

Chapter 14

Chemical Kinetics

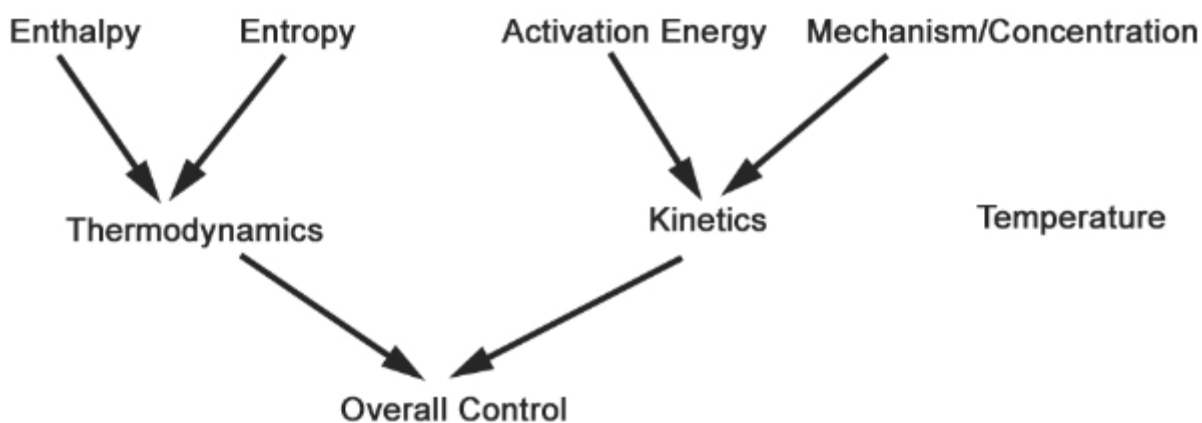
-bv, 2-7-2009

I. Introduction

Gasoline and air in a car engine explode violently, but left untouched, they will not react for years at a time. Meat left out will invite biochemical reactions that, among other things, generate bad smelling gases. If kept at lower temperatures, these reactions take a much longer time to occur. Enzymatic reactions occur slowly at low temperatures and at high temperatures, but rapidly at intermediate temperatures. Why do some occur quickly, while others slowly? Why do some reactions occur at all while others do not? In other words, what controls chemical reactivity?

Chemical reactivity is controlled by two broad factors: thermodynamics and kinetics. Thermodynamics considers the question: which state is more stable, reactants or products. Thermodynamics answers the question: should this reaction occur? Kinetics- the subject of this chapter- considers the question: what controls the rate of a reaction?

Control of Chemical Reactivity



In order for a reaction to occur in a practical sense, it must be both thermodynamically and kinetically favored. These are relative terms: the reaction must be thermodynamically favored *enough* to form the amount of product desired, and it must be kinetically favored *enough* to be complete on the timescale required.

Thermodynamic control of reactions arises from enthalpy, entropy and the temperature. Kinetic control of a reaction arises from the manner in which the reaction takes place- its mechanism, the energy barrier required to be overcome- the activation energy, the concentration of reactants, and again the temperature. In this chapter we analyze:

- how concentration controls reaction rate
- the mathematics connecting concentration, rate and time
- how activation energy controls reaction rate
- how temperature controls reaction rate
- how each of these is related to the reaction's mechanism

II. Collision Theory

Collision theory relates how we think of reactions to the reaction rates we observe. The idea of collision theory, is that molecules are colliding all the time and some fraction- but not all- of those collisions will lead to transformation of the reactants to the products.

1. The molecules must come into contact. This is a collision.
2. They must collide with enough energy to overcome an energy barrier to reaction called the activation energy.
3. They must collide in an orientation that allows the necessary bond-breaking and forming needed to transform the reactants to the products.

Relationships to reaction rate:

1. Collisions: This is simple. If some fraction of collisions will lead to creation of products, then the more collisions per second, the faster the reaction will proceed. This collision requirement does have a large effect on what media are chosen to perform chemical reactions. Solids tend to be very slow reactors because only the atoms on the surface can have collisions with other atoms on other molecules. Ever notice how slow iron rusts? Most reactions are done either in solution or in the gas phase where freedom of movement of the reactant molecules allows them to easily come into contact.

Conclusion: The more collisions, the faster the reaction.

2. Overcoming the Activation Barrier: Any sample of reactants will have a Boltzmann distribution of molecular energies. Some molecules will have high energy; some low; many intermediate. Only those with energies greater than the activation energy will be able to react. Figure 15.1a shows Boltzmann plots for a set of reactants at two different temperatures. Only those reactants with energy greater than (to the right of, in the plot) the activation energy will be able to react. Because a greater fraction of molecules in the high temperature sample exceed the activation energy, the high-temperature sample will have effective collisions and will experience a faster reaction rate.

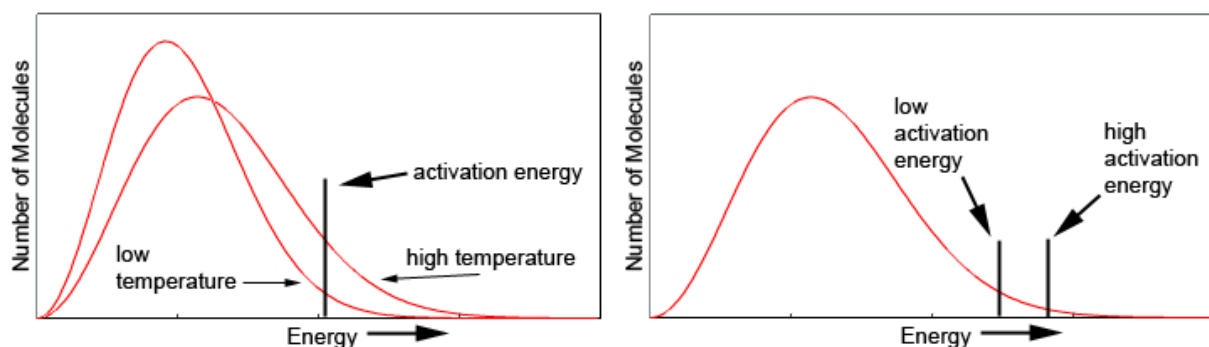


Figure 15.1 a: Boltzmann distributions of molecular energies at different temperatures show that more molecules exceed the activation energy at higher temperature. b: At a given temperature, more molecules exceed a lower activation energy than a high one.

Figure 15.1 b shows a Boltzmann distribution of molecular energies for a single sample, but shows two different activation energies. A greater fraction of the sample molecules exceed the energy of the lower activation energy than do the higher activation energy. Therefore, those reactant molecules will undergo the reaction with the lower activation barrier more rapidly than would with the higher activation barrier.

Conclusion: The higher the temperature and the lower the activation energy, the faster the reaction.

3. Collision Orientation: Consider the reaction where a chloride ion bonds to an electron deficient C atom in the unstable $\text{C}(\text{CH}_3)_3^+$ carbocation. The reaction in terms of Lewis structures is shown in Figure 15.2a.

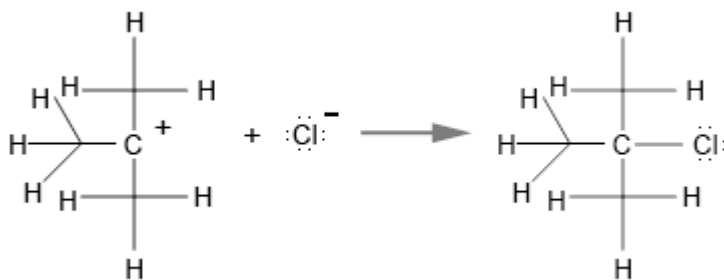


Figure 15.2 a

The reaction is more clear when viewed using 3-dimensional molecular models. These are shown in Figure 15.2b and c. In (a) the Cl^- ion approaches the $\text{C}(\text{CH}_3)_3^+$ ion from the open side, so the Cl^- lone pair of electrons can reach the open site on the central C atom and form the bond to make the product.

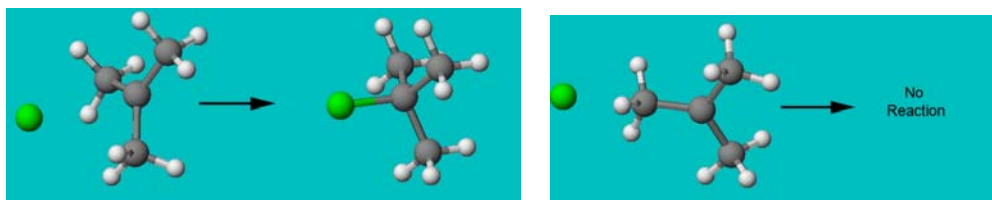


Figure 15.2 b and c

In (c) the Cl^- ion approaches from the end and is blocked by one of the CH_3 groups. It collides, but not in the right place. So, no reaction. In this reaction many of the collisions will be in the proper “orientation” but many will not. Orientation effects slow the reaction, but not by much. Some reactions involve very large molecules with very specific reaction sites, and in these a low fraction of collisions occurring lead to products.

