

Lecture Presentation

Chapter 13 Chemical Kinetics

13.1, 13.3, 13.4, 13.6,
13.9, 13.11, 13.14,
13.15, 13.17, 13.23,
13.25, 13.31, 13.56,
13.58, 13.78

John E. McMurry
Robert C. Fay

Reaction Rates

Chemical Kinetics: The area of chemistry concerned with **reaction rates** and the sequence of steps by which reactions occur

Reaction Rate: Either the *increase* in the concentration of a **product per unit time** or the *decrease* in the concentration of a **reactant per unit time** (how fast does the reaction go ?)

Reaction Rates

TABLE 13.1 Concentrations as a Function of Time at 55 °C for the Reaction
 $2 \text{N}_2\text{O}_5(g) \longrightarrow 4 \text{NO}_2(g) + \text{O}_2(g)$

Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note that the concentrations of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.

Reaction Rates



Rate of decomposition of N_2O_5 :
Reactant disappearing with time

$$\begin{aligned} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} &= \frac{-(0.0101 \text{ M} - 0.0120 \text{ M})}{(400 \text{ s} - 300 \text{ s})} \\ &= -1.9 \times 10^{-5} \frac{\text{M}}{\text{s}} \end{aligned}$$

Reaction Rates

General Reaction:



$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$$

disappearing reactant
(negative sign)

appearing product
(positive sign)

reaction:

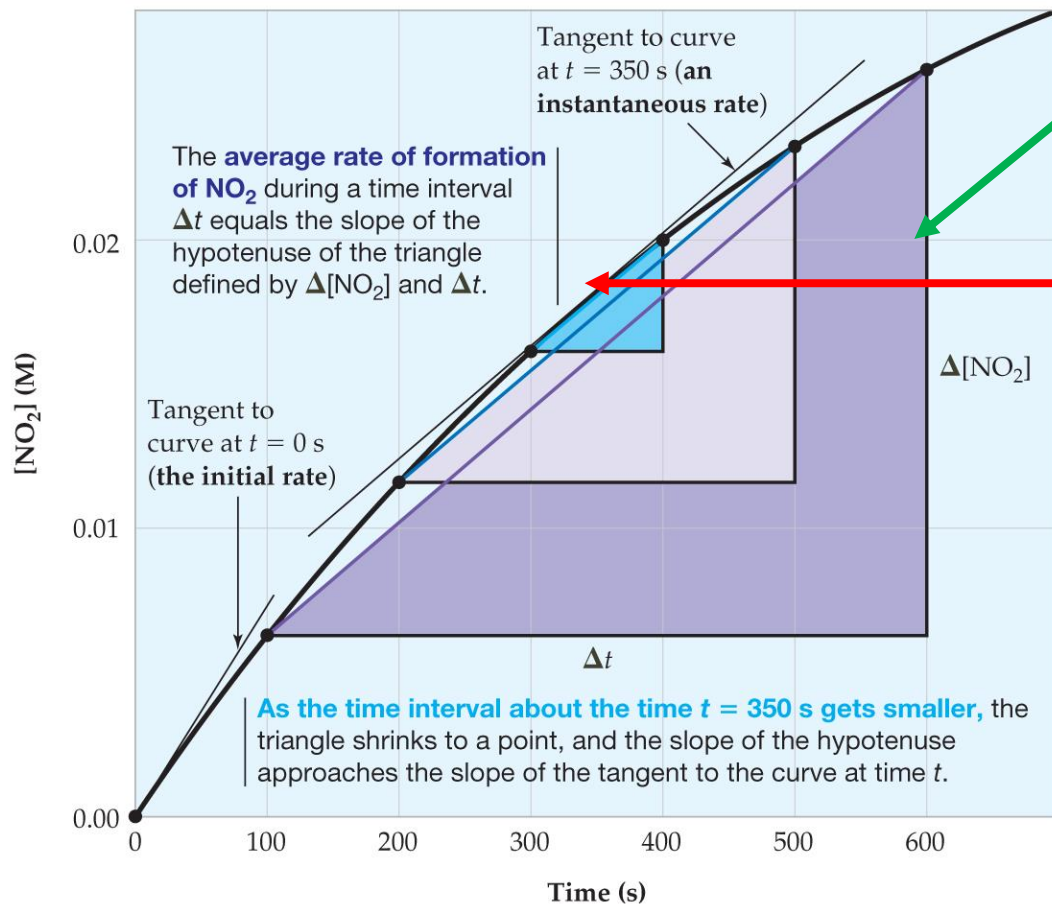


$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

disappearing
reactant

appearing product

Reaction Rates – rate changes w time



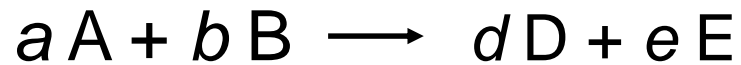
Average rate over area

tangent to curve give rate at a single point in time

The slope of the tangent at time t is defined as the instantaneous rate at that particular time. The initial rate is the slope of the tangent to the curve at $t = 0$.

Reaction Rates

General Reaction:

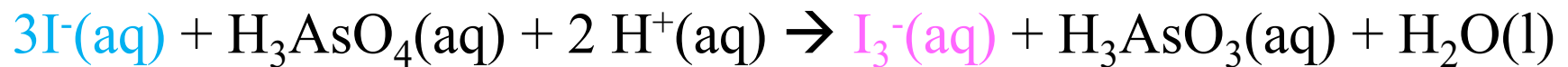


$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$$

Given a balanced chemical reaction, if you know the rate of one component, can get all others from stoichiometry

For the reaction shown, if the $-\Delta[I^-] / \Delta t = 4.8 \times 10^{-4} \text{M/s}$

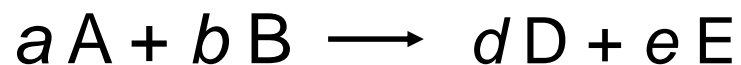
(a) what is the value of the $\Delta[I_3^-] / \Delta t$ during the same time ?



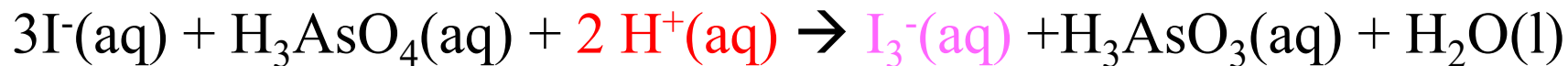
$$\frac{-1}{3} \frac{\Delta[I^-]}{\Delta t} = \frac{\Delta[I_3^-]}{\Delta t} = -1/3 (4.8 \times 10^{-4} \text{M/s}) = 1.6 \times 10^{-4} \text{ M/s}$$

HW13.1: Reaction Rates

General Reaction:



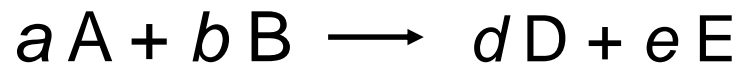
$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$$



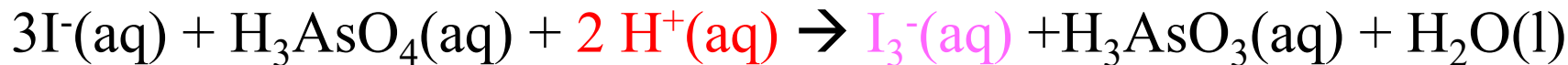
(b) What is the value of the $\Delta[\text{H}^+]/\Delta t$? Given $\Delta[\text{I}_3^-]/\Delta t = 1.6 \times 10^{-4} \text{M/s}$

HW13.1: Reaction Rates

General Reaction:



$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$$



(b) What is the value of the $\Delta[\text{H}^+]/\Delta t$? Given $\Delta[\text{I}_3^-]/\Delta t = 1.6 \times 10^{-4} \text{M/s}$

$$= \frac{\Delta[\text{I}_3^-]}{\Delta t} = 1.6 \times 10^{-4} \text{M/s} = \frac{-1 \Delta[\text{H}^+]}{2 \Delta t}$$

End 2/12 Wed
section A
section

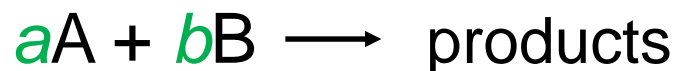
$$\frac{\Delta[\text{H}^+]}{\Delta t} = -2 * 1.6 \times 10^{-4} \text{M/s} = -3.2 \times 10^{-4} \text{M/s}$$

END QUIZ 4

END TEST 2

Rate Laws and Reaction Order

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant



$$\text{rate} \propto [A]^m[B]^n$$

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

k is the **rate constant**.

$$m, n \neq a, b$$

Rate Laws and Reaction Order

The values of the **exponents in the rate law must be determined by experiment**; they cannot be deduced from the stoichiometry of the reaction.

