# Chapter 13

# Chemical Kinetics

# Goals/Objectives

Rates of reaction & conditions affecting rates

Rate eqn, rate constant, and order of a rxn

Calcns involving integrated rate laws

Collision theory and activation energy

Link between rxn mechanism and the rate law

# Chemical Kinetics

- **KINETICS** — the study of **REACTION RATES** and their relation to the way the reaction proceeds @ the molecular level, i.e., its **MECHANISM**.

- The reaction mechanism is our goal!

# Chemical Kinetics

- there are 5 factors that influence the speed (rate) of a reaction:

  - ✓nature of the reactants (tendency to change)
  - ✓ability of reactants to make contact
  - ✓Temperature (T ↑, rate ↑)
  - ✓Catalysts (↑ rate)
  - ✓Concentration (concn ↑, rate ↑)

# The Rate

- **rate is how much a quantity changes in a given period of time**

- **the speed a car is driven is a rate – the distance a car travels (miles) in a given period of time (1 hour)**

  ✓ so the speed of a car has units of mi/hr

$$\text{rate} = \text{speed} = \frac{\Delta\,\text{distance}}{\Delta\,\text{time}}$$

# Reaction Rates

- **Rate of a chemical reaction = change in concentration (mol/L) of a reactant or product with time (s, min, hr);**

$$\text{rate of rxn} = \frac{\text{change in concn}}{\text{change in time}} = \frac{\Delta[H_2]}{\Delta t}$$

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

# Initial Rate

## (rate at the start)

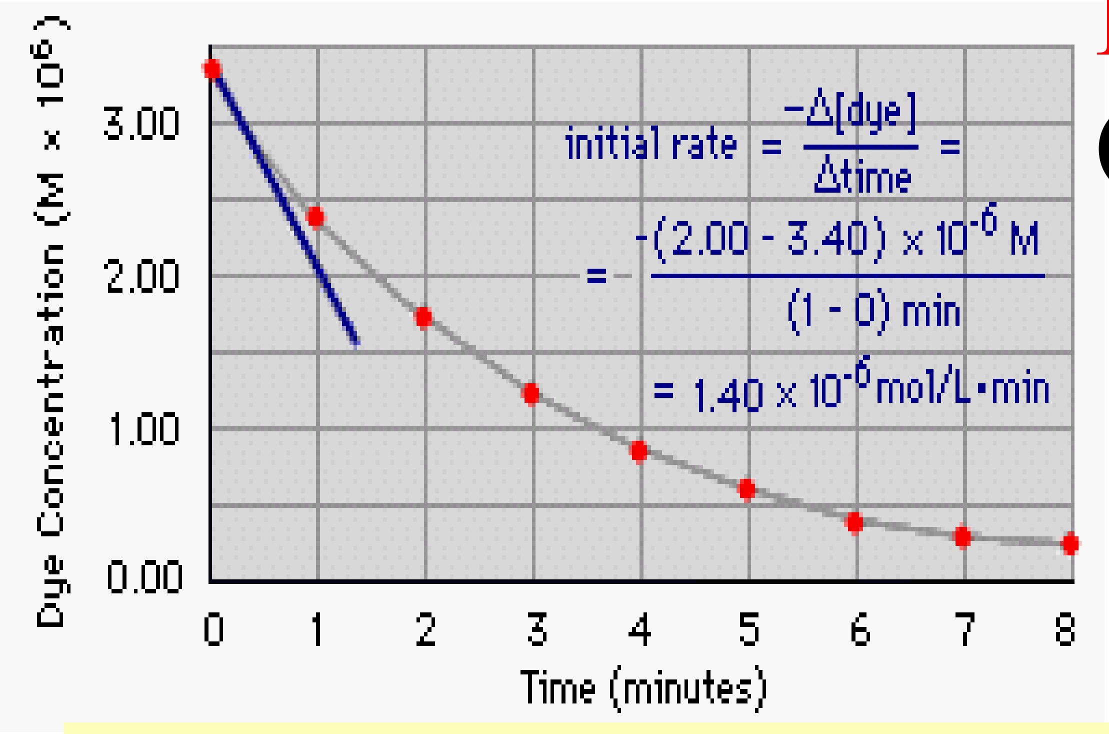


Figure shows change in concentration (decreases exponentially) with time.

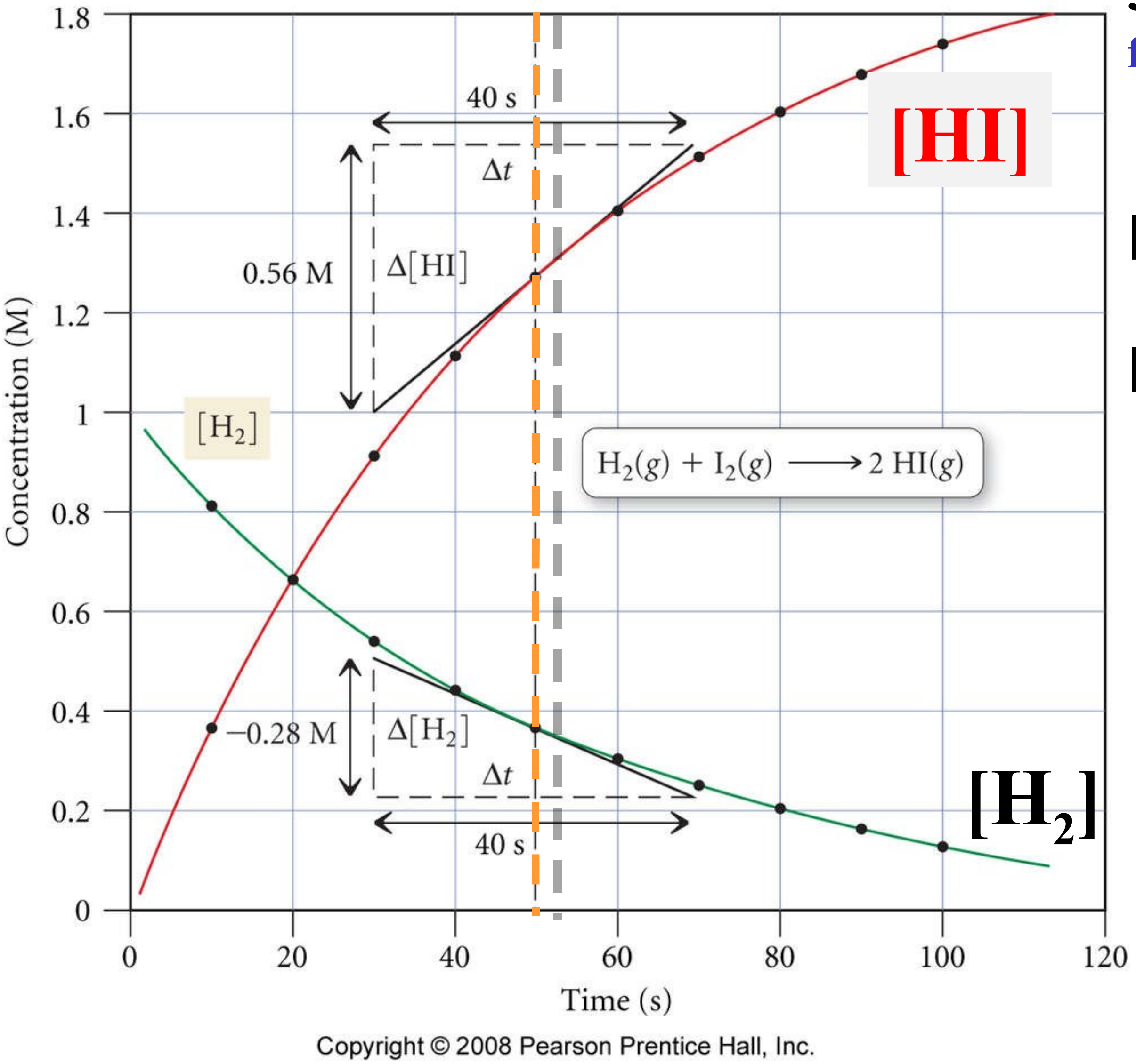
**The initial rate = the change in dye conc with time — can be determined from the slope.**

# Instantaneous Rate

- the instantaneous rate is the change in concentration at any one particular time
  - ✓ **slope at one point of a curve**

- **determined by taking the slope of a line tangent to the curve at that particular point**
  - ✓ **first derivative of the function**
    - ➢ **for you calculus fans**

# $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$



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**Using $[H_2]$, the instantaneous rate at 50 s is** (30, 0.50); (70, 0.22) from Δy/Δx :

