Chemical Kinetics

$A + D \rightarrow C + D$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Chemical Kinetics

The area of chemistry that concerns reaction rates.

Kinetics

In kinetics we study the rate at which a chemical process occurs.

Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

Factors That Affect Reaction Rates

Physical state of the reactants.

- In order to react, molecules must come in contact with each other.
- The more homogeneous the mixture of reactants, the faster the molecules can react.

Factors That Affect Reaction Rates

Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly

Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

Concentration of reactants.

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

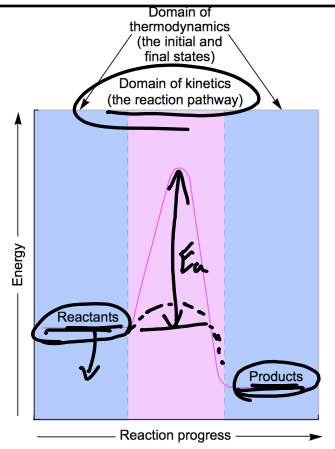
Factors That Affect Reaction Rates

Temperature

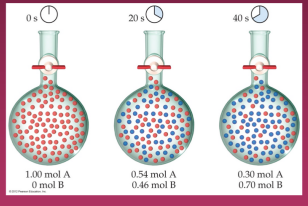
- At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

Factors That Affect Reaction Rates

- Presence of a catalyst.
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.



Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

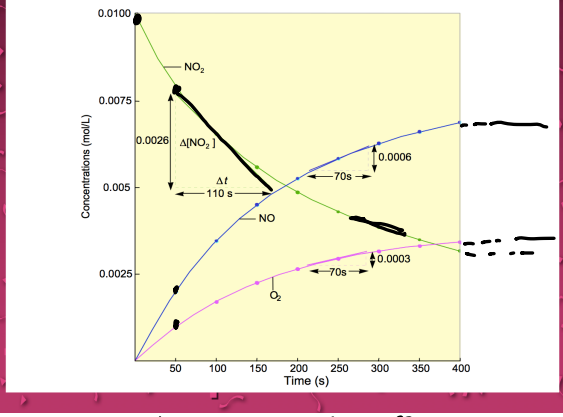
$$\text{Rate} = \frac{\Delta[A]}{\Delta t}$$

Reaction Rate

Change in concentration (conc) of a reactant or product per unit time.

$$\text{Rate} = \frac{\text{conc of A at time } t_2 - \text{conc of A at time } t_1}{t_2 - t_1}$$

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



$$2NO_2 \rightleftarrows 2NO + O_2$$

Rate Laws

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

k = rate constant

n = rate order

$$2NO_2 \rightarrow 2NO + O_2$$

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

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\text{Rate} = k[CH_4]^m[O_2]^n$$

Problem

The decomposition of N_2O_5 in carbon tetrachloride proceeds as follows:

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

The rate law is 1st order in N_2O_5. At 64°C the rate constant is $4.82 \times 10^{-3}\ s^{-1}$.

a. Write the rate law.

b. What is the reaction rate when $[N_2O_5] = 0.0243$ M?

a.) $Rate = k[N_2O_5]$ $n=1$

b.) $Rate = \left(4.82\times10^{-3}\frac{1}{s}\right)(0.0243M) =$

$Rate = 1.17\times10^{-4}\frac{M}{s}$

$Rate = \frac{\Delta[N_2O_5]}{\Delta t}$

Problem

Consider the following reaction:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

(a) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law.

(b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4\ M^{-2}\ s^{-1}$, what is the reaction rate when $[NO] = 0.025$ M and $[H_2] = 0.015$ M?

a.) $Rate = k[NO]^2[H_2]$

b.) $Rate = \left(6.0\times10^4\frac{1}{M^2s}\right)(0.025M)^2(0.015M)$

$= 0.56\ \frac{M}{s}$

Types of Rate Laws

Differential Rate Law: expresses how rate depends on concentration.

Integrated Rate Law: expresses how concentration depends on time.

Exp

Find the Rate Law order k

Method of Initial Rates

Initial Rate: the "instantaneous rate" just after the reaction begins.

The initial rate is determined in several experiments using different initial concentrations.

A → P

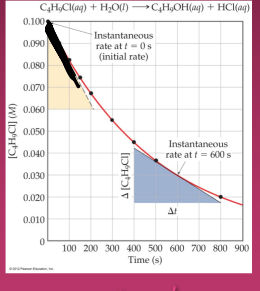
.1M

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

A plot of $[C_4H_9Cl]$ versus time for this reaction yields a curve like this.

