

Chemistry, The Central Science, 10th edition
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Chapter 14

Chemical Kinetics



Kinetics

- Chemical Kinetics is the study of 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. If the reaction is happening between a solid and a liquid it will react only on the surface.
 - 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.

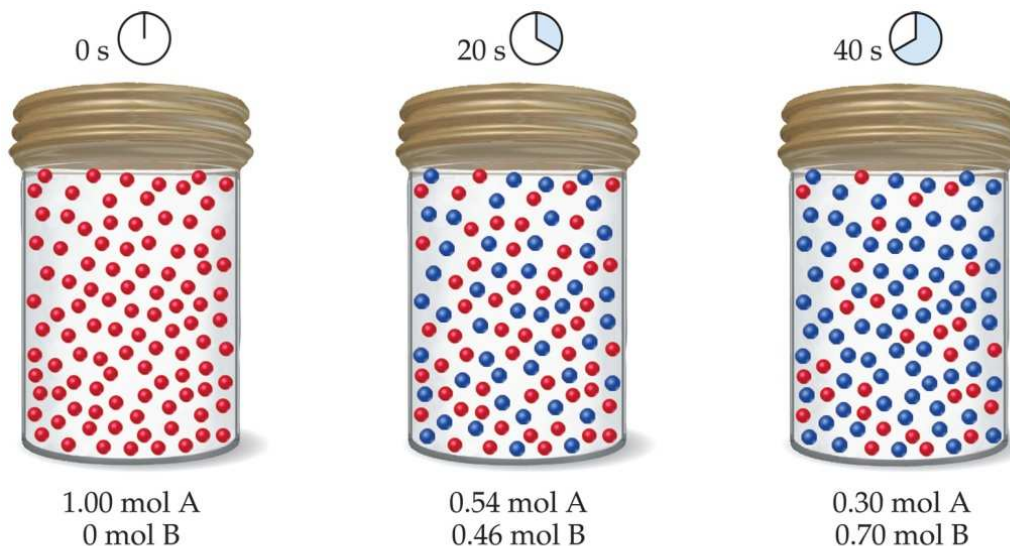


Factors That Affect Reaction Rates

- 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



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (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, $\text{C}_4\text{H}_9\text{Cl}$, was measured at various times.



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

- $$\text{Average rate} = \frac{[X]_{t_2} - [X]_{t_1}}{t_2 - t_1} = \frac{\Delta[X]}{\Delta t}$$

$$\text{Average rate} = \frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}$$



Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (M)	Average Rate (M/s)
0.0	0.1000	
50.0	0.0905	1.9×10^{-4}
100.0	0.0820	1.7×10^{-4}
150.0	0.0741	1.6×10^{-4}
200.0	0.0671	1.4×10^{-4}
300.0	0.0549	1.22×10^{-4}
400.0	0.0448	1.01×10^{-4}
500.0	0.0368	0.80×10^{-4}
800.0	0.0200	0.560×10^{-4}
10,000	0	

$$\text{Average rate} = \frac{[0.0905] - [0.1000]}{50 - 0} = -\frac{0.0095}{50} = -1.9 \times 10^{-4}$$



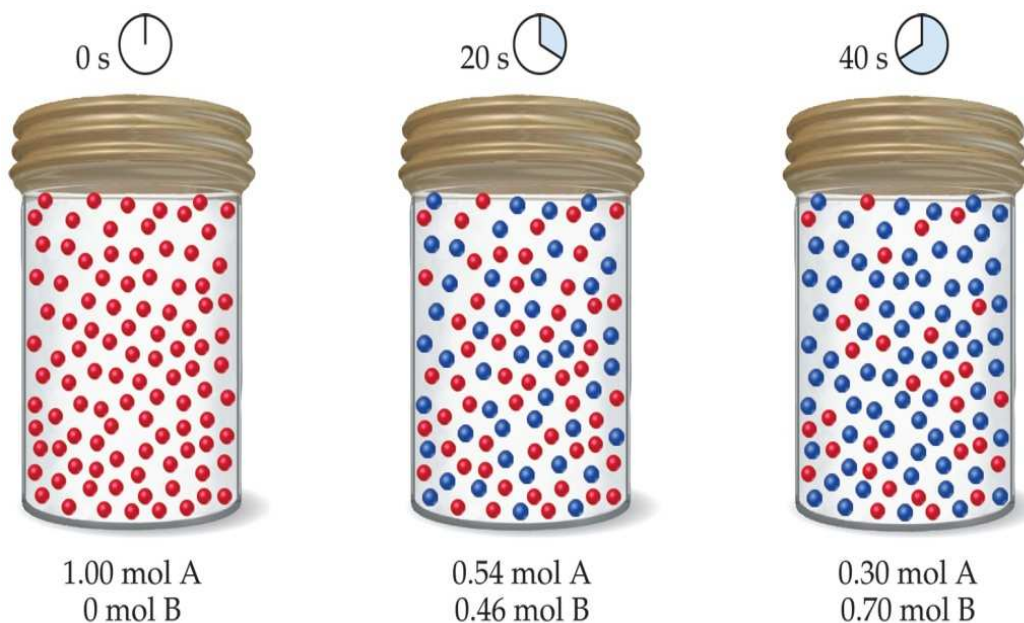
Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
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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	

- 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.



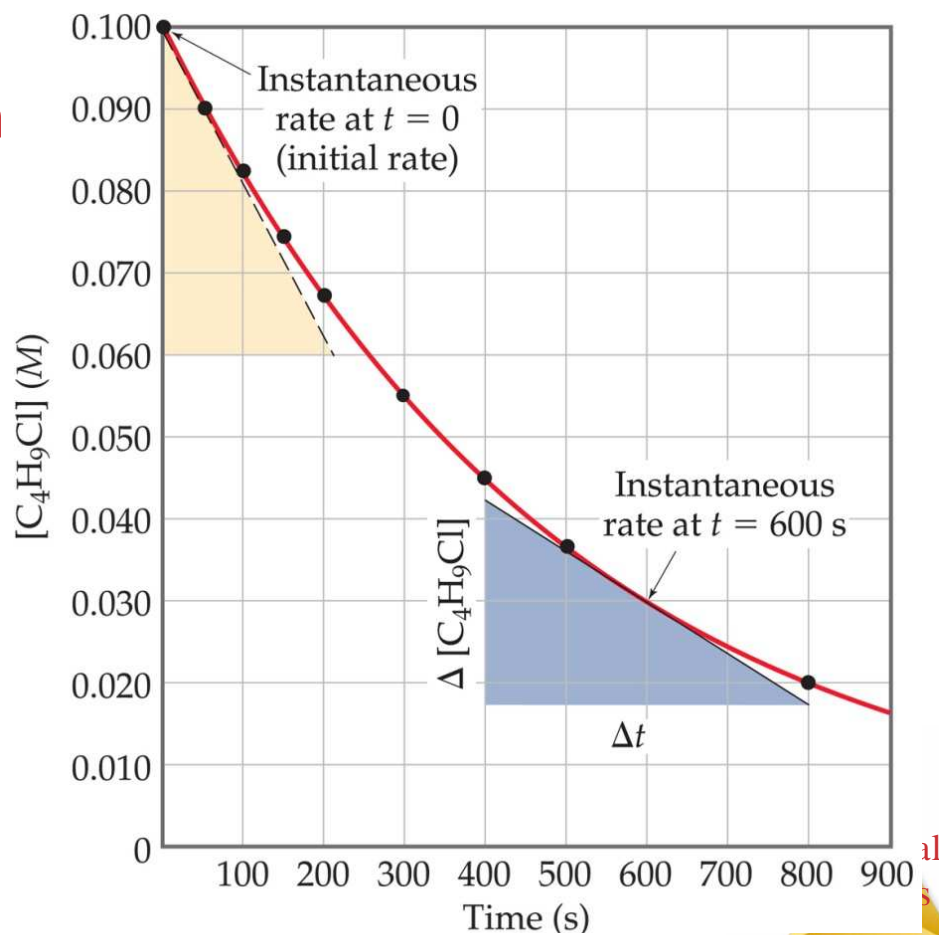


- calculate the average rate of appearance of B over the time interval from 0 to 40 s.

Reaction Rates



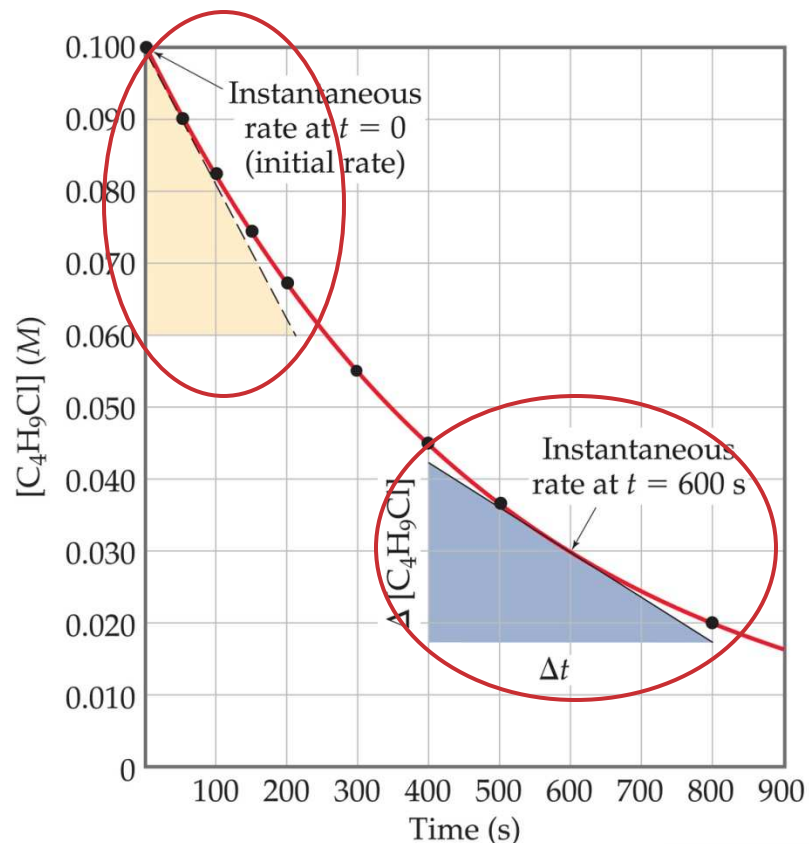
- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.



Reaction Rates



- All reactions slow down over time.
- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the beginning.



