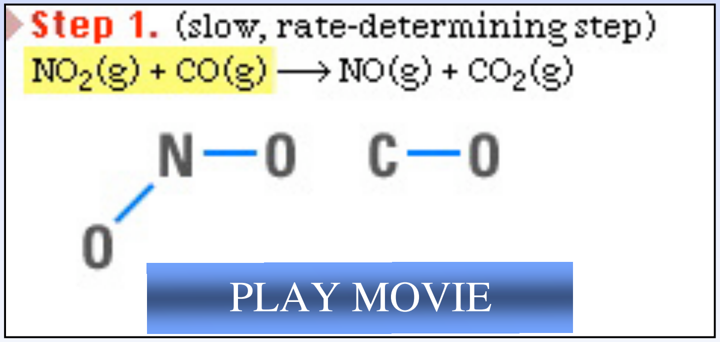
Step 1. (slow, rate-determining step)

$2\ NO_2(g) \longrightarrow NO_3(g) + NO(g)$

Step 2. (fast)

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

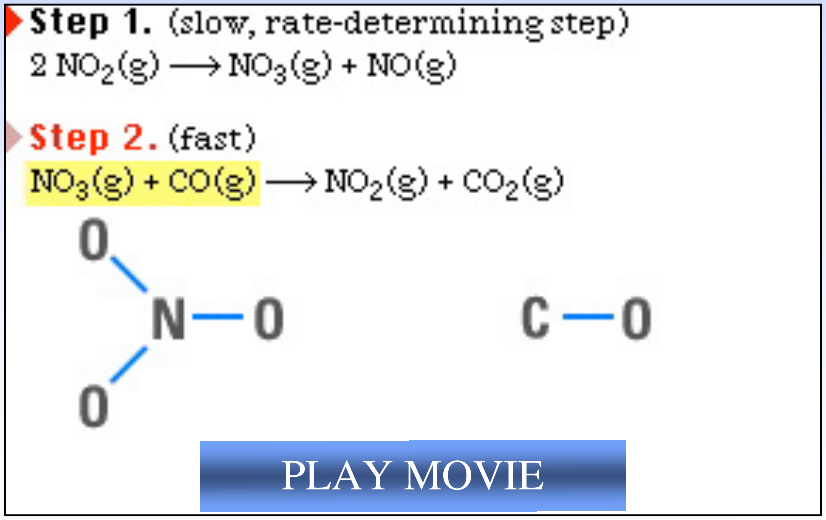
Two steps: step 1



Step 1. (slow, rate-determining step)

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Single step



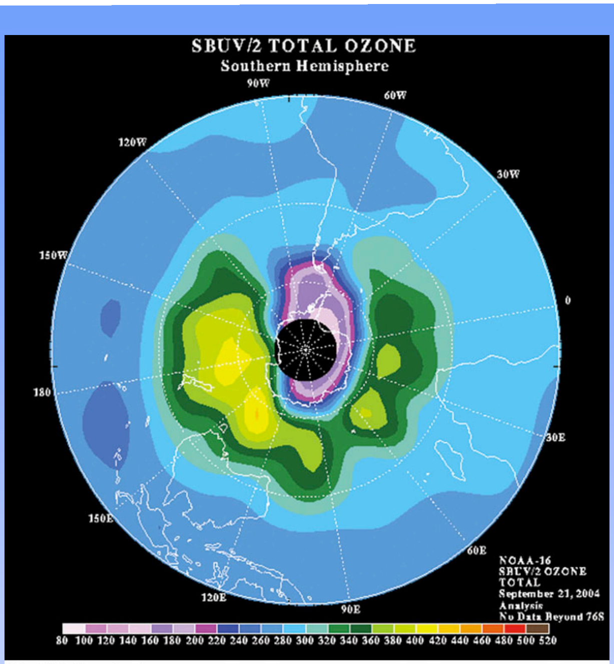
Step 1. (slow, rate-determining step)

$2\ NO_2(g) \longrightarrow NO_3(g) + NO(g)$

Step 2. (fast)

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

Two steps: step 2



Ozone Decomposition Mechanism

$$2\ O_3\ (g)\ \ f\ \ 3\ O_2\ (g)$$

Proposed mechanism

Step 1: fast, equilibrium

$$O_3\ (g)\ e\ O_2\ (g)\ +\ O\ (g)$$

Step 2: slow $O_3\ (g)\ +\ O\ (g)\ \ f\ 2\ O_2\ (g)$

$$\text{Rate} = k\ \frac{[O_3]^2}{[O_2]}$$