$$\text{Rate} = -\frac{-0.28\text{M}}{40\text{s}}$$

$$\text{Rate} = 0.0070\frac{\text{M}}{\text{s}}$$

**Using [HI], the instantaneous rate at 50 s is:**

$$\text{Rate} = \left(\frac{1}{2}\right)\frac{0.56\text{M}}{40\text{s}}$$

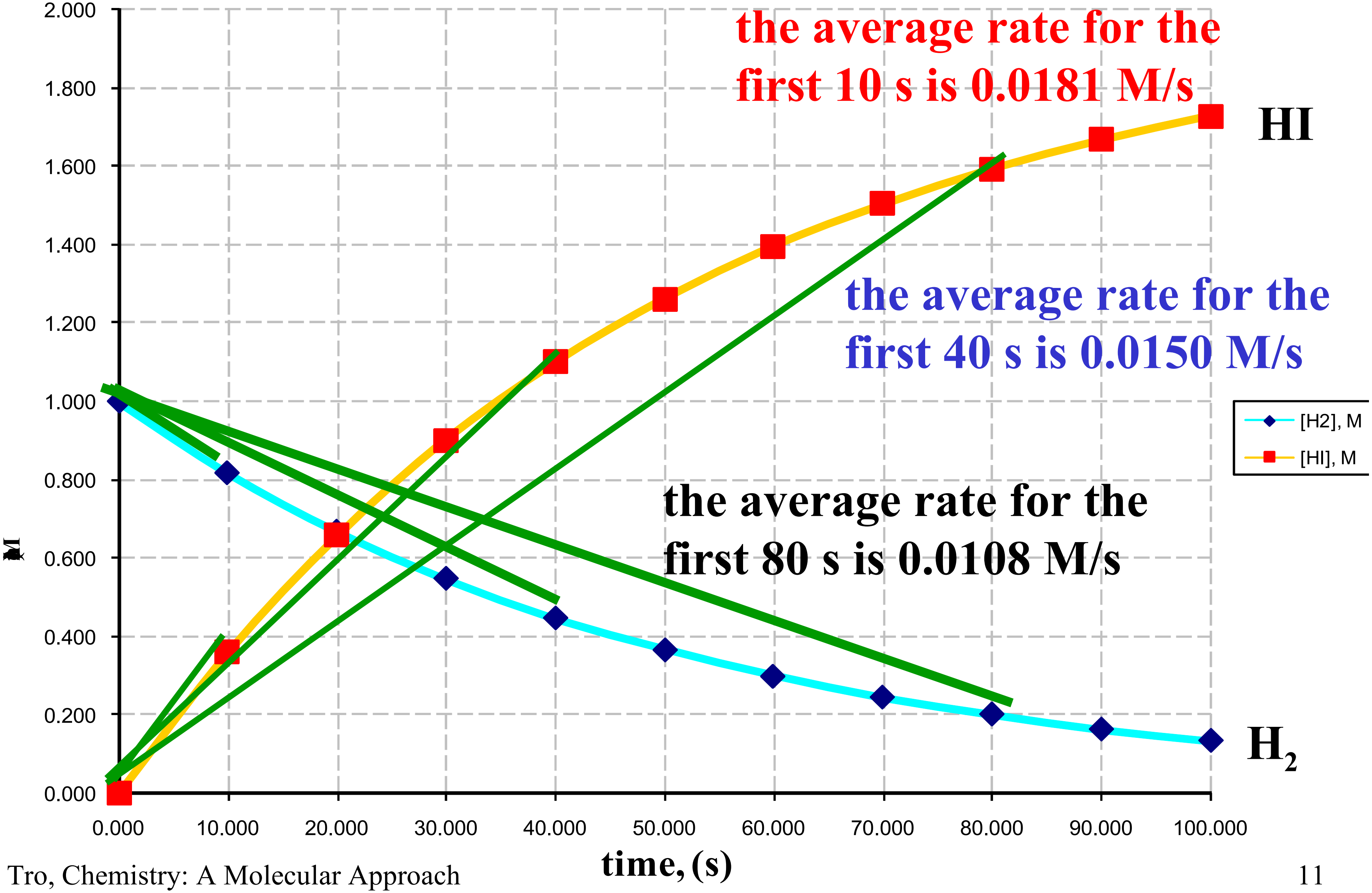
$$\text{Rate} = 0.0070\text{M/s}$$

# Average Rate

- **the average rate is the change in measured concentrations in any particular time period**

- **can be over large or small time interval (see next diagram)**

# Concentration vs. Time for $H_2 + I_2 \text{-->} 2HI$



the average rate for the first 10 s is 0.0181 M/s

the average rate for the first 40 s is 0.0150 M/s

the average rate for the first 80 s is 0.0108 M/s

# Rate of a Chemical Reaction

**Consider:** $2N_2O_5 \rightarrow 4NO_2 + O_2$

The rate of a reaction is measured w.r.t Δ[product] or Δ[reactant] per unit time.

$$rate\ of\ reaction = \frac{\text{change in }[N_2O_5]}{\text{change in time}} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

$$rate\ of\ reaction = +\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

To equate rates, divide by stoichiometric coefficients in the balanced equation (relative rates).

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

$$rate\ of\ reaction = -\frac{1}{2}\left(\frac{\Delta[N_2O_5]}{\Delta t}\right) = +\frac{1}{4}\left(\frac{\Delta[NO_2]}{\Delta t}\right) = +\frac{\Delta[O_2]}{\Delta t}$$

**The rate of reaction must reflect the stoichiometric coefficients in the reaction**

**NB: coefficients written as fractions…**

For the reaction, [I⁻] changes from 1.000 M to 0.868 M in the first 10 s. Calculate the average rate in the first 10 s.

$$H_2O_{2\,(aq)} + 3\,I^-_{(aq)} + 2\,H^+_{(aq)} \rightarrow I_3^-{}_{(aq)} + 2\,H_2O_{(l)}$$

$$\text{Rate} = -\left(\frac{1}{3}\right)\frac{\Delta[I^-]}{\Delta t} = -\left(\frac{1}{3}\right)\frac{(0.868\,M - 1.000\,M)}{10\,s}$$

$$\text{Rate of rxn} = -\left(\frac{1}{3}\right)\frac{(-0.132\,M)}{10\,s}$$

$$\text{Rate of rxn} = 4.40 \times 10^{-3}\,\frac{M}{s}$$

If the rate of formation (disappearance) of one substance is known, the stoichiometry can be used to deduce the rates of formation (disappearance) of other participants in the rxn.

- Rate of disappearance of $H_2 = 4.5 \times 10^{-4}$ mol $L^{-1}$ $min^{-1}$.

  $\mathbf{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}$

  Rate of consumption $N_2 = ?$

  Rate of formation of $NH_3 = ?$

**Rate of disappearance of $H_2$ = $4.5 \times 10^{-4}$ mol $L^{-1}$ $min^{-1}$.**

**$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$**

**Rate of consumption $N_2$ = ?**

**Rate of formation of $NH_3$= ?**

## SOLUTION

-rate of consumptn $H_2 \equiv 4.5 \times 10^{-4}$ mol $L^{-1}$ min $^{-1}$,

-rate of consumption $N_2 \equiv$

$$\frac{1\ \text{mol}\ \text{N}_2(\text{g})}{3\ \text{mol}\ \text{H}_2(\text{g})} \times 4.5 \times 10^{-4}\ \text{mol}\ \text{L}^{-1}\ \text{min}^{-1} = 1.5 \times 10^{-4}\ \text{mol}\ \text{L}^{-1} \text{min}^{-1}$$

rate of formation $NH_3 \equiv$

$$\frac{2\ mol\ \text{NH}_3(g)}{3\ mol\ \text{H}_2(g)} \times 4.5 \times 10^{-4}\ mol\ L^{-1}\ \text{min}^{-1} = 3.0 \times 10^{-4}\ mol\ L^{-1}\ \text{min}^{-1}$$

# The Rate Law

**mathematical relationship between the rate of the reaction and the concentrations of the reactants/products** (also catalysts)

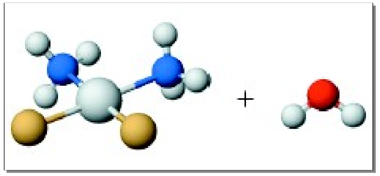
**-the rate of a reaction is directly proportional to the concentration of each reactant/product raised to a power**

- **for the reaction $aA + bB \rightarrow$ products the rate law would have the form given below:**

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

***m* and *n* are called the orders for each reactant;**

***k* is called the rate constant.**



# Reaction Order

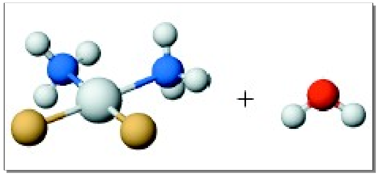
-the order of a reaction w.r.t a reactant, is the exponent of its concentration term in the rate expression,

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

(m is the order w.r.t A)(n is the order w.r.t B)

can be 0, 1, 2 or fractions,-ve

order must be determined by experiment!!!

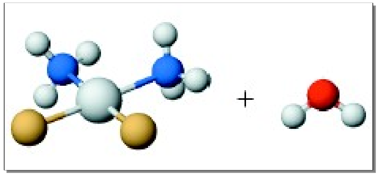


# Reaction Order

-the **total reaction order** is the sum of all exponents on all concentration terms;

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

$$\text{Total order} = m + n + p$$



# Interpreting Rate Laws

**Rate = k [A]$^{m}$**

- If m = 1, rxn is 1st order w.r.t A: rate = k [A]$^{1}$

  i.e., if [A] doubles, then the rate goes up by factor of 2 ($2^1 = 2$)

- If m = 2, rxn is 2nd order in A: rate = k [A]$^{2}$

  Doubling [A] increases rate by 4 ($2^2 = 4$)

- If m = 0, rxn is zero order: rate = k [A]$^{0}$

  If [A] doubles, rate __________?

# k, rate constant

Rate = k $[A]^m$

The rate constant is a proportionality constant that relates rate of rxn and conc’n at a given temp.

Rate constants have units consistent with the units for other terms in the rate equation.

0 order: k = mol/L· time ($M\ s^{-1}$)

1 st order: k = $time^{-1}$ ( $s^{-1}$)

2 nd order: k = L/mol · time ($M^{-1}\ s^{-1}$)

General: $M^{1-n}$ $time^{-1}$

# Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the experimental data below.

**Write a general rate law including all reactants**

**Examine the data and find two experiments in which the concentration of one reactant <u>changes</u>, but the other concentrations are the <u>same</u>**

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

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

Comparing Expt #1 and Expt #2, the $[NO_2]$ changes but the [CO] does not;

**-the rate of rxn also changes!**

# Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Determine by what factor the **concentrations** and **rates** change in these two experiments.

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

$$\frac{[NO_2]_{\text{expt 2}}}{[NO_2]_{\text{expt 1}}} = \frac{0.20\ \text{M}}{0.10\ \text{M}} = 2 \qquad \frac{\text{Rate}_{\text{expt 2}}}{\text{Rate}_{\text{expt 1}}} = \frac{0.0082\ {}^{\text{M}}\!/_{\text{s}}}{0.0021\ {}^{\text{M}}\!/_{\text{s}}} \approx 4$$

# Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Determine to what power the concentration factor must be raised to equal the rate factor.

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

$$\frac{[NO_2]_{\text{expt 2}}}{[NO_2]_{\text{expt 1}}} = \frac{0.20\text{ M}}{0.10\text{ M}} = 2$$

$$\frac{\text{Rate}_{\text{expt 2}}}{\text{Rate}_{\text{expt 1}}} = \frac{0.0082\ {}^{\text{M}}\!/\!_{\text{s}}}{0.0021\ {}^{\text{M}}\!/\!_{\text{s}}} \approx 4$$

$$\left(\frac{[NO_2]_{\text{expt 2}}}{[NO_2]_{\text{expt 1}}}\right)^n = \frac{\text{Rate}_{\text{expt 2}}}{\text{Rate}_{\text{expt 1}}}$$

$$2^n = 4$$

$$n = 2\ (2nd\ order)$$

# Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Repeat for the other reactant(s):

**CO**

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

$$\frac{[\mathrm{CO}]_{\mathrm{expt\ 3}}}{[\mathrm{CO}]_{\mathrm{expt\ 2}}} = \frac{0.20\ \mathrm{M}}{0.10\ \mathrm{M}} = 2$$

$$\frac{\mathrm{Rate}_{\mathrm{expt\ 3}}}{\mathrm{Rate}_{\mathrm{expt\ 2}}} = \frac{0.0083\ \mathrm{M}/\mathrm{s}}{0.0082\ \mathrm{M}/\mathrm{s}} \approx 1$$

$$\left(\frac{[\mathrm{CO}]_{\mathrm{expt\ 3}}}{[\mathrm{CO}]_{\mathrm{expt\ 2}}}\right)^m = \frac{\mathrm{Rate}_{\mathrm{expt\ 3}}}{\mathrm{Rate}_{\mathrm{expt\ 2}}}$$

$$2^m = 1$$

$$m = 0\ (zero\ order)$$

# Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.