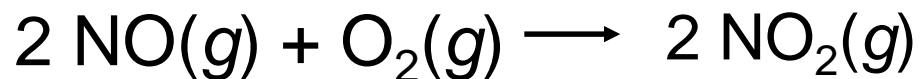
TABLE 13.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

Reaction*	Rate Law
$(\text{CH}_3)_3\text{CBr}(\text{soln}) + \text{H}_2\text{O}(\text{soln}) \longrightarrow (\text{CH}_3)_3\text{COH}(\text{soln}) + \text{H}^+(\text{soln}) + \text{Br}^-(\text{soln})$	$\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$
$\text{HCO}_2\text{H}(\text{aq}) + \text{Br}_2(\text{aq}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) + \text{CO}_2(\text{g})$	$\text{Rate} = k[\text{Br}_2]$
$\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$	$\text{Rate} = k[\text{H}_2][\text{I}_2]$

In general, the exponents in the rate law **are not the same** as the stoichiometric coefficients in the balanced chemical equation for the reaction.

*In the first reaction, “(soln)” denotes a nonaqueous solution.

Experimental Determination of a Rate Law (Method of Initial Rates)



$$\text{rate} = k[\text{NO}]^m [\text{O}_2]^n \quad (\text{m and n} \neq \text{coefficients of reaction a,b})$$

Compare the initial rates to the changes in initial concentrations.

TABLE 13.3 Initial Concentration and Rate Data for the Reaction
 $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	Initial Reaction Rate (M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

Experimental Determination of a Rate Law



The concentration of NO **doubles**, the concentration of O₂ remains constant, and the rate **quadruples**.

$$\text{rate 2}/\text{rate 1} = 0.096/0.024 = [0.030/0.015]^m [0.015/0.015]^n$$

$$4 = [2]^m [1]^n \quad \rightarrow \quad 2^m = 4 \quad m = 2$$

End 2/12 Wed
C section

TABLE 13.3 Initial Concentration and Rate Data for the Reaction
 $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	Initial Reaction Rate (M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

HW13.2: Experimental Determination of a Rate Law



Given $m = 2$, what is n given the following chart.

TABLE 13.3 Initial Concentration and Rate Data for the Reaction
 $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	Initial Reaction Rate (M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

HW13.2: Experimental Determination of a Rate Law



Given $m = 2$, what is n given the following chart.

TABLE 13.3 Initial Concentration and Rate Data for the Reaction
 $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	Initial Reaction Rate (M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

HW13.2: Experimental Determination of a Rate Law



Given $m = 2$, what is n given the following chart.

$$\text{rate 3}/\text{rate 1} = 0.048/0.024 = [0.015/0.015]^m [0.030/0.015]^n$$

$$2 = [1]^m [2]^n \rightarrow n = 1$$

or

$$\text{rate 4}/\text{rate 2} = 0.192/0.096 = [0.030/0.030]^m [0.030/0.015]^n$$

$$2 = [1]^m [2]^n \rightarrow n = 1$$

$$2^n = 2$$

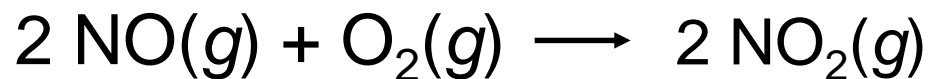
$$n = 1$$

End
2/14
Friday
A sect

TABLE 13.3 Initial Concentration and Rate Data for the Reaction
 $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	Initial Reaction Rate (M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

Experimental Determination of a Rate Law



$$\text{rate} = k[\text{NO}]^2 [\text{O}_2]$$

Reaction Order With Respect to a Reactant

- NO: second-order
- O₂: first-order

Overall Reaction Order

- 2 + 1 = 3 (third-order)

Order for heterogenous reactant/products

zero like gas in a reaction in solution or

H₂O(l) in a reaction in water solution

HW 13.3: Experimental Determination of a Rate Law

Given the following experimentally determined rate law: what is the overall order of the reaction? Write down the overall order in the blank provided.

(a) $\text{Rate} = k[\text{A}][\text{B}]^2$ _____

(b) $\text{Rate} = k [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ _____

(c) $\text{Rate} = k[\text{A}]^2$ _____

HW 13.3: Experimental Determination of a Rate Law

Given the following experimentally determined rate law: what is the overall order of the reaction ?

(a) Rate = $k[A][B]^2$ 3

(b) Rate = $k [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ 4

(c) Rate = $k[A]^2$ 2

End 2/14
Friday C
section

Note additional questions not in HW:

Order of [B] in (a) is ? 2

Order of [A] in (a) is ? 1

Order of [A] in (c) is ? 2

Experimental Determination of a Rate Law (can get value of k if know rate law)



$$\text{rate} = k[\text{NO}]^2 [\text{O}_2]$$

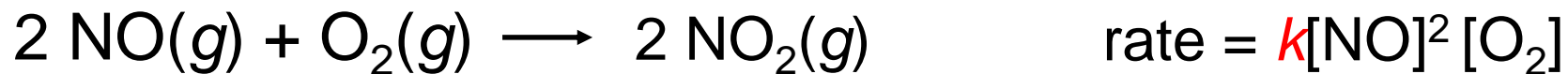
Units of k for this third-order reaction:

$$k = \frac{\text{rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{\frac{\text{M}}{\text{s}}}{(\text{M}^2) (\text{M})} = \frac{1}{\text{M}^2 \text{s}}$$

To get k .

- (a) Get order (m, n) of rate law experimentally.
- (b) use any one experimental data to calculate k (watch the units)

Experimental Determination of a Rate Law



Experiment 3 (from chart 13.3) solving for k

$$0.048 \text{ M/s} = k [0.015 \text{ M}]^2 [0.030 \text{ M}]$$

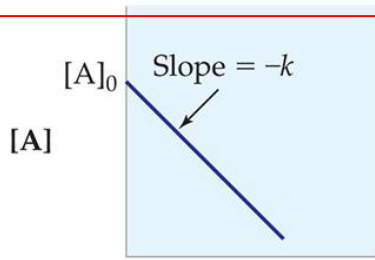
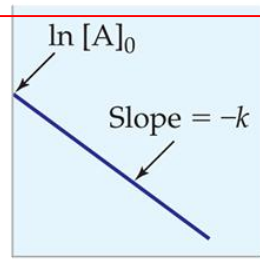
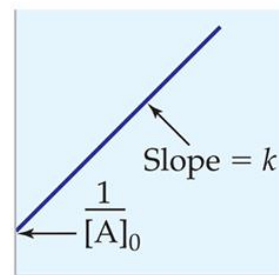
$$k = \frac{0.048}{[0.015]^2 [0.030]}$$

$$k = \frac{0.048 \text{ M/s}}{6.75 \times 10^{-6} \text{ M}^3}$$

$$k = 7.1 \times 10^3 / (\text{M}^2 \cdot \text{s})$$

(integrated rate law – summary of next few slides)

TABLE 13.4 Characteristics of Zeroth-, First-, and Second-Order Reactions of the Type $A \rightarrow \text{Products}$

	Zeroth-Order	First-Order	Second-Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Linear graph	$[A]$ versus t	$\ln [A]$ versus t	$\frac{1}{[A]}$ versus t
$y = mx + b$ eqn of line			
Graphical determination of k	$k = -(\text{Slope})$	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (not constant)	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)

Zeroth-Order Reactions (integrated rate law)

For a zeroth-order reaction, the rate is independent of the concentration of the reactant.



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

$$-\frac{\Delta[A]}{\Delta t} = k$$

Calculus can be used to derive an **integrated** rate law.