Conclusion: The more specific a reaction site, the slower the reaction.

II. Expressing Reaction Rate

How fast is a reaction? We know it when we see it, but how is it expressed quantitatively? We do this by writing a ratio of change in concentration over change in time. Consider Figure 15.3, which shows the changes in concentration over a period of 8 seconds for a reaction, $\text{A} \rightarrow 2\text{B}$. Reactant A starts at a concentration of 0.50 M and drops to 0 M over 8 seconds. Product B starts at 0 M and increases to 1.0 M over 8 seconds. There are three common ways we measure rate.

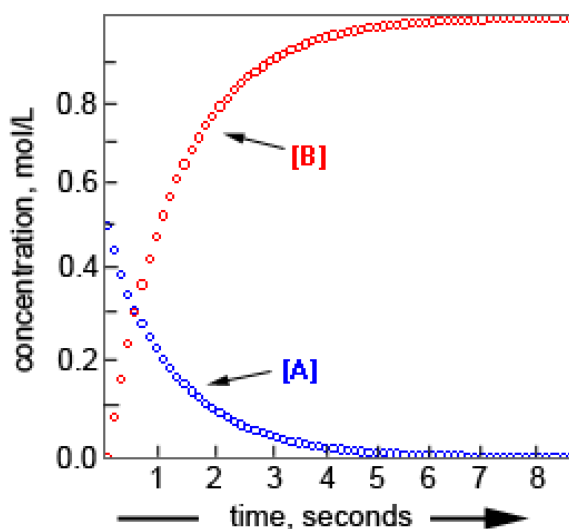
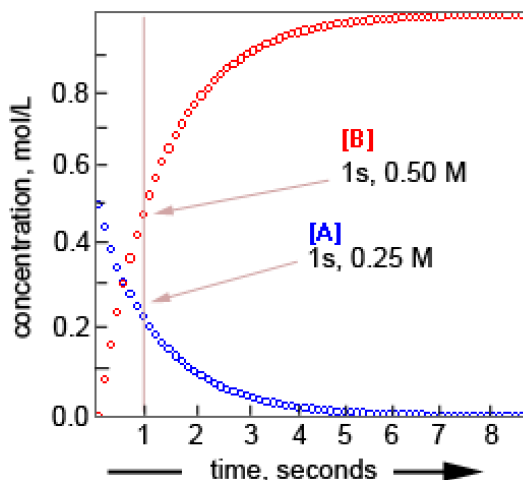


Figure 15.3 Concentration-Time plots during the course of the reaction of $\text{A} \rightarrow 2\text{B}$

Average Rate Over Time

One way we could express the rate is the change in concentration over the period of 8 seconds. The rate of production of B would be $1.00\text{ M}/8\text{ s}$, or 0.125 M/s . This is not particularly useful because the reaction was already done. Better is to look at the rate of the reaction while it is occurring. If we look at the plot in more detail, we see that the change in concentration in the first second, is:



In the first second, the concentration of B changes from 0 M to 0.50 M. The rate of change is therefore,

$$\frac{\Delta[B]}{\Delta t} = \frac{(0.50\text{M} - 0.0\text{M})}{1.0\text{s} - 0.0\text{s}} = 0.50\text{M} / \text{s}$$

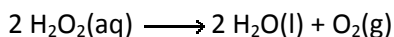
Likewise, in the first second, the concentration of A changes from 0.50 M to 0.25 M. The rate of change of A is therefore,

$$\frac{\Delta[A]}{\Delta t} = \frac{-(0.25\text{M} - 0.50\text{M})}{1.0\text{s} - 0.0\text{s}} = 0.25\text{M} / \text{s}$$

Why the negative sign? Rates are always considered to be positive. When expressing a rate in terms of a reactants (for which the concentration decreases) we change the sign to make sure the rate comes out positive. **Rule:** Rates expressed for products don't use the negative sign; those for reactants do.

Example 1.

For the decomposition of hydrogen peroxide in dilute sodium hydroxide at 20 °C



the following data have been obtained:

Time, minutes	[H ₂ O ₂], mol/L
0	9.12 x 10 ⁻²
434	5.66 x 10 ⁻²
868	3.51 x 10 ⁻²
1302	2.18 x 10 ⁻²

What is the average rate of disappearance of H₂O₂ over the time period from 0 min to 434 min?

Solution:

The rate over time is given by the change in concentration over the change in time. For a reactant, we add a minus sign to make sure the rate comes out as a positive value.

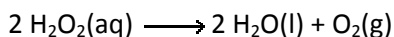
$$\text{Rate} = \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta\text{time}} = \frac{-(5.66 \times 10^{-2} \text{ M} - 9.12 \times 10^{-2})}{434 \text{ min} - 0 \text{ min}} = 7.97 \times 10^{-5} \text{ M / min}$$

We can relate the rates of change of A and B using the reaction equation. Because 2 mol of B are produced for each mol of A reacting, the change in concentrations of A and B are related by a factor of -2.

$$\frac{\Delta[B]}{\Delta t} = 2 \times \frac{-\Delta[A]}{\Delta t}$$

Example 2.

For the decomposition of hydrogen peroxide in dilute sodium hydroxide at 20 °C



the average rate of disappearance of H_2O_2 over the time period from $t = 0$ to $t = 516$ min is found to be $8.08 \times 10^{-5} \text{ M/min}$. What is the rate of appearance of O_2 over the same time period?

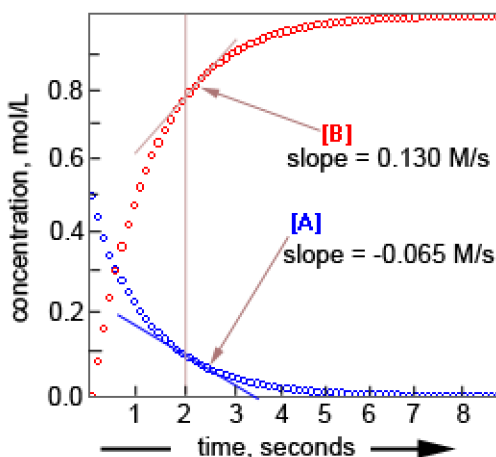
Solution:

The reaction equation shows that for every two moles of H_2O_2 that react, one mole of O_2 is formed. Therefore the rate of formation of O_2 is half the rate of H_2O_2 consumption.

$$\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \times \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \times \frac{8.08 \times 10^{-5} \text{ M}}{\text{min}} = 4.04 \times 10^{-5} \text{ M / min}$$

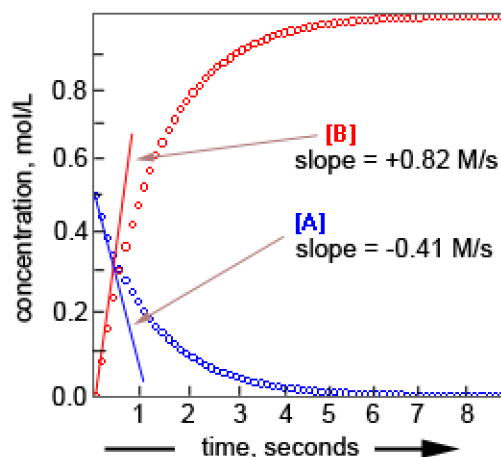
Instantaneous Rate

We are often interested in how fast a reaction is going, *right now*. This is called the instantaneous rate and is equal to the slope of the concentration-time curve. If draw tangents on the curve at the 2-second point and measure their slopes, we see that the instantaneous rate at 2 seconds is $+0.130 \text{ M/s}$ for the production of B and -0.065 M/s for consumption of A.



Initial Rate

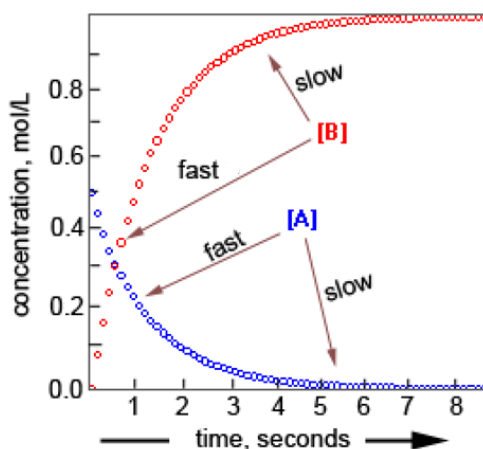
The initial rate is the instantaneous rate right when the reaction starts. This is of interest experimentally because it is the easiest time for us to know the exact concentrations of the different species in solution. After the reaction goes awhile, we need to make instantaneous measurements to know what the concentrations are. Sometimes that's easy, but sometimes not. But the concentrations at the start of the reaction are always easy to know. You made the solutions, after all.