Substitute the exponents into the general rate law to get the rate law for the reaction

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

$n = 2, m = 0$

$$\text{Rate} = k[NO_2]^n[CO]^m$$

$$\text{Rate} = k[NO_2]^2[CO]^0$$

$$\text{Rate} = k[NO_2]^2$$

## **Determine the rate law and rate constant for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ given the data below.**

Substitute the concentrations and rate for **any** experiment into the rate law and solve for *k*

| Expt. Number | Initial $[NO_2]$, (M) | Initial [CO], (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1. | 0.10 | 0.10 | 0.0021 |
| 2. | 0.20 | 0.10 | 0.0082 |
| 3. | 0.20 | 0.20 | 0.0083 |
| 4. | 0.40 | 0.10 | 0.033 |

$$\text{Rate} = k[NO_2]^2$$

for expt 1

$$0.0021\,{}^{M}\!/_{s} = k(0.10\text{ M})^2$$

$$k = \frac{0.0021\,{}^{M}\!/_{s}}{0.10\text{ M}^2} = 0.21\text{ M}^{-1} \bullet \text{s}^{-1}$$

$$\text{Rate} = 0.21\text{M}^{-1}\text{s}^{-1}[NO_2]^2$$

# #2. Deriving Rate Laws

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

| Expt | [NO], M | $[H_2]$, M | Rate, mol/L·s |
|---|---|---|---|
| 1. | 0.420 | 0.122 | 0.136 |
| 2. | 0.210 | 0.122 | 0.0339 |
| 3. | 0.210 | 0.244 | 0.0678 |

**-order of the reaction for NO & $H_2$?**

**-rate law (rate equation)?**

**-value of k (units)?**

# SOLUTION

$$\frac{rate\ \exp 1}{rate\ \exp 2} = \left[\frac{[NO]}{[NO]}\right]^{n} \qquad \frac{\overset{\text{rate}}{0.136}}{0.0339} = \left[\frac{[\overset{\text{concn}}{0.420}}{[0.210}\right]^{n}$$

$$\underset{\text{rate}}{4} = \underset{\text{concn}}{2^{n}} \Rightarrow 2^{2} = 2^{n}\ (n = 2 \text{ for } [NO])$$

$$\frac{rate\ \exp 3}{rate\ \exp 2} = \left[\frac{[H_2]}{[H_2]}\right]^{m} \qquad \frac{0.0678}{0.0339} = \left[\frac{[0.244]}{[0.122]}\right]^{m}$$

$$2 = 2^{\overset{\text{concn}}{m}} \Rightarrow 2^{1} = 2^{m}\ (m = 1 \text{ for } [H_2])$$

# Rate Law = $k[NO]^2[H_2]$

**-value of k (units)?**

**Use exp 1 data + rate law**

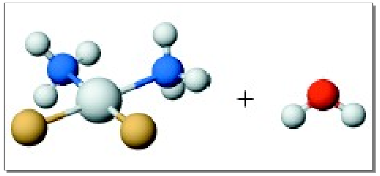
$k\,[NO]^2[H_2] = 0.136\ mol/L\cdot s$

$k\,[0.420\ mol/L]^2[0.122\ mol/L] = 0.136\ mol/L\cdot s$

$$k = \frac{0.136\ mol/L\cdot s}{0.0215\ mol^3/L^3} = 6.32\ L^2/mol^2\cdot s$$

or, $k = 6.32\ M^{-2}\cdot s^{-1}$

**Rate Law = $6.32\ M^{-2}\cdot s^{-1}\,[NO]^2[H_2]$**



# Concentration/Time Relations

-What is the conc’n of a reactant/product as a function of time?

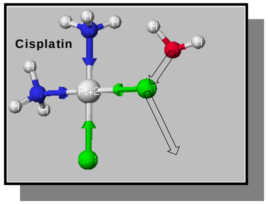
-How much time has elapsed?

Need an equation linking time & concentration

Consider **FIRST ORDER REACTIONS.**

This is the rate law:

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta\text{time}} = \mathrm{k}[\mathrm{A}]$$



# Concentration/Time Relations

**Integrating - ($\Delta$ [A] / $\Delta$ time) = k [A], we get**

[A] at time = t

**natural logarithm** →

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

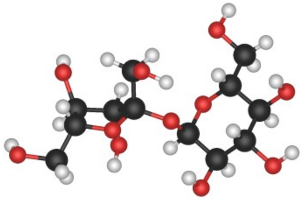
[A] at time = 0

**'ln' on computer not 'log'**

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

**-can determine** amount reacted/used up: [A]: $[A]_0$: k: t

**-called the** integrated first-order rate law.

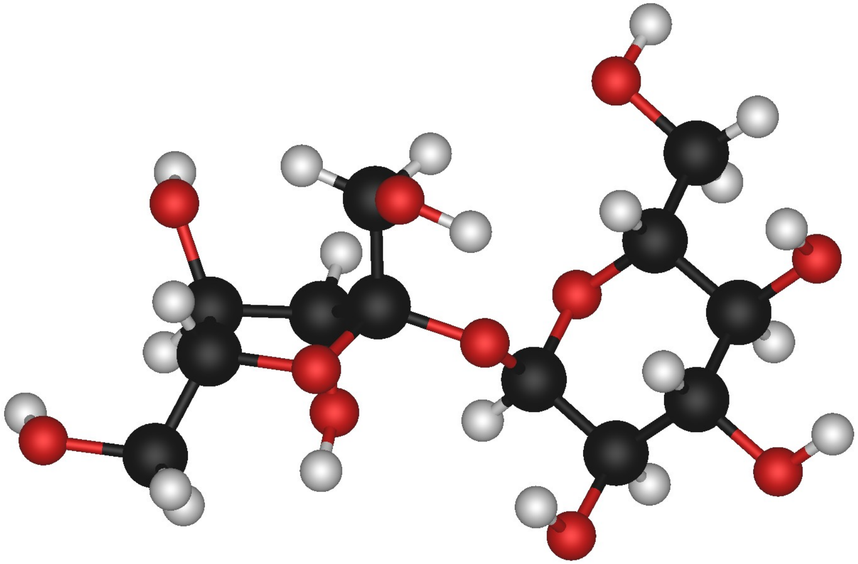


# Concentration/Time Relations

**Sucrose decomposes to simpler sugars**

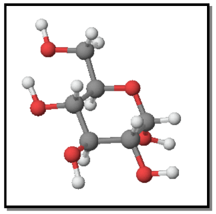
**Rate of disappearance of sucrose = k [sucrose]**

**If $k = 0.21\ hr^{-1}$**
**and $[sucrose]_0 = 0.010$ M,**
**how long does it take for**
**the concn of sucrose to dec by**
**90% (to 0.0010 M)?**



sucrose

Q1. calculating time



# Concentration/Time Relations

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

Use the first order integrated rate law

$$\ln \frac{[A]}{[A]_o} = -k \cdot t$$

$$\ln\left[\frac{0.0010\ \mathrm{M}}{0.010\ \mathrm{M}}\right] = -(0.21\ \mathrm{hr}^{-1}) \cdot t$$

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

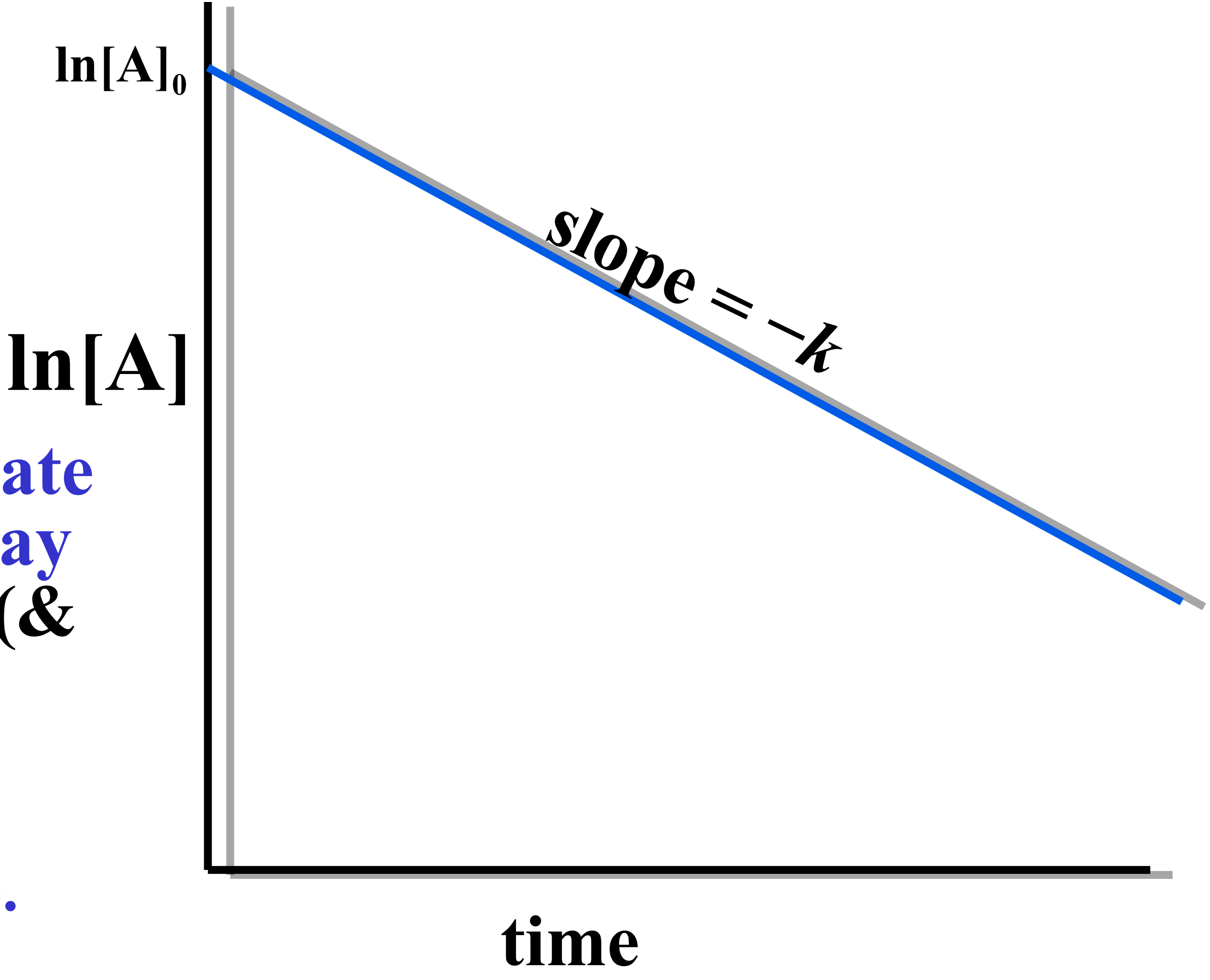
**time = 11 hours**

## Q2. The reaction $SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$ is first order with a rate constant of $2.90 \times 10^{-4}\ s^{-1}$ at a given set of conditions. Find the $[SO_2Cl_2]$ at 865 s when $[SO_2Cl_2]_0 = 0.0225$ M

| | |
|---|---|
| **Given:** | $[SO_2Cl_2]_0 = 0.0225$ M, t = 865, $k = 2.90 \times 10^{-4}\ s^{-1}$ |
| **Find:** | $[SO_2Cl_2]$ |
| **Concept Plan:** | $[SO_2Cl_2]_0$, t, $k$ $\rightarrow$ $[SO_2Cl_2]$ |
| **Relationships:** | for a 1st order process : $\ln[A] = -kt + \ln[A]_0$ |
| **Solution:** | $\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0$ SAME<br>$\ln[SO_2Cl_2] = -\left(2.90\times10^{-4}\ \cancel{s^{-1}}\right)\left(865\ \cancel{s}\right) + \ln\left(0.0225\right)$<br>$\ln[SO_2Cl_2] = -0.251 - 3.79 = -4.04$<br>$[SO_2Cl_2] = e^{(-4.04)} = 0.0175\ \text{M}$ |
| **Check:** | the new concentration is less than the original, as expected |