The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.



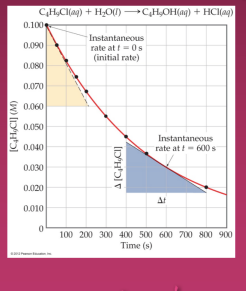
A + B → C + D

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

All reactions slow down over time.

Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the *beginning* of the reaction.

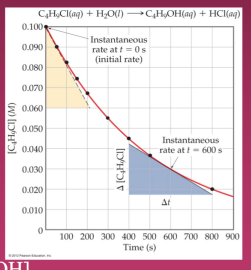


Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.

Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Use the Method of Initial Rates to find Rate Law for:

$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$m = 1$ $n = 1$

$\text{Rate} = k[NH_4^+]^m[NO_2^-]^n$

$\frac{32.3 \times 10^{-7}}{5.4 \times 10^{-7}} = \frac{k[0.0600]^m(0.200)^n}{k(0.0100)^n(0.200)^n}$

$5.98 = 6^m$ $\ln x^n = n \ln x$

$\ln 5.98 = \ln 6^m = m \ln 6$

$m = \frac{\ln 5.98}{\ln 6} = 0.998 \approx 1$

$\text{Rate} = k[NH_4^+][NO_2^-]$

$k = \frac{\text{Rate}}{[NH_4^+][NO_2^-]} = \frac{(5.4 \times 10^{-7} M/s)}{(0.0100 M)(0.200 M)}$

$k_1 = 2.7 \times 10^{-4}\ M^{-1}\ s^{-1}$

k_2

overall 2nd order

Overall Reaction Order

Sum of the order of each component in the rate law.

$$\text{rate} = k[H_2SeO_3][H^+]^2[I^-]^3$$

The overall reaction order is 1 + 2 + 3 = 6.

$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$

Experiment	$[ClO_2]$ M	$[OH^-]$ M	Rate, M s^{-1}
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

1. Determine the order with respect to each reactant.
2. Calculate the rate constant. $230\ s^{-1}\ M^{-2}$
3. Write the rate law for the reaction.
4. What is the overall reaction order? 3rd order

First-Order Rate Law

$A \rightarrow B$

For $aA \rightarrow$ Products in a 1st-order reaction,

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

Integrated first-order rate law is

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

initial

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

$y = mx + b$

First-Order Processes

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

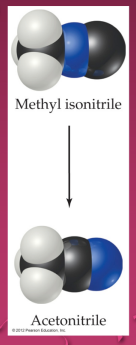
Therefore, if a reaction is first-order, a plot of ln [A] vs. t will yield a straight line, and the slope of the line will be $-k$.

Types of Rate Laws

Differential Rate Law: expresses how rate depends on concentration.

Integrated Rate Law: expresses how concentration depends on time.

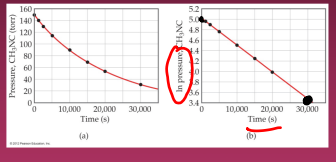
First-Order Processes



Consider the process in which methyl isonitrile is converted to acetonitrile.

$CH_3NC \longrightarrow CH_3CN$

First-Order Processes



When ln P is plotted as a function of time, a straight line results.

Therefore,

- The process is first-order.
- k is the negative of the slope: $5.1 \times 10^{-5}\ s^{-1}$.

$m = -k$

$m = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[A]}{\Delta t} = \frac{3.95 - 5.0}{30{,}000 - 0\,s}$

$= -5.16 \times 10^{-5}\ s^{-1}$

$k = 5.16 \times 10^{-5}\ s^{-1}$

$CH_3NC \rightarrow CH_3CN$

We now know conversion of methyl isonitrile to acetonitrile follows first order kinetics.

a. Find the rate constant for this reaction under slightly different conditions.

b. What is the pressure of CH_3NC at 3200 seconds?