Average vs. instantaneous rxn rate

- Average rxn rate

$$\text{rate of reaction (rate)} = \frac{\left(\begin{array}{l} \text{change of chemical concentration} \\ \text{between beginning of rxn and end} \end{array} \right)}{\text{total time elapsed}} = \frac{\Delta[A]}{\Delta t}$$

- Instantaneous rxn rate (tangent to curve)

$$\text{rate of reaction (rate)} = \frac{\left(\begin{array}{l} \text{change of chemical concentration} \\ \text{over a short period of time} \end{array} \right)}{\text{the short time elapsed}} = \frac{\Delta[A]}{\Delta t}$$

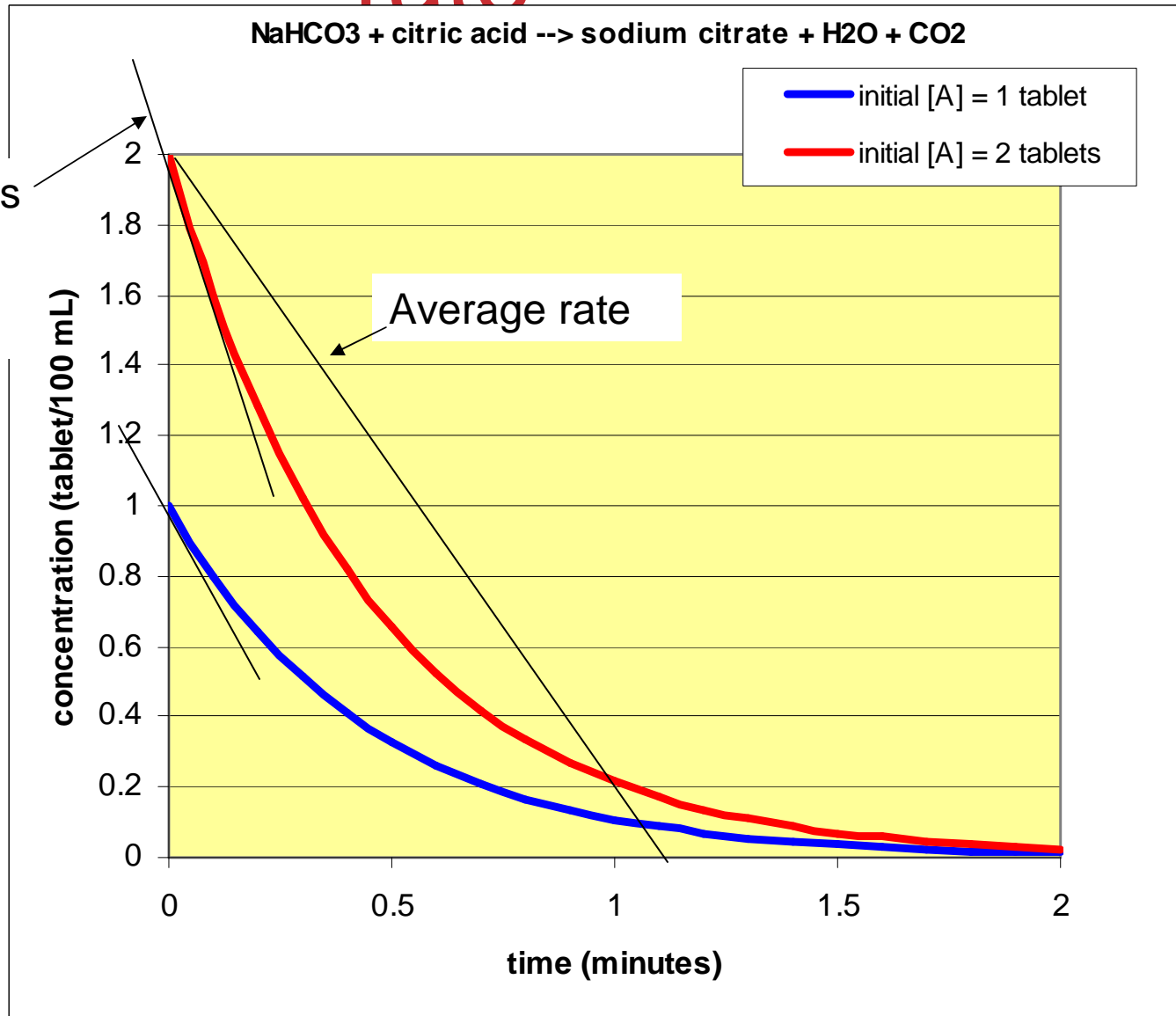
Usually in chemistry, we are interested in the instantaneous rxn rate at the very beginning (at $t = 0$)

INITIAL REACTION RATE

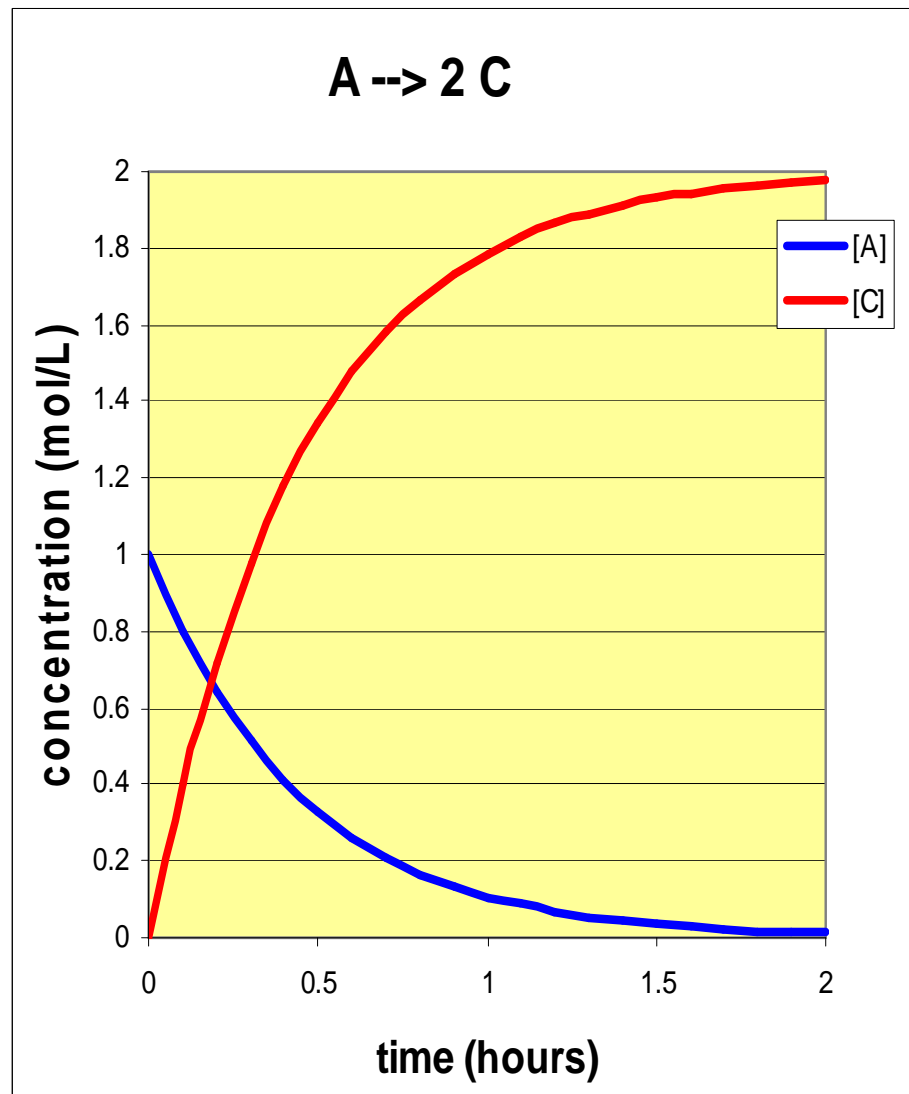
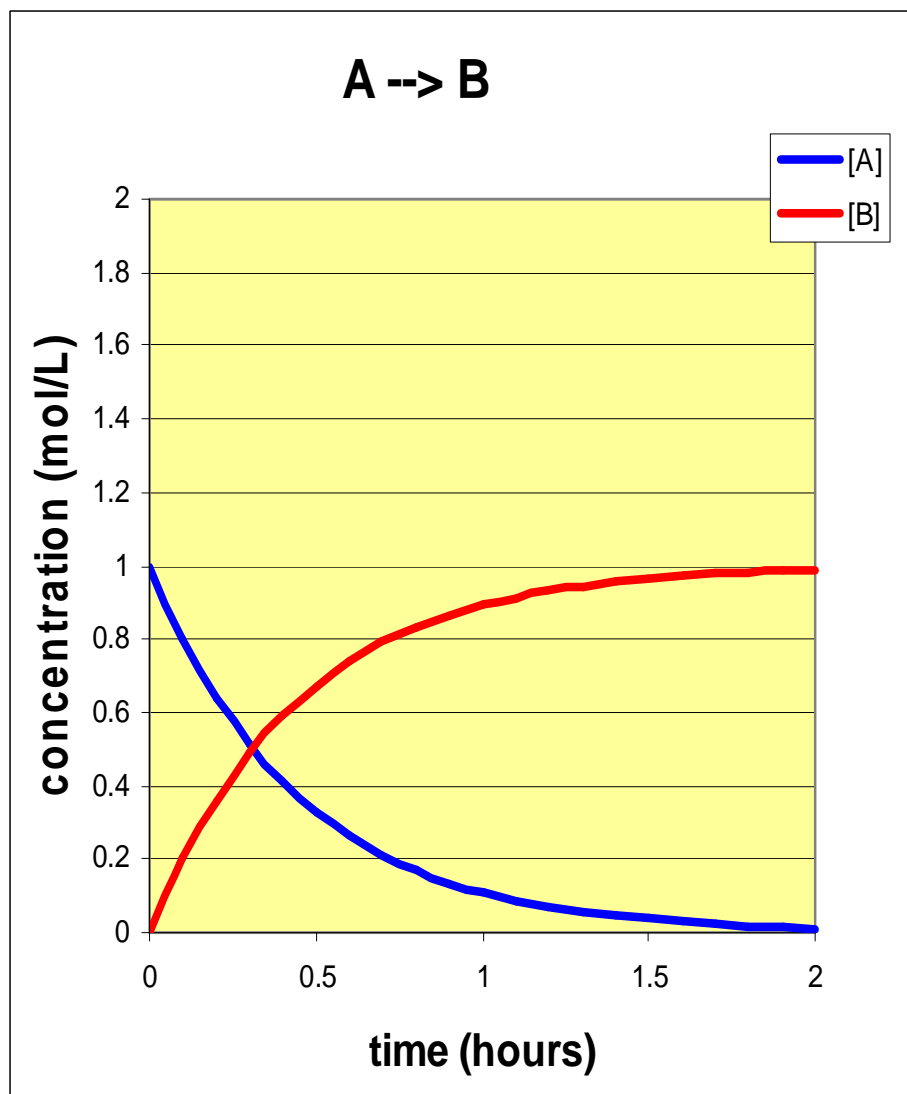
Chemical
Kinetics



Average vs. instantaneous rxn rate



Comparing concentrations of chemicals in a reaction

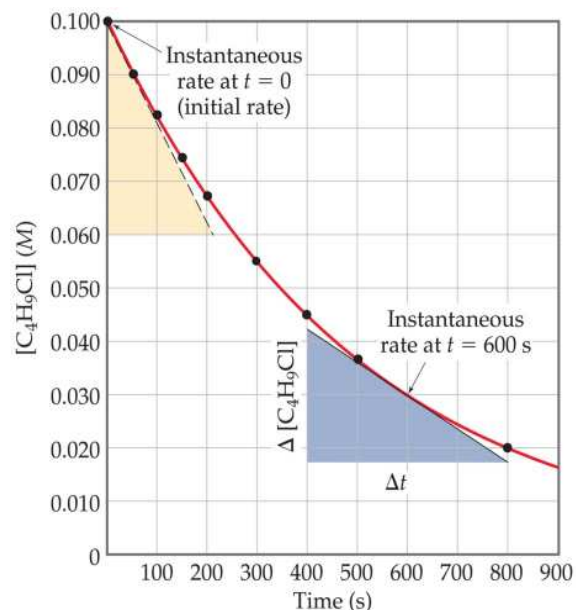


What we're after in kinetics

- We want to be able to understand and predict how much reactants remain (or products get formed) in a certain amount of time
- Change with time is rate
- Rate means calculus must be used, so we need to be careful which rate we are talking about
- We will use instantaneous rate at the start of a reaction (initial rate)
- Several factors affect the rate of a reaction
 - Initial concentration
 - Temperature
 - Amount of reactant exposed (surface area)
 - Presence of a catalyst
- A theory (equations) that predicts kinetics must explain these