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

$$y = mx + b$$

$$[A]_t$$

concentration of A at time t

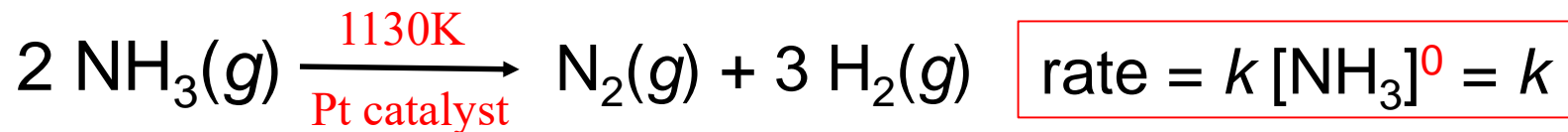
$$[A]_0$$

initial concentration of A

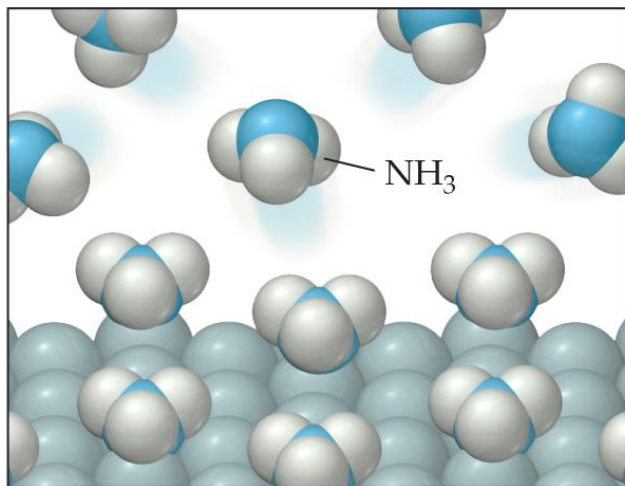
Order for heterogenous reactant/products zero like gas in a reaction in solution or $\text{H}_2\text{O}(l)$ in a reaction in water solution

Zeroth-Order Reactions - uncommon

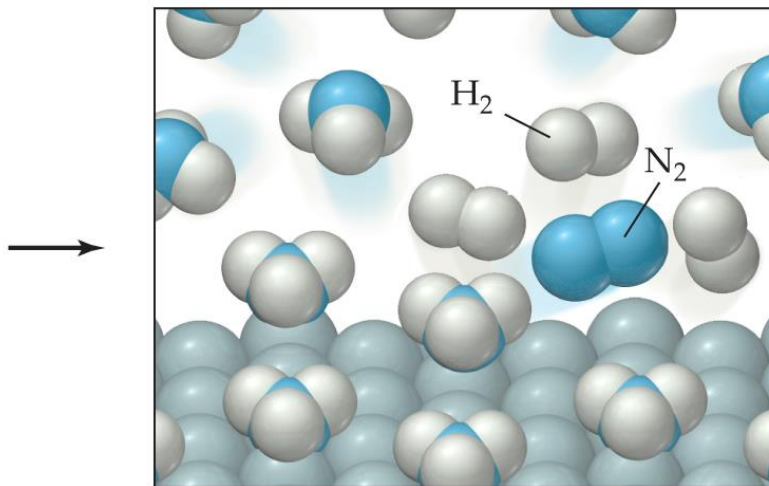
What kind of reaction would have rate not dependent on concentration of reactants ?



Most of the NH_3 molecules are in the gas phase above the surface and are unable to react.



As NH_3 molecules on the surface decompose, they are replaced by molecules from the gas phase, so the number of NH_3 molecules on the surface remains constant.



Because only the NH_3 molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of NH_3 .

Integrated Rate Law for a First-Order Reaction



$$\text{rate} = k[A] \qquad -\frac{\Delta[A]}{\Delta t} = k[A]$$

Calculus can be used to **derive an integrated rate law**.

$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt \left\{ \begin{array}{l} [A]_t \quad \text{concentration of A at time } t \\ [A]_0 \quad \text{initial concentration of A} \end{array} \right.$$

Using: $\ln \left(\frac{x}{y} \right) = \ln(x) - \ln(y)$

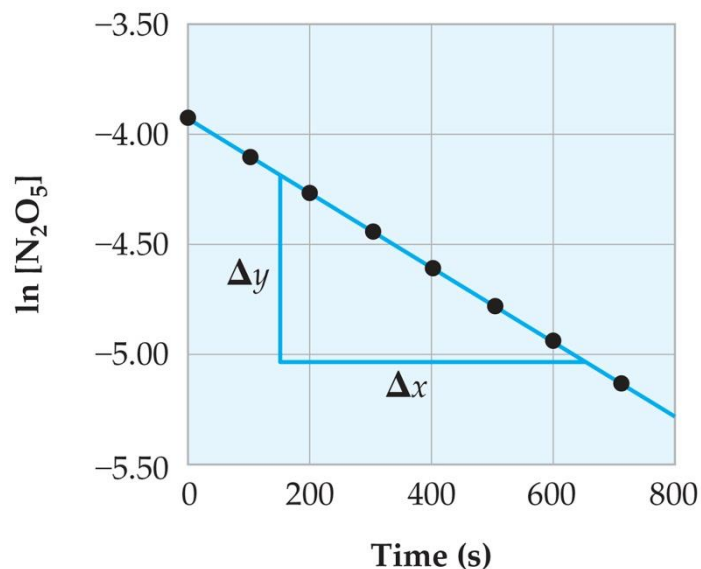
$$\ln[A]_t = -kt + \ln[A]_0$$
$$y = mx + b$$

Integrated Rate Law for a First-Order Reaction



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

X		Y
Time (s)	$[\text{N}_2\text{O}_5]$	$\ln [\text{N}_2\text{O}_5]$
0	0.0200	-3.912
100	0.0169	-4.080
200	0.0142	-4.255
300	0.0120	-4.423
400	0.0101	-4.595
500	0.0086	-4.756
600	0.0072	-4.934
700	0.0061	-5.099



$$\text{Slope} = -k$$

$$\text{Slope} = \frac{\Delta y}{\Delta x}$$

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

$$y = mx + b$$

Half-Life of a First-Order Reaction

Half-Life: The **time** required for the **reactant concentration** to drop to one-half of its initial value



$$\text{rate} = k[A]$$

$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt \left\{ \begin{array}{l} t = t_{1/2} \\ [A]_{t_{1/2}} = \frac{[A]_0}{2} \end{array} \right.$$

$$\ln \left(\frac{1}{2} \right) = -kt_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k}$$

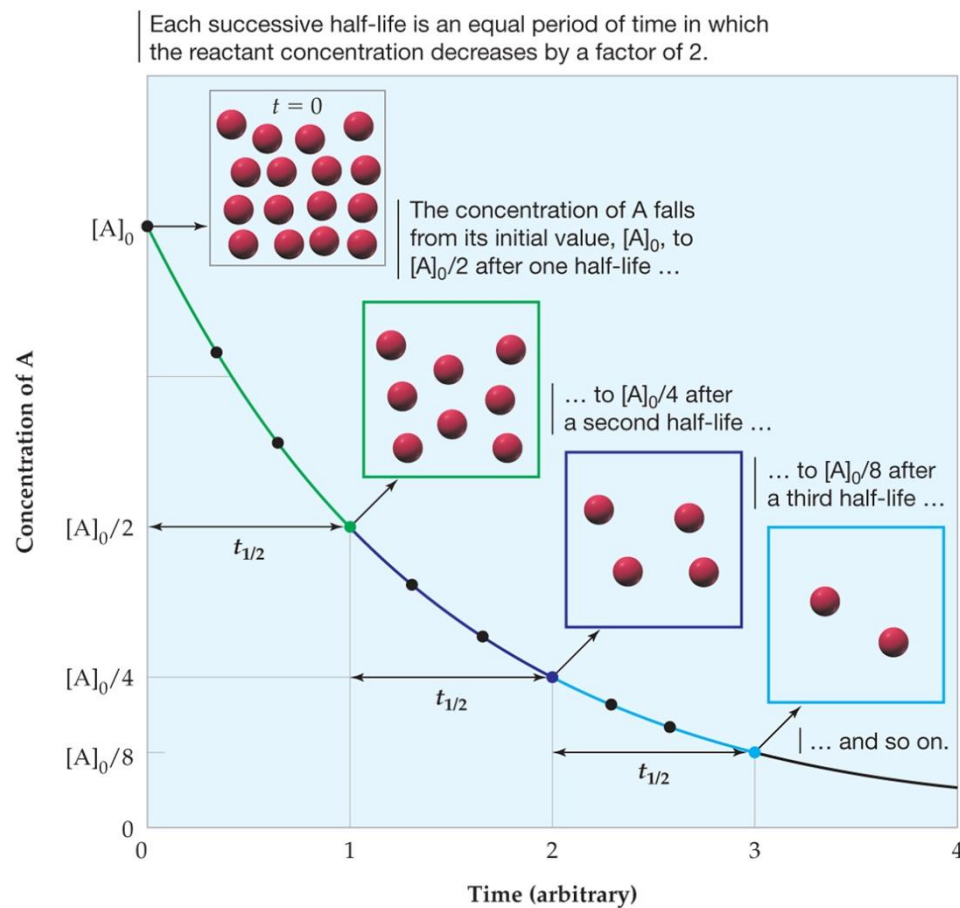
Half Life

Half-Life of a First-Order Reaction

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

For a **first-order reaction**, the **half-life** is **independent** of the **initial concentration**.

Each successive half-life is an equal period of time.