Time (s)	Pres. CH_3NC (torr)	ln Pres
0	502	
2000	335	
5000	180	

$Rate = k[CH_3NC]$

$k = .0$ s^{-1}

-2.05×10^{-4}

$m = -k$

$m = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln(A_t)}{\Delta\ time} = \frac{\ln(180) - \ln(502)}{5000 - 0\,s}$

$= -2.05 \times 10^{-4}$

$k = 2.05 \times 10^{-4}\ s^{-1}$

1st order

$\ln[CH_3NC] = -kt + \ln[CH_3NC]_0$

$\ln[CH_3NC] = -(2.05 \times 10^{-4}\ s^{-1})(3200\ s) + \ln(502)$

$e^{\ln[CH_3NC]} = e^{5.564}$

$[CH_3NC] = e^{5.564} = 261$ torr

Half-Life of a First-Order Reaction

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

$\ln 2$

$t_{1/2}$ = half-life of the reaction

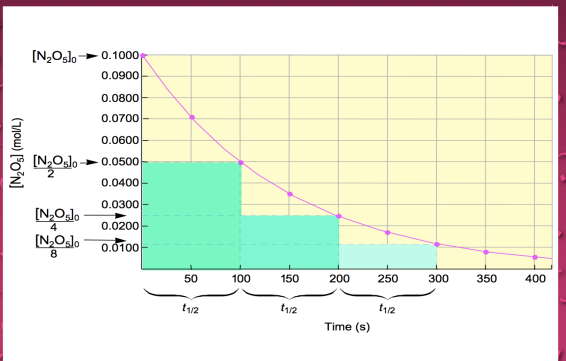
k = rate constant

For a first-order reaction, the half-life does not depend on concentration.

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

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

Half-Life of a First Order Rx

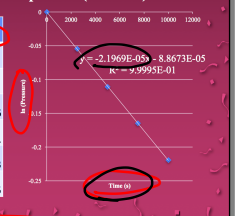


$SO_2Cl_2 \rightarrow SO_2 + Cl_2$

Experimental Data

Time (s)	Pressure (atm)	ln(Pressure)
0	1	0
2500	0.947	-0.054456186
5000	0.895	-0.110931561
7500	0.848	-0.164874643
10000	0.803	-0.219400565

Graph of ln (Pressure) vs. Time



Rate = $k[SO_2Cl_2]$

$k = 2.197 \times 10^{-5}\ s^{-1}$

$\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0$

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.2 \times 10^{-5}/s} = 31500\ s$

Table 12.6 Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = k[A]	Rate = k[A]^2
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Second-Order Rate Law

For $aA \rightarrow$ products in a second-order reaction,

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

Integrated rate law is

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

Second-Order Processes

The decomposition of NO_2 at 300 ° C is described by the equation

$$NO_2(g) \longrightarrow NO(g) + \tfrac{1}{2}O_2(g)$$

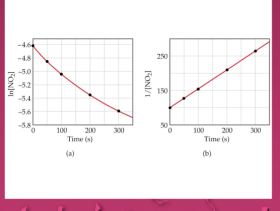
and yields data comparable to this table:

Time (s)	$[NO_2]$, M
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

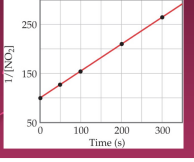
Second-Order Processes

- Plotting ln $[NO_2]$ vs. t yields the first graph at the right.
- The plot is *not* a straight line, so the process is *not* first-order in [A].

Time (s)	$[NO_2]$, M	ln $[NO_2]$
0.0	0.01000	–4.610
50.0	0.00787	–4.845
100.0	0.00649	–5.038
200.0	0.00481	–5.337
300.0	0.00380	–5.573



Second-Order Processes



- Graphing $\frac{1}{[NO_2]}$ vs. t, however, gives this plot
- Because this *is* a straight line, the process is second-order in [A].

Time (s)	$[NO_2]$, M	$1/[NO_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

Half-Life of a Second-Order Reaction

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

$t_{1/2}$ = half-life of the reaction
k = rate constant
A_o = initial concentration of A

The half-life is dependent upon the initial concentration.

Zero Order Rate Laws

Rate = k $[A]^0$

Integrated Form

$[A] = -kt + [A]_o$

Table 12.6 Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]

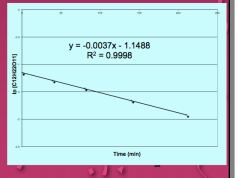
	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = k[A]	Rate = k[A]^2
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Sucrose Problem

Time (min)	$[C_{12}H_{22}O_{11}]$ (M)
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

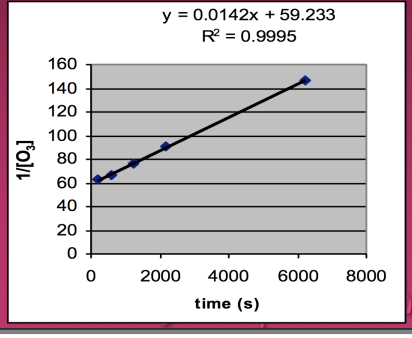
Sucrose ($C_{12}H_{22}O_{11}$), which is commonly known as table sugar, reacts in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the formula $C_6H_{12}O_6$: At 23° C and in 0.5 M HCl, the following data were obtained for the disappearance of sucrose:

(a) Is the reaction first order or second order with respect to $[C_{12}H_{22}O_{11}]$?
(b)What is the value of the rate constant?
(c)How much sucrose is left after 3.0 hours?



