Chemistry, The Central Science, 11th edition
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Chapter 14
Chemical Kinetics

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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

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

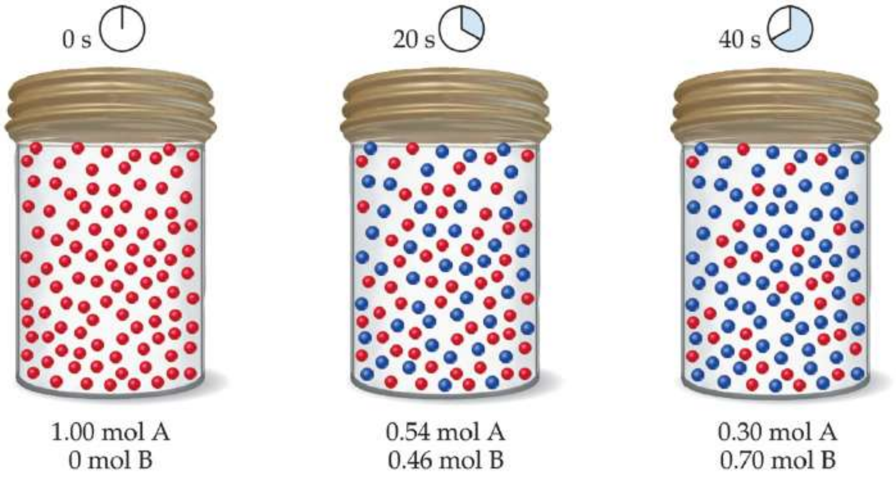
Factors That Affect Reaction Rates

- 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.

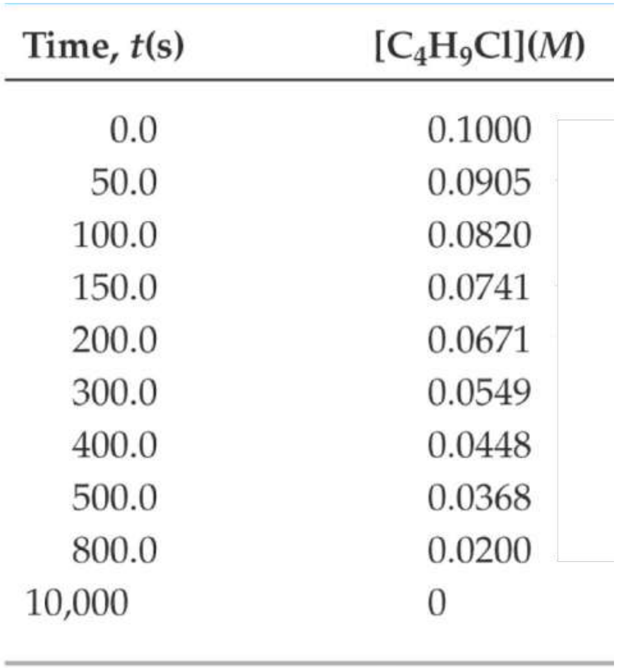
Reaction Rates



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

Reaction Rates

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



Time, t(s)	$[C_4H_9Cl](M)$
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, C_4H_9Cl, was measured at various times.

Reaction Rates

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

Time, t(s)	$[C_4H_9Cl]$(M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{Average rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t}$$

Chemical Kinetics

Reaction Rates

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

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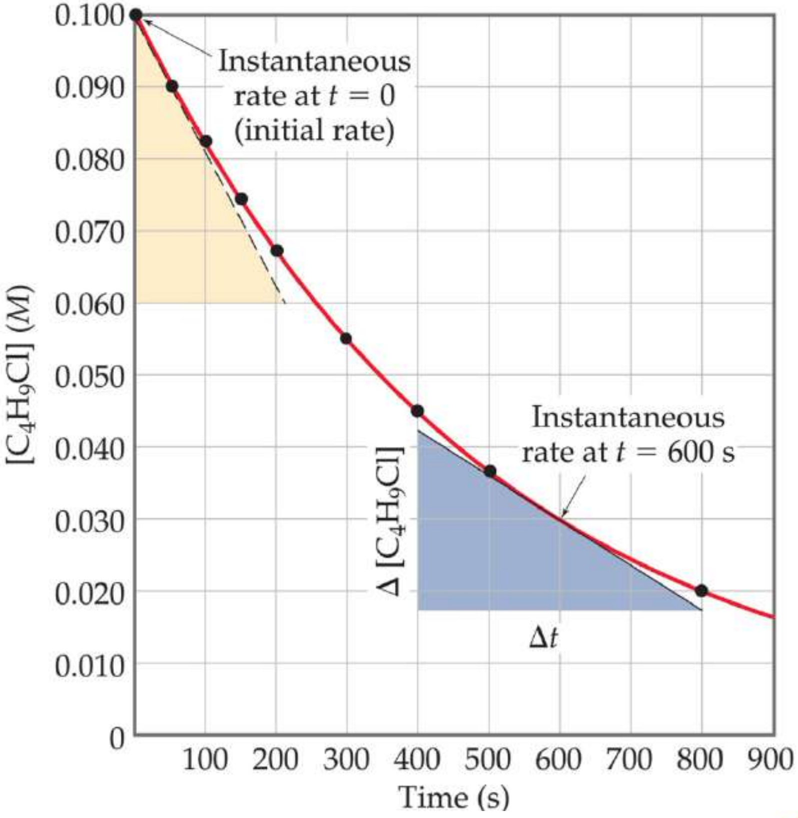
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates

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

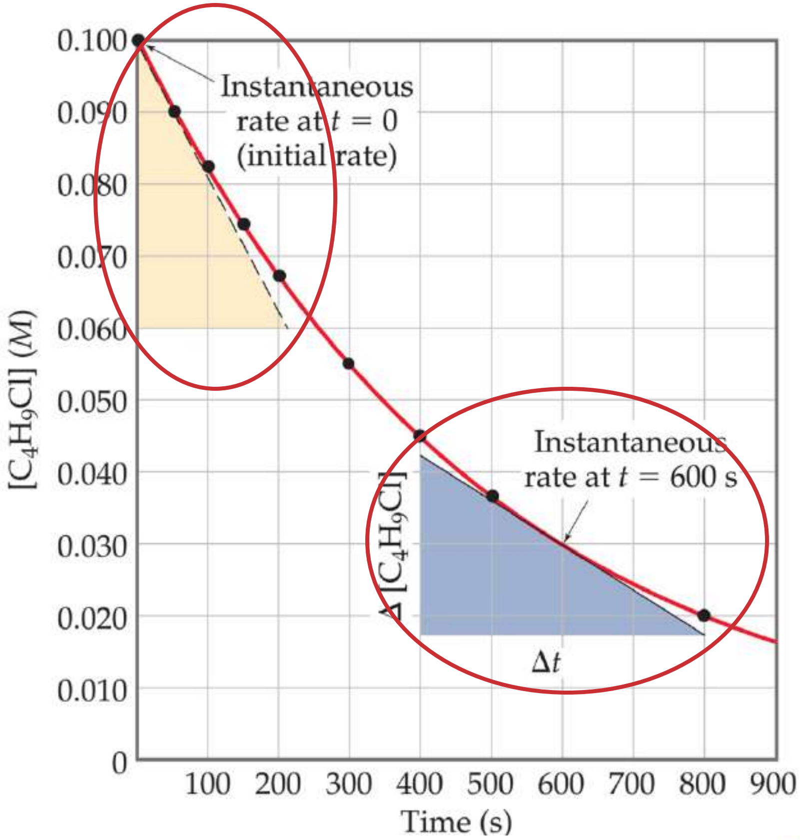
- A plot of [C_4H_9Cl] vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.