The instantaneous rate is the slope of the concentration-time curve at the time = 0 point. Again, though, we see that the rate of production of B is twice the rate of consumption of A.

A Final Point

You can use a concentration-time curve to say a lot about a reaction. We've already noted that the concentration-time curve identifies A as a reactant because it decreases in concentration over time, and B as a product because it increases. We can also see that 2 mol of B are formed for each mol of A that reacts because B goes up twice as much as A goes down.

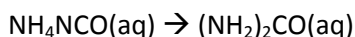


But we can also see in this plot that the reaction slows down as it proceeds. Not all reactions do. What this tells us is that the reaction rate depends on the concentration of A available to react. Notice that when [A] is large, the slope of the curve is steep. The reaction is fast when [A] is large. Later in the reaction, [A] is much smaller, and so is the slope. The reaction slows down as A is used up. There is a concentration dependence of rate on concentration. Which, not coincidentally, is the subject of the next section.

III. Concentration Effects

The frequency of collisions was the first consideration we examined when thinking about what controls reaction rates. The more collisions, the faster the rate should be. And that's generally but not always true. There are two ways to increase the frequency of collisions between molecules: crowd more of them together in a space or make them move faster. Moving faster is accomplished by raising the temperature, and we'll deal with that later. As for crowding more molecules together, we're talking about concentration. The greater the concentration of a compound, the more molecules will be present in the same volume, and the more collisions will occur. This is why crowded dance floors are popular, and empty ones are not. In addition to that being true by definition, of course.

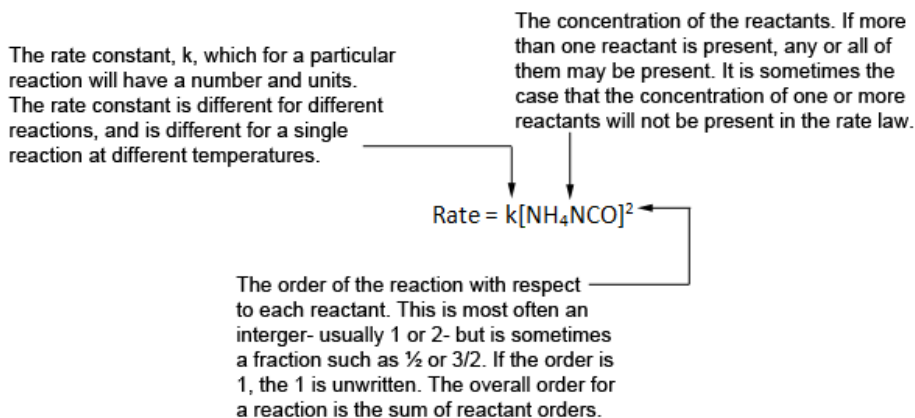
The dependence of a rate on the concentration of the reactants is expressed in a rate law (or sometimes called a rate equation). Consider the decomposition reaction of NH_4NCO .



The rate law for the reaction is

$$\text{Rate} = k[\text{NH}_4\text{NCO}]^2$$

The rate law has three parts:



What does this mean, anyway? Well, for this reaction, it means that the rate of the reaction is proportional to the square of the concentration of the reactant. You might think that if you double the reactant concentration, the rate would double. In this reaction, not true. It will quadruple.

More examples:

Reaction(all gas phase)	Rate Law	Overall Order
$2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$	$\text{Rate} = k[\text{N}_2\text{O}_5]$	first order
$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$	$\text{Rate} = k[\text{NO}_2]^2$	second order in NO_2 , zero order in CO , second order overall
$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$	$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$	second order in NO , first order in O_2 , third order overall

A couple things to notice in the examples above:

1. The rate laws are not derived from the reaction equations. Sometimes they match. Sometimes they do not.
2. Although the rate constant is really a number with units, when describing a general rate law, we usually just write "k." This is because the rate law is true at all temperatures, but any numerical k value is true only at one temperature. We indicate a number when we want to use the rate law in calculations.

Annoying Box About the Units of k

Assuming time is measured in seconds, the rate of a reaction is always expressed in terms of M/s. What are the units of k? Well, it depends on the reaction order.

Zero Order

If the reaction is zero order, the rate law is,

$$\text{Rate} = k$$

The units of k must be the same as that of rate, M/s.

First Order

In a first order reaction, the rate law is,

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

In terms of units, this is $\frac{M}{s} = k \times M$. The units of k must be 1/s, or s^{-1} .

Second Order

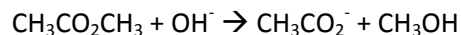
In a second order reaction, the rate law is,

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

In terms of units, this is $\frac{M}{s} = k \times M^2$. The units of k must be 1/Ms, or $M^{-1}s^{-1}$.

Example 3:

Methyl acetate reacts with hydroxide ion according to the following equation,



with the rate law,

$$\text{Rate} = k[\text{CH}_3\text{CO}_2\text{CH}_3][\text{OH}^-]$$

What is the order of reaction for each reactant, and the overall reaction order?

Solution:

Because there are no superscripts to the right of each concentration in the rate law, it means they are each first order. The reaction is first order in $\text{CH}_3\text{CO}_2\text{CH}_3$ and first order in OH^- . It is second order overall, because $1 + 1$ does equal 2.

Determining Rate Laws Using the Method of Initial Rates

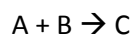
Rate laws are not derived from the reaction equation. No matter how many times we say, people keep thinking it's true. But it's not.

Rate laws are derived from experimental data. There are two methods: the method of initial rates, and the graphical method. Here we cover the method of initial rates in which a reaction is run multiple times with different initial concentrations of each reactant. The initial rates of each experiment are compared to the initial concentrations of the reactants to determine the order of each. The method is most often performed in the following way:

1. For each reactant, run a pair of reactions in which that reactant's concentration is doubled while all other reactant concentrations are held constant. This isolates the effect on rate to that single reactant.
2. Most often one of three things happens to the initial rate when the reactant concentration is doubled:
 - a. The rate does not change: this means the rate is independent of that reactant. The reaction is zero order with respect to that reactant.
 - b. The rate doubles: this means the rate is proportional to the concentration of that reactant. The reaction is first order with respect to that reactant.
 - a. The rate quadruples: this means the rate is proportional to the square of the concentration of that reactant. The reaction is second order with respect to that reactant.
3. Once the order for each reactant is found, take any of the experiments and plug in concentration values and the measured rate to determine the numerical value of k .

Example 4.

A reaction is performed between two reactant, A and B,



The following data was obtained for the initial rate of the reaction in four separate experiments.

TABLE			
	[A], mol/L	[B], mol/L	rate, mol/L-min
Trial 1	0.573	0.252	0.0204
Trial 2	1.146	0.252	0.0817
Trial 3	0.573	0.504	0.0409
Trial 4	0.761	0.630	0.0901

What is the rate law for the reaction, and what is the numerical value of k?

Solution:

The idea is to identify two trials for which one reactant concentration is doubled and the other is held constant.

For A, the pair to use is Trial 1 and Trial 2. Notice the [B] is constant at 0.252 M. When [A] is doubled, the rate increases from 0.0204 M/min to 0.0817 M/min. This is an increase of 4 times. The reaction rate quadruples, so we know that the reaction is second order in A.

For B, the pair of trials to use is Trial 1 and Trial 3. [A] is held constant at 0.573 M while [B] is doubled. When [B] is doubled, the rate increases from 0.0204 M/min to 0.0409 M/min. The rate doubles when [B] is doubled, so the reaction is first order in B.

The rate law is then, $\text{Rate} = k[A]^2[B]$

Finally, we find the value of k by choosing any of the trials, inserting the values for rate, [A], and [B], and solving for k. Choosing Trial 4 (for no particular reason), we see,

$$0.0901 \text{ M/min} = k[0.761 \text{ M}]^2[0.630]$$

$$k = \frac{0.0901 \text{ M} / \text{min}}{[0.761]^2 [0.630]} = 0.247 \text{ M}^{-2} \text{ min}^{-1}$$

Concentration-Time Relationships for Single Reactant Reactions

For reactions that involve a single reactant, we have derived mathematical equations that relate the concentration at any time during the course of the reaction to the initial concentration and the rate constant. These are called integrated rate equations because, perhaps without surprise, they are derived by integration of the rate equation. Because the rate equations depend on the reaction order, so do the integrated rate equations. Table 13.1 shows the three equations in two forms. The first is the regular equation. The second is a version in the form of a straight line equation. We'll use that later to make straight line plots, which are always useful in science. In each case, $[A]_o$ represents the concentration of A before the reaction starts. $[A]_t$ represents the concentration of A after time t passes. Two algebraic versions are given for the first order case, because both are useful.