ICA

$2O_3 \rightarrow 3O_2$



Rate Law Determination

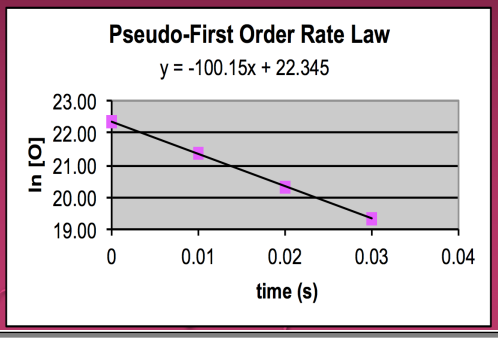
Concentration vs. Rate: use the method of initial rates.

Concentration v. time: use the integrated forms of the rate laws - graphically.

For several reactants: choose conditions under which only one reactant varies significantly (pseudo n-order conditions).

Reactions with more than one reactant

$O_{(g)} + NO_{2\,(g)} \rightarrow NO_{(g)} + O_{2\,(g)}$



Collision Model

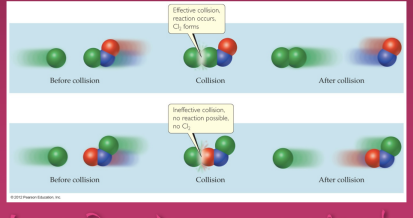
Key Idea: Molecules must collide to react.

However, only a small fraction of collisions produces a reaction. Why?

Arrhenius: An activation energy must be overcome.

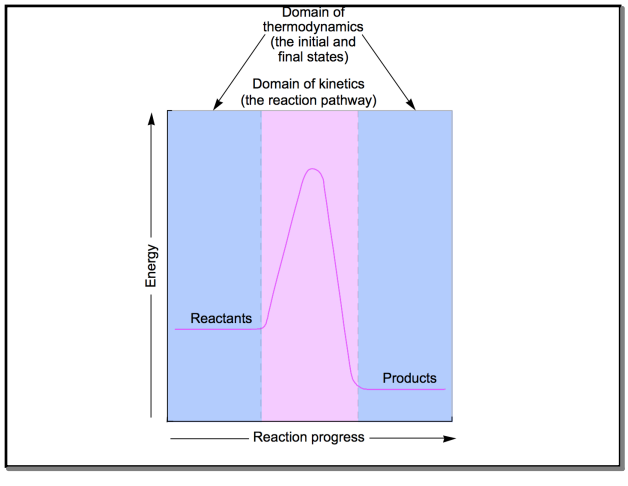
The Collision Model

Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.



Arrhenius Equation

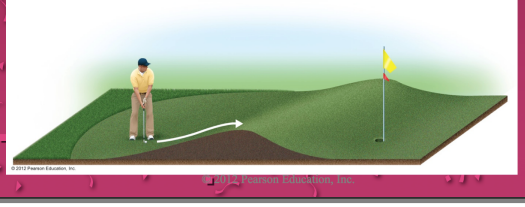
- Collisions must have enough energy to produce the reaction (must equal or exceed the activation energy).
- Orientation of reactants must allow formation of new bonds.



Activation Energy

In other words, there is a minimum amount of energy required for reaction: the **activation energy**, E_a.

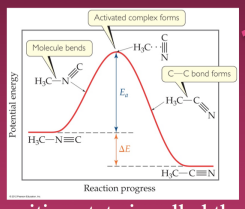
Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation-energy barrier.



Reaction Coordinate Diagrams

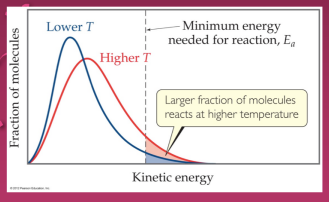
The diagram shows the energy of the reactants and products (and, therefore, ΔE).

The high point on the diagram is the **transition state**.