HW 13.4: Integrated Rate Law for a First-Order Reaction

The following reaction is first order in $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ with an initial concentration of 0.100 M. The rate constant $k = 6.3 \times 10^{-6} \text{ s}^{-1}$.



(a) What is the molarity of the $\text{Co}(\text{NH}_3)_5\text{Br}^{2+} (\text{aq})$ after 10.0 hours ?

$$\ln[\mathbf{A}]_t = -kt + \ln[\mathbf{A}]_0 \quad \ln \neq \log$$

HW 13.4: Integrated Rate Law for a First-Order Reaction

The following reaction is first order in $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ with an initial concentration of 0.100 M. The rate constant $k = 6.3 \times 10^{-6} \text{ s}^{-1}$.



(a) What is the molarity of the $\text{Co}(\text{NH}_3)_5\text{Br}^{2+} (\text{aq})$ after 10.0 hours ?

$$\ln[\mathbf{A}]_t = -kt + \ln[\mathbf{A}]_0 \quad \ln \neq \log$$

$$\ln[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = -(6.3 \times 10^{-6} \text{ s}^{-1})(10.0 \text{ hours}) + \ln[0.100\text{M}]$$

$$10.0 \text{ hrs} \times 60 \text{ min/hr} \times 60 \text{ s/min} = 36,000 \text{ s}$$

$$\ln[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = -(6.3 \times 10^{-6} \text{ s}^{-1})(36,000 \text{ s}) + (-2.303 \text{ M})$$

$$\ln[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = -0.2268 - 2.303 = -2.5298$$

$$[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = e^{-2.5298} \text{ (antilog for e based log)} = 0.080 \text{ M}$$

HW 13.5: Integrated Rate Law for a First-Order Reaction

The following reaction is first order in $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ with an initial concentration of 0.100 M. The rate constant $k = 6.3 \times 10^{-6} \text{ s}^{-1}$.



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

(b) What is the half life time ?

HW 13.5: Integrated Rate Law for a First-Order Reaction

The following reaction is first order in $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ with an initial concentration of 0.100 M. The rate constant $k = 6.3 \times 10^{-6} \text{ s}^{-1}$.



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

End 2/21 Friday
section A

(b) What is the half life time ?

$$t_{1/2} = 0.693 / 6.3 \times 10^{-6} \text{ s}^{-1} = 110,000 \text{ sec}$$

$$t_{1/2} = 110,000 \text{ sec} \times 1 \text{ min}/60 \text{ sec} \times 1 \text{ h} / 60 \text{ min} = 31 \text{ hours}$$

Second-Order Reactions



$$\text{rate} = k[A]^2 \qquad - \frac{\Delta[A]}{\Delta t} = k[A]^2$$

Calculus can be used to derive an **integrated** rate law.

$$\boxed{\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}}$$

$y = mx + b$

$[A]_t$ concentration of A at time t

$[A]_0$ initial concentration of A

Second-Order Reactions



Calculate the slope:

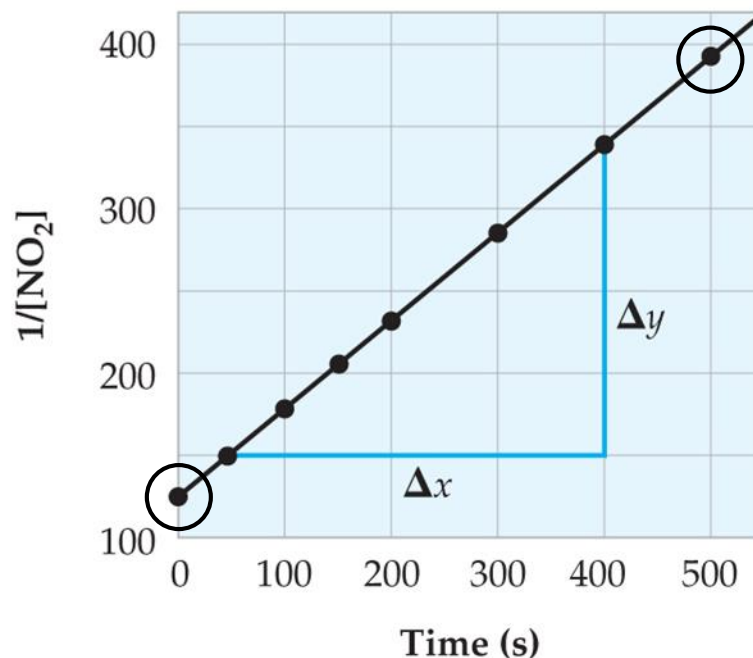
$$\frac{(340 - 150) \frac{1}{\text{M}}}{400 \text{ s} - 50 \text{ s}} = 0.54 \frac{1}{\text{M s}}$$

$$k = 0.54 \frac{1}{\text{M s}}$$

$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$$

$$y = mx + b$$

Slope = k



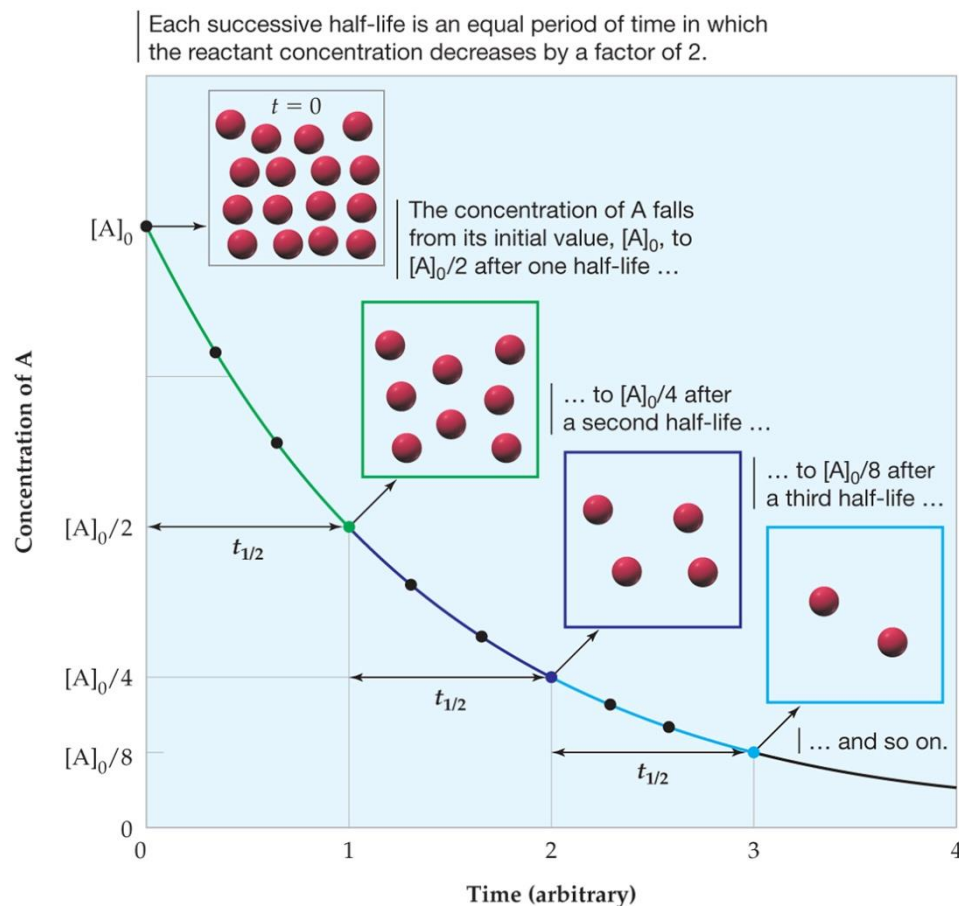
Second-Order Reactions

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a **second-order** reaction, the **half-life is dependent on the initial concentration.**

Each successive half-life is twice as long as the preceding one.

Mistake on textbook powerpoint – wrong figure should be fig 13.9



HW 13.6: Integrated Rate Law for a First-Order Reaction

For the following reaction what would you plot in order to get a linear plot.

Assume that the reaction is **first order. MC question**



$$[A]_t = -kt + [A]_0 \quad \text{zero order}$$

$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{first order}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad \text{second order}$$

$$y = mx + b \quad \text{generalized equation for a line}$$

(a) $y = \text{time}$ vs. $x = \ln[\text{SO}_2\text{Cl}_2]$

(b) $y = \ln [\text{SO}_2\text{Cl}_2]$ vs. $x = \text{time}$

(c) $y = 1/[\text{SO}_2\text{Cl}_2]$ vs. $x = \text{time}$

(d) $y = \ln[\text{SO}_2\text{Cl}_2]$ vs. $x = k$

HW 13.6: Integrated Rate Law for a First-Order Reaction

For the following reaction what would you plot in order to get a linear plot.