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.

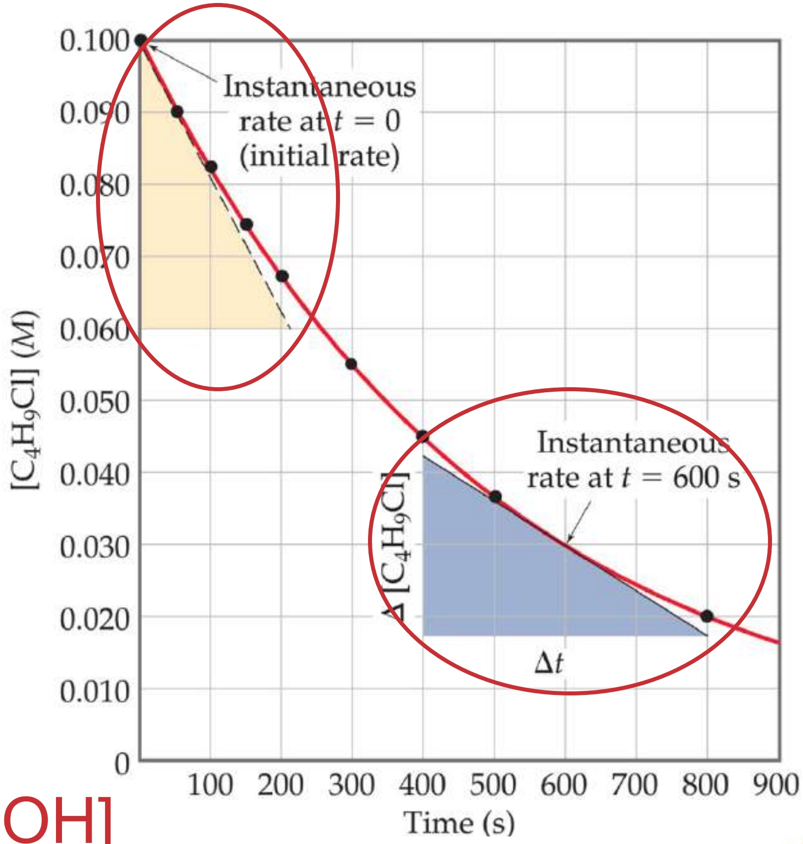


Chemical Kinetics

Reaction Rates and Stoichiometry

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

- 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.



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

Chemical Kinetics

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?

$$2\,\mathrm{HI}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

- In such a case,

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\mathrm{HI}]}{\Delta t} = \frac{\Delta[\mathrm{I_2}]}{\Delta t}$$

Reaction Rates and Stoichiometry

- To generalize, then, for the reaction

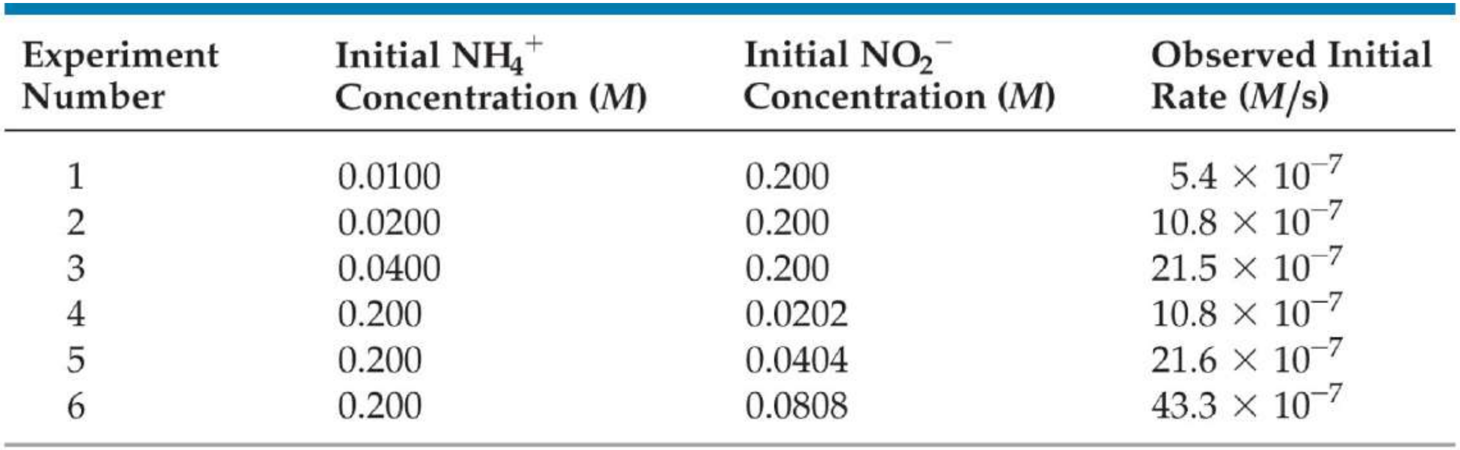
$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Concentration and Rate

One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

Concentration and Rate



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	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

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

If we compare Experiments 1 and 2, we see that when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate

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	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

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

Likewise, when we compare Experiments 5 and 6, we see that when $[NO_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

- This means

$$\text{Rate} \propto [NH_4^+]$$

$$\text{Rate} \propto [NO_2^-]$$

Therefore, $\text{Rate} \propto [NH_4^+]\,[NO_2^-]$

which, when written as an equation, becomes

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

- This equation is called the **rate law**, and *k* is the **rate constant**.

Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The exponents tell the order of the reaction with respect to each reactant.
- Since the rate law is

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

the reaction is

First-order in $[\mathrm{NH_4}^+]$ and

First-order in $[\mathrm{NO_2}^-]$.

Rate Laws

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

- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is second-order overall.

Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process gives us

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

Where

$[A]_0$ is the initial concentration of A, and

$[A]_t$ is the concentration of A at some time, t, during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces…

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

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

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

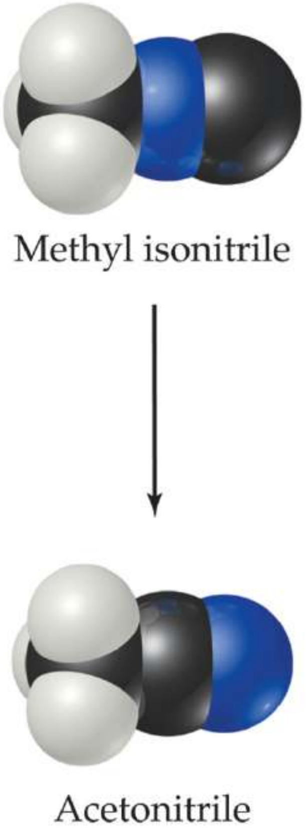
…which is in the form $y = mx + b$

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*.

First-Order Processes



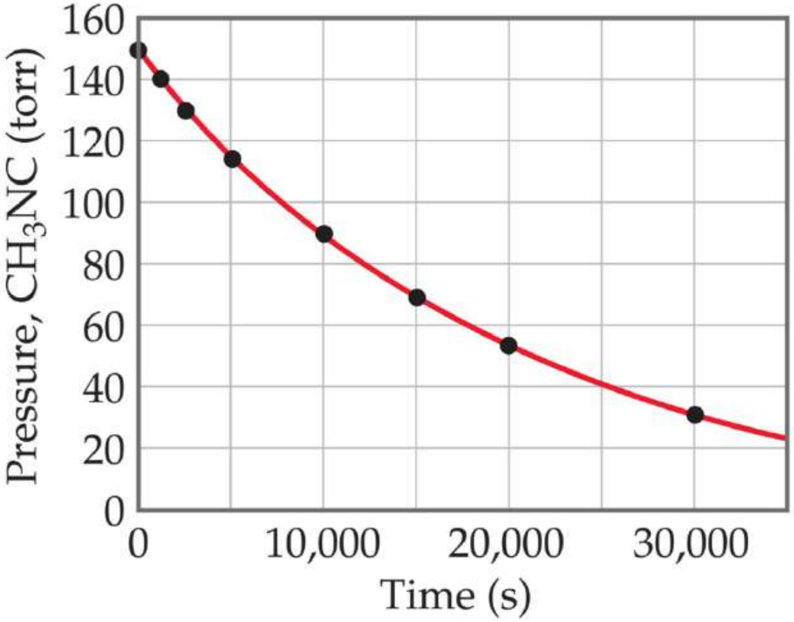
Consider the process in which methyl isonitrile is converted to acetonitrile.

$$CH_3NC \longrightarrow CH_3CN$$

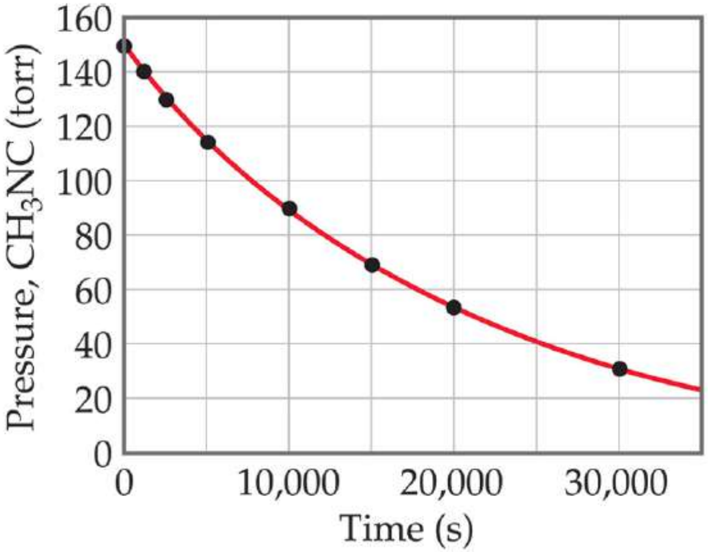
First-Order Processes

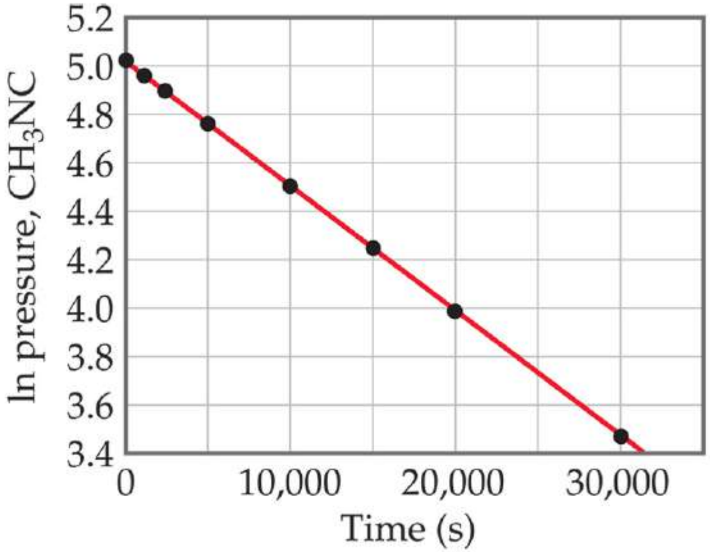
$$CH_3NC \longrightarrow CH_3CN$$

This data was collected for this reaction at 198.9 °C.



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: 5.1×10^{-5} s^{-1}.

Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A, we get

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

also in the form

$$y = \mathrm{mx} + b$$

Second-Order Processes

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

So if a process is second-order in A, a plot of $\frac{1}{[A]}$ vs. t will yield a straight line, and the slope of that line is k.