- The species present at the transition state is called the **activated complex**.
- The energy gap between the reactants and the activated complex is the **activation-energy barrier**.

Maxwell–Boltzmann Distributions

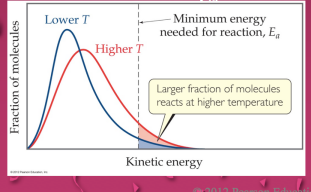


As the temperature increases, the curve flattens and broadens.

Thus, at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

If the dotted line represents the activation energy, then as the temperature increases, so does the fraction of molecules that can overcome the activation-energy barrier.



- As a result, the reaction rate increases.

Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

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

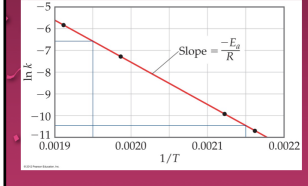
where A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation (continued)

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

k = rate constant
A = frequency factor
E_a = activation energy
T = temperature
R = gas constant

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

$$y = mx + b$$

Therefore, if k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of ln k vs. $\frac{1}{T}$.

Reaction Mechanism

- The series of steps by which a chemical reaction occurs.
- A chemical equation does not tell us how reactants become products - it is a summary of the overall process.

Reaction Mechanisms

Reactions may occur all at once or through several discrete steps.

Each of these processes is known as an **elementary reaction** or **elementary process**.

Often Used Terms

Intermediate: formed in one step and used up in a subsequent step and so is never seen as a product.

Molecularity: the number of species that must collide to produce the reaction indicated by that step.

Elementary Step: A reaction whose rate law can be written from its molecularity.

uni, bi and termolecular

Reaction Mechanisms

TABLE 14.3 • Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	A ⟶ products	Rate = k[A]
*Bi*molecular	A + A ⟶ products	Rate = k[A]^2
*Bi*molecular	A + B ⟶ products	Rate = k[A][B]
*Ter*molecular	A + A + A ⟶ products	Rate = k[A]^3
*Ter*molecular	A + A + B ⟶ products	Rate = k[A]^2[B]
*Ter*molecular	A + B + C ⟶ products	Rate = k[A][B][C]

The **molecularity** of a process tells how many molecules are involved in the process.

Reaction Mechanism
(continued)

- The reaction

$$O_3 + O \rightarrow 2O_2$$

has several steps in the reaction mechanism.

Rate-Determining Step

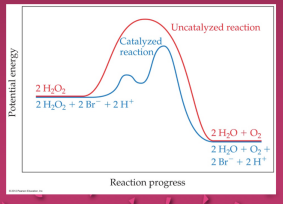
In a multistep reaction, it is the slowest step. It therefore determines the rate of reaction.

Problem 14.67 and 14.69

Catalysts

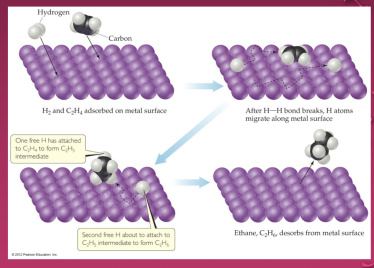
Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.

Catalysts change the mechanism by which the process occurs.

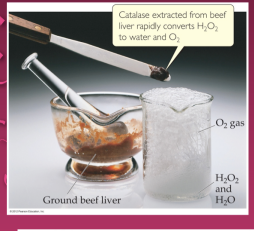


Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.

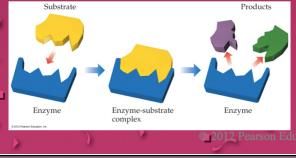


Enzymes

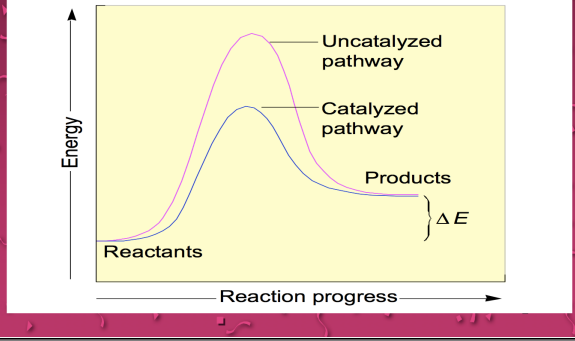


Enzymes are catalysts in biological systems.

The substrate fits into the active site of the enzyme much like a key fits into a lock.



Lower E_a for Catalyzed Rx



END

$2N_2O_5 \rightarrow 4NO_2 + O_2$