Assume that the reaction is **first order**.



$$[A]_t = -kt + [A]_0 \quad \text{zero order}$$

$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{first order}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad \text{second order}$$

$$y = mx + b \quad \text{generalized equation for a line}$$

(a) $y = \text{time}$ vs. $x = \ln[\text{SO}_2\text{Cl}_2]$

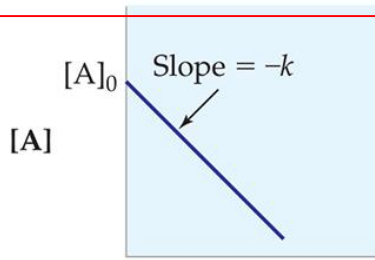
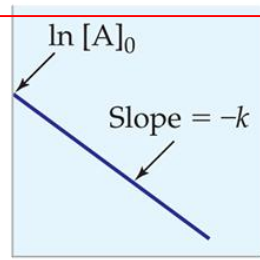
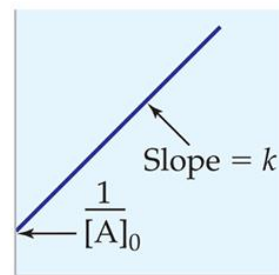
(b) $y = \ln [\text{SO}_2\text{Cl}_2]$ vs. $x = \text{time}$

(c) $y = 1/[\text{SO}_2\text{Cl}_2]$ vs. $x = \text{time}$

(d) $y = \ln[\text{SO}_2\text{Cl}_2]$ vs. $x = k$

(integrated rate law – summary of last few slides)

TABLE 13.4 Characteristics of Zeroth-, First-, and Second-Order Reactions of the Type $A \rightarrow \text{Products}$

	Zeroth-Order	First-Order	Second-Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Linear graph	$[A]$ versus t	$\ln [A]$ versus t	$\frac{1}{[A]}$ versus t
$y = mx + b$ eqn of line			
Graphical determination of k	$k = -(\text{Slope})$	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (not constant)	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)

Reaction Rates and Temperature: The Arrhenius Equation

Typically, as the temperature increases, the rate of reaction increases.



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

The **rate constant** is dependent on temperature.

NOT RESPONSIBLE

Omit from departmental syllabus

omit sections 13.7, 13.8

End 2/21 Friday

Section C

Reaction Mechanisms

Reaction Mechanism: A sequence of reaction steps that describes the pathway from reactants to products

Elementary Reaction (step): A single step in a reaction mechanism (NOT overall rxn)

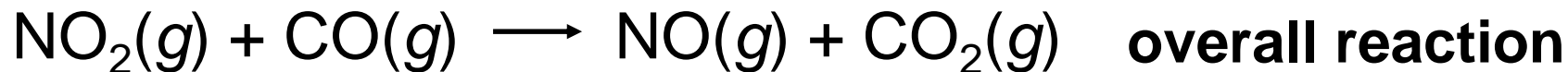
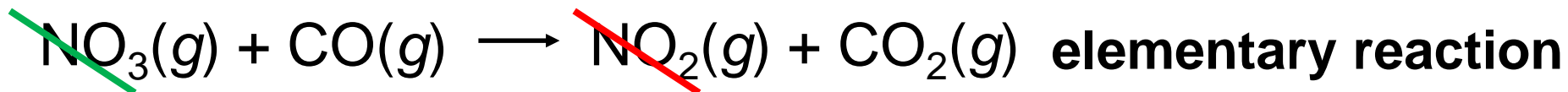
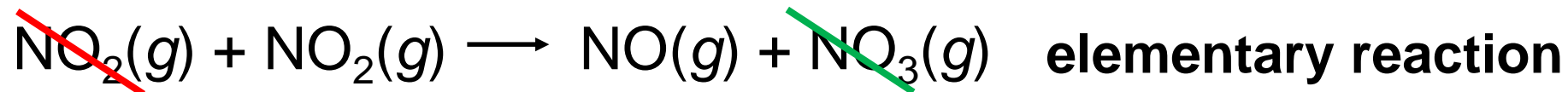
Reaction Mechanisms

An **elementary reaction** describes an individual molecular event.

The **overall reaction** describes the reaction stoichiometry and is a **summation of elementary reactions**.

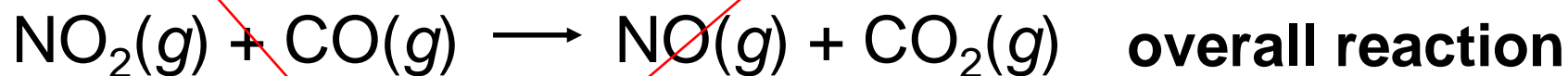
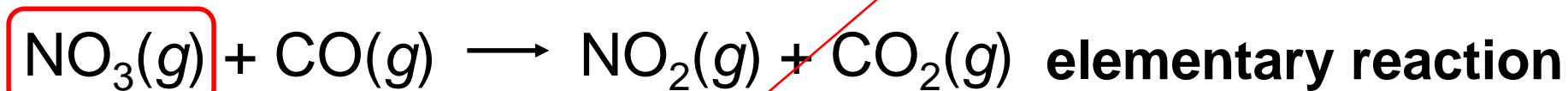
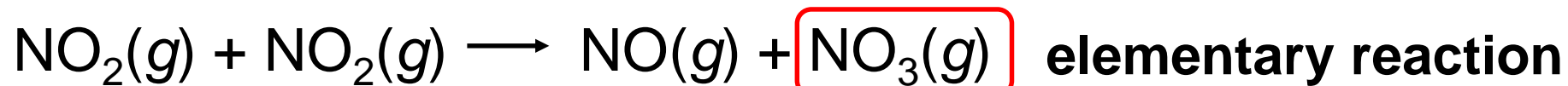
Reaction Mechanisms

Experimental evidence suggests that the reaction between NO_2 and CO takes place by a two-step mechanism:



Reaction Mechanisms

Experimental evidence suggests that the reaction between NO_2 and CO takes place by a two-step mechanism:



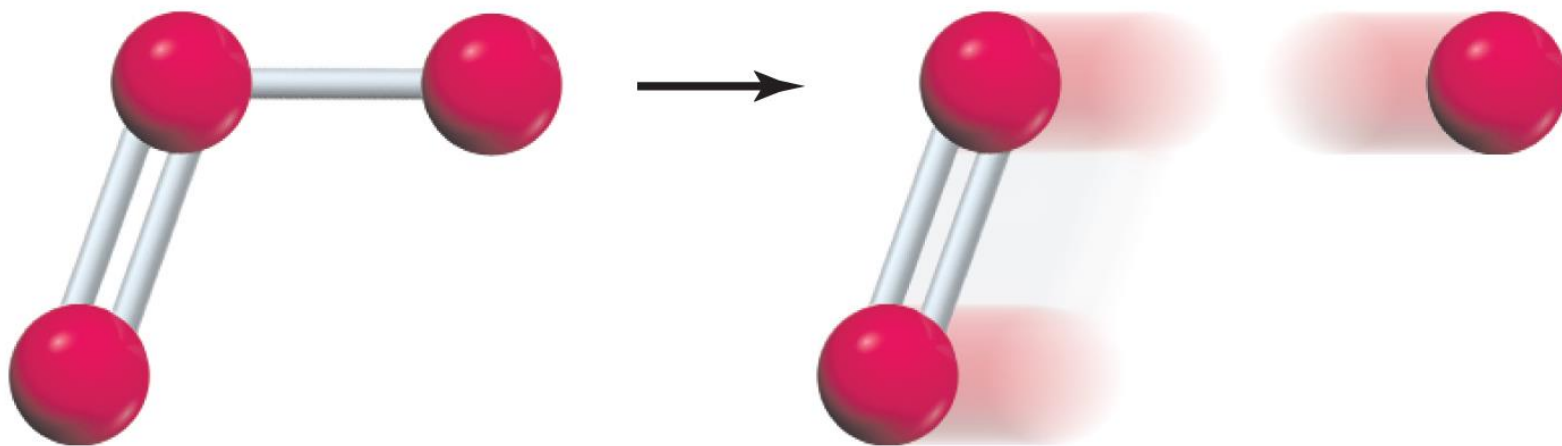
A **reactive intermediate** is formed in one step and consumed in a subsequent step.