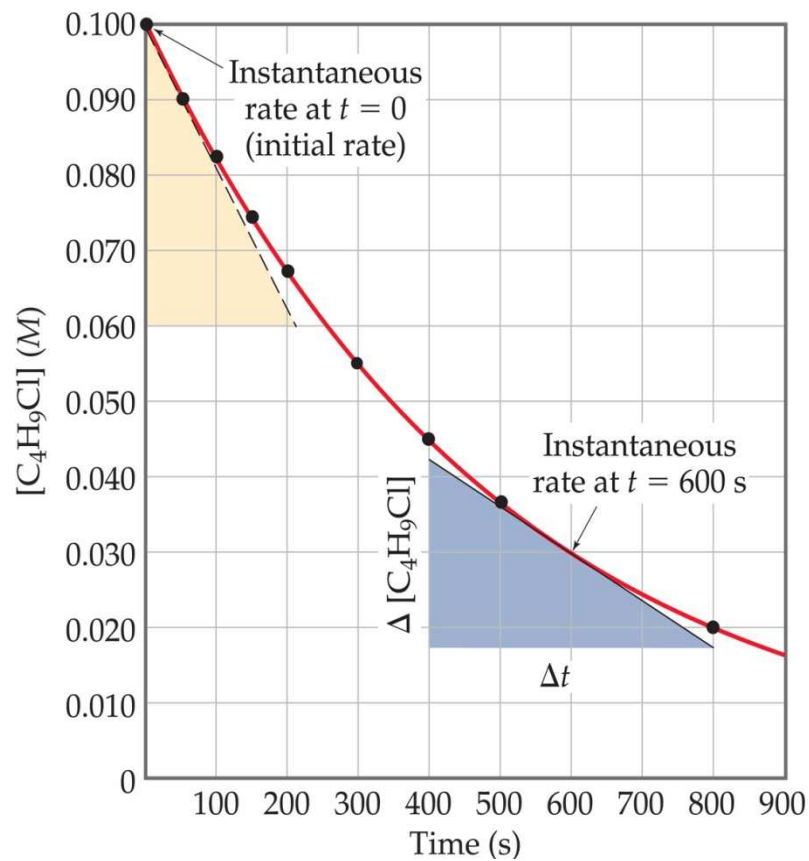
Calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).



$$\text{Rate} = -\frac{\Delta [C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100) M}{(200 - 0) s} = 2.0 \times 10^{-4} M/s$$



Determine the instantaneous rate of disappearance of C_4H_9Cl at $t = 300$ s.



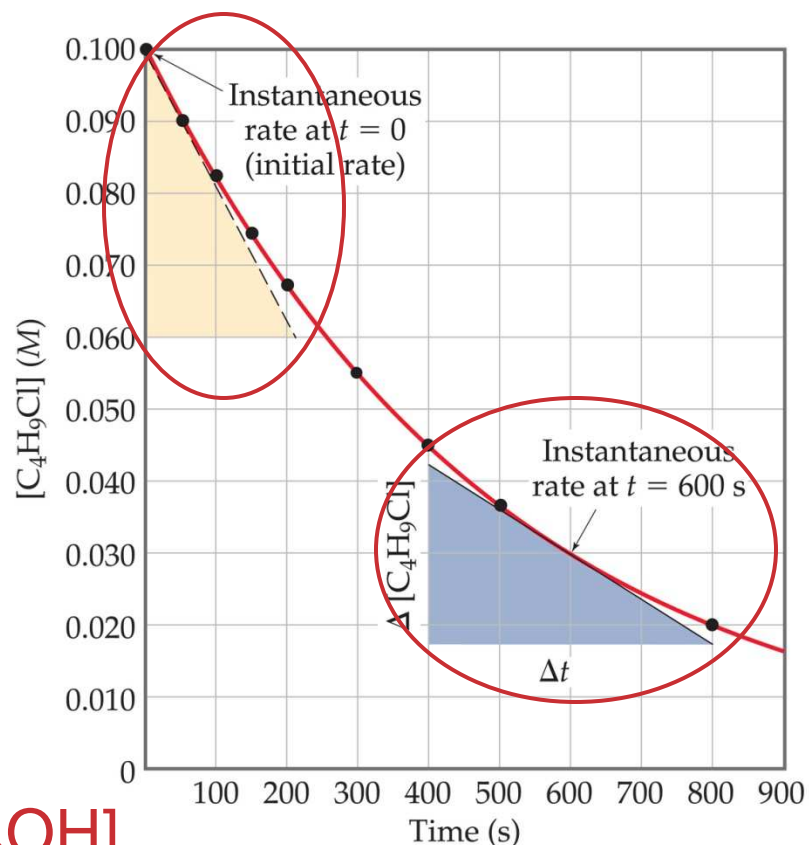
Answer: $1.1 \times 10^{-4} M/s$



Reaction Rates and Stoichiometry



- In this reaction, the ratio of $\text{C}_4\text{H}_9\text{Cl}$ to $\text{C}_4\text{H}_9\text{OH}$ is 1:1.
- Thus, the rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ is the same as the rate of appearance of $\text{C}_4\text{H}_9\text{OH}$.



$$\text{Rate} = \frac{-\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$



Reaction Rates and Stoichiometry

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



in such a case ,

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$



Reaction Rates and Stoichiometry

- To generalize, then, for the reaction



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



Key points about kinetics so far

- Study the vocabulary
- Reaction rate has weird units
- Be clear whether you are talking about average reaction rate or instantaneous reaction rate
- The equations which we will study all talk about instantaneous reaction rate, most easily measured at the beginning of a reaction (initial rate)
- Relating rates at which products appear (+) and reactants disappear (-) has to do with inverse stoichiometric coefficients
- Reaction rate depends on several factors: initial concentration, temperature, surface area of reactants exposed, presence of a catalyst



(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

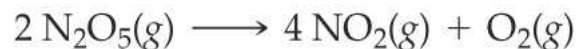
(b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$



SAMPLE EXERCISE 14.3 continued

The decomposition of N_2O_5 proceeds according to the following equation:



If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of (a) NO_2 , (b) O_2 ?

Answers: (a) $8.4 \times 10^{-7} \text{ M/s}$, (b) $2.1 \times 10^{-7} \text{ M/s}$



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	0.0600	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}



Comparing Experiments 1 and 2, when $[\text{NH}_4^+]$ 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}
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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}



Likewise, comparing Experiments 5 and 6, when $[\text{NO}_2^-]$ doubles, the initial rate doubles.



Concentration and Rate

- This means

$$\text{Rate} \propto [\text{NH}_4^+]$$

$$\text{Rate} \propto [\text{NO}_2^-]$$

$$\text{Rate} \propto [\text{NH}_4^+] [\text{NO}_2^-]$$

or

$$\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

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



- If you want your concepts to be clearer do the visualizing concepts part of the problems at the back of your chapter.



Rate Law

- An equation that shows how the rate depends on the concentration of the reactants is called the rate law
- The exponents tell the **order** of the reaction with respect to each reactant.
- This reaction is

First-order in $[\text{NH}_4^+]$

First-order in $[\text{NO}_2^-]$



Rate Laws

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



- For a general reaction:



Rate law has the form

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

where k is the rate constant and is dependant on temperature.



If we know the rate law and the rate for a set of reaction conditions we can calculate the value of k .



To calculate the rate constant:

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

Rate law

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

$$\text{Rate} = k[\text{NH}_4] [\text{NO}_2]$$

For experiment 1:

$$5.4 \times 10^{-7} \text{ M/s} = k (0.0100\text{M})(0.200\text{M})$$

$$k = \frac{5.4 \times 10^{-7} \text{ M/s}}{k (0.0100\text{M})(0.200\text{M})}$$

$$= 2.7 \times 10^{-4} / \text{Ms}$$



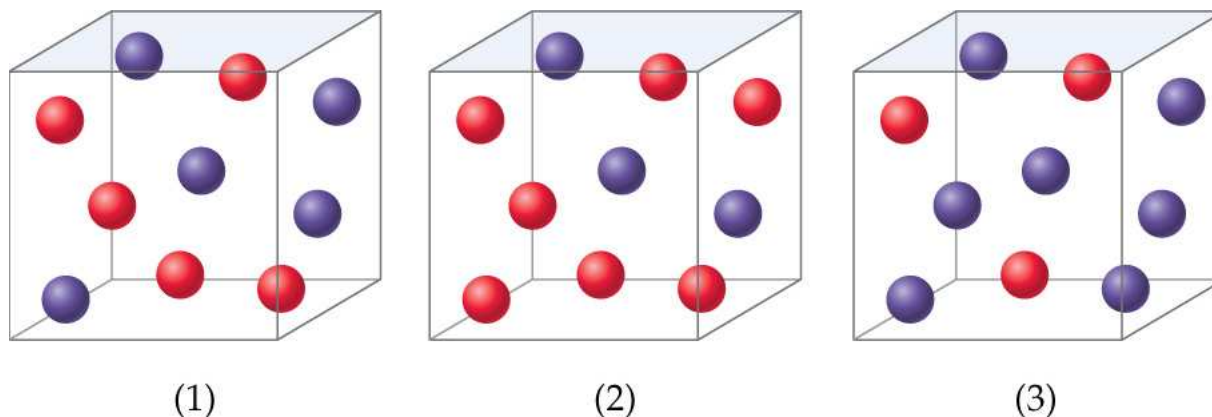
Exponents in the rate law

The exponent in the rate law indicates how the rate is affected by the concentration of each reactant.



SAMPLE EXERCISE 14.4 Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $A + B \longrightarrow C$ for which rate = $k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.

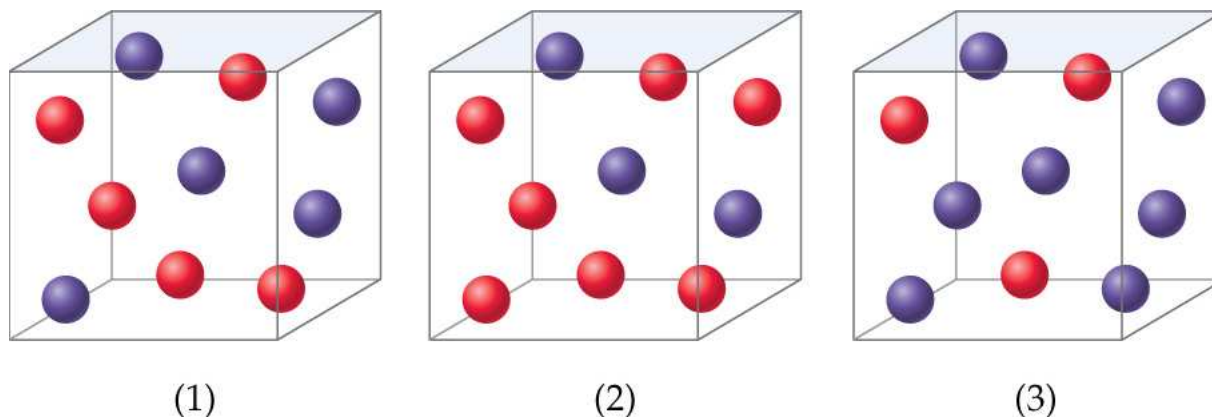


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SAMPLE EXERCISE 14.4 Relating a Rate Law to the Effect of Concentration on Rate

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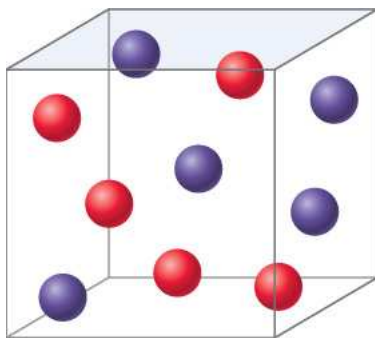


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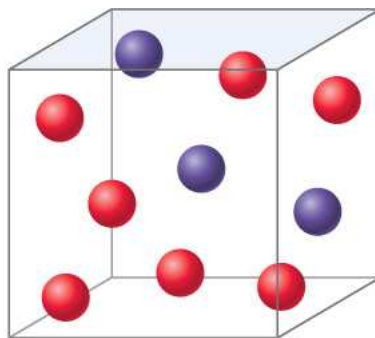
Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a higher reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.