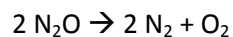
Equation/Order	Zero Order	First Order	Second Order
Rate Law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Equation	$[A]_o - [A]_t = kt$	$\ln \frac{[A]_t}{[A]_o} = -kt$ $[A]_t = [A]_o e^{-kt}$	$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$
Linear Form	$[A]_t = -kt + [A]_o$ $y = mx + b$	$\ln [A]_t = -kt + \ln [A]_o$ $y = mx + b$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$ $y = mx + b$
Straight Line Plot	$y = [A]$ $x = \text{time}$ slope = $-k$	$y = \ln[A]$ $x = \text{time}$ slope = $-k$	$y = 1/[A]$ $x = \text{time}$ slope = k

These equations are generally useful in three ways:

1. To predict the concentration at some future time, given t , k and $[A]_o$.
2. Determine the time required for $[A]_o$ to decrease to $[A]_t$.
3. To determine the rate constant, k , given $[A]_o$ and $[A]_t$ at time t .

Example 5.

The decomposition of nitrous oxide at 565 °C



is second order in N_2O with a rate constant of $1.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. If the reaction is initiated with $[\text{N}_2\text{O}]$ equal to 0.108 M, what will its concentration be after 1250 s have elapsed?

Solution

Because the reaction is first order, we use the first order integrated rate equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

We know $[\text{N}_2\text{O}]_o$, k , and t . We solve for $[\text{N}_2\text{O}]_t$.

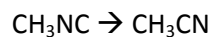
$$\frac{1}{[\text{N}_2\text{O}]_t} - \frac{1}{0.108\text{M}} = (1.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}) 1250 \text{ s}$$

$$\frac{1}{[\text{N}_2\text{O}]_t} = 9.26 \text{ M}^{-1} + 1.38 \text{ M}^{-1}$$

$$[\text{N}_2\text{O}]_t = 0.940 \text{ M}$$

Example 6. Finding the time required for $[A]_o$ to Decrease to $[A]_t$

The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250 °C



is first order with a rate constant of $3.00 \times 10^{-3} \text{ s}^{-1}$. If the initial concentration of CH_3NC is 0.107 M, how much time must pass for the concentration of CH_3NC to drop to 0.0142 M?

Solution

Because the reaction is first order, we use the first order integrated rate equation. The version better suited to finding time (or k , for that matter) is,

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

We know $[\text{CH}_3\text{NC}]_t$, $[\text{CH}_3\text{NC}]_o$, and k . We solve for t .

$$\begin{aligned}\ln \frac{[\text{CH}_3\text{NC}]_t}{[\text{CH}_3\text{NC}]_o} &= \ln \frac{0.0142 \text{ M}}{0.107 \text{ M}} = -3.00 \times 10^{-3} \text{ s}^{-1} t \\ -2.02 &= -3.00 \times 10^{-3} \text{ s}^{-1} t \\ t &= \frac{-2.02}{-3.00 \times 10^{-3} \text{ s}^{-1}} = 673 \text{ s}\end{aligned}$$

Example 7. Determining the Value of k

The gas phase decomposition of dinitrogen pentoxide at 335 K



is first order in N_2O_5 . During one experiment it was found that an initial concentration of 0.249 M dropped to 0.0496 M in 230 s. What is the value of the rate constant, k, in s^{-1} ?

Solution:

Because the reaction is first order, we use the first order integrated rate equation. The version better suited to finding k is,

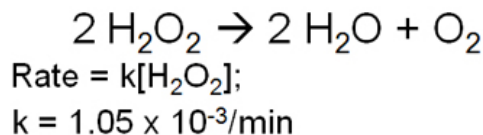
$$\ln \frac{[\text{A}]_t}{[\text{A}]_o} = -kt$$

We know $[\text{N}_2\text{O}_5]_t$, $[\text{N}_2\text{O}_5]_o$, and t. We solve for k.

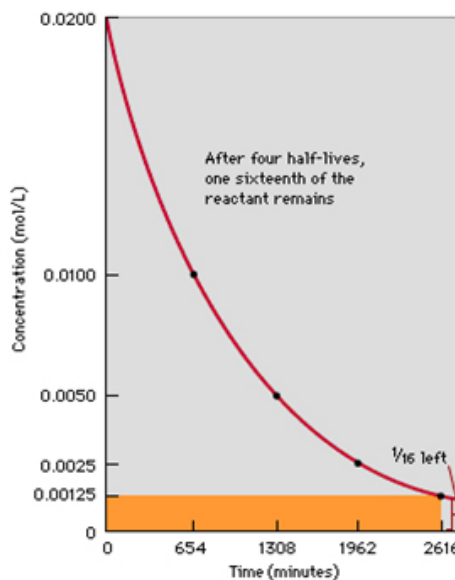
$$\begin{aligned}\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_o} &= \ln \frac{0.0496 \text{ M}}{0.249 \text{ M}} = -k \text{ s}^{-1} 230 \text{ s} \\ -1.61 &= -k \text{ s}^{-1} 230 \text{ s} \\ k &= \frac{-1.61}{-230 \text{ s}} = 7.02 \times 10^{-3} \text{ s}^{-1}\end{aligned}$$

Half-Life and Radioactive Dating

The concept of half-life is useful for describing the rough speed of a reaction. The half-life of a reaction is the time it takes for $\frac{1}{2}$ of the reactants to turn into products. Consider the first order decomposition of hydrogen peroxide. The table below shows the concentration of H_2O_2 in increments of 654 min. The data are plotted as well.



Time (min)	Number Half-lives	Fraction remaining	$[\text{H}_2\text{O}_2]$, M
0	0	1	0.020
654	1	$\frac{1}{2}$	0.010
1308	2	$\frac{1}{4}$	0.0050
1962	3	$\frac{1}{8}$	0.0025
2616	4	$\frac{1}{16}$	0.0013

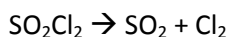


Notice that in the first 654 min, the concentration drops from 0.020 M to 0.010 M. That is, it drops in half. The half-life of the reaction is therefore 654 min. Then, when another 654 min passes (from $t = 654$ to $t = 1308$) the concentration drops in half again: from 0.010 M to 0.0050 M. The half-life is still 654 min. Successive half-lives cut the original concentration to fractions of,

# half-lives	1	2	3	4	5	6
fraction remaining	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$

Example 8.

The following data are for the decomposition of sulfuryl chloride at 383 oC.



time, min	0	166	332
$[\text{SO}_2\text{Cl}_2]$, M	5.18×10^{-3}	2.59×10^{-3}	1.30×10^{-3}

What is the half-life of the reaction starting at time 0 min, and at time 166 min?

Solution:

The concentration drops in half from to 2.59×10^{-3} over the first 166 min of reaction. Therefore the half-life starting at $t = 0$ min is 166 min (by definition).

Starting at 166 minutes, the concentration drops from 2.59×10^{-3} to 1.30×10^{-3} of 166 min (from 166 min to 332 min). This is again dropping in half over that same time period. The half-life remains 166 min.

Mathematical Relationships for Half-Life and k

For any first order reaction, the half-life can be related to the rate constant in the following way:

At the half-life, the concentration for reactant A is $\frac{1}{2}$ of what it was at the start of the reaction. So,

$$\ln \frac{[A]_t}{[A]_0} = \ln \frac{\frac{1}{2}[A]_0}{[A]_0}$$

$$\ln \frac{1}{2} = -kt$$

Therefore,

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

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

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

Radioactive Decay

All radioactive isotopes decay via first order reactions. For these cases we write the rate law and time-based equations in terms of numbers of atoms or amount present instead of concentration, where the letter N is used to denote how much of the radioactive isotope is present at any particular time.

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

$$[N]_t = [N]_0 e^{-kt}$$

Example 9.

The isotope ^{32}P has a half-life of 14.3 days. If a sample contains 0.884 g of ^{32}P , what mass of ^{32}P will remain after 22 days?

Solution:

The path for this problem is to use the half-life to determine the rate constant k. Then use the first order concentration-time equation to determine the final amount.