Second-Order Processes

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

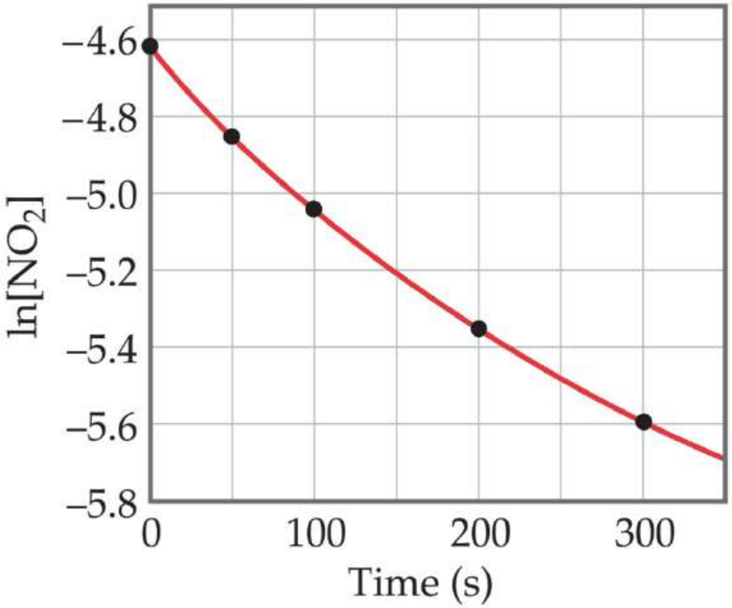
$$NO_2\,(g) \longrightarrow NO\,(g) + \frac{1}{2}O_2\,(g)$$

and yields data comparable to this:

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

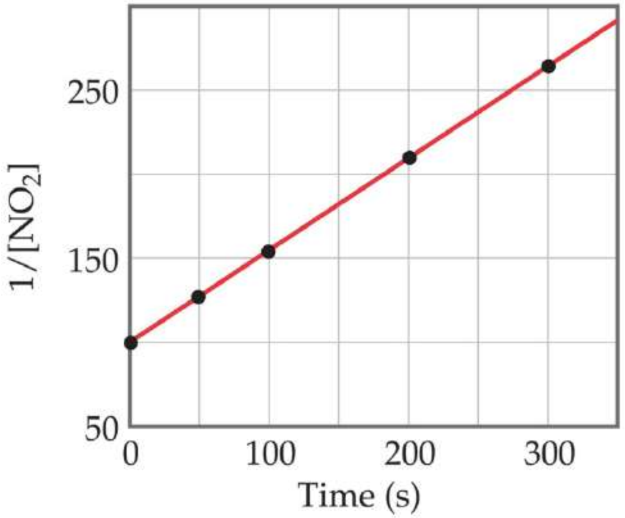
Second-Order Processes

- Plotting ln [NO_2] vs. *t* yields the 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

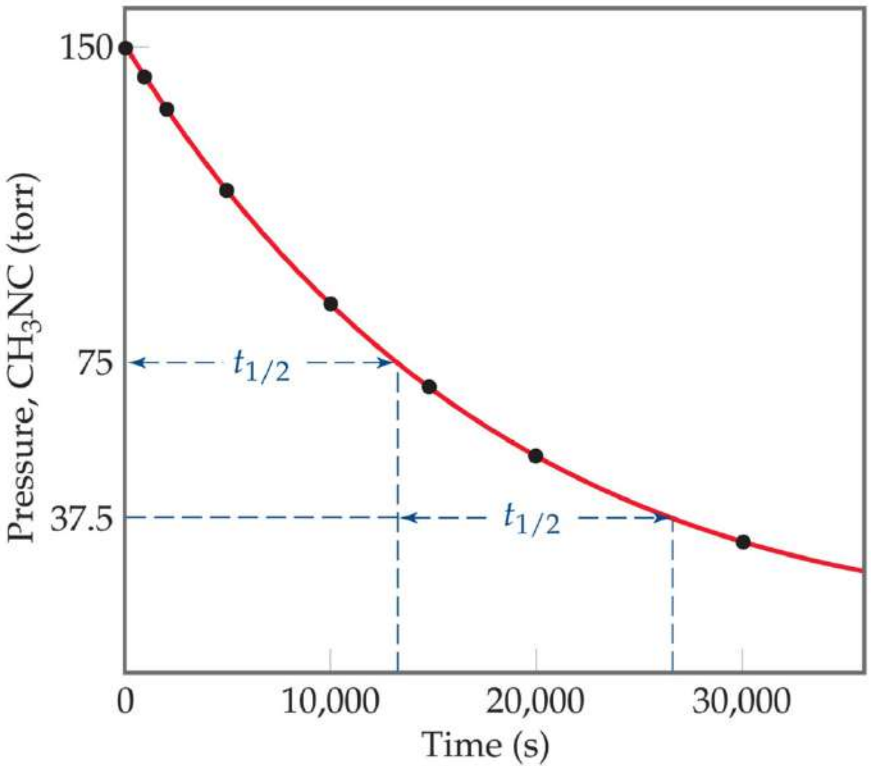


Time (*s*)	$[NO_2]$, *M*	$1/[NO_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- Graphing ln $\frac{1}{[NO_2]}$ vs. *t*, however, gives this plot.

- Because this *is* a straight line, the process is second-order in [A].

Half-Life



- Half-life is defined as the time required for one-half of a reactant to react.
- Because [A] at $t_{1/2}$ is one-half of the original [A],

  $[A]_t = 0.5\ [A]_0$.

Half-Life

For a first-order process, this becomes

$$\ln \frac{0.5\,[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

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

NOTE: For a first-order process, then, the half-life *does not* depend on $[A]_0$.

Half-Life

For a second-order process,

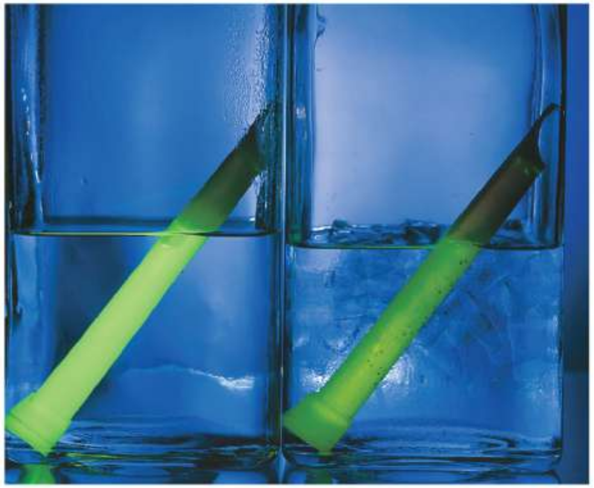
$$\frac{1}{0.5\,[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

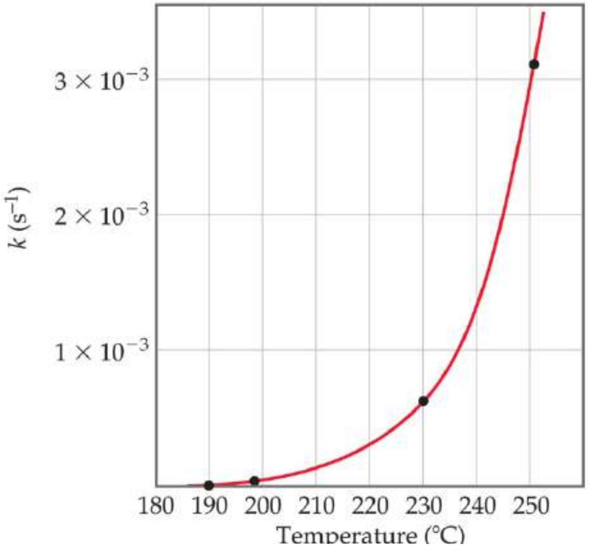
$$\frac{2-1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