# First order: $\ln[A] = -kt + \ln[A]_0$

Plot of ln[A] vs. time gives straight line with **slope = -*k* and y-intercept = $\ln[A]_0$**

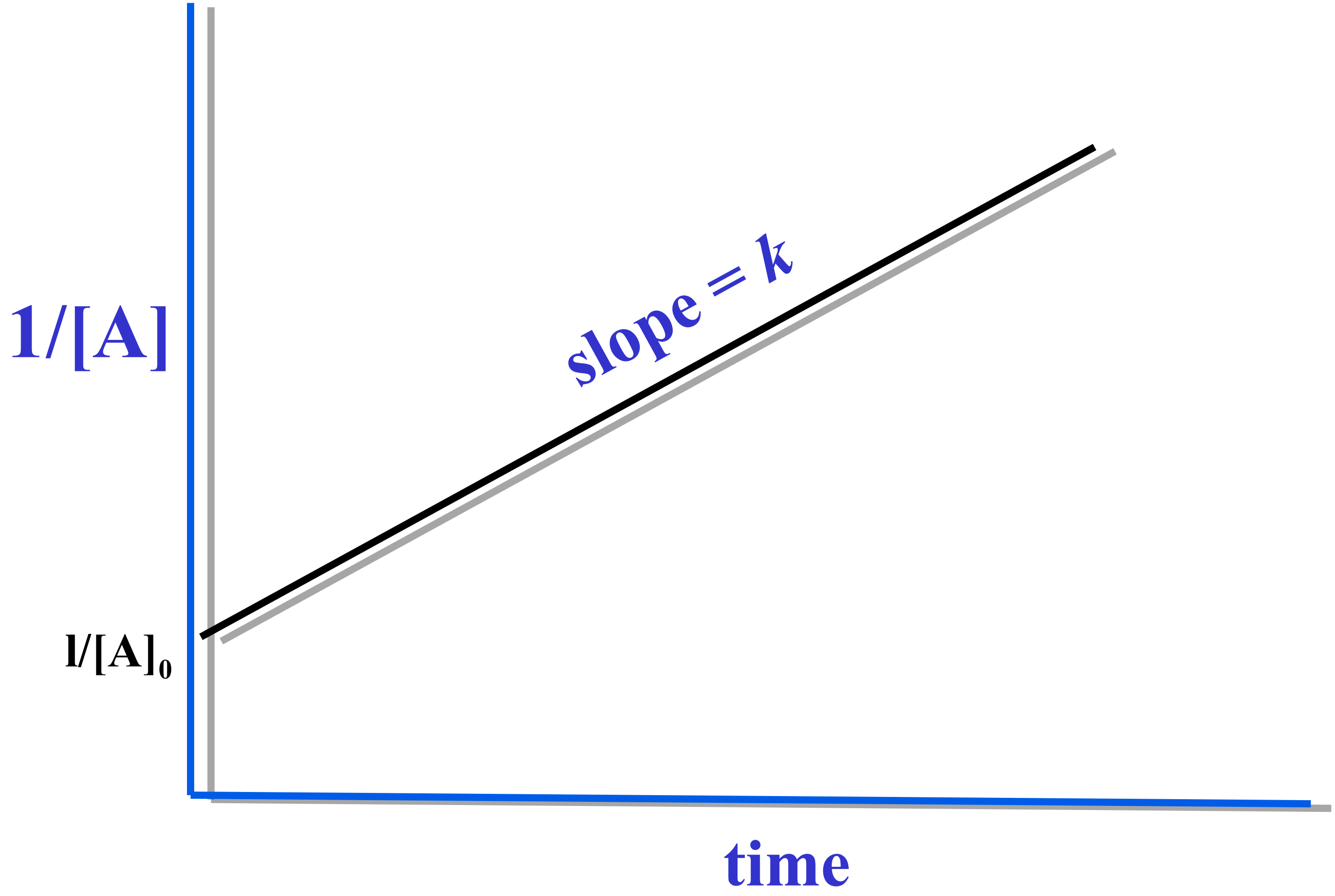


The integrated rate law suggests a way to tell the order **(& rate constant, k)** based on experiment (graphical method).

## Using the Integrated Rate Laws: k, order

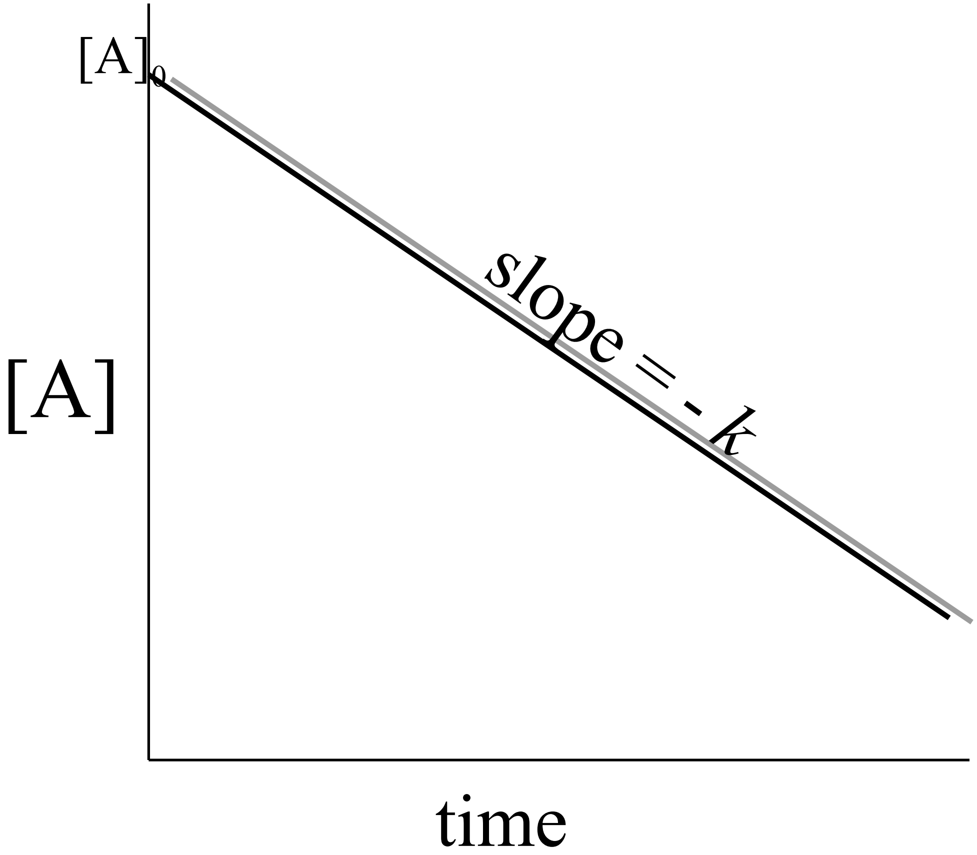
# Second order: $1/[A] = kt + 1/[A]_0$

Plot of 1/[A] vs. time gives straight line with **slope = +$k$ and y-intercept = $1/[A]_0$**



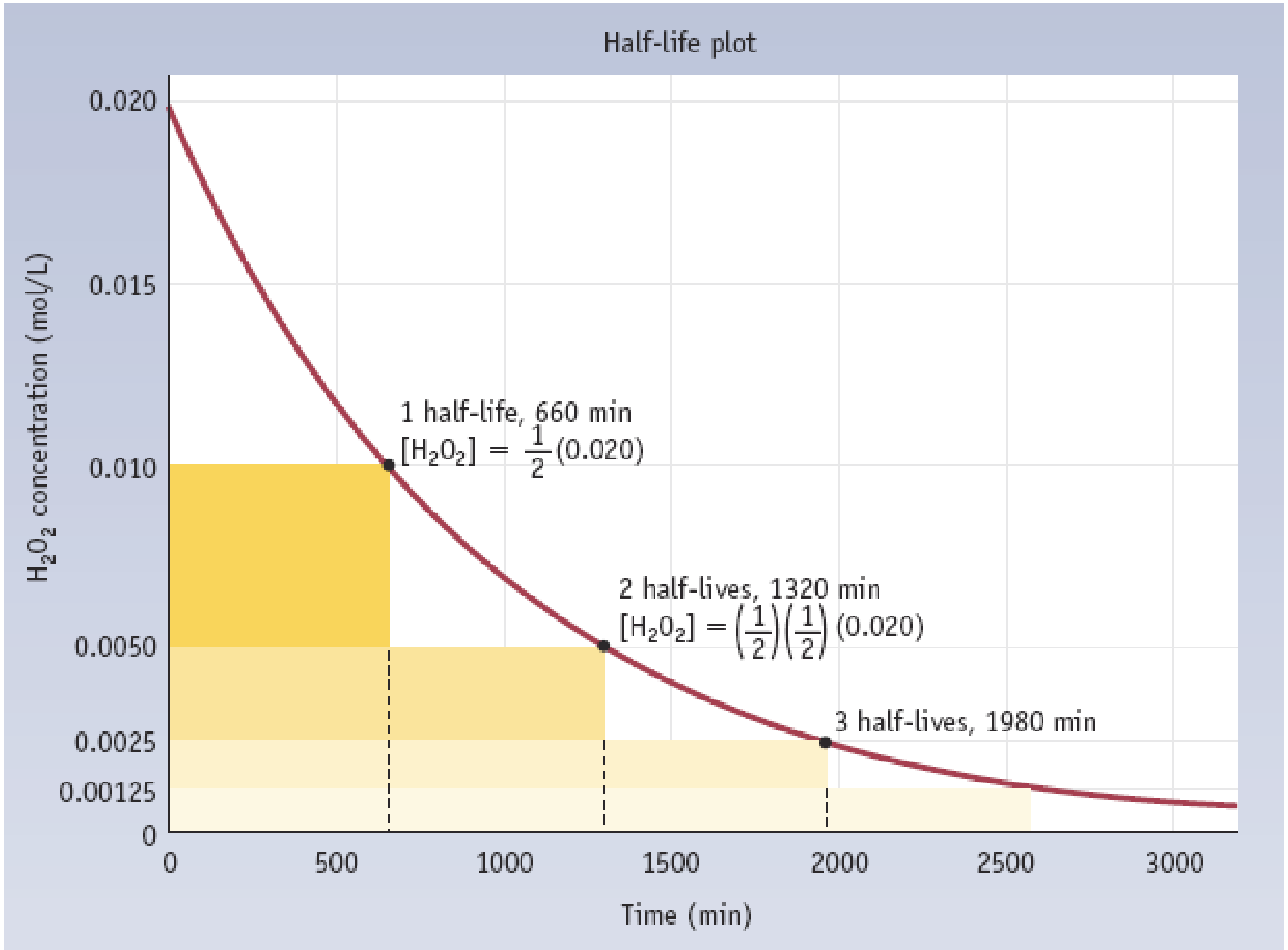
# Zero order: $[A] = -kt + [A]_0$

Plot of [A] vs. time is straight line with **slope = -*k*** **and y-intercept = $[A]_0$**