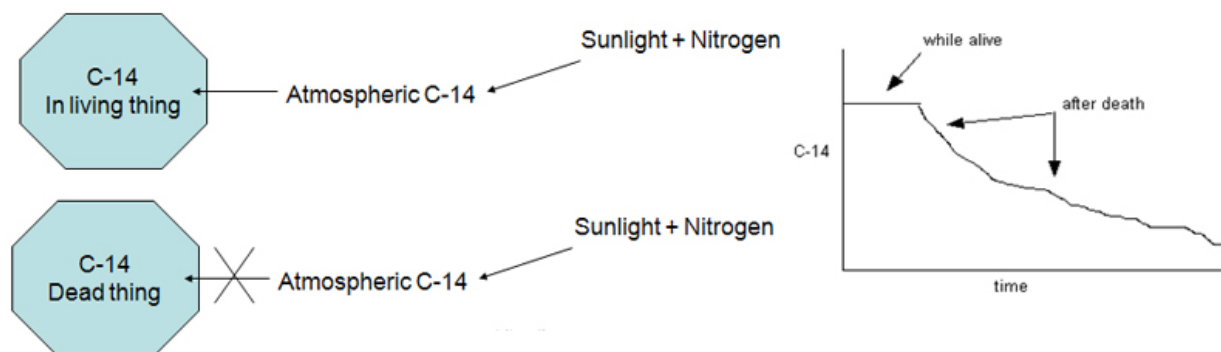
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ days}} = 0.0485 \text{ days}^{-1}$$

$$N_t = N_0 e^{-kt} = 0.884 \text{ g} e^{-(0.0485 \text{ days}^{-1})(22 \text{ days})} = 0.304 \text{ g}$$

Radioactive Carbon Dating

Carbon exists as mostly ^{12}C , with about 1% of ^{13}C , and a very small fraction of radioactive ^{14}C . It is formed in the upper atmosphere by reaction of ^{14}N with high energy solar radiation. Because it is constantly decaying and being reformed in the upper atmosphere, there is a relatively constant concentration of ^{14}C present as CO_2 in the atmosphere. That CO_2 , like all CO_2 , can be sequestered by photosynthesis to form plants. Those plants live their plant-like life, sometimes being eaten by animals, sometimes just dying. As a plant or animal lives it keeps exchanging C with the atmosphere, and the fraction of ^{14}C in the plant or animal stays equal to that in the atmosphere.

Once the thing dies, however, its C content is “locked” and it no longer receives new ^{14}C . Because the ^{14}C is radioactive, the fraction of it present in the dead thing starts to decrease. If we compare the fraction present today with the fraction we presume to be the steady state ^{14}C amount, we can estimate the time since death. This is shown in Figure 14.5.



The actual experiment involves measuring the ^{14}C radioactivity from a sample. It is generally reported in units of counts per minute per gram of C. The half-life of ^{14}C is 5730 years, and this technique is good for dating items as old as 50,000 years.

Example 10.

A wooden bowl is found in a cave in France is found to have a ^{14}C radioactivity of 10.2 counts per minute per gram of carbon. Living wood has an activity of 13.6 counts per minute per gram of carbon. How long ago did the tree die?

Solution.

To make this calculation, we make the assumption that the fraction of ^{14}C in the atmosphere has been constant over time. Therefore, the activity at $t = 0$ is assumed to have been 13.6 counts/min·g. Because the radioactivity of a sample is directly proportional to the amount of radioisotope present, the ratio of ^{14}C present now and then is equal to the ratio of radioactivity now and then. So,

$$\ln \frac{N_t}{N_o} = -kt$$

$$k = \frac{0.693}{5730\text{y}} = -1.21 \times 10^{-4} \text{y}^{-1}$$

$$\ln \frac{10.2}{13.6} = -1.21 \times 10^{-4} \text{y}^{-1} t$$

$$-0.288 = -1.21 \times 10^{-4} \text{y}^{-1} t$$

$$t = 2380\text{y}$$

Determining the Rate Law: The Graphical Method

Concentration-time plots can be used to determine the rate law for single-reactant reactions. The linear forms of the concentration-time equations for zero, first, and second order reactions predict different forms of equations that will yield a linear plot.

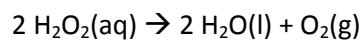
Equation/Order	Zero Order	First Order	Second Order
Linear Form	$[A]_t = -kt + [A]_o$ $y = mx + b$	$\ln [A]_t = -kt + \ln [A]_o$ $y = mx + b$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$ $y = mx + b$
Straight Line Plot	$y = [A]$ $x = \text{time}$ $\text{slope} = -k$	$y = \ln [A]$ $x = \text{time}$ $\text{slope} = -k$	$y = 1/[A]$ $x = \text{time}$ $\text{slope} = k$

The graphical method for determining rate laws involves these steps:

1. Collect concentration-time data while the reaction proceeds.
2. Make three plots: $[A]$ vs. t , $\ln[A]$ vs. t , and $1/[A]$ vs. t .
3. Determine the reaction order:
 - if $[A]$ vs. t is linear, the reaction is zero order
 - if $\ln[A]$ vs. t is linear, the reaction is first order
 - if $1/[A]$ vs. t is linear, the reaction is second order
4. The slope of the plot that gives a straight line is the rate constant for the reaction.

Example 11.

Concentration vs. time data is collected for the decomposition of H₂O₂.



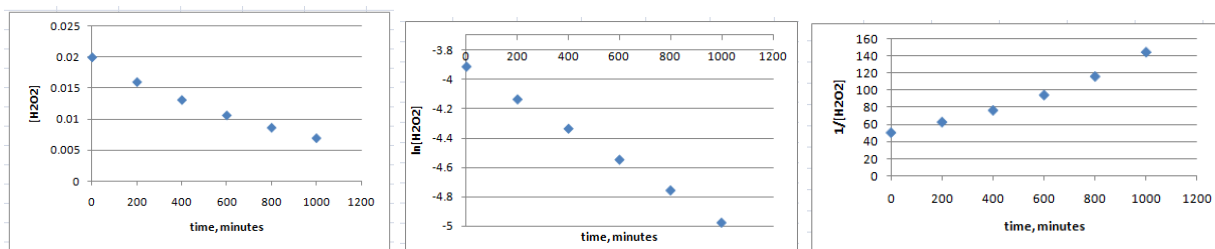
Use these data to determine the rate law, and the numerical value of the rate constant.

Solution

The first step is to enter the data into a graphing program such as Excel and use the calculation functions to create columns for $\ln[\text{H}_2\text{O}_2]$ and $1/[\text{H}_2\text{O}_2]$.

	A	B	C	D
1	time	[H ₂ O ₂]	ln[H ₂ O ₂]	1/[H ₂ O ₂]
2	0	0.02	-3.91202	50
3	200	0.016	-4.13517	62.5
4	400	0.0131	-4.33514	76.33588
5	600	0.0106	-4.5469	94.33962
6	800	0.0086	-4.75599	116.2791
7	1000	0.0069	-4.97623	144.9275

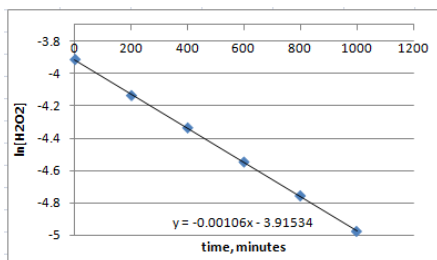
Next, create three plots: $[\text{H}_2\text{O}_2]$ vs. t , $\ln[\text{H}_2\text{O}_2]$ vs. t , and $1/[\text{H}_2\text{O}_2]$ vs. t .



The $\ln[\text{H}_2\text{O}_2]$ plot gives a straight line. This means that the reaction is first order and the rate law is,

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

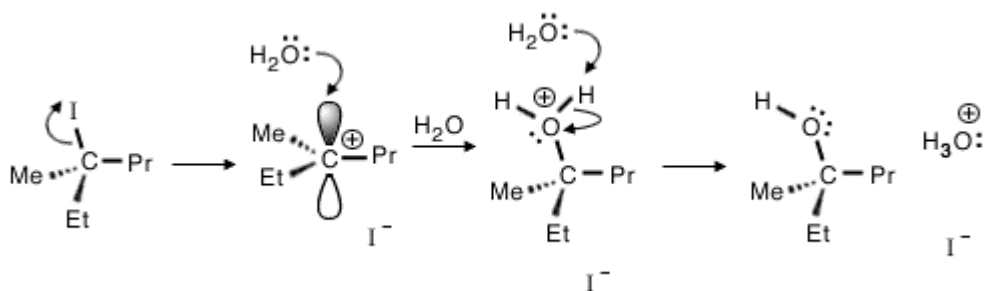
Finally, the numerical value of the rate constant is the absolute value of the slope of the straight line plot. The slope can be found in Excel by right-clicking on one of the data points, and choosing Add Trendline/Linear/Display Equation on Chart.



In this reaction, $k = 0.00106 \text{ min}^{-1}$.

IV. Activation Energy and Temperature

We all have the feeling that reactions go faster at higher temperatures, and that's true. Given equal concentrations, all reactions will proceed more rapidly as temperature increases. Why? All reactions have an "activation barrier," an energy they must overcome before proceeding to products. Consider the case of the reaction of this organic iodide compound.