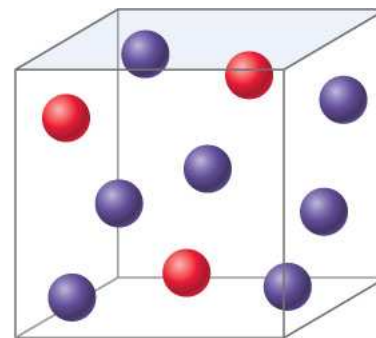
Assuming that rate = $k[A][B]$, rank the mixtures represented in this Sample Exercise in order of increasing rate.



(1)



(2)



(3)

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Answer: $2 = 3 < 1$



Unit for k depends on the overall order of the reaction.

For example for a second order reaction

$$k = \frac{\text{Unit of Rate}}{(\text{Units of concentration})^2} = \frac{\text{M/s}}{\text{M}^2} = \frac{\text{M}}{\text{M}^2 \text{ s}} = /\text{Ms}$$

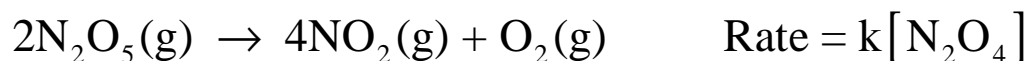


(a) What are the overall reaction orders for the rate laws described in Equations 14.9 and 14.10?

(b) What are the units of the rate constant for the rate law for Equation 14.9?



(a) What are the overall reaction orders for the rate laws described in Equations 14.9 and 14.10?



Answer:

The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.10 is first order in CHCl_3 and one-half order in Cl_2 . The overall reaction order is three halves.

(b) What are the units of the rate constant for the rate law for Equation 14.9?

Answer:

$$\text{Rate} = k[\text{N}_2\text{O}_4]$$

So Units of rate = (units of rate constant)(units of concentration)

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{\text{M/s}}{\text{M}} = \text{s}^{-1}$$

Notice that the units of the rate constant change as the overall order of the reaction changes.



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}

1. The reaction is first order in a reactant

If the concentration of a particular component is doubled the rate doubles and triples when the concentration triples.



2. If the reaction is second order with respect to a component:

If the rate is second order with respect to a particular component, doubling its concentration increases the rate by a factor of $2^2 = 4$

Tripling its concentration increases the rate by a factor of $3^2 = 9$
and so forth



- 3. If a reaction is zero order with respect to a component:

If a reaction is zero order in a particular reactant, changing its concentration will have no effect on the rate as long as long as the reactant is present.

It is because any concentration raised to zero is one



Order of reaction rate

- Rate of reaction can depend on how much reactant is present in more than one way:

Zero order: $\text{rate} \propto [A]^0$

First order: $\text{rate} \propto [A]$

Second order: $\text{rate} \propto [A]^2$





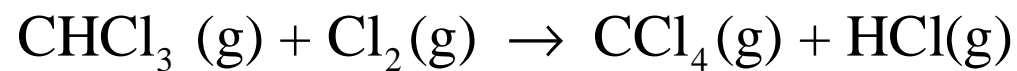
What does “order” mean?

- Zero order
rate = $k [A]^0$
if you double $[A]$
 $[A] \times 2$
if you triple A , $[A] \times 3$
rate stays the same
rate $\times 2^0 =$ stays same
rate $\times 3^0 =$ stays same
- First order
rate = $k [A]^1$
if you double $[A]$
 $[A] \times 2$
if you triple A , $[A] \times 3$
rate doubles
rate $\times 2^1$
rate $\times 3^1$
- Second order
rate = $k [A]^2$
if you double $[A]$
 $[A] \times 2$
if you triple A , $[A] \times 3$
rate quadruples
rate $\times 2^2 =$ rate $\times 4$
rate $\times 3^2 =$ rate $\times 9$





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



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$



$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$



Some Reactions and Their Experimental Rate Laws



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



$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$



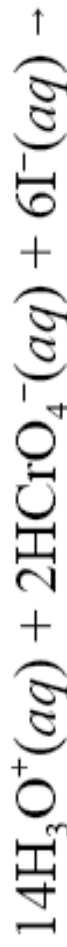
$$\text{Rate} = k[\text{N}_2\text{O}_5]$$



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



$$\text{Rate} = k[\text{CH}_3\text{CHO}]^{3/2}$$



$$\text{Rate} = k[\text{HCrO}_4^-][\text{I}^-][\text{H}_3\text{O}^+]$$



- Although the exponents in the rate law are often the same as the coefficients in the balanced reaction, this is not necessarily the case.
- The values of these exponents must be determined experimentally.
- Most reaction orders are 0, 1 or 2. However we may encounter reaction orders in fraction.

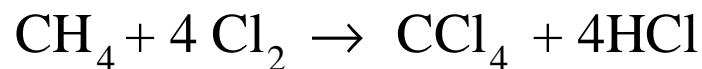


- The rate of the reaction depends on the concentration but the rate constant , k, does not.
- k is dependent only on temperature.



- a. Consider the reaction $\text{CH}_4(\text{g}) + 4\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + 4\text{HCl}(\text{g})$, for which the rate is defined as $\text{Rate} = -d[\text{CH}_4]/dt$. At any time in the course of this reaction, the rate of appearance of $\text{HCl}(\text{g})$ is equal to

Rate

 $4 \times \text{Rate}$ $\frac{1}{4} \times \text{Rate}$ $2 \times \text{Rate}$ $\frac{1}{2} \times \text{Rate}$ 

$$\text{Rate} = - \frac{1}{1} \frac{\Delta[\text{CH}_4]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{HCl}]}{\Delta t}$$

$$\text{Rate} = - \text{rate of disappearance of } \text{CH}_4 = \frac{1}{4} \text{rate of appearance of HCl}$$

$$\text{Rate} \times 4 = \text{Rate of appearance of HCl}$$



Change in Concentration with Time

From the rate law we can calculate the rate of the reaction if we know the the rate constant and the reactant concentration

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

Rate laws can also be converted into equations that tell us what the concentration of reactants and products are at any time during the reaction.



Change of Concentration with Time for the First Order Reactions

The first order reaction is one whose rate depends on the concentration of a single reactant raised to the first power

reactant $A \rightarrow$ product

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

This form of rate law, which expresses how rate depends upon concentration is called differential rate law.



Instantaneous Rate

- The approximation that the curve is nearly a straight line becomes better as Δt becomes smaller.
- At the limit where Δt becomes infinitesimally small, the segment of the curve *is* a straight line, the negative of whose slope gives the *instantaneous rate* at a point in time.
- To indicate instantaneous rate, we use the notation d instead of Δ :

$$\text{Rate} = \frac{-d[\text{Cl}_2]}{dt} = \text{-slope}$$



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

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{[A]} = k dt$$

Integrating for time = 0 to time = t

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k \int_0^t dt$$

From this

$$-(\ln[A]_t + \ln[A]_0) = k(t-0)$$

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

$$-\ln \frac{[A]_t}{[A]_0} = kt \quad \left(\begin{array}{l} \infty \\ \ln a - \ln b \\ = \ln \frac{a}{b} \end{array} \right)$$

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

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

Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process we get:

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

Where

$[A]_0$ is the initial concentration of A.

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



Integrated Rate Laws

Manipulating this equation produces...

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

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

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

$$y = mx + b$$

Where m is the slope of the line and b is the y intercept of the line.

Which is a general equation of a straight line.



Integrated Rate Laws

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

..which is in the form $y = mx + b$

Where m is the slope of the line and b is the y intercept of the line.

Which is a general equation of a straight line.



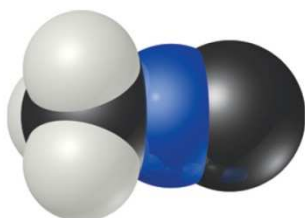
First-Order Processes

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

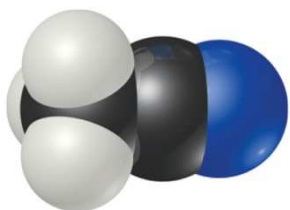
Therefore, if a reaction is first-order, a plot of $\ln [A]_t$ vs. t will yield a straight line, and the slope of the line will be $-k$.



First-Order Processes



Methyl isonitrile



Acetonitrile

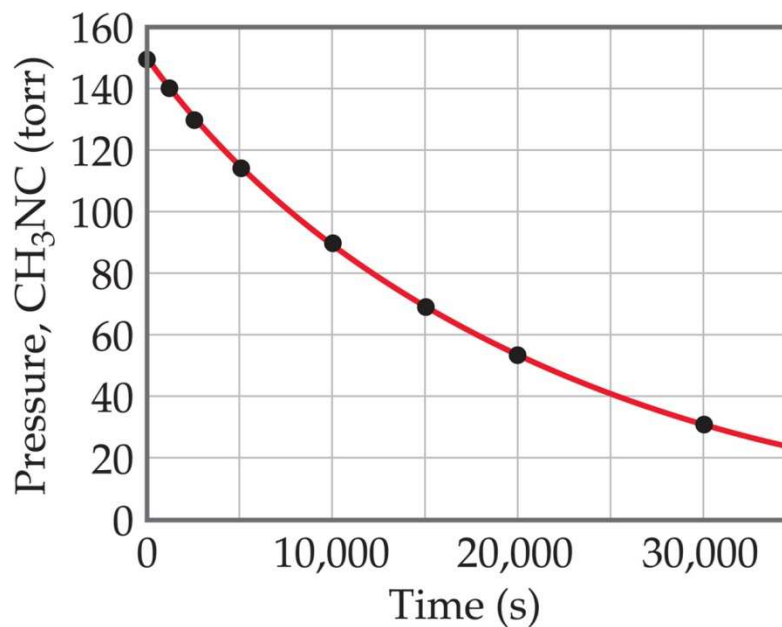
Consider the process in which methyl isonitrile is converted to acetonitrile.