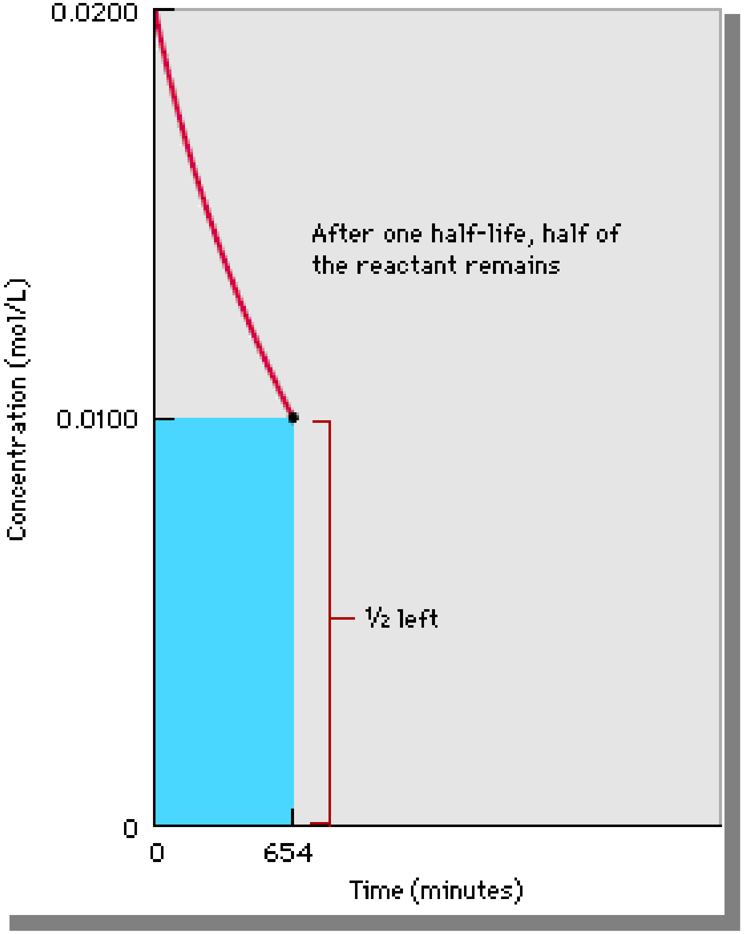
**See summary in Table 13.2**

# Half-Life



**HALF-LIFE** is the time it takes for half the sample to disappear.

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

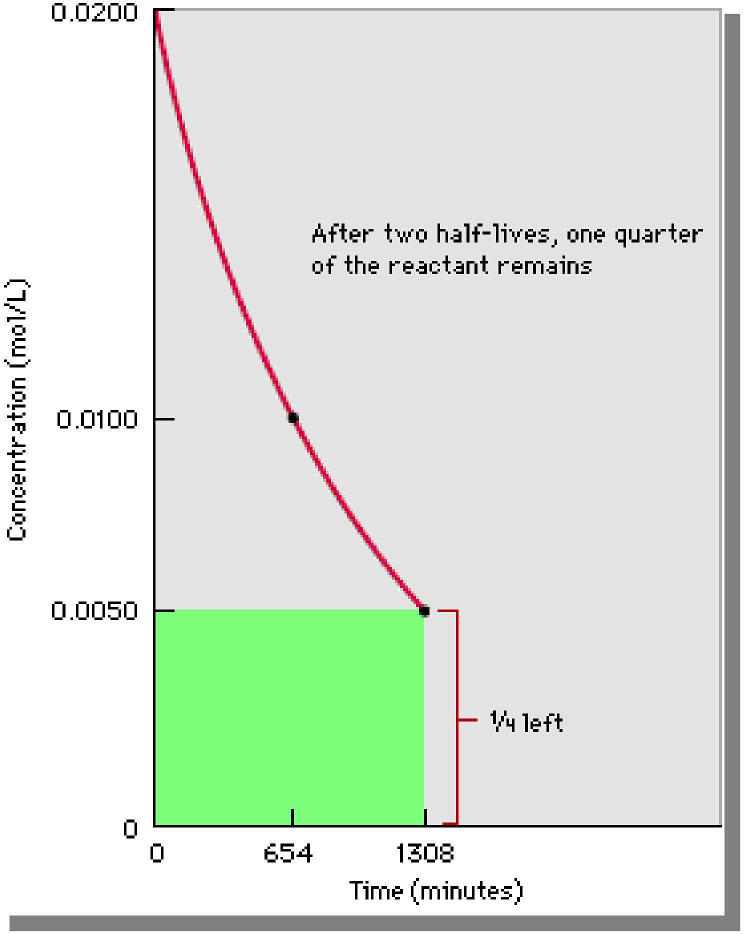


# Half-Life

- Reaction after 1 half-life.
- 1/2 of the reactant has been consumed (0.0100 M) and 1/2 remains (0.0100 M).

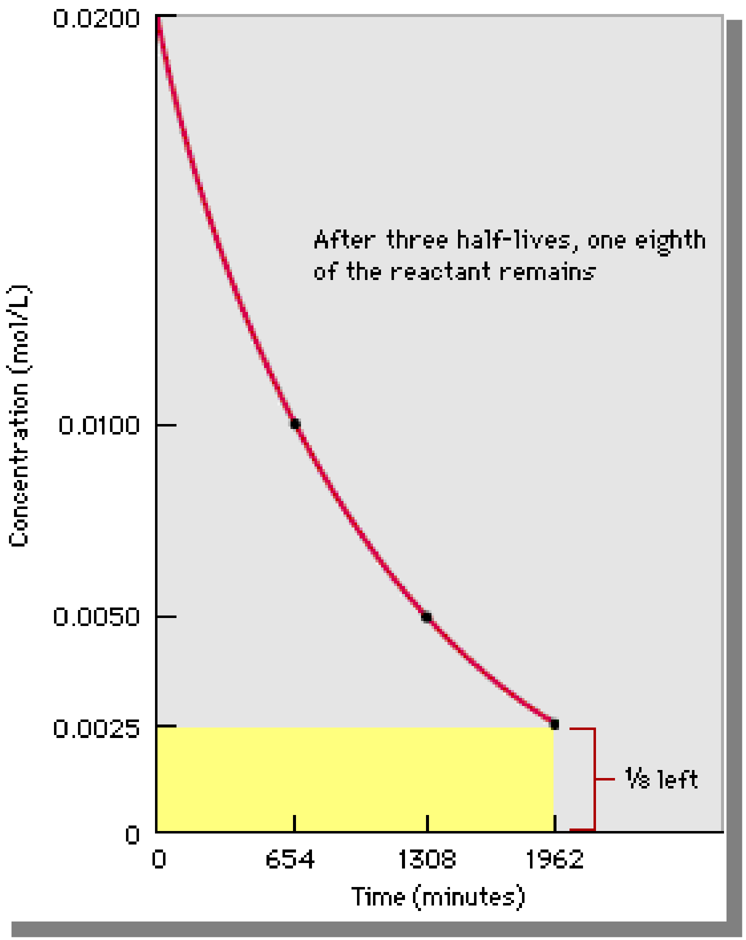
- **Remaining = $(\frac{1}{2})^{\text{1 half life}}$**

# Half-Life



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

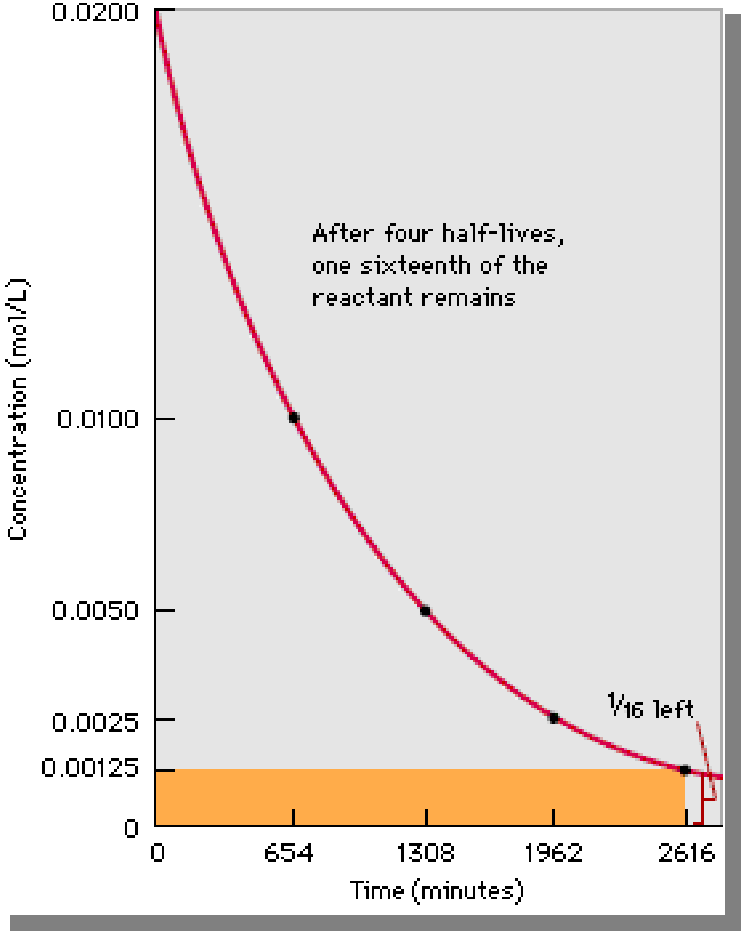
**Remaining = ¼ = (½ )$^{\text{2 half lives}}$**



# Half-Life

- After 3 half-lives, 1/8 of the reactant remains.

$$\text{remaining} = \frac{1}{8} = \left(\frac{1}{2}\right)^{\text{3 half lives}}$$



# Half-Life

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

$$\text{remaining} = \frac{1}{16} = \left(\frac{1}{2}\right)^{\text{4 half lives}}$$

# Half-Life

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

$$sugar + enzyme \rightarrow products$$

**Rate of disappear of sugar = k[sugar]**

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

**What is the half-life of this reaction?**

**-need a formula linking half-life and rate constant, k!**

# Half-Life

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

**Solution**

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

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

**Therefore, ln (1/2) = - k • $t_{1/2}$**

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

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

**So, for sugar,**

**$t_{1/2} = 0.693/3.3 \times 10^{-4}\ s^{-1}$ = 2100 sec = 35 min**

# Half-Life (time for ½ sample to disappear)

**Rate = k[sugar] and k = $3.3 \times 10^{-4}$ 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 = 140/35 = 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 |

$$\text{remaining} = \left(\frac{1}{2}\right)^{\text{4 half lives}} = \frac{1}{16} \times 5.00\ \text{g} = 0.313\ \text{g}$$

# Half-Lives of Radioactive Elements (ch. 19)

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

| | |
|---|---|
| $^{238}\mathrm{U} \rightarrow {}^{234}\mathrm{Th} + \mathrm{He}$ | $4.5 \times 10^{9}$ y |
| $^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N}$ + beta | 5730 y |
| $^{131}\mathrm{I} \rightarrow {}^{131}\mathrm{Xe}$ + beta | 8.05 d |
| Element 106 - seaborgium | |
| $^{263}\mathrm{Sg}$ | 0.9 s |

# Half-Life

Radioactive decay is a first order process.