Reaction Mechanisms-Molecularity

Molecularity: A classification of an elementary reaction based on the **number of molecules (or atoms)** on the reactant side of the chemical equation

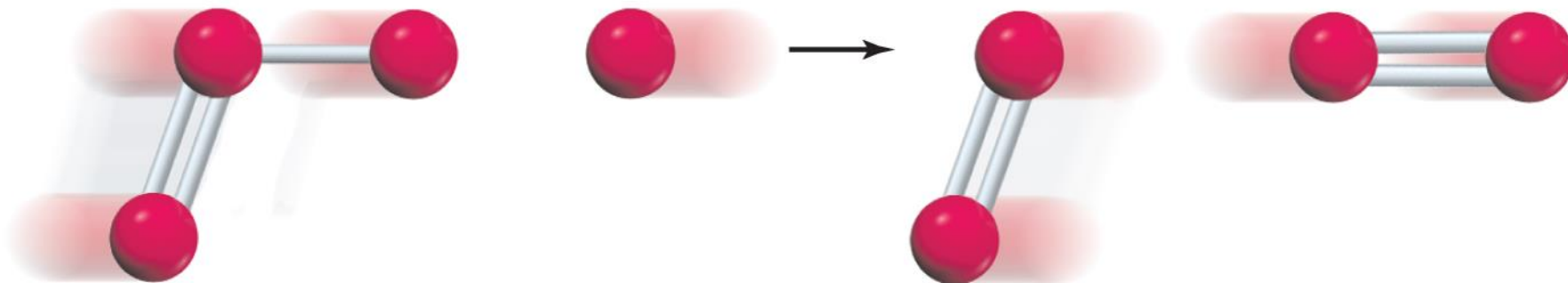
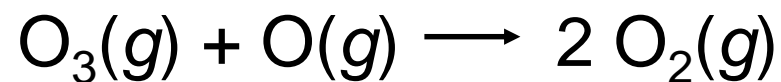
Reaction Mechanisms-Molecularity

Unimolecular Reaction



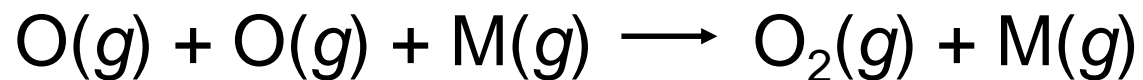
Reaction Mechanisms-Molecularity

Bimolecular Reaction



Reaction Mechanisms-Molecularity

Termolecular Reaction



Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an elementary reaction is an individual molecular event.

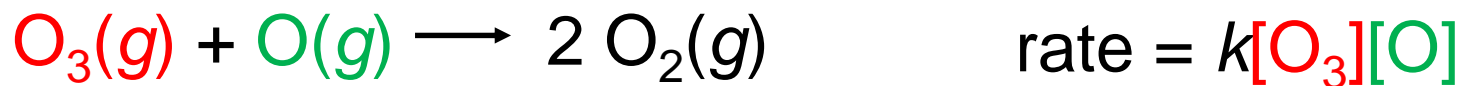
Rate Laws for Elementary Reactions

(reaction mechanism step) (if know elementary reaction mechanism step **CAN** write rate law directly from rxn)

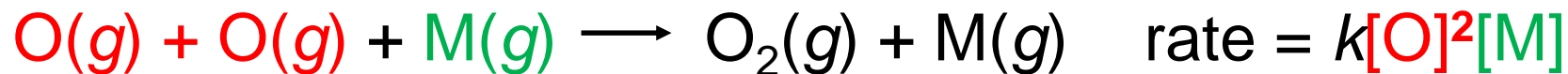
Unimolecular Reaction



Bimolecular Reaction



Termolecular Reaction



Rate Laws for Elementary Reactions

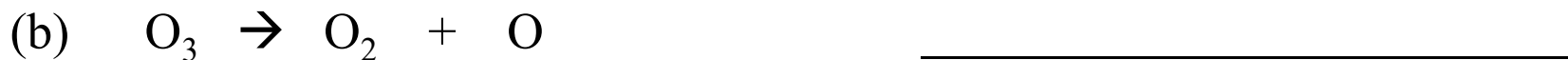
Rate laws for elementary reactions is just the reactants by inspection
{rate = k [all reactants, write as individual concentration]}

TABLE 13.5 Rate Laws for Elementary Reactions

Elementary Reaction	Molecularity	Rate Law
$A \rightarrow \text{Products}$	Unimolecular	Rate = $k[A]$
$A + A \rightarrow \text{Products}$	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow \text{Products}$	Bimolecular	Rate = $k[A][B]$
$A + A + B \rightarrow \text{Products}$	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{Products}$	Termolecular	Rate = $k[A][B][C]$

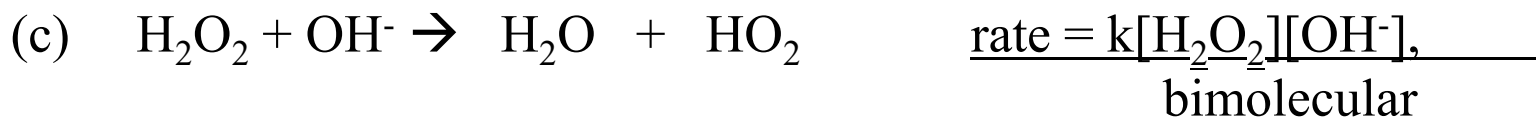
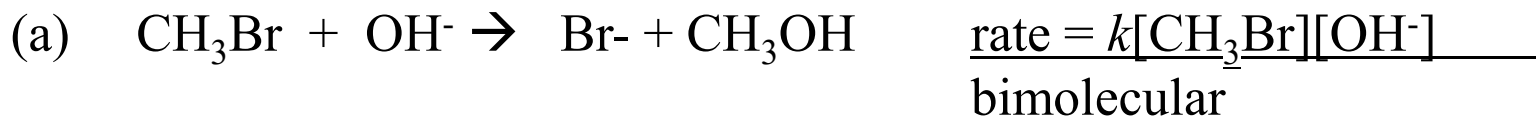
HW 13.7: Rate Laws for Elementary Reactions (reaction mechanism steps)

For the following elementary reactions (reaction mechanism steps) give the **rate law and the molecularity** of the reaction mechanism step (unimolecular, bimolecular, trimolecular, etc.)



HW 13.7: Rate Laws for Elementary Reactions (reaction mechanism steps)

For the following elementary reactions (reaction mechanism steps) give the **rate law and the molecularity** of the reaction mechanism step (unimolecular, bimolecular, trimolecular, etc.)



End 2/24 Monday A section

Rate Laws for Overall Reactions

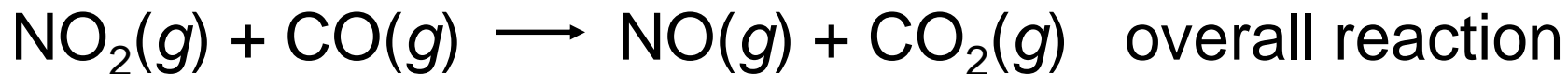
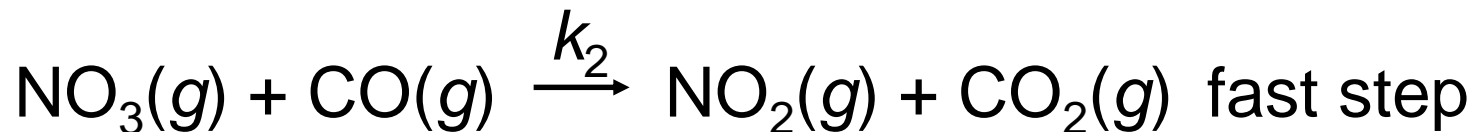
Rate-Determining Step: The slow step in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products (Slow step elementary reaction step determines rate law of overall reaction.)

To Determine rate law for overall reactions:

- **Propose reaction mechanism elementary steps**
- **Compare experimental rate law with rate law suggested by proposed reaction mechanism.**

Rate Laws for Overall Reactions

Multistep Reactions with an Initial Slow Step

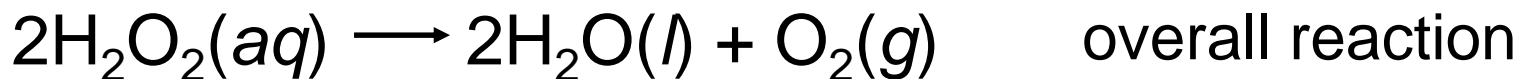
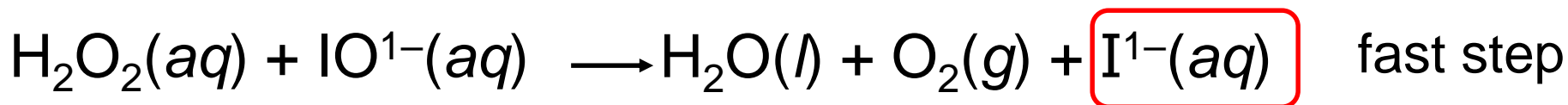
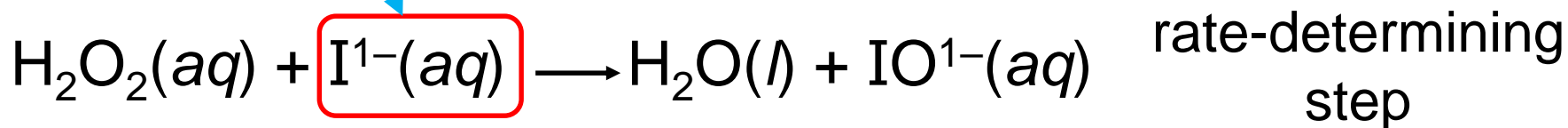


Based on the **slow step**: **rate = $k_1[\text{NO}_2]^2$**

Catalysis

Catalyst: A substance that increases the rate of a reaction without itself being consumed in the reaction.