First-Order Processes



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



- The experiments show this reaction to be first order so we can write the rate equation as

$$\ln[\text{CH}_3\text{NC}]_t = -kt + \ln[\text{CH}_3\text{NC}]_0$$



- For gas we can use pressure as a unit of concentration as from the ideal gas law equation the pressure is directly proportional to the number of moles per unit volume

$$PV = nRT$$

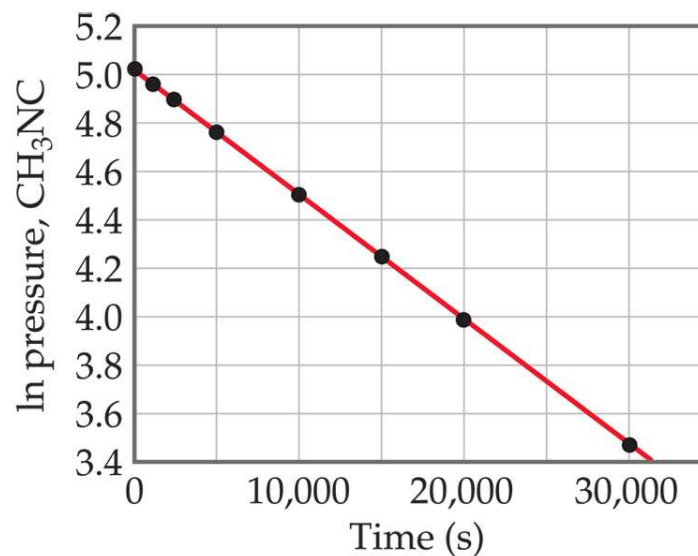
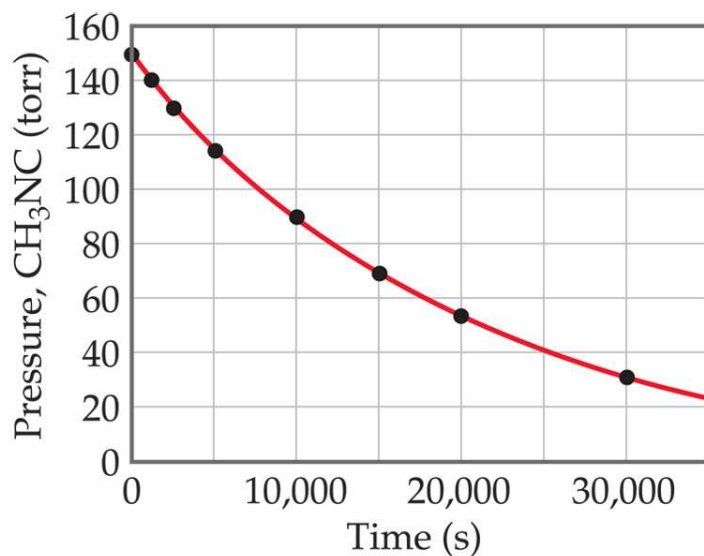
$$P = \frac{n}{V}RT$$

At constant temperature

$$P \propto \frac{n}{V}$$



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 slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.



- How to get the natural log value on your calculator

LN will give the natural log value.

Pressing LN will show

In (key in the value)

and press enter



The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine

- (a) the rate law for the reaction,
- (b) the magnitude of the rate constant,
- (c) the rate of the reaction when $[A] = 0.050 \text{ M}$ and $[B] = 0.100 \text{ M}$.



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- (b) the magnitude of the rate constant,
- (c) the rate of the reaction when $[A] = 0.050 \text{ M}$ and $[B] = 0.100 \text{ M}$

a.

$$\text{Rate} = k[A]^2[B]^0 = k[A]^2$$

(b) Using the rate law and the data from experiment 1, we have

$$k = \frac{\text{rate}}{[A]^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.100 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(c) Using the rate law from part (a) and the rate constant from part (b), we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.050 \text{ M})^2 = 1.0 \times 10^{-5} \text{ M/s}$$



PRACTICE EXERCISE

The following data were measured for the reaction of nitric oxide with hydrogen:



Experiment Number	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. (b) Calculate the rate constant. (c) Calculate the rate when [NO] = 0.050 M and [H₂] = 0.150 M.



PRACTICE EXERCISE

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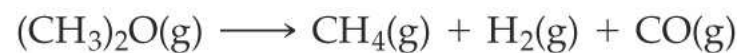
(a) Determine the rate law for this reaction. (b) Calculate the rate constant. (c) Calculate the rate when [NO] = 0.050 M and [H₂] = 0.150 M.

Answers: (a) rate = $k[\text{NO}]^2[\text{H}_2]$; (b) $k = 1.2 \text{ M}^{-2}\text{s}^{-1}$; (c) rate = $4.5 \times 10^{-4} \text{ M/s}$



PRACTICE EXERCISE

The decomposition of dimethyl ether, $(\text{CH}_3)_2\text{O}$, at 510°C is a first-order process with a rate constant of $6.8 \times 10^{-4}\text{s}^{-1}$:

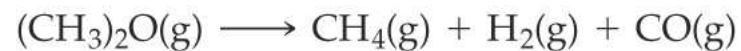


If the initial pressure of $(\text{CH}_3)_2\text{O}$ is 135 torr, what is its partial pressure after 1420 s?



PRACTICE EXERCISE

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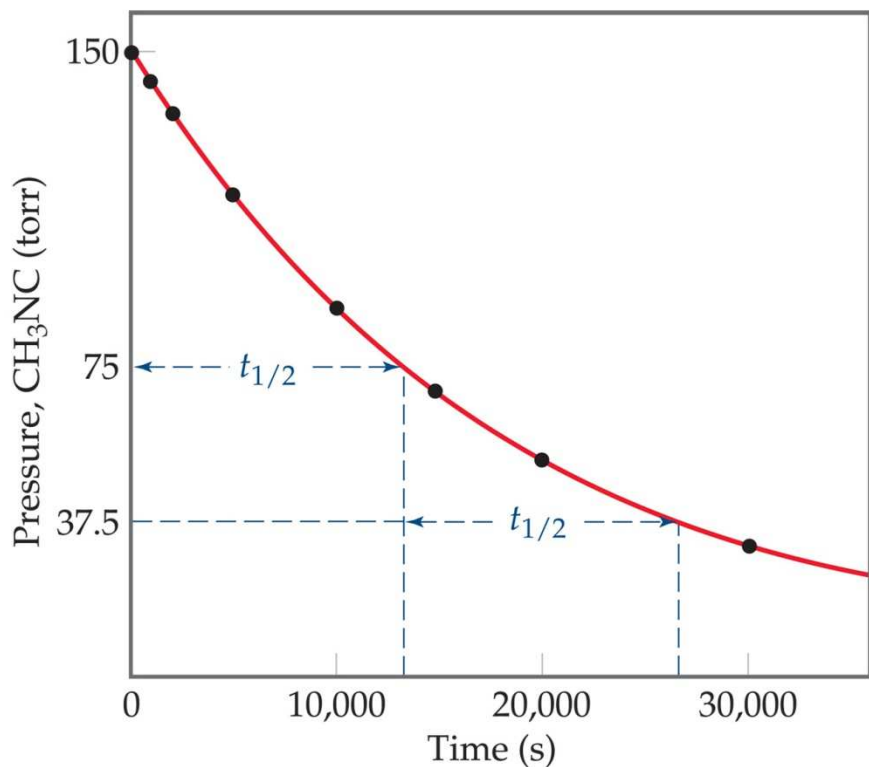


If the initial pressure of $(\text{CH}_3)_2\text{O}$ is 135 torr, what is its partial pressure after 1420 s?

Answer: 51 torr



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 $[A]$,

$$[A]_t = 1/2 [A]_0.$$



Half-Life

For a first-order process, this becomes

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

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

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

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

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



- The half life of a first order reaction remains the same throughout the reaction.
- The concentration of the reactant keeps becoming half of the previous value after every half life.



- In the first order reaction, the concentration of reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely $t_{1/2}$
- The concept of a first order reaction is widely used in describing radioactive decay, a first order process.



SAMPLE EXERCISE 14.7 Using the Integrated First-Order Rate Law

- The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12°C . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$. Assume that the average temperature of the lake is 12°C .
- **(a)** What is the concentration of the insecticide on June 1 of the following year?
- **(b)** How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?



SAMPLE EXERCISE 14.7 Using the Integrated First-Order Rate Law

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- **(a)** What is the concentration of the insecticide on June 1 of the following year?
- **(b)** How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?

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

Solve: **(a)** Substituting the known quantities into Equation 14.13, we have

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7})$$

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -1.45 + (-14.51) = -15.96$$

$$[\text{insecticide}]_{t=1 \text{ yr}} = e^{-15.96} = 1.2 \times 10^{-7} \text{ g/cm}^3$$

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(b) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7} \text{ g/cm}^3$, gives

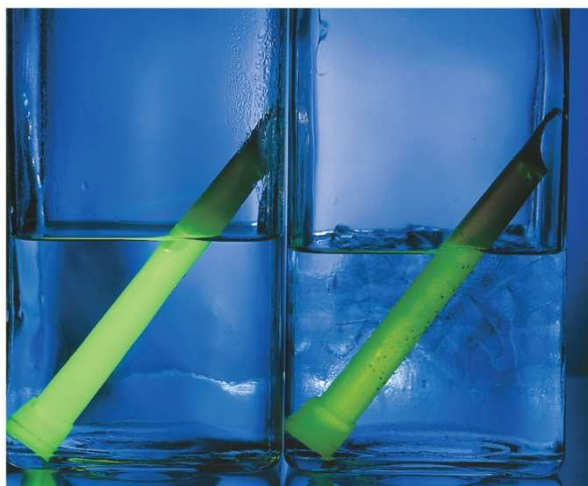
$$\ln(3.0 \times 10^{-7}) = -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

Solving for t gives

$$\begin{aligned} t &= -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45 \text{ yr}^{-1} \\ &= -(-15.02 + 14.51)/1.45 \text{ yr}^{-1} = 0.35 \text{ yr} \end{aligned}$$



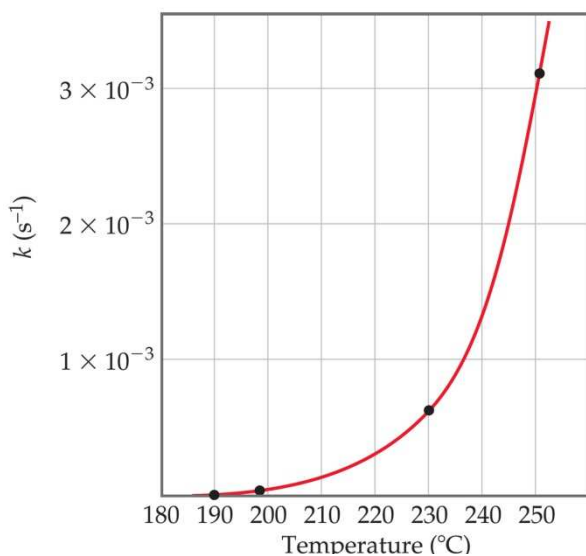
Temperature and Rate



Higher temperature

Lower temperature

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



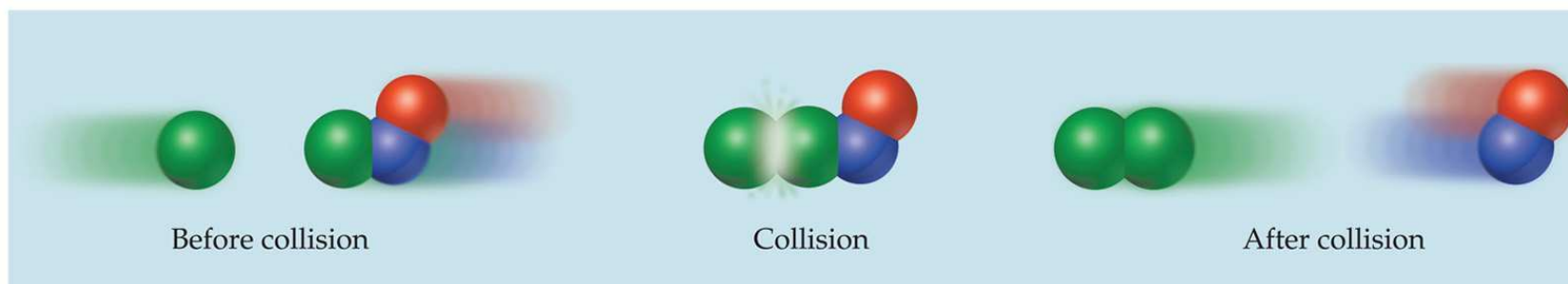
The Collision Model

- 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

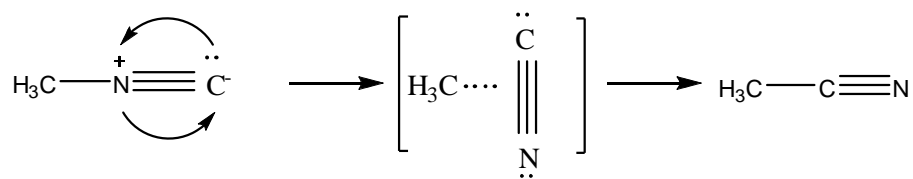
Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.