Tritium → electron + helium

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

$t_{1/2} = 12.3$ 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

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

12.3 yrs

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

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

Therefore, $k = 0.0564\ y^{-1}$

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

$= -2.77$

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, then $[A] = 0.0941$ mg**

**But notice that 49.2 y = 4.00 half-lives**

**1.50 mg → 0.750 mg after 1 half-life**
**→ 0.375 mg after 2 half-lives**
**→ 0.188 mg after 3 half-lives**
**→ 0.094 mg after 4 half-lives**

$$\text{fraction remaining} = \left(\frac{1}{2}\right)^{\text{4 half lives}} = \frac{1}{16} \times 1.50\ mg = 0.094\ \text{mg}$$

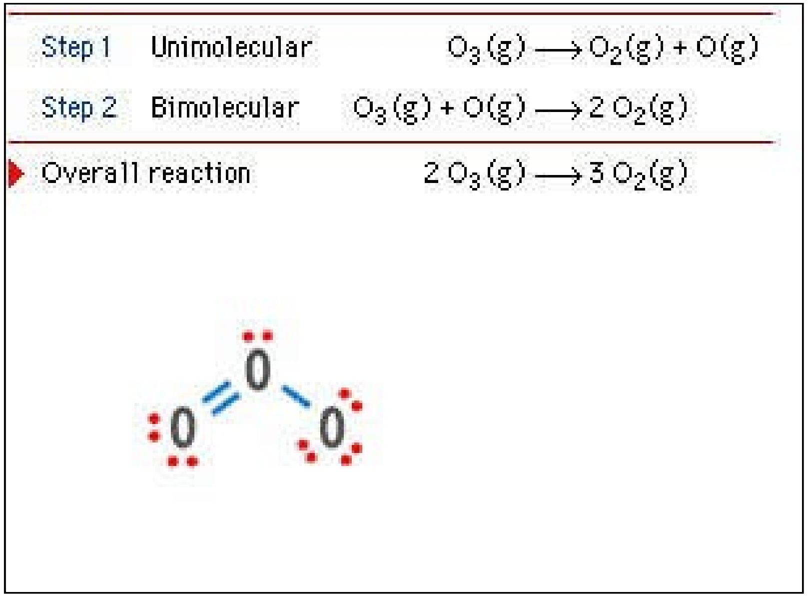
# MECHANISMS

## A Microscopic View of Reactions

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

**RXN RATES = RATE LAW → MECHANISM**

**experiment → 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 | | $2\,O_3(g) \longrightarrow 3\,O_2(g)$ |

# Collision Theory

For any reaction to occur -

(a) Molecules must collide with each other.

once molecules collide they may react together or they may not -

(b) Molecules must have sufficient energy, and

(c) Molecules must have correct geometry.

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

$O{=}O\text{-}O + NO \rightarrow [O{=}O\text{-}O\cdots\cdots NO] \rightarrow O{=}O(g) + ONO(g)$ ✓

$O{=}O\text{-}O + ON \rightarrow [O{=}O\text{-}O\cdots\cdots ON] \rightarrow O{=}O(g) + OON(g)$

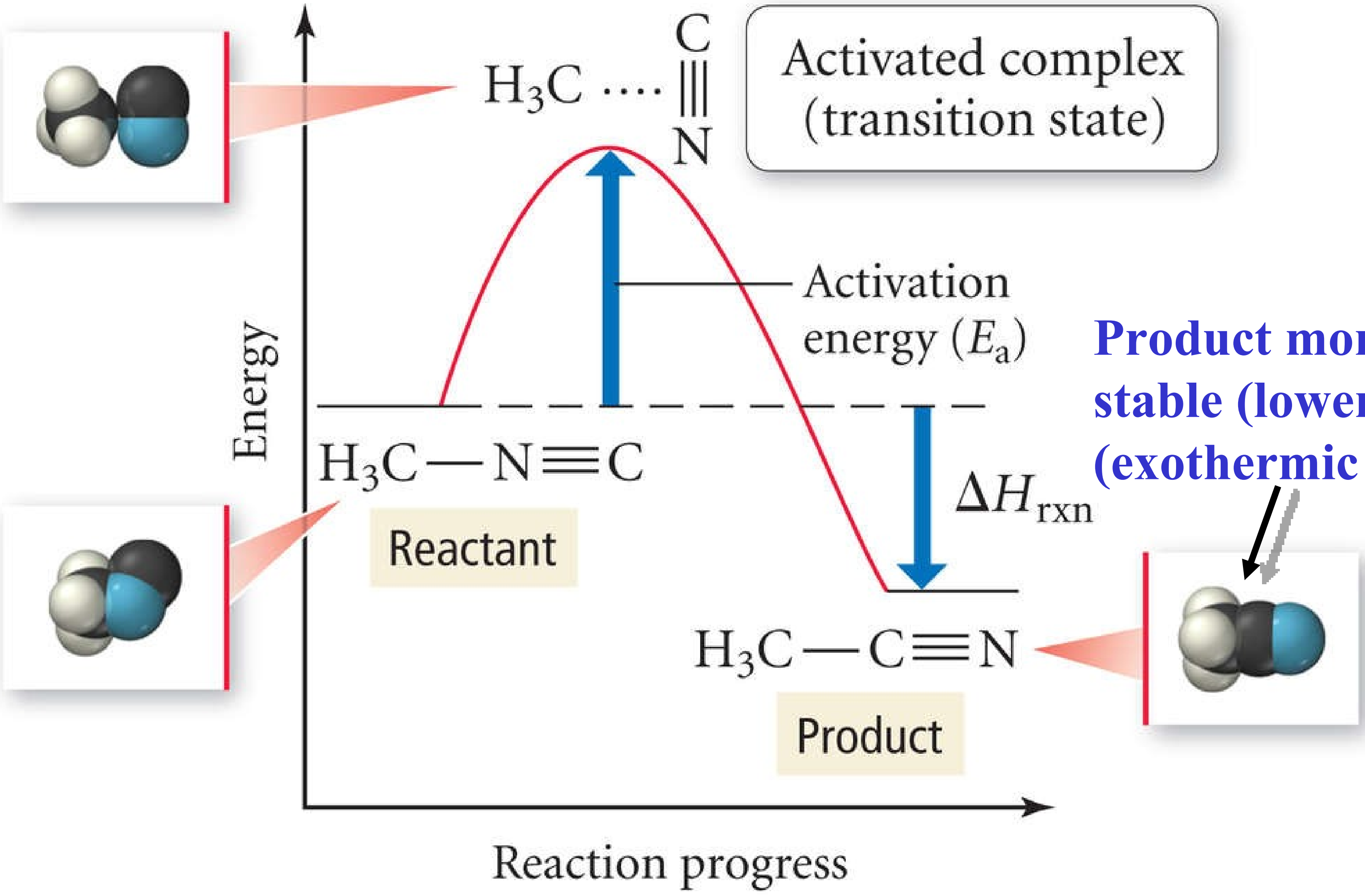
?

# Activation Energy and the Activated Complex

- **energy barrier to the reaction**
- **amount of energy needed to convert reactants into the activated complex**

- **the activated complex is a chemical species with partially broken and partially formed bonds**
  - ✓ **always very high in energy because of partial bonds**

# Energy Profile for the Isomerization of Methyl Isonitrile



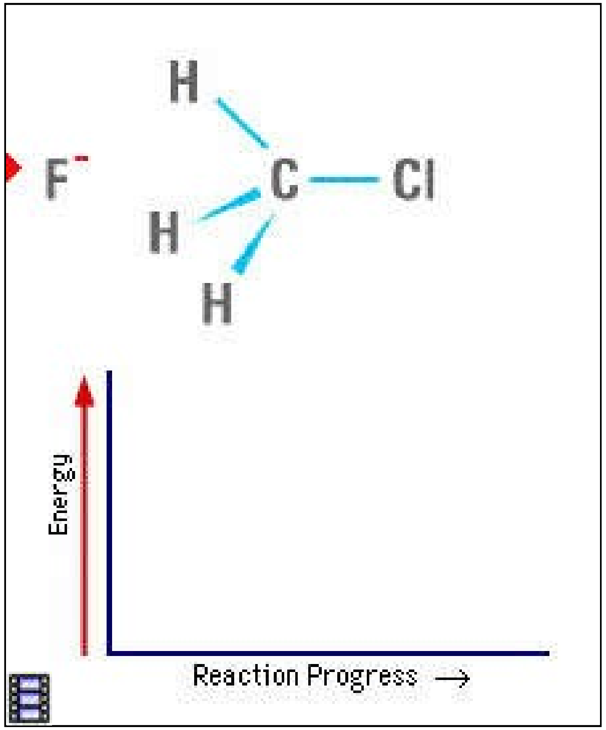
**Product more stable (lower E); (exothermic rxn)**

# Activation Energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier - activation energy, $E_a$.

**Figure 15.12** **An analogy to chemical activation energy.** For the volleyball to go over the net, the player must give it sufficient energy.