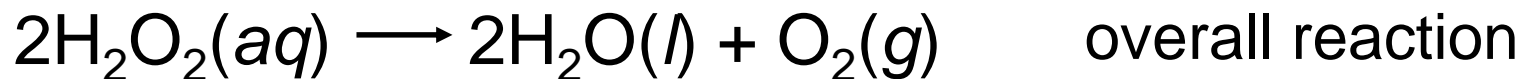
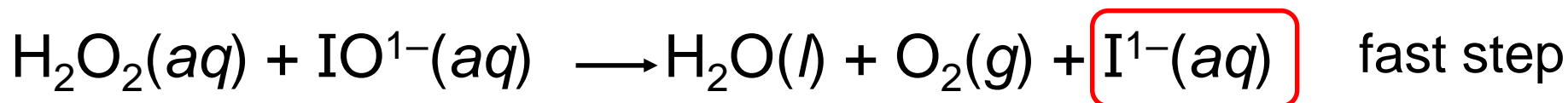
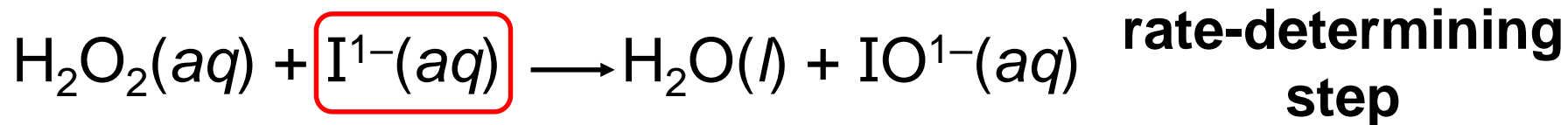
A catalyst is used in one step and regenerated in a later step.



Catalysis

Since the **catalyst is involved in the rate determining step (slow step)**, it often appears in the rate law.

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^{1-}]$$



End class 2/24/20
Monday A section

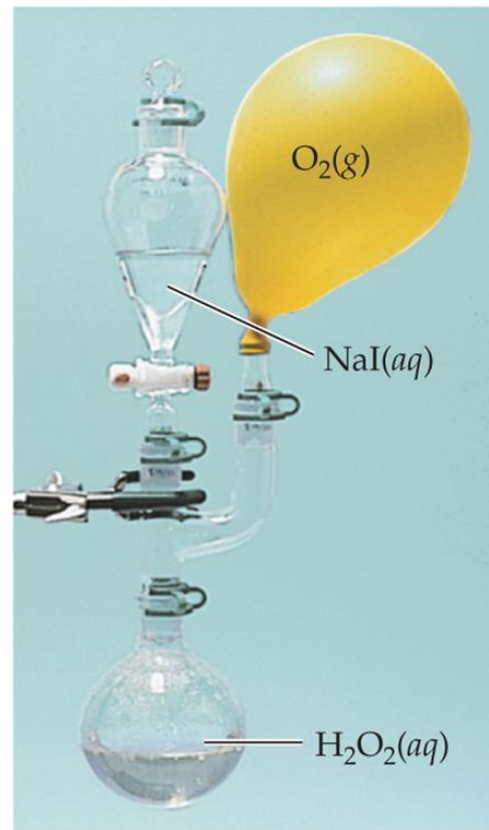
Catalysis

The rate of decomposition of aqueous hydrogen peroxide can be monitored qualitatively by collecting the evolved oxygen gas in a balloon.



In the absence of a catalyst, little O₂ is produced.

without catalyst



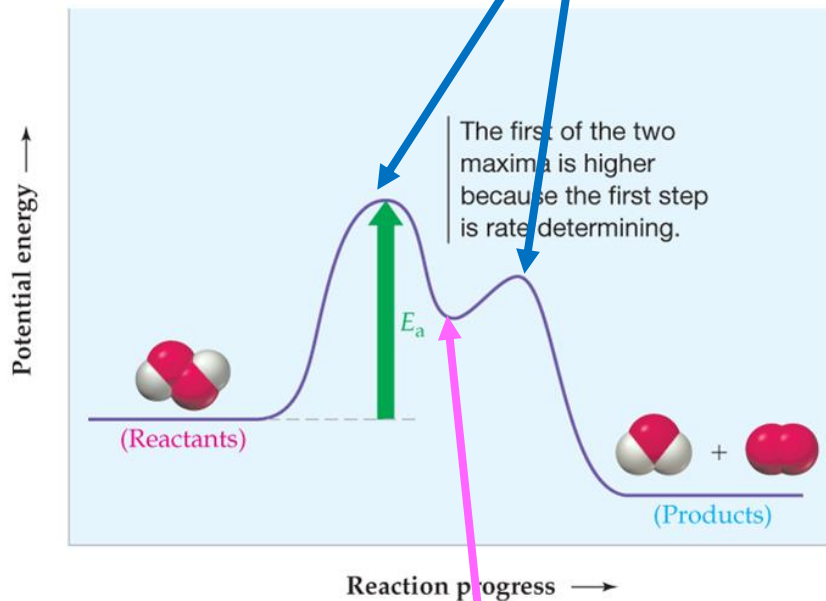
After addition of aqueous sodium iodide, by opening the stopcock to add NaI, the balloon rapidly inflates with O₂.

with catalyst (I⁻)

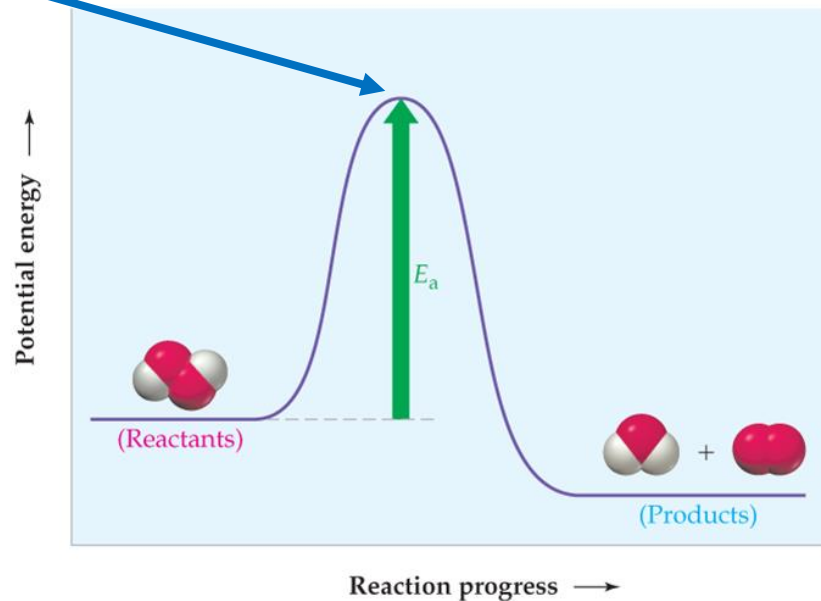
Catalysis

Transition state – short lived high energy, not reactant or product

(a) Catalyzed pathway



(b) Uncatalyzed pathway



The activation energy E_a is lower for the catalyzed pathway. The shape of the barrier for the catalyzed pathway applies to the decomposition of H₂O₂.