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.

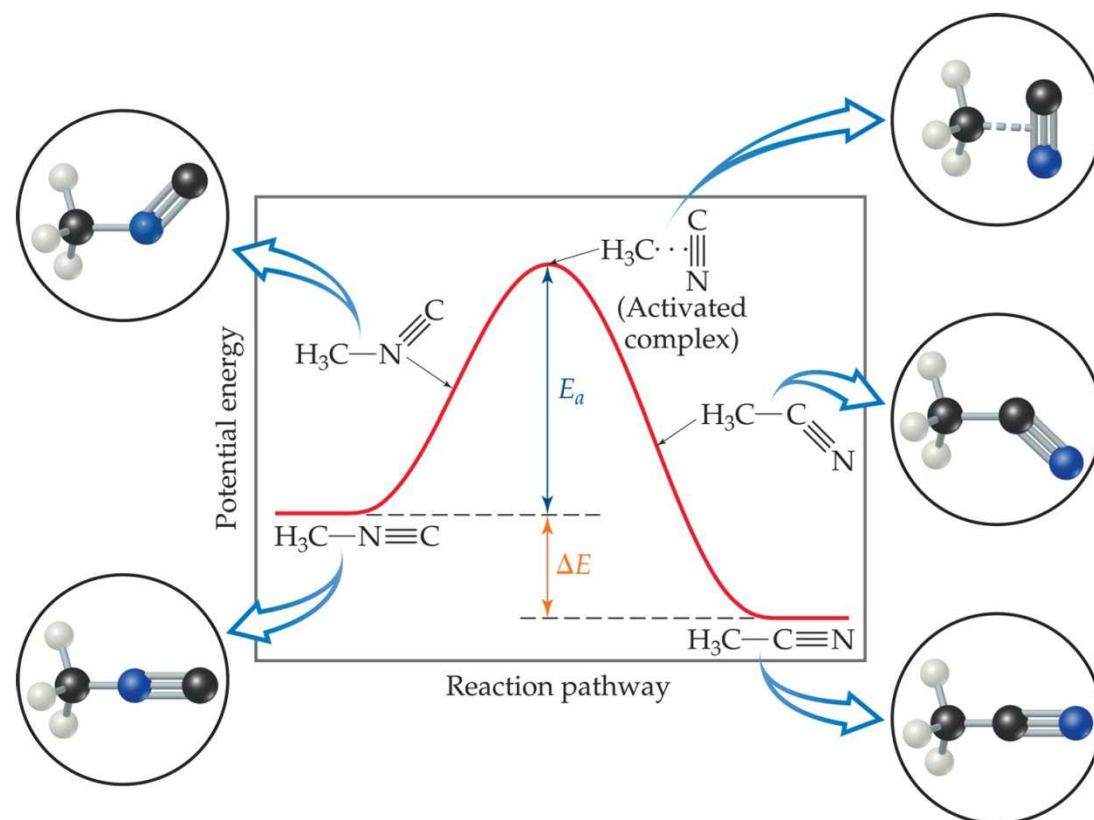




- This is a reaction where methyl isonitrile is rearranging to acetonitrile
- This reaction passes through an intermediate state in which the $\text{N} \equiv \text{C}$ is sitting sideways.

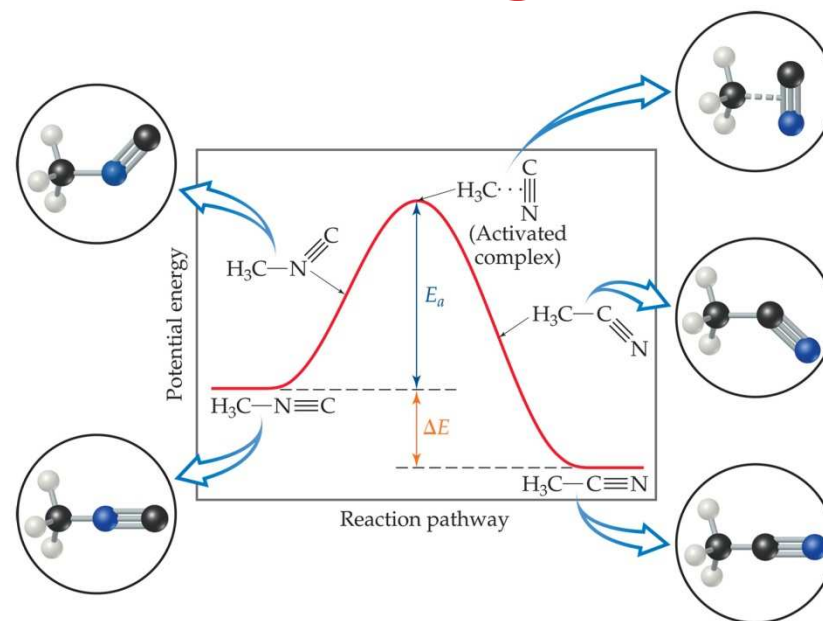
Reaction Coordinate Diagrams

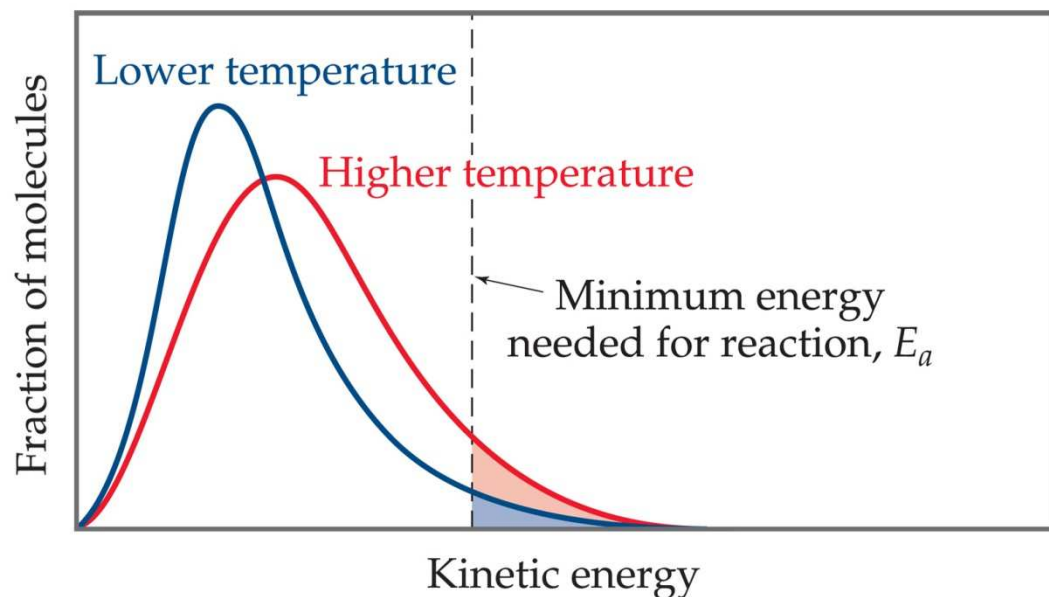
It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.



Reaction Coordinate Diagrams

- It 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.

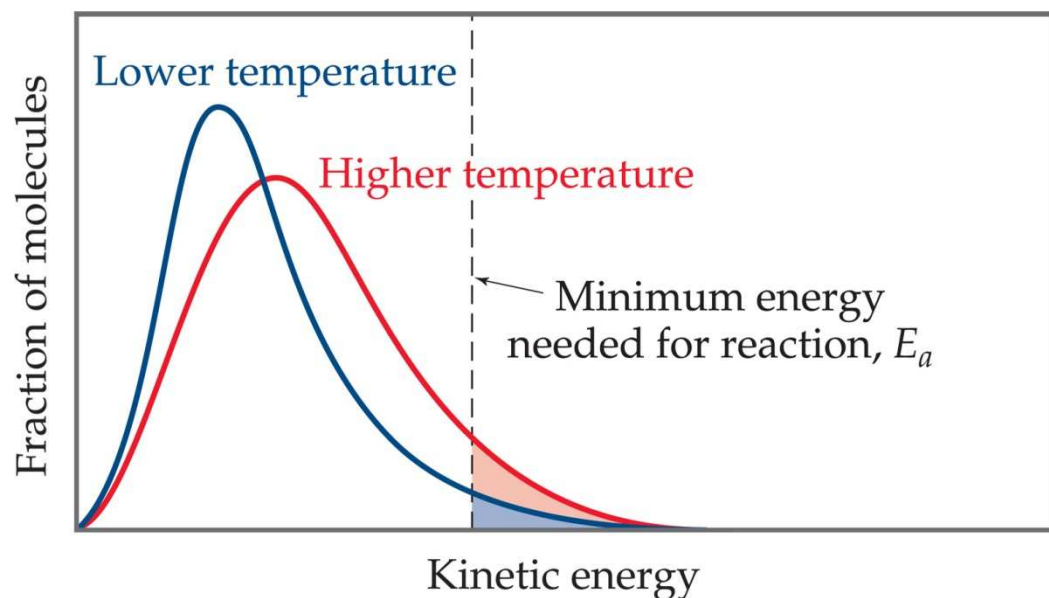




- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.
- At any temperature there is a wide distribution of kinetic energies.



Maxwell–Boltzmann Distributions

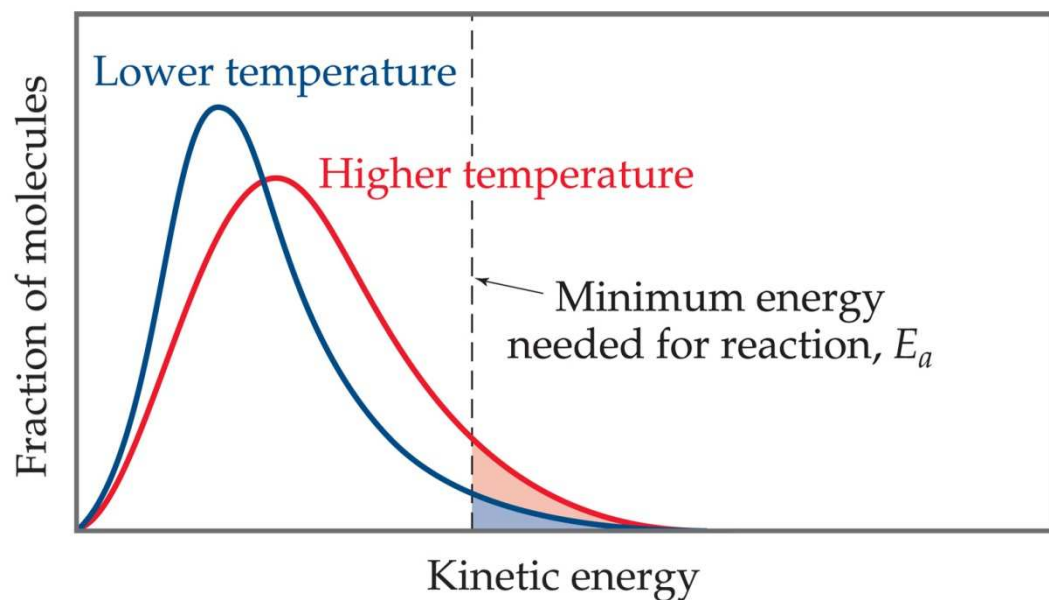


- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.