Reaction coordinate diagram

# The Effect of Temperature on Rate

- changing the temperature changes the rate constant of the rate law

**Svante Arrhenius investigated this relationship and showed that:**

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

# More on Activation Energy

**Arrhenius equation —**

Temp (K)

Rate constant

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

Frequency factor

Activation energy

$8.31 \times 10^{-3}$ kJ/K•mol

**Frequency factor is related to frequency of <u>collisions</u> with correct <u>geometry.</u>**

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

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

# The $E_a$ can also be evaluated mathematically if 2 rate constants are known at 2 diff temps: **2-point form**

R = 8.3145 J/(mol·K)

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

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

# The reaction $NO_{2(g)} + CO_{(g)} \rightarrow CO_{2(g)} + NO_{(g)}$ has a rate constant of $2.57\ M^{-1}\cdot s^{-1}$ at 701 K and $567\ M^{-1}\cdot s^{-1}$ at 895 K. Find the activation energy in kJ/mol

**Given:** $T_1 = 701\ K,\ k_1 = 2.57\ M^{-1}\cdot s^{-1},\ T_2 = 895\ K,\ k_2 = 567\ M^{-1}\cdot s^{-1}$

**Find:** $E_a$, kJ/mol

**Concept Plan:**

$$T_1, k_1, T_2, k_2 \longrightarrow E_a$$

**Relationships:**

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

**Solution:**

$$\ln\left(\frac{567\ \cancel{M^{-1}\cdot s^{-1}}}{2.57\ \cancel{M^{-1}\cdot s^{-1}}}\right) = \frac{E_a}{8.314\ \frac{J}{mol\bullet K}}\left(\frac{1}{701\ K} - \frac{1}{895\ K}\right)$$

$$5.39\underline{6}5 = \frac{E_a}{8.314\ \frac{J}{mol}\cancel{\bullet K}}\left(3.0\underline{9}2\times10^{-4}\ \cancel{K^{-1}}\right)$$

$$E_a = 1.45\times10^5\ \frac{J}{mol} = 145\ \frac{kJ}{mol}$$

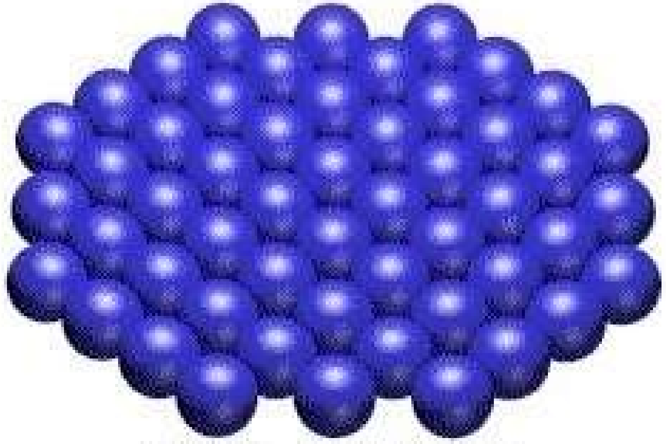
**Check:** most activation energies are tens to hundreds of kJ/mol – so the answer is reasonable

# 5th factor: CATALYSIS

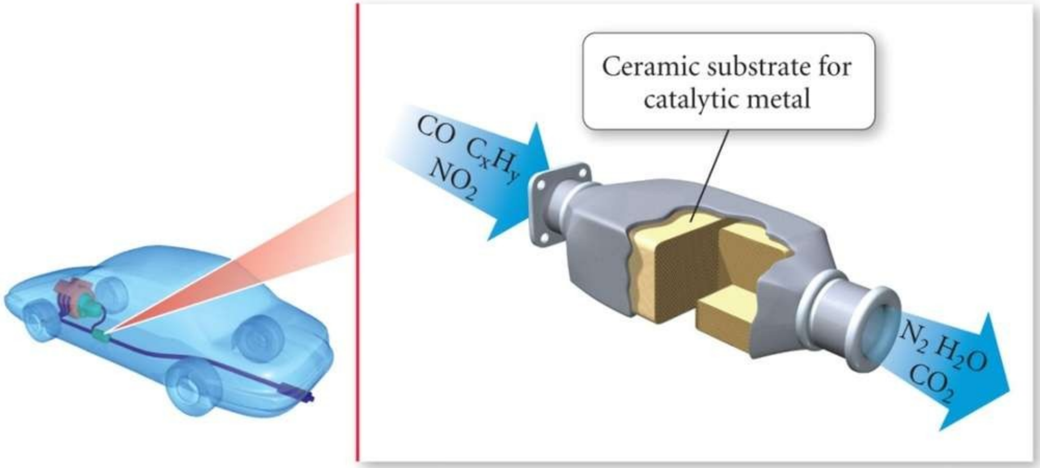
1. **In auto exhaust systems — Pt, NiO**

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

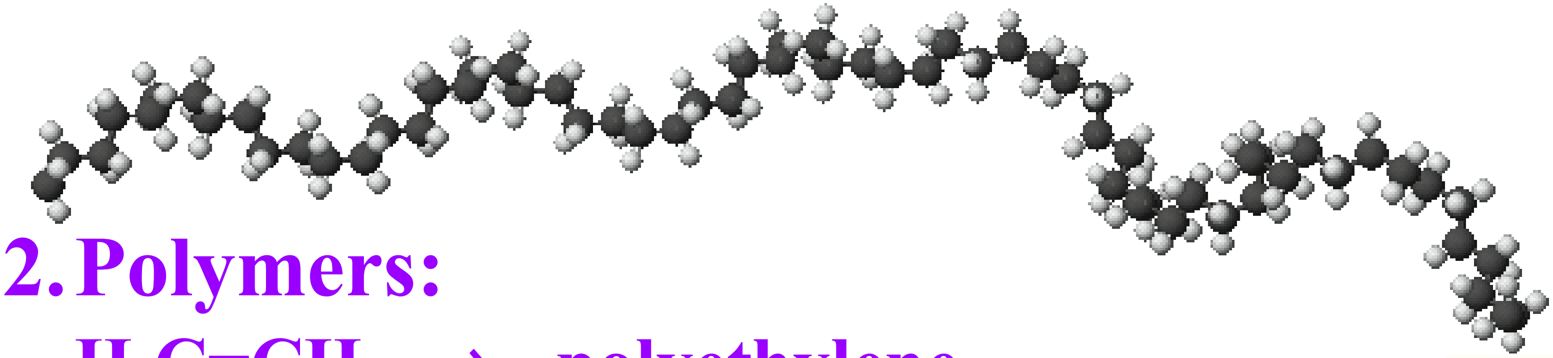
$2\,NO \rightarrow N_2 + O_2$



$2\,NO(g) \longrightarrow O_2(g) + N_2(g)$

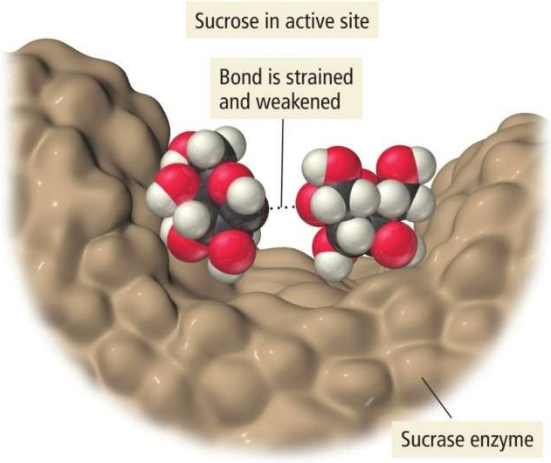


# CATALYSIS



2. **Polymers:**

   $H_2C{=}CH_2 \rightarrow$ polyethylene



3. **Acetic acid:**

   $CH_3OH + CO \rightarrow CH_3CO_2H$

4. **Enzymes — biological catalysts**

# 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, $E_a$**
- **catalysts are consumed in an early mechanism step, then made in a later step**

**mechanism without catalyst**

$O_{3(g)} + O_{(g)} \rightarrow 2\,O_{2(g)}$ V. Slow

**mechanism with catalyst, Cl**

$Cl_{(g)} + O_{3(g)} \Leftrightarrow O_{2(g)} + ClO_{(g)}$ Fast

$ClO_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl_{(g)}$ Slow

# CATALYSIS

## Catalysis and activation energy

$MnO_2$ catalyzes decomposition of $H_2O_2$

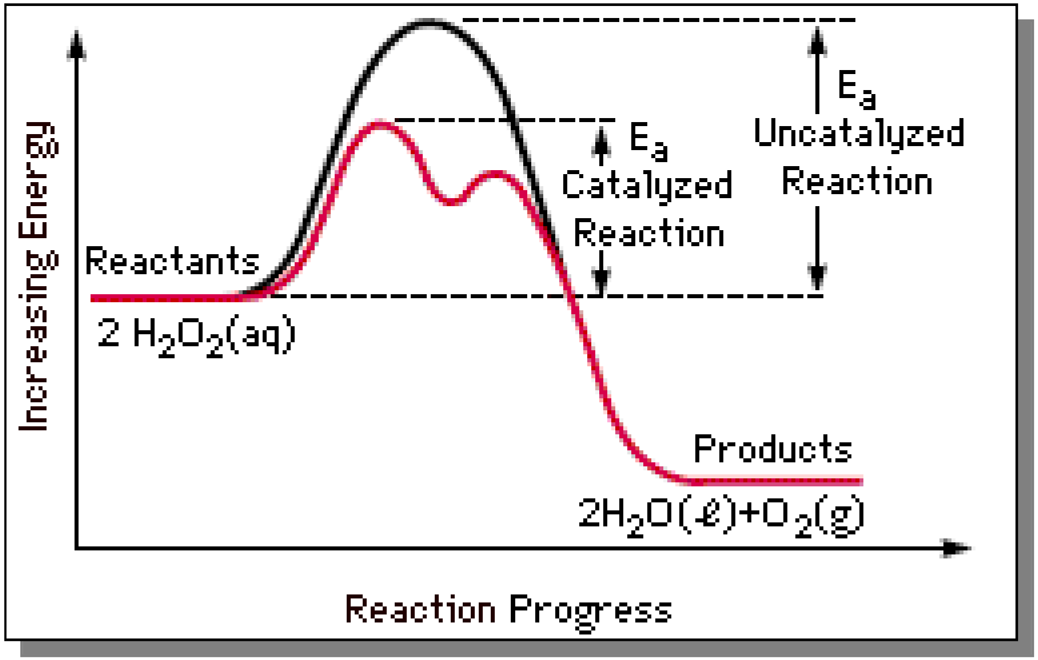
$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

Uncatalyzed reaction

alternative mechanism

lower activation energy

Catalyzed reaction

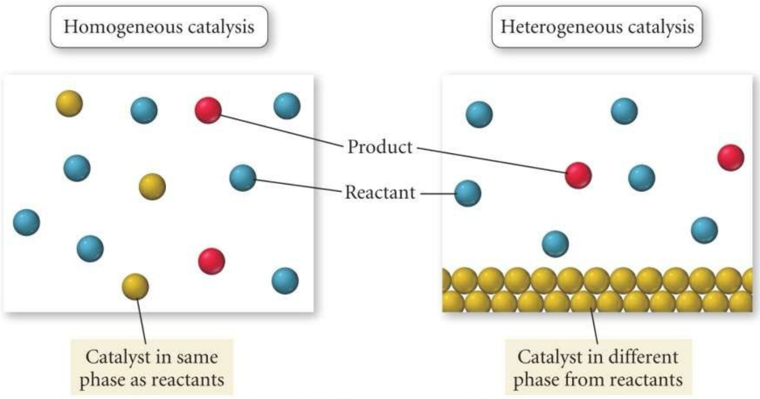


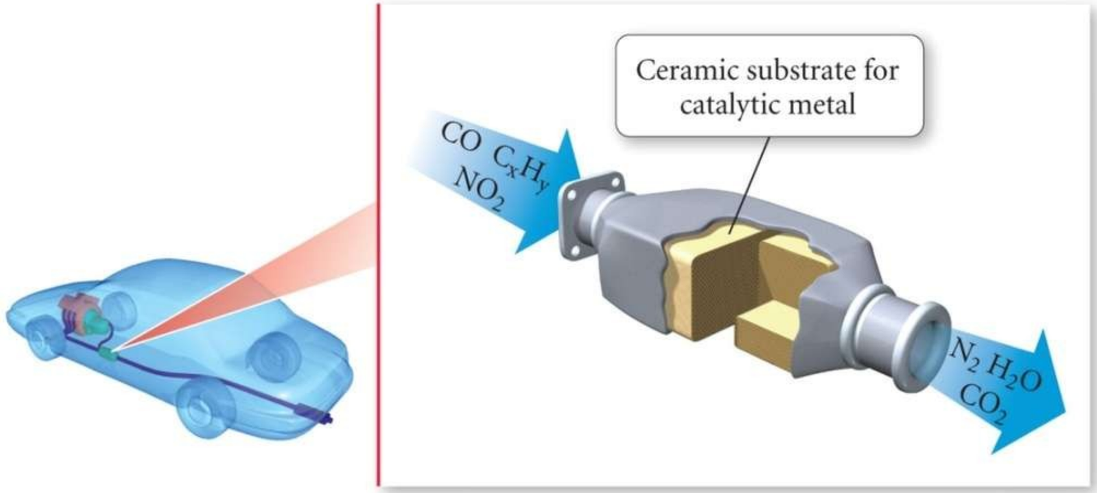
# Catalysts

**homogeneous catalysts** are in the same phase as the reactant particles

**$Cl_{(g)}$ in the destruction of $O_{3(g)}$**

- **heterogeneous catalysts** are in a different phase than the reactant particles
  - ✓**solid catalytic converter in a car's exhaust system**
  - ✓**solid $MnO_2$ catalyses liq $H_2O_2$**