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

Temperature and Rate



Higher temperature Lower temperature



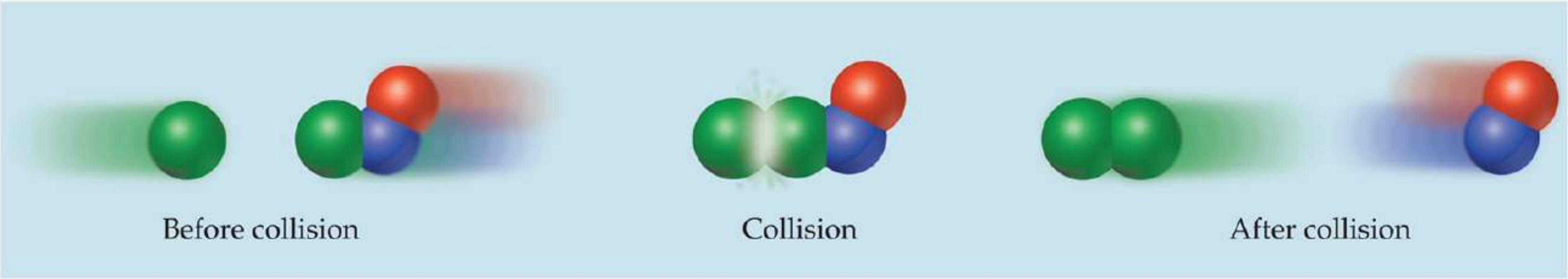
- Generally, as temperature increases, so does the reaction rate.
- This is because *k* is temperature dependent.

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

The Collision Model

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

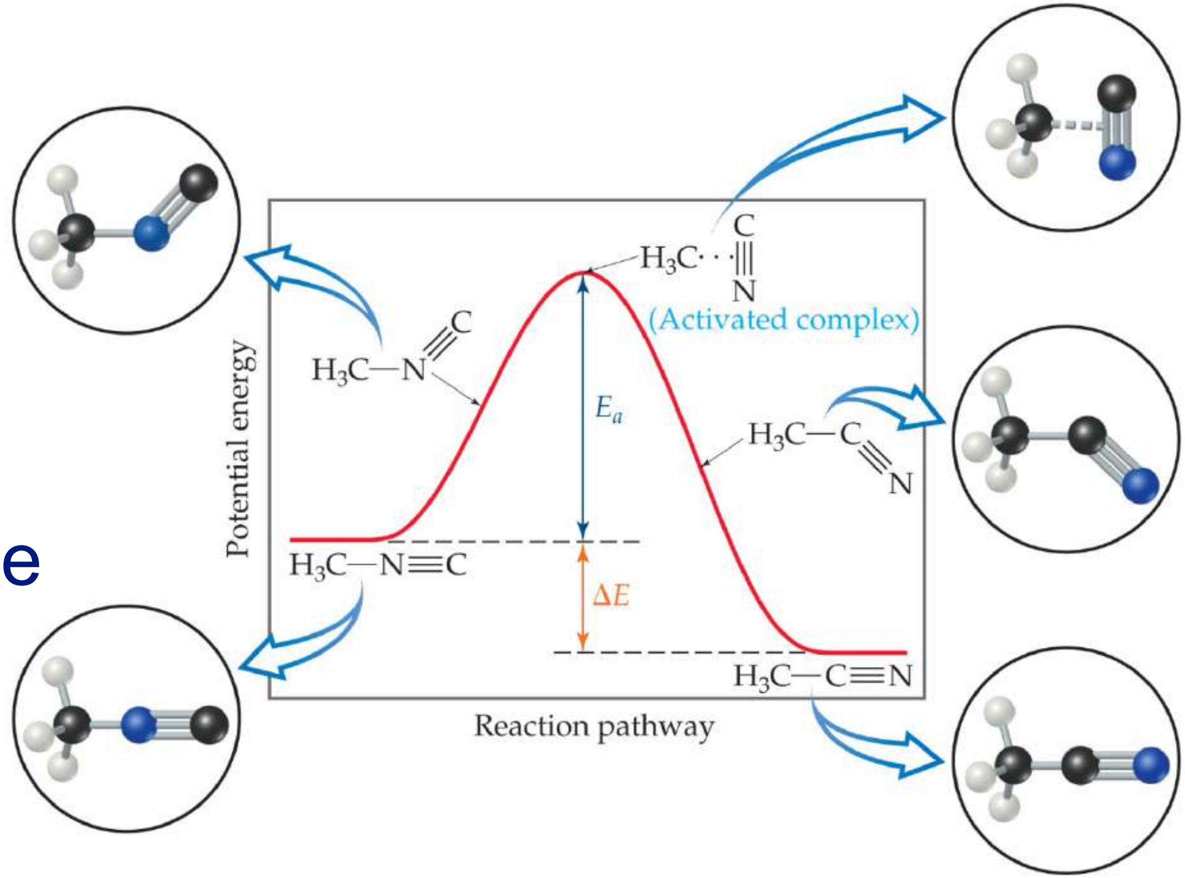


Activation Energy

- 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.

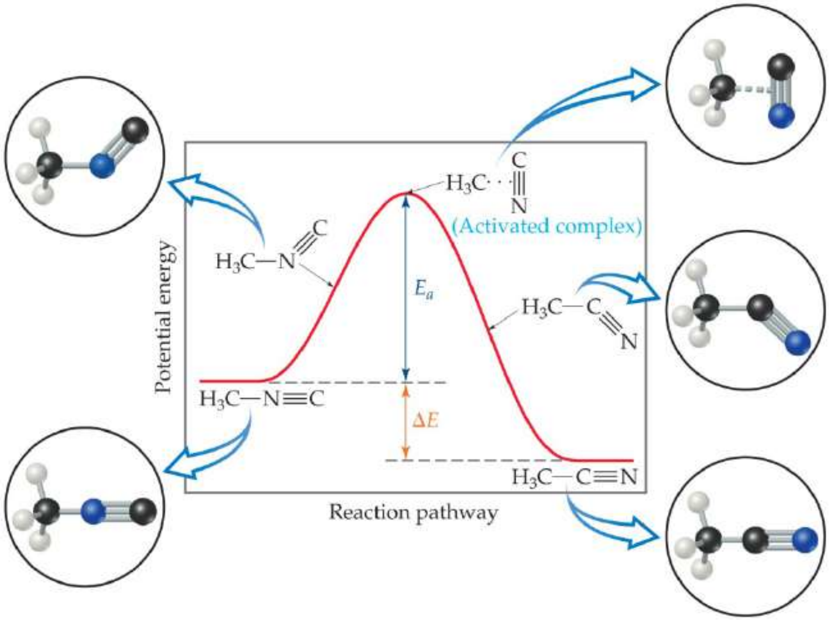
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a **reaction coordinate diagram** like this one for the rearrangement of methyl isonitrile.