The first step involves the breaking of the C-I bond. This is an endothermic process and requires energy to make happen. Even though later steps involve bond formation and are exothermic, and can make the overall reaction exothermic, energy must be used to get the first step to occur.

Reaction Coordinate Diagrams

The energetic changes that occur during the progress of a reaction are often displayed graphically using a reaction coordinate diagram. This is a plot with energy of the chemical system on the y axis and the progress of the reaction- from reactants on the left to products on the right- along the x axis.

Figure 14.5 shows representative reaction coordinate diagrams for two simple reactions, one exothermic and the other endothermic.

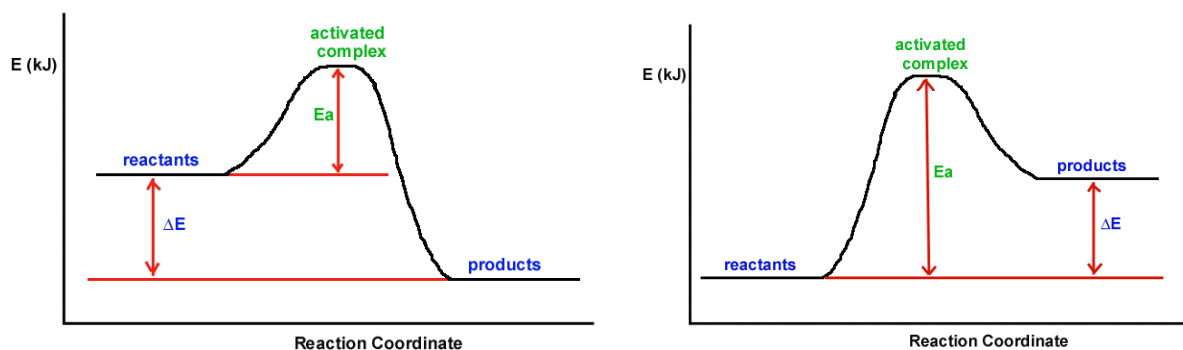


Figure 14.5 Reaction coordinate diagrams for an exothermic reaction and an endothermic reaction.

Important facts about reaction coordinate diagrams:

- Energy must be gained by the reactants in order to reach the activated complex (also called the transition state)
- The energy required is the reaction's activation energy, and the symbol given is E_a .
- The activation energy is always the energy difference between that of the reactants and that of the activated complex.
 - Activation energy is always positive.
- The energy change for the reaction (ΔE) is the energy difference between the reactants and the products.
 - ΔE can be either positive or negative

When introducing collision theory, we saw that any sample of reactants will have a Boltzmann distribution of molecular energies. Only those with energies greater than the activation energy will be

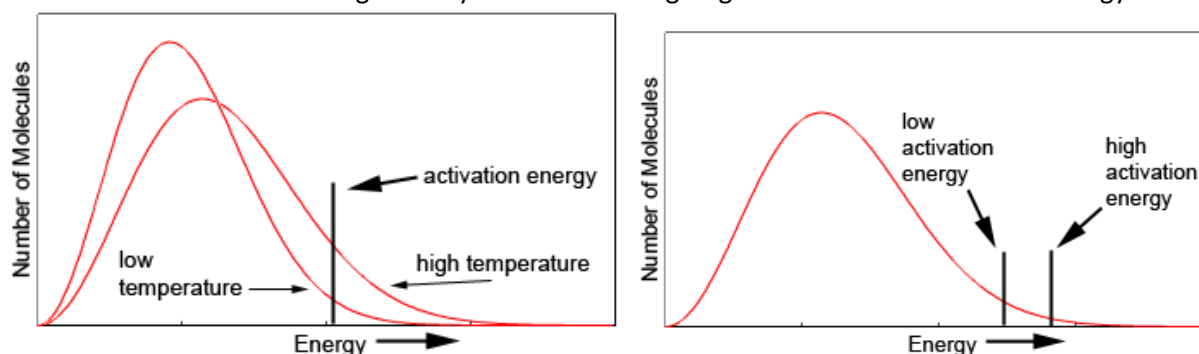


Figure 14.6 a and b. Boltzmann distributions of molecular energies at different temperatures show that more molecules exceed the activation energy at higher temperature. b: At a given temperature, more molecules exceed a lower activation energy than a high one.

able to react. Figure 14.6a shows Boltzmann plots for samples at low and high temperature. A greater fraction of molecules exceed the activation energy in the high temperature sample. This leads to a greater frequency of effective collisions and a faster reaction rate. Figure 14.6b shows how activation energy affects rate. High activation energy leads to a smaller fraction of molecules that can react, and a slower rate.

Temperature and activation energy therefore play off each other to control reaction rate. Greater activation energy decreases the fraction of collisions with sufficient energy to react. But high activation energy can be overcome with higher temperatures.

Consider the concentration-time curves in Figure 14.7a. If two reactions are run at the same temperature, the one with the greater activation energy will be slower. Figure 14.7b shows that a single reaction will proceed faster at a higher temperature.

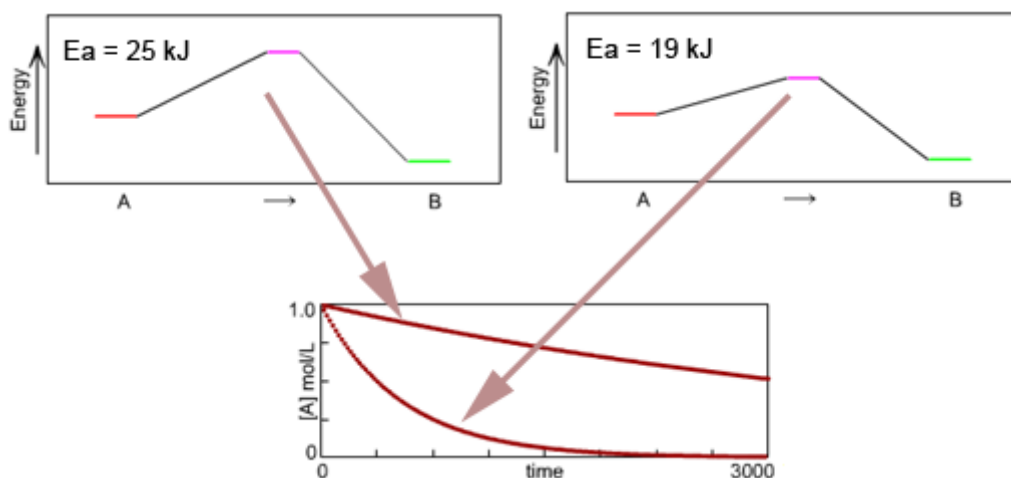


Figure 14.7a Two reactions run at the same temperature, but with different activation energies. The high activation energy case gives the slower reaction.

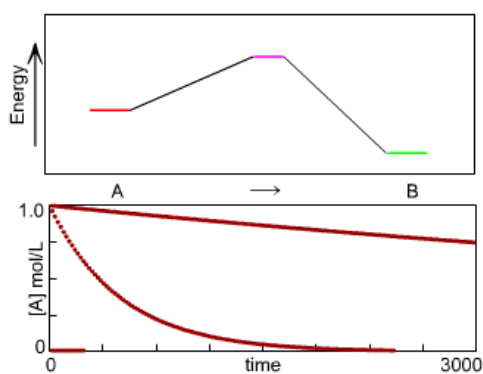


Figure 14.7b The same reaction run at two different temperatures. The high temperature case gives the faster reaction.

Remember the rate law? It was supposed to control rate, and so it still does. Recall that for a simple first order reaction, $A \rightarrow B$, the rate law is,

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

Temperature and activation energy effects are part of the rate constant, k , as described by the Arrhenius equation.

$$k = Ae^{-\frac{E_a}{RT}}$$

rate constant \downarrow k

activation energy, usually in kJ \downarrow E_a

frequency factor: the frequency of collisions that occur with correct orientation \uparrow A

temperature, in K \leftarrow T

gas constant: $8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}$ \uparrow R

The Arrhenius equation shows us that:

- a higher fraction of collisions with correct orientation leads to larger value of A and a faster rate (we generally do not report values of A for reactions, but they do matter)
- $e^{-\frac{E_a}{RT}}$ is the fraction of collisions exceeding the activation energy
- as E_a increases, $e^{-\frac{E_a}{RT}}$ decreases and the rate is slower
- as T increases, $e^{-\frac{E_a}{RT}}$ increases and the rate is faster
- the fraction E_a/T controls rate: the smaller this fraction, the faster the rate

Using the Arrhenius Equation

The two-point version of the Arrhenius equation is

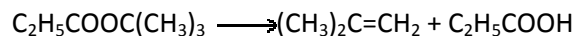
$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

and is most often used in two ways:

1. predicting the rate of reaction at a different temperature if you know E_a and the rate at another temperature
2. determining the activation energy

Example 12. Finding k at a New Temperature

The activation energy for the gas phase decomposition of t-butyl propionate is 164 kJ.