# More on Mechanisms

## Elementary steps; Molecularity (order)

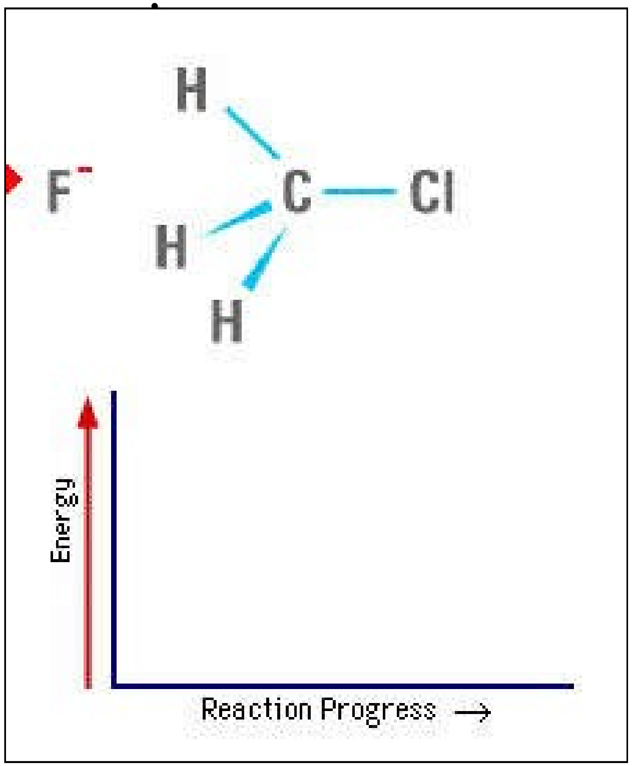
Based on the derived rate eqn & chemical intuition, the rxn

**trans-butene → cis-butene**

is UNIMOLECULAR - only one reactant is involved.

**BIMOLECULAR — two molecules must collide → products**

A bimolecular



Exo- or endothermic?

# Mechanisms

$O_3$ + NO reaction occurs in a single **ELEMENTARY**

step: $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

**Most others involve a sequence of <u>elementary</u> steps.**

**bond forms**
**bond breaks**
**atom displacement**

**Mechanism**

**Step 1** **bimolecular** $NH_3 + OCl^- \rightarrow \cancel{NH_2Cl} + \cancel{OH^-}$

**Step 2** **bimolecular** $\cancel{NH_2Cl} + NH_3 \rightarrow \cancel{N_2H_5^+} + Cl^-$

**Step 3** **bimolecular** $\cancel{N_2H_5^+} + \cancel{OH^-} \rightarrow N_2H_4 + H_2O$

**Overall rxn** $2NH_3 + OCl^- \rightarrow N_2H_4 + H_2O + Cl^-$

Adding elementary steps, gives the NET

# Mechanisms

**Most rxns. involve a sequence of elementary steps.**

$$2\ I^- + H_2O_2 + 2\ H^+ \rightarrow I_2 + 2\ H_2$$

**Rate of rxn = 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 a multistep reaction.

# Mechanisms

Most rxns. involve a sequence of elementary steps.

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

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

## Proposed Mechanism

**Step 1 — slow** $HOOH + I^- \rightarrow HOI + OH^-$

**Step 2 — fast** $HOI + I^- \rightarrow I_2 + OH^-$

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

Rate of the reaction controlled by slow step —

**RATE DETERMINING STEP**, rds.

Rate can be no faster than rds!

# Mechanisms

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

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

**Step 1 — slow** $HOOH + I^- \rightarrow HOI + OH^-$

**Step 2 — fast** $HOI + I^- \rightarrow I_2 + OH^-$

**Step 3 — fast** $2\,OH^- + 2\,H^+ \rightarrow 2\,H_2O$

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

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

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

# Another Reaction Mechanism

$\mathbf{NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}}$ $\mathbf{Rate_{obs} = \mathit{k}[NO_2]^2}$ **1)**

$\mathbf{NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}}$ $\mathbf{Rate = \mathit{k}_1[NO_2]^2}$ **slow**

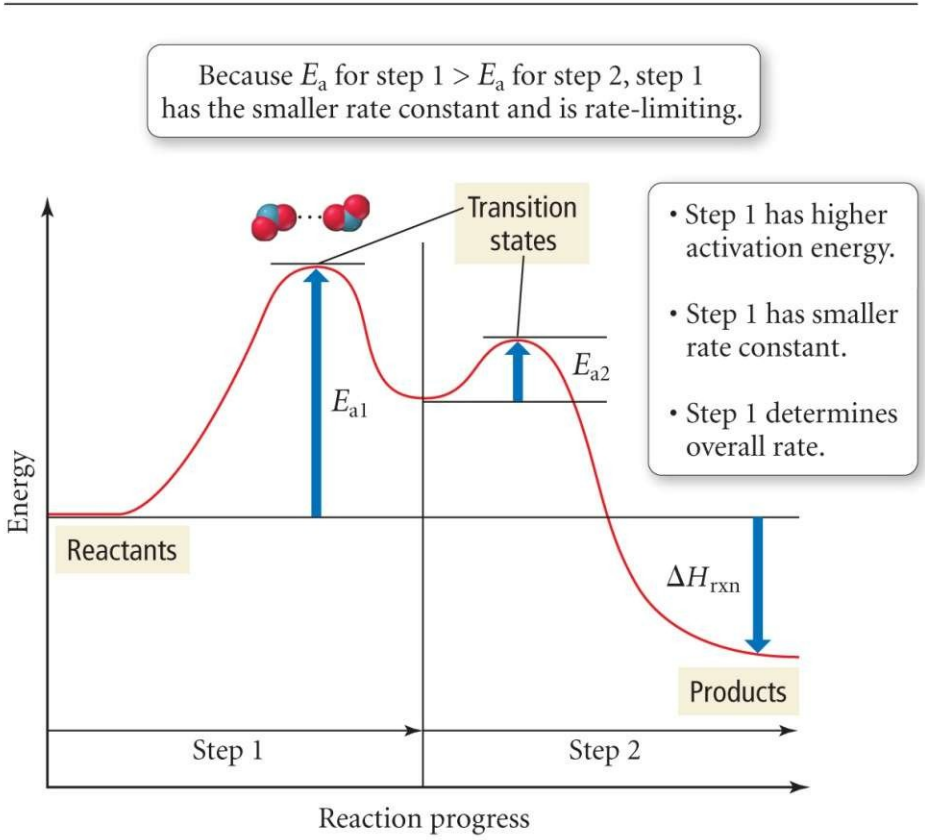
2) $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ $\text{Rate} = k_2[NO_3][CO]$ fast

**The first step is slower than the second step because its activation energy is larger.**

**The first step in this mechanism is the rate determining step.**

**The rate law of the first step (slow) is the same as the rate law of the overall reaction.**

**Energy Diagram for a Two-Step Mechanism**



Because $E_a$ for step 1 > $E_a$ for step 2, step 1 has the smaller rate constant and is rate-limiting.

- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

# Rate Laws and Mechanisms

**More than one possible mechanisms!**

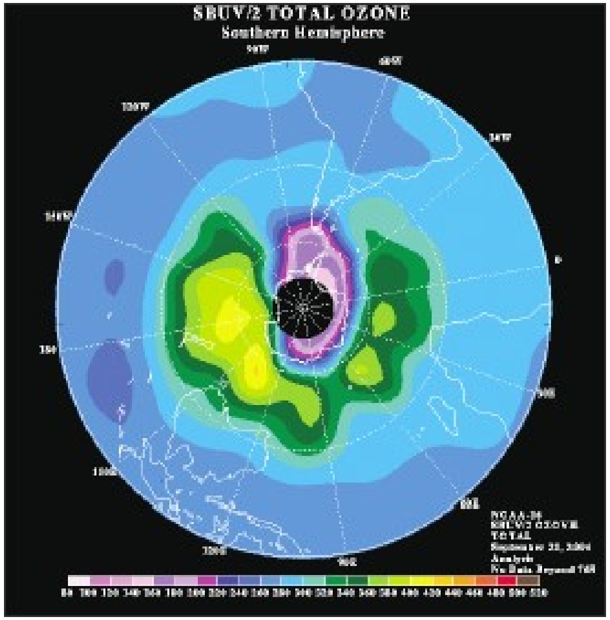
**things to do….**

**Derive rate laws (not mechanisms)**

**Deduce eqn for an elementary step**

**Determine overall eqn from elementary steps**

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



# Ozone Decomposition Mechanism

**Overall reaction:**

$$2\,O_3\,(g) \rightarrow 3\,O_2\,(g)$$

***Proposed mechanism***

**Step 1: fast, equilibrium**

$$O_3\,(g) \rightleftarrows O_2\,(g) + O\,(g) \qquad (k_1, k_{-1})$$

**Step 2: slow** $O_3\,(g) + O\,(g) \rightarrow 2\,O_2\,(g) \quad (k_2)$

**So what is the rate law??**

**rate = $k_2[O_3][O]$**

**O is an intermediate**

(the rate of an elementary step must be written w.r.t the reactants only)

**Rate of formation of O = $k_1[O_3]$**

**Rate of conversion to $O_3$ = $k_{-1}[O_2][O]$**

**$k_1[O_3] = k_{-1}[O_2][O]$ @ <u>equilibrium</u>**

$$\frac{k_1}{k_{-1}}\frac{[O_3]}{[O_2]} = [O]$$

$$\frac{k_1}{k_{-1}} = K$$

$$[O] = K\frac{[O_3]}{[O_2]}$$

Substituting for [O] in: rate = $k_2[O_3][O]$

$$rate = k_2[O_3]K\frac{[O_3]}{[O_2]}$$

$$\textbf{Rate} = \textbf{k}\,\frac{[\mathbf{O_3}]^2}{[\mathbf{O_2}]}$$