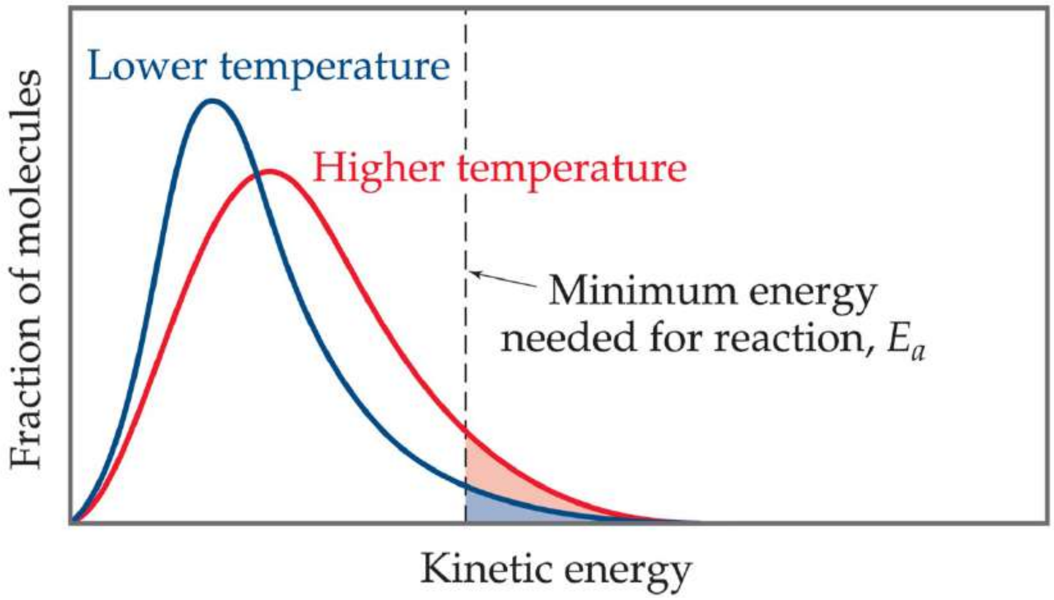
Reaction Coordinate Diagrams

- 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.

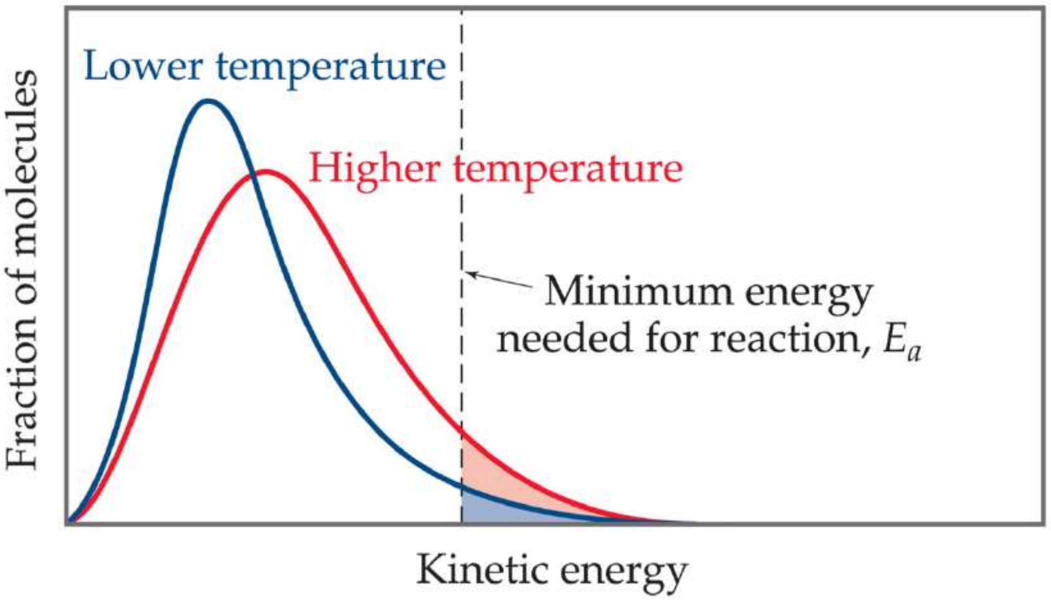
Maxwell–Boltzmann Distributions



- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.

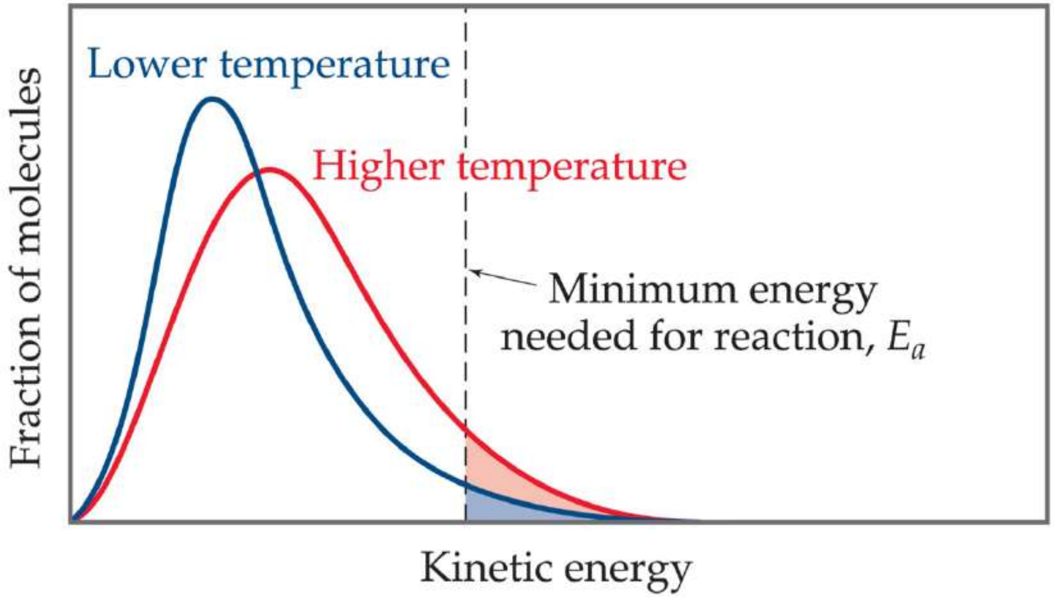
Maxwell–Boltzmann Distributions



- 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.