The rate constant at 528 K is $3.80 \times 10^{-4} / \text{s}$. What will the rate constant be at 569 K?

Solution:

In this case, we know:

$$T_1 = 528 \text{ K}$$

$$T_2 = 569 \text{ K}$$

$$k_1 = 3.80 \times 10^{-4} / \text{s}$$

$$k_2 = ?$$

$$E_a = 164 \text{ kJ/mol and } R = 8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}$$

We insert these into the Arrhenius equation,

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = -\frac{164 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}} \left[\frac{1}{569 \text{ K}} - \frac{1}{528 \text{ K}} \right]$$

$$\ln \frac{k_2}{3.80 \times 10^{-4} / \text{s}} = 2.69$$

$$\frac{k_2}{3.80 \times 10^{-4} / \text{s}} = e^{2.69} = 14.8$$

$$k_2 = 5.61 \times 10^{-3} / \text{s}$$

What of this can we control?

Although we discuss how changes in E_a will affect reaction rate, the activation energy is inherent to any reaction. We can control the temperature, but not E_a . For some reactions, E_a can be lowered through use of a catalyst, but not in a controlled way. If you want to change reaction rate, you change either concentration or temperature.

Example 13. Finding E_a

For the gas phase decomposition of ethyl chloroformate,



the rate constant at 470 K is $1.05 \times 10^{-3} / \text{s}$ and the rate constant at 508 K is $1.11 \times 10^{-2} / \text{s}$. What is the activation energy for this reaction?

Solution:

In this case, we know:

$$T_1 = 470 \text{ K}$$

$$T_2 = 508 \text{ K}$$

$$k_1 = 1.05 \times 10^{-3} / \text{s}$$

$$k_2 = 1.11 \times 10^{-2} / \text{s}$$

$$E_a = ?$$

$$R = 8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}$$

We insert these into the Arrhenius equation,

$$\ln \frac{1.11 \times 10^{-2} / \text{s}}{1.05 \times 10^{-3} / \text{s}} = - \frac{E_a}{8.314 \times 10^{-3} \text{ kJ} / \text{K}\cdot\text{mol}} \left[\frac{1}{508 \text{ K}} - \frac{1}{470 \text{ K}} \right]$$
$$2.36 = - \frac{E_a}{8.314 \times 10^{-3} \text{ kJ} / \text{K}\cdot\text{mol}} \left[-1.59 \times 10^{-4} / \text{K} \right]$$

$$E_a = 123 \text{ kJ/mol}$$

Graphical Determination of E_a

The Arrhenius equation can be written in the form of a straight-line equation.

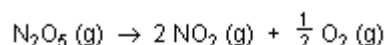
$$\ln k = - \frac{E_a}{R} \frac{1}{T} + \ln A$$

$$y = m x + b$$

In a straight line plot, $y = \ln k$, $x = 1/T$, and the slope $= -E_a/R$. To determine E_a , we run the reaction at a series of temperatures and measure the rate constant at each. Then we plot $\ln k$ vs. $1/T$.

Example 14.

The rate of the reaction



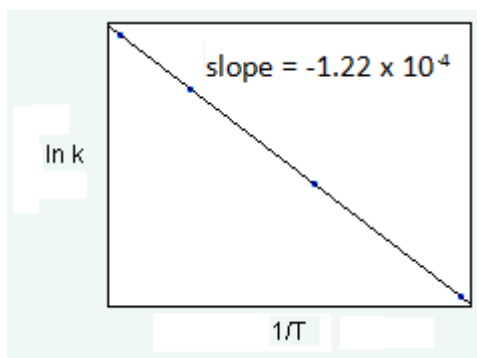
is measured at different temperatures, with the following rate constants, k , determined:

Temperature, K	k , s^{-1}
298	3.46×10^{-5}
328	1.5×10^{-3}
358	3.34×10^{-2}
378	0.21

What is the activation energy, E_a , for this reaction in units of kilojoules?

Solution:

The first step is to create a plot of the natural log of the measured rate constants vs. the inverse temperature. This can be done in Excel or another graphing program. Find the slope using least squares analysis (in Excel this is called a trendline).



The activation energy is given by,

$$E_a = -R \times \text{slope} = - (8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}) (-1.22 \times 10^4) = 102 \text{ kJ/mol}$$

V. Reaction Mechanisms

Chemical reactions involve rearranging atoms. Atoms on one molecule end up on another; some molecules fall apart; other molecules form. A reaction mechanism is a detailed description of the bond breaking and forming steps involved in the pathway from reactant to products. An overall reaction is composed of a series of individual steps. Each of these discrete steps is called an **elementary step**.

Reaction mechanisms cannot be calculated or predicted with assuredness. Instead, all reaction mechanisms must be determined experimentally. In sections Vf and Vg we review some of the methods used to elucidate mechanisms.

Va. Types of Mechanism Steps

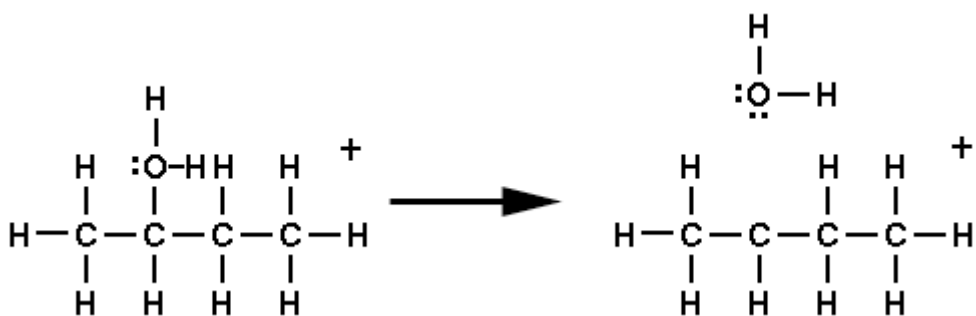
Molecularity

Chemical events can be categorized simply by the number of reacting species in an elementary step. Almost all events are **unimolecular**, involving a single reactant, or **bimolecular**, involving two reactants. Of the millions of chemical events observed, only a handful involve **termolecular** steps, in which three species react together at the same instant. Therefore, we will deal with unimolecular and bimolecular steps, but not termolecular steps.

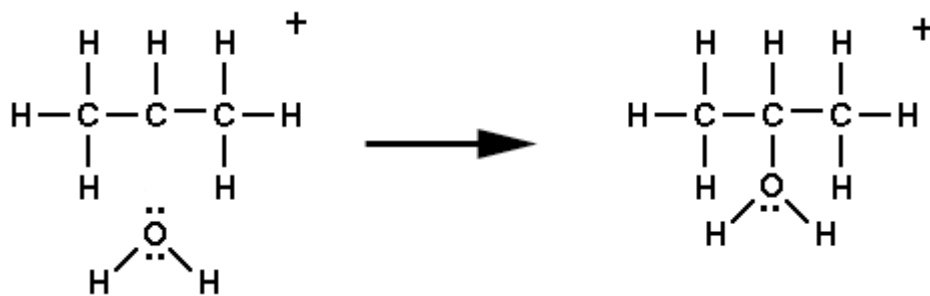
From a more chemical perspective, any reaction we observe is the sum of a series of events that occur in sequence. There are three kinds of chemical events:

- bond breaking
- bond forming
- concerted bond breaking and forming

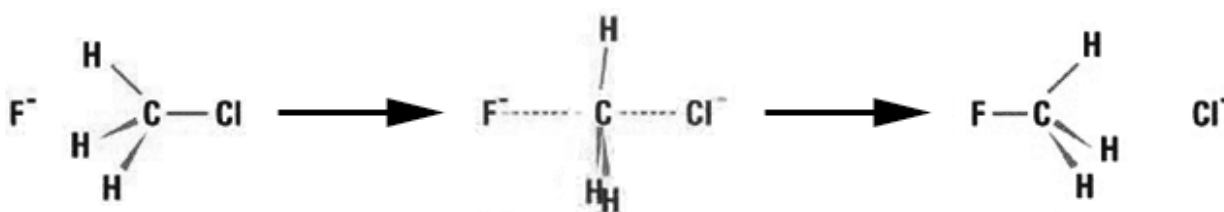
A **bond breaking step** involves a single entity breaking up into two pieces. In the example below, a C-O bond breaks. A single reactant forms two products. Because only one reactant molecule is involved, this step is also termed **unimolecular**.