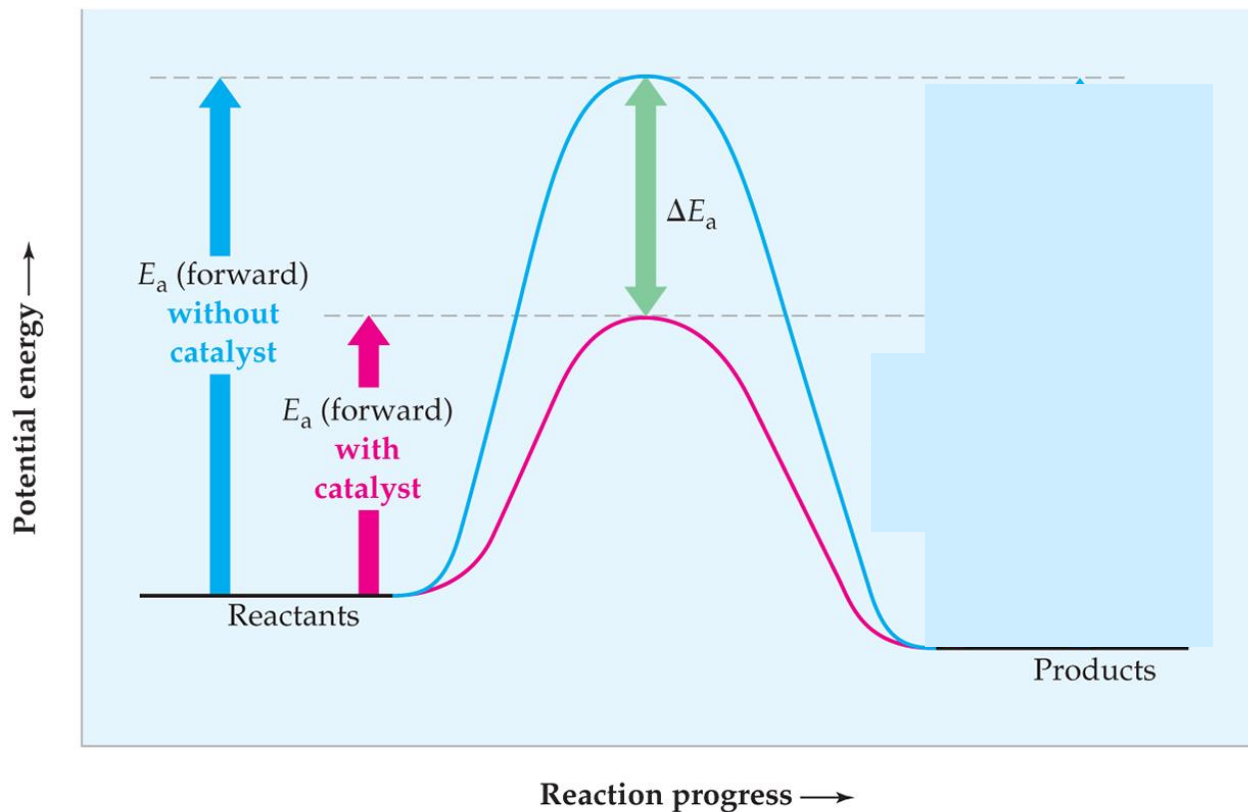
Intermediate – short lived higher energy than reactant or product, in valley between 2 transition states

*lower activation energy with catalyst

*often catalyst pathway does not have an intermediate so (a) is just one hill but lower activation energy

Catalysis

The activation energy for the **catalyzed pathway** (red curve) is lower than that for the **uncatalyzed pathway** (blue curve) by an amount ΔE_a .



End 2/26 Wed
C section

END QUIZ 5

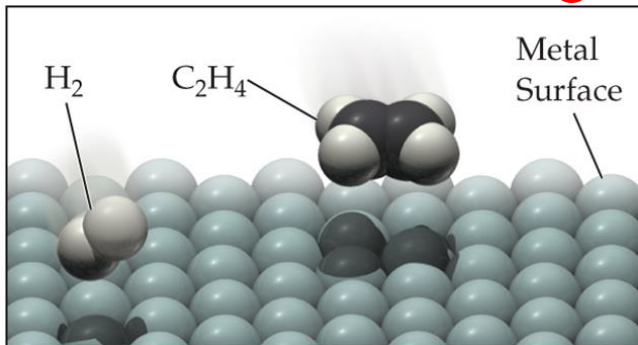
Homogeneous and Heterogeneous Catalysts

Homogeneous Catalyst: A catalyst that exists in the same phase as the reactants

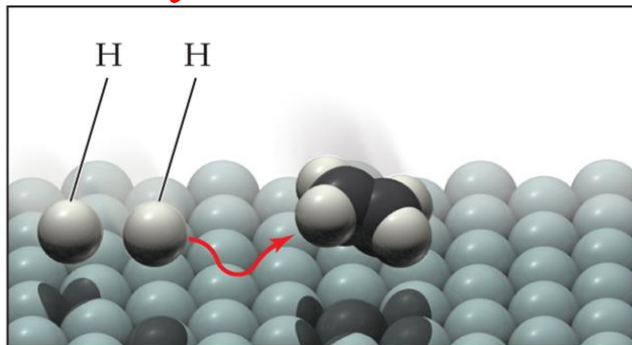
Heterogeneous Catalyst: A catalyst that exists in a different phase from that of the reactants

Homogeneous and Heterogeneous Catalysts

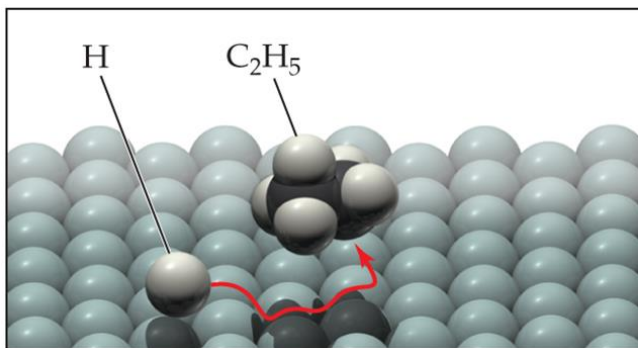
heterogeneous catalyst



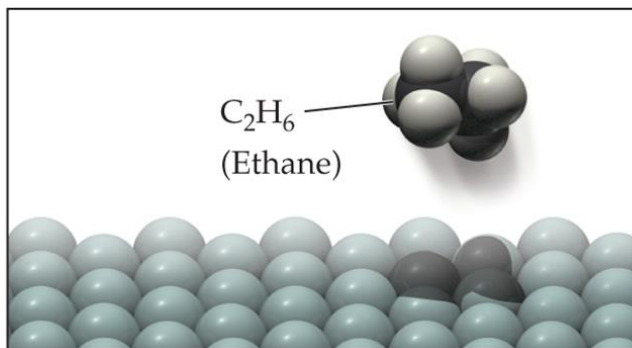
(a) H_2 and C_2H_4 are adsorbed on the metal surface.



(b) The $H-H$ bond breaks as H -metal bonds form, and the H atoms move about on the surface.



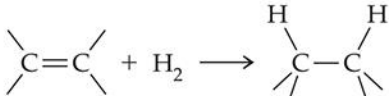
(c) One H atom forms a bond to a C atom of the adsorbed C_2H_4 to give a metal-bonded C_2H_5 group. A second H atom bonds to the C_2H_5 group.



(d) The resulting C_2H_6 molecule is desorbed from the surface.

Homogeneous and Heterogeneous Catalysts (not responsible for this slide)

TABLE 13.6 Some Heterogeneous Catalysts Used in Commercially Important Reactions

Reaction	Catalyst	Commercial Process	Product: Commercial Uses
$2 \text{SO}_2 + \text{O}_2 \longrightarrow 2 \text{SO}_3$	Pt or V_2O_5	Intermediate step in the contact process for synthesis of sulfuric acid	H_2SO_4 : Manufacture of fertilizers, chemicals; oil refining
$4 \text{NH}_3 + 5 \text{O}_2 \longrightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$	Pt and Rh	First step in the Ostwald process for synthesis of nitric acid	HNO_3 : Manufacture of explosives, fertilizers, plastics, dyes, lacquers
$\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$	Fe, K_2O , and Al_2O_3	Haber process for synthesis of ammonia	NH_3 : Manufacture of fertilizers, nitric acid
$\text{H}_2\text{O} + \text{CH}_4 \longrightarrow \text{CO} + 3 \text{H}_2$	Ni	Steam-hydrocarbon re-forming process for synthesis of hydrogen	H_2 : Manufacture of ammonia, methanol
$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$	ZnO and CuO	Water-gas shift reaction to improve yield in the synthesis of H_2	H_2 : Manufacture of ammonia, methanol
$\text{CO} + 2 \text{H}_2 \longrightarrow \text{CH}_3\text{OH}$	Cu, ZnO, and Al_2O_3	Industrial synthesis of methanol	CH_3OH : Manufacture of plastics, adhesives, gasoline additives; industrial solvent
 $\text{C}=\text{C} + \text{H}_2 \longrightarrow \text{C}-\text{C}$	Ni, Pd, or Pt	Catalytic hydrogenation of compounds with $\text{C}=\text{C}$ bonds as in conversion of unsaturated vegetable oils to solid fats	Food products: margarine, shortening