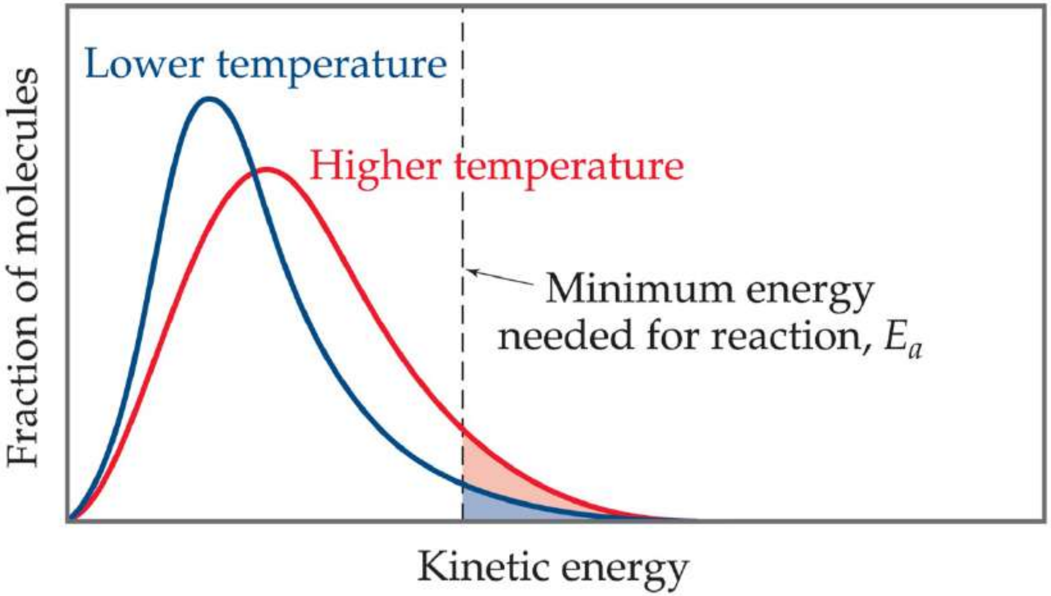
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{\frac{-E_a}{RT}}$$

where *R* is the gas constant and *T* is the Kelvin temperature.



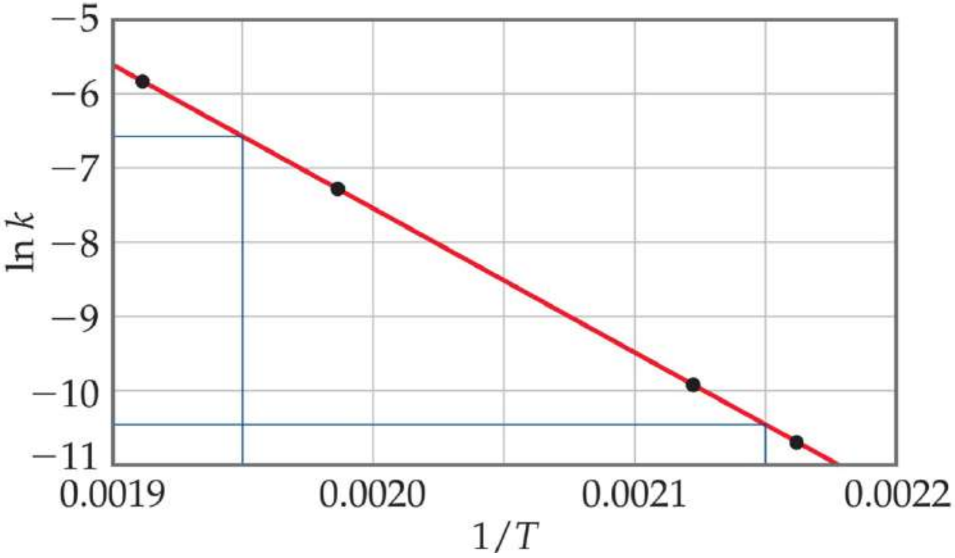
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

$$k = A e^{\frac{-E_a}{RT}}$$

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

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

$$y \quad = \quad m \quad x \quad + \quad b$$

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 Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism**.

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**.

Reaction Mechanisms

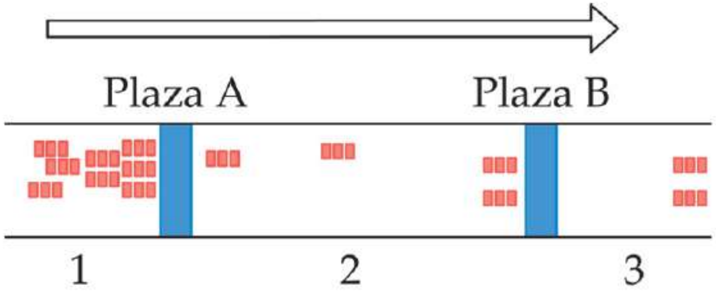
Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
*Bi*molecular	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
*Bi*molecular	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

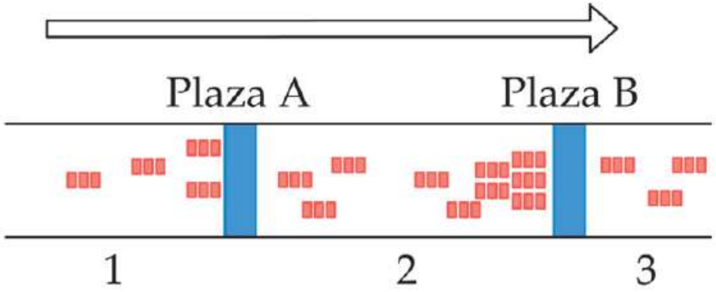
The molecularity of a process tells how many molecules are involved in the process.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.



Cars slowed at plaza A



Cars slowed at plaza B

Slow Initial Step

$$\mathrm{NO_2}\ (g) + \mathrm{CO}\ (g) \longrightarrow \mathrm{NO}\ (g) + \mathrm{CO_2}\ (g)$$

- The rate law for this reaction is found experimentally to be

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

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

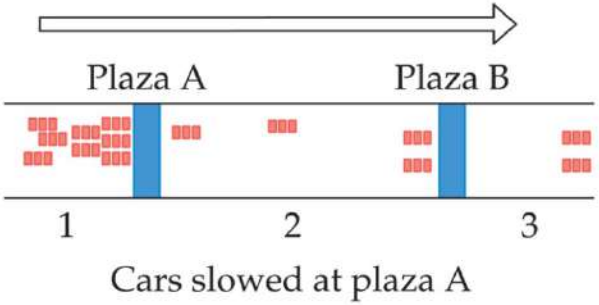
Slow Initial Step

- A proposed mechanism for this reaction is

  Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

  Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)

- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



Cars slowed at plaza A

Fast Initial Step

$$2\ \text{NO}\ (g) + \text{Br}_2\ (g) \longrightarrow 2\ \text{NOBr}\ (g)$$

- The rate law for this reaction is found to be

$$\text{Rate} = k\ [\text{NO}]^2\ [\text{Br}_2]$$

- Because termolecular processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

- A proposed mechanism is

Step 1: $NO + Br_2 \rightleftharpoons NOBr_2$ (fast)

Step 2: $NOBr_2 + NO \longrightarrow 2\ NOBr$ (slow)

Step 1 includes the forward *and* reverse reactions.