Maxwell–Boltzmann Distributions

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



- As a result, the reaction rate increases.

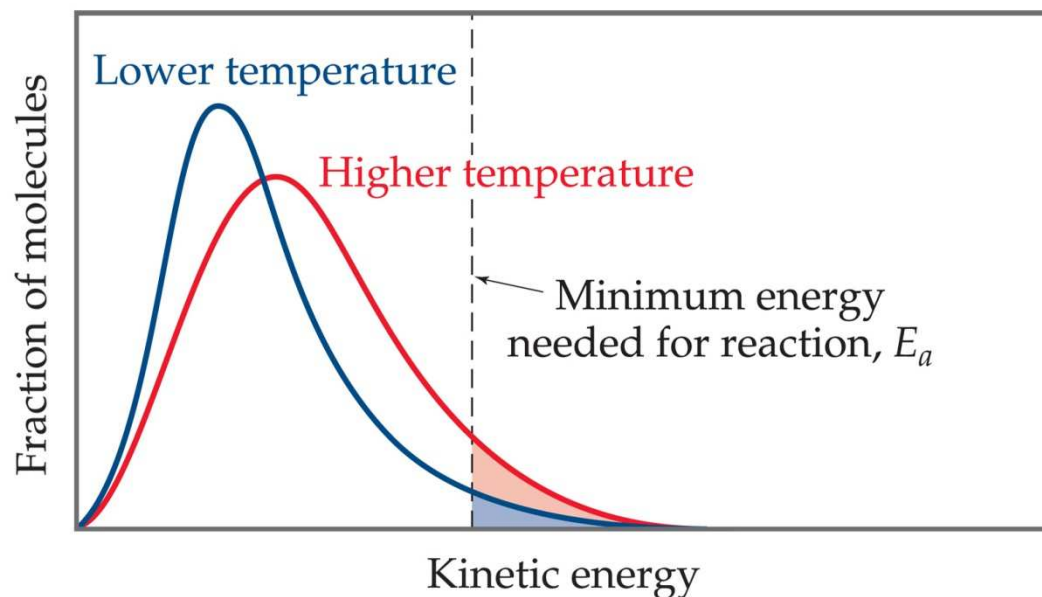


Maxwell–Boltzmann Distributions

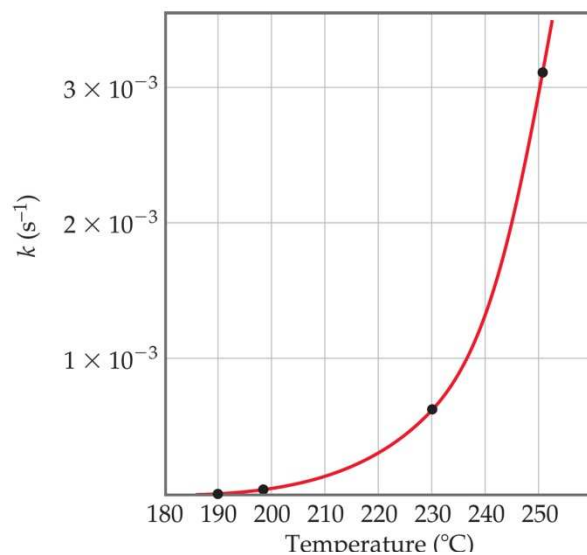
This fraction of molecules can be found through the expression

$$f = e^{-E_a/RT}$$

where R is the gas constant (8.314J/mol-K) and T is the Kelvin temperature. E_a is the minimum energy needed for reaction.



- Arrhenius noted that the increase in reaction rate is not linear with increase in temperature in most reactions.



- Arrhenius observed that most reaction rates depend on the following three factors
 - A. Fraction of molecules possessing E_a or greater
 - B. number of collisions per second
 - C. fraction of molecules having the correct orientation



Arrhenius Equation

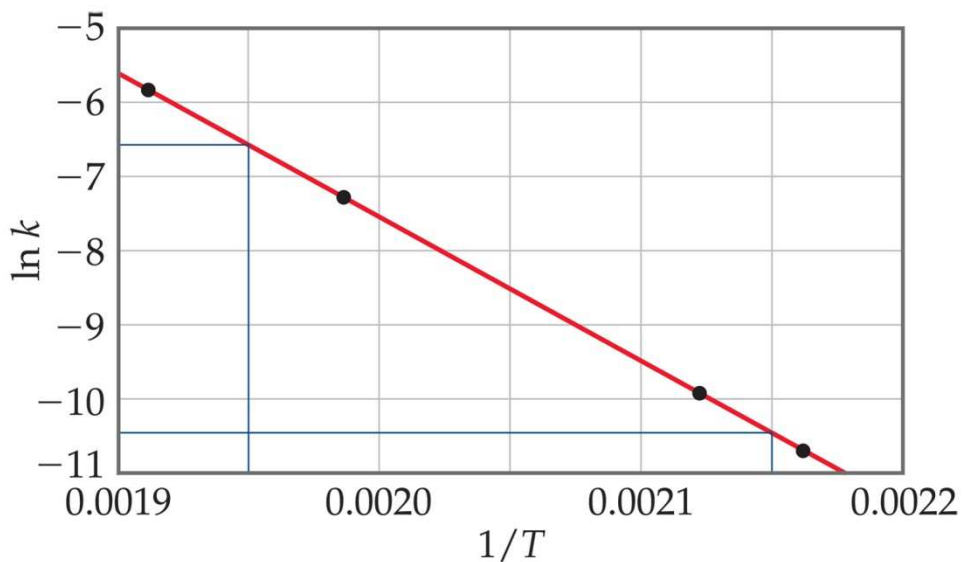
Svante Arrhenius developed a mathematical relationship between k (the rate constant) and E_a :

$$k = A e^{-E_a/RT}$$

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

$$\ln k = -E_a \left(\frac{1}{RT} \right) + \ln A$$
$$y = mx + b$$

Therefore, if k is determined experimentally at several temperatures, and $\ln k$ vs $1/T$ is plotted E_a can be calculated from the slope of the plot.



- If we know the constant k at two or more temperatures
At temperatures T_1 and T_2 the rate constant is k_1 and k_2

$$\ln k_1 = \frac{-E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = \frac{-E_a}{RT_2} + \ln A$$

$$\ln k_1 - \ln k_2 = \left[\frac{-E_a}{RT_1} + \ln A \right] - \left[\frac{-E_a}{RT_2} + \ln A \right]$$

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



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



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.



Rate laws for elementary reactions

- The rate law of an elementary reaction is directly based on its molecularity or concentration.



Reaction Mechanisms

Molecularity	Elementary Reaction	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	Rate = $k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

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

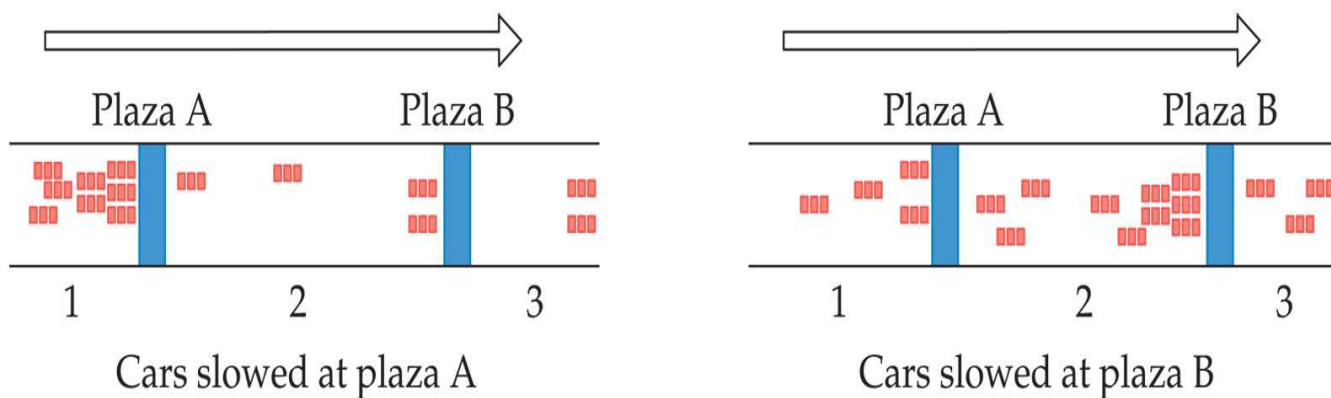


- In a multistep reaction each step will have its own rate constant and activation energy.
- The slowest step determines the overall rate.

Example Relay race



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**.



- A balanced chemical equation often occurs in a series of elementary reactions
- A balanced chemical reaction itself could have a multi step mechanism



Slow Initial Step



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

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

- 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



- 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.
- Since step 1 is the slow rate determining step the rate law is going to be

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



Practice exercise

Ozone reacts with NO_2 to give dinitrogen pentoxide and oxygen:



The reaction occurs in the following two steps:

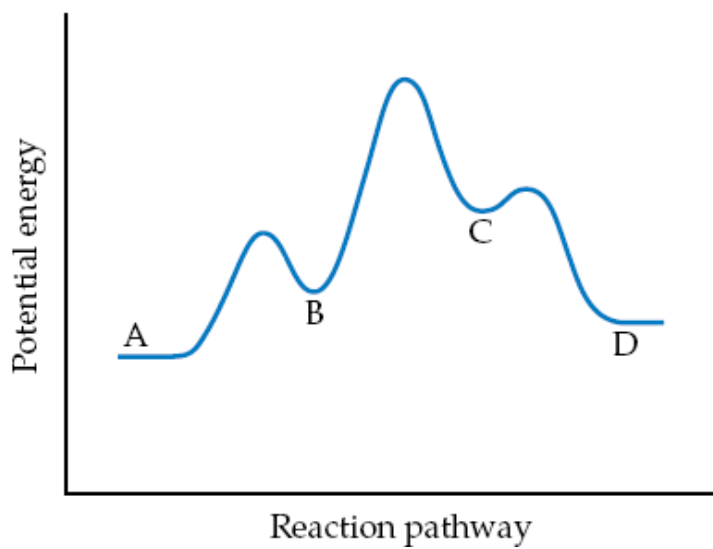


The experimental rate law is

$$\text{Rate} = [\text{O}_3][\text{NO}_2]$$

What can you say about the relative rate of the two steps of the mechanism?

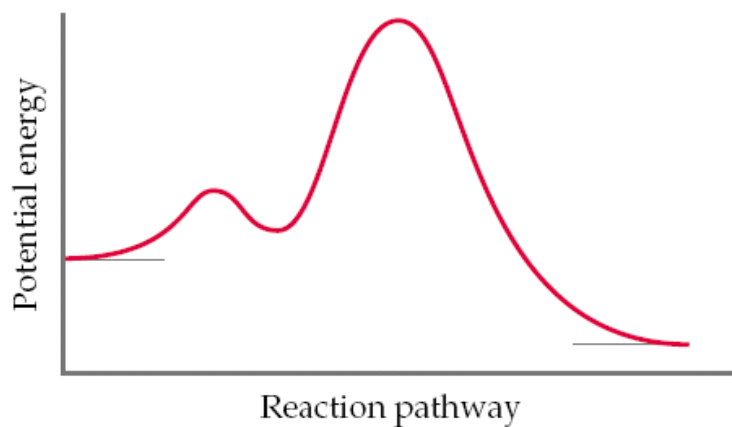




- How many elementary reactions are there in the mechanism?
- How many intermediates?
- Which step is rate limiting?
- Which is the fastest step?
- Exo or endothermic?