Fast Initial Step

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$\text{Rate} = k_2\,[\text{NOBr}_2]\,[\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?

Fast Initial Step

- $NOBr_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$\text{Rate}_f = \text{Rate}_r$$

Fast Initial Step

- Because Rate$_f$ = Rate$_r$,

$$k_1\,[\mathrm{NO}]\,[\mathrm{Br_2}] = k_{-1}\,[\mathrm{NOBr_2}]$$

- Solving for $[\mathrm{NOBr_2}]$ gives us

$$\frac{k_1}{k_{-1}}\,[\mathrm{NO}]\,[\mathrm{Br_2}] = [\mathrm{NOBr_2}]$$

Fast Initial Step

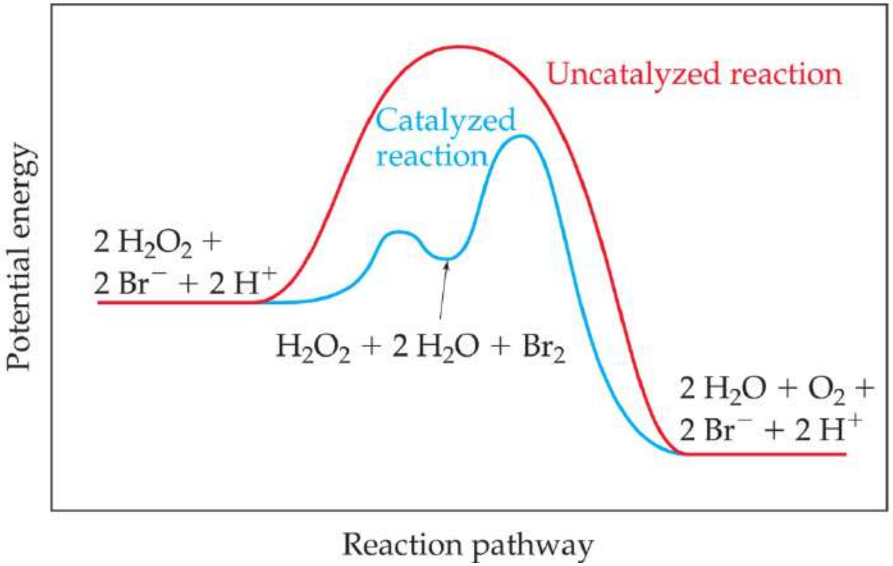
Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step gives

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [NO] [Br_2] [NO]$$

$$= k [NO]^2 [Br_2]$$

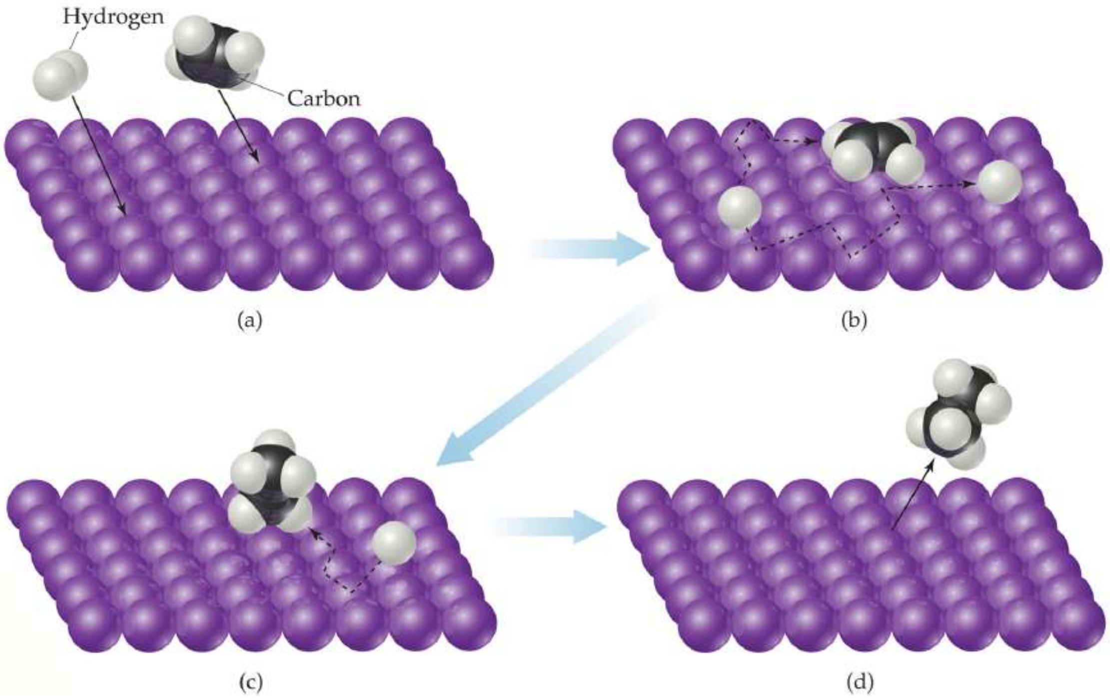
Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.

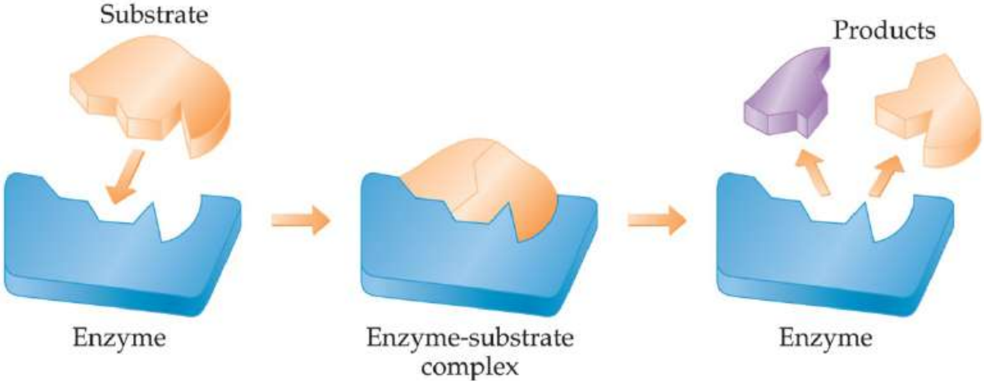


Catalysts

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.