Problems



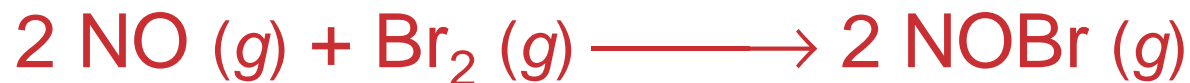
- How many elementary reactions are there in the mechanism?
- How many intermediates?
- Which step is rate limiting?
- Which is the fastest step?
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Figure Number: 14.20.12 (M304)

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Fast Initial Step



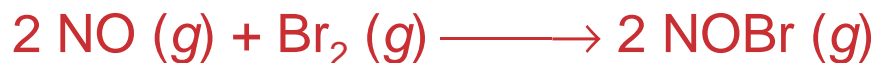
- Experimentally the rate law for this reaction is found to be

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

- Because *ter* molecular processes are rare, this rate law suggests a two-step mechanism.



Fast Initial Step



- A proposed mechanism is



Step 1 includes the forward *and* reverse reactions.

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

$$k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]$$

Pay attention to the fact that the reverse k
is k_{-1}

- Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$



Fast Initial Step

From before Rate = k_2 [NOBr₂] [NO]

From the previous equation:

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$

Substituting this expression for [NOBr₂] in the rate law for the rate-determining step gives

$$\begin{aligned} \text{Rate} &= \frac{k_2 k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] [\text{NO}] \\ &= k [\text{NO}]^2 [\text{Br}_2] \end{aligned}$$

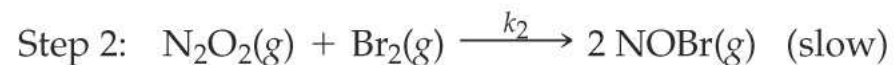
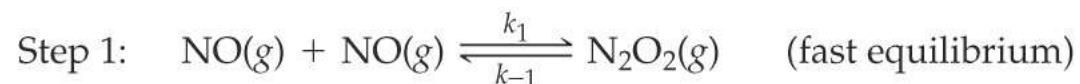


- In general when ever a fast step precedes a slow step we can solve the problem of the concentration of the intermediate step by assuming that an equilibrium is established in the fast step.



SAMPLE EXERCISE 14.15 Deriving the Rate Law for a Mechanism with a Fast Initial Step

Show that the following mechanism for Equation 14.24 also produces a rate law consistent with the experimentally observed one:

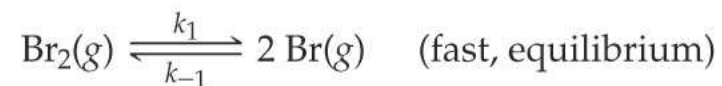


- Write down the rate law for the overall reaction.



PRACTICE EXERCISE

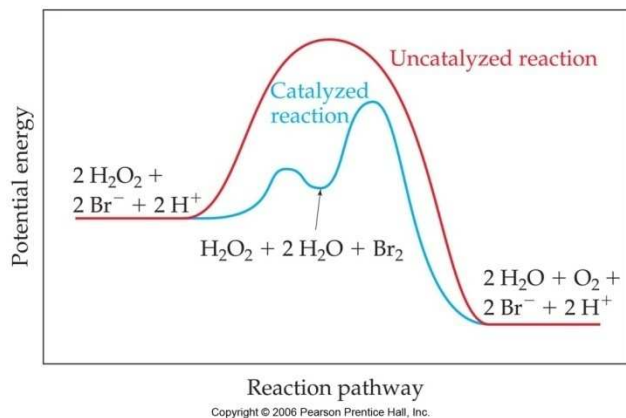
The first step of a mechanism involving the reaction of bromine is



What is the expression relating the concentration of Br (g) to that of Br₂(g)?



Catalysts



Arrhenius equation

- $K = A e^{-E/RT}$

A= frequency factor and

E= Energy of activation

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



- Homogeneous catalysts

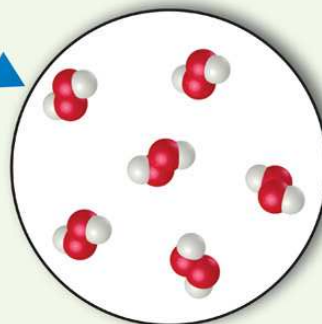


NaBr in an acidic solution acts as a catalyst for this reaction

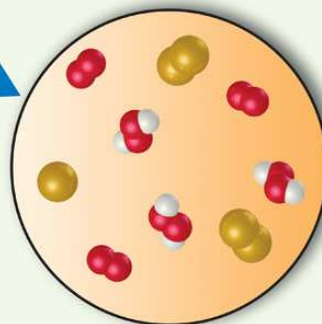


HOMOGENEOUS CATALYSIS

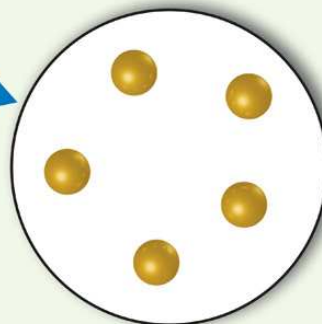
A catalyst that is present in the same phase as the reacting molecules is a homogeneous catalyst.



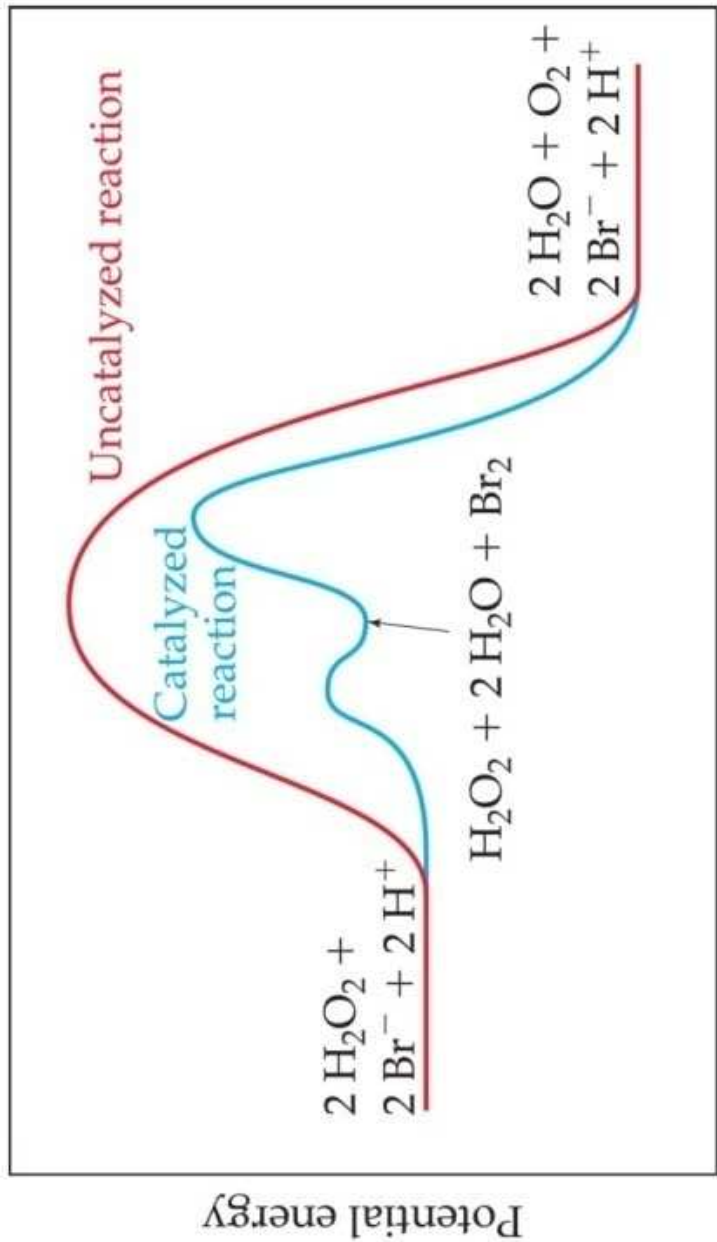
In the absence of a catalyst, $\text{H}_2\text{O}_2(\text{aq})$ decomposes very slowly.



Shortly after the addition of a small amount of $\text{NaBr}(\text{aq})$ to $\text{H}_2\text{O}_2(\text{aq})$, the solution turns brown because Br_2 is generated (Equation 14.30). The buildup of Br_2 leads to rapid evolution of O_2 according to Equation 14.31.



After all of the H_2O_2 has decomposed, a colorless solution of $\text{NaBr}(\text{aq})$ remains. Thus, NaBr has catalyzed the reaction even though it is not consumed during the reaction.



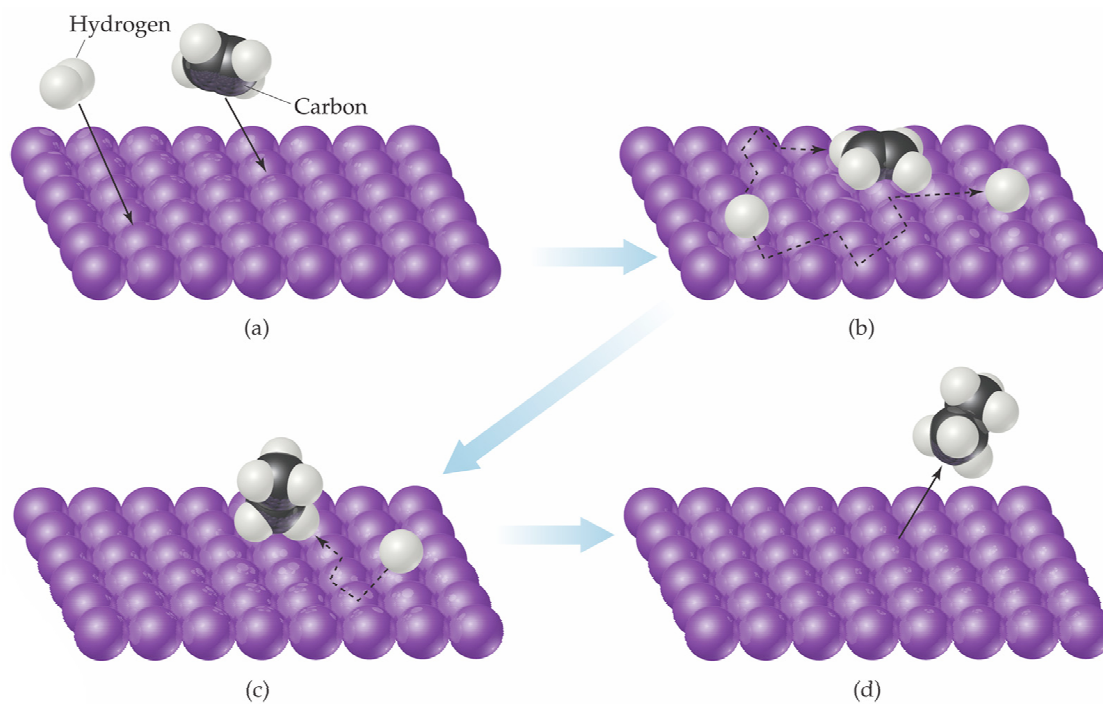
Reaction pathway

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Heterogeneous Catalyst

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

The reactants are adsorbed on the surface of the catalyst.



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.