A **bond forming step** involves bringing two molecular fragments together to form a single product. In the example below, a C-O bond is formed. Two reactants form a single product. Because two reactant molecules are involved, this step is also termed **bimolecular**.

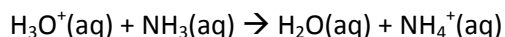


A **concerted bond breaking and forming step** involves one bond breaking while another is forming. In the example below a C-F bond is formed while a C-Cl bond breaks. Two reactants form two products. This step is also bimolecular because two reactant molecules are involved.



Vb. Examples of Single Step Reactions

Many chemical reactions are simple events that occur in a single step. Many of these you have seen before. Acid-base reactions mostly occur in a single step. The protonation of ammonia by hydronium ion involves the transfer of an H^+ ion from H_3O^+ to NH_3 . This single step is a concerted bond-breaking and forming process.



The decomposition of N_2O_4 is a single bond breaking step.

Vc. Multistep Reactions, Intermediates and Catalysts

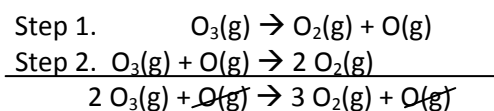
Most chemical processes that we observe occur in a series of elementary steps. Here are some rules:

1. The overall reaction is the sum of the reaction steps.
2. A species that is formed in one step and then used up in a later step is an **intermediate**.
3. A species that is used in one step and then reformed in a later step is a **catalyst**.
4. Neither intermediates nor catalysts are seen in the overall reaction equation.
5. A catalyst will normally be seen in the reaction's rate law, but an intermediate is not.

The decomposition of ozone takes place in two steps.



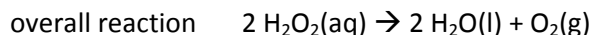
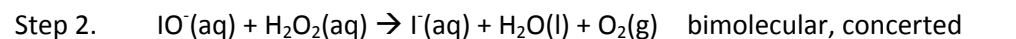
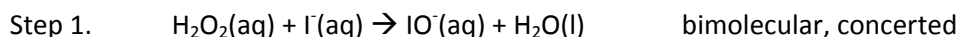
When studying Hess's Law in Chapter 5 we introduced the idea of adding a series of reactions to give a net reaction. The same technique is used here to determine the overall reaction that takes place in a series of steps. This is performed by adding all the reactants to the left of the reaction arrow and all the products to the right of the reaction arrow, and cancelling like items that are present on both sides. In this case, the $\text{O}(\text{g})$ is present on both sides.



Let's not just yet completely write off that $\text{O}(\text{g})$ atom. Sure, it doesn't appear in the overall reaction equation, but that doesn't mean it does not exist at least for a little while. A chemical species that is formed in one step of a mechanism and then used in a later step is called an intermediate.

Intermediates never appear in the overall reaction equation. Sometimes they can be observed while the reaction progresses, but other times they are formed and used up so quickly they are not seen, nor heard.

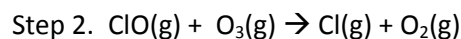
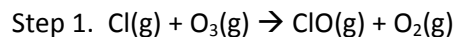
The decomposition of hydrogen peroxide in the presence of iodide ion occurs in two steps.



In this case, the IO^- ion is formed in the first step and then consumed in the second step. IO^- is an intermediate in this reaction. Conversely, I^- ion is used in the first step and then reformed in the second step. I^- is a catalyst.

Example 15.

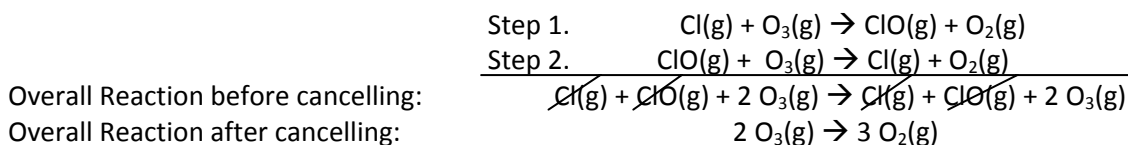
Chlorofluorocarbons break down in the upper atmosphere to give chlorine atoms. These are involved in the breakdown of ozone via the following mechanism.



- What is the molecularity of each step?
- What is the overall reaction equation?
- Identify any intermediates and/or catalysts.

Solution:

- Both steps involve two reactants. They are both bimolecular.
- The overall reaction is found by adding the two steps and cancelling like species present on both sides. In this case, both ClO and Cl are cancelled.



- Cl(g) is a reactant in the Step 1, but is regenerated in Step 2. Cl is therefore a catalyst. ClO is generated in Step 1, but is consumed in Step 2. ClO is therefore an intermediate.

Reaction Coordinate Diagrams and Mechanisms

Reaction coordinate diagrams are used to relate the progress of a reaction to the energy of the system at any particular step. Figure 14.8 shows reaction coordinate diagrams for a 1-step and a 2-step reaction.

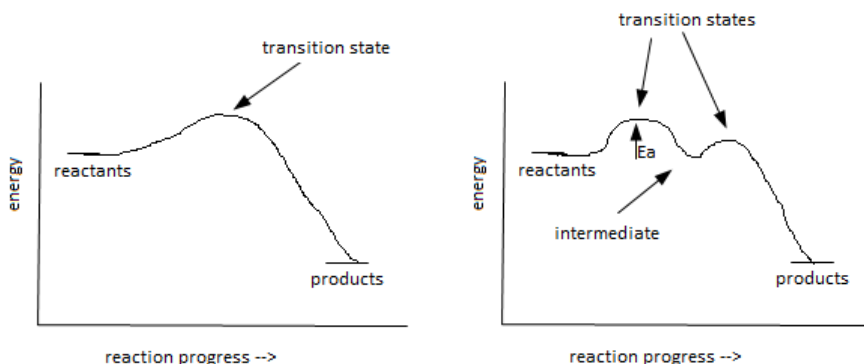
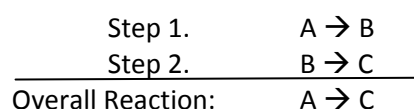


Figure 14.8 Reaction Coordinate diagrams for 1-step ($\text{R} \rightarrow \text{P}$) and 2-step ($\text{R} \rightarrow \text{In} \rightarrow \text{P}$) reactions.

In the one step reaction, the energy of the reactants (R) must increase to that of the transition state before proceeding to form products (P). In the two step reaction, a transition state must first be reached to allow the reactants (R) to undergo the first step to form the intermediate (In). The intermediate lies in an energy well. A second activation barrier must be overcome for the intermediate to react further to form the final products (P). Any reaction's overall activation energy is the energy difference between the reactants and the transition state of highest energy.

Vd. Complex Reaction Mechanisms and Concentration-Time Curves

Consider a two step reaction.



How will the concentrations of A, B, and of C change over time. Clearly the concentration of the reactant A will decrease as the reaction proceeds, and the concentration of the product C will increase. But what about the concentration of the intermediate, B? It is formed in one step and consumed in another. Its concentration must be zero at the start of the reaction, and must be zero when the reaction is complete, but non-zero inbetween. This is best observed by examining concentration-time curves. Figure 14.9 shows concentration-time curves for A(red), B(yellow), and C(blue) for three cases.

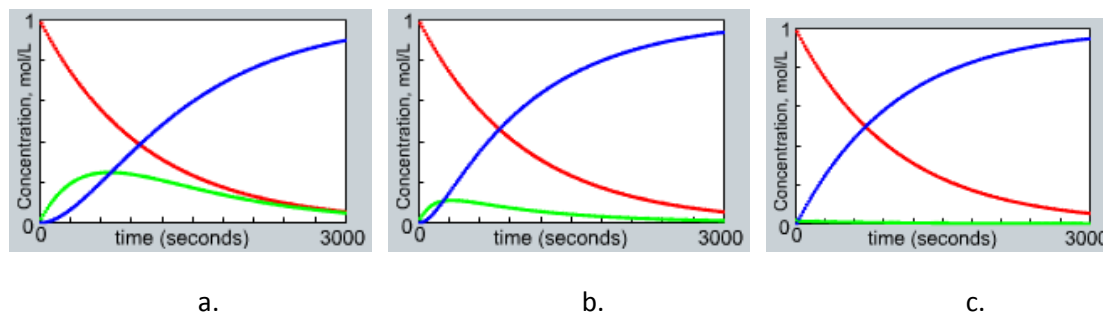


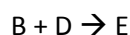
Figure 14.9 a. Step 1 faster than Step 2. b. Step 2 a little faster than Step 1. c. Step 2 must faster than Step1.

In (a) the first step is somewhat faster than the second step. Initially, as $A \rightarrow B$ occurs, the rate of formation of B is greater than its rate of consumption in Step 2. So, the concentration of B increases over time. Then, as reactant A is depleted and the concentration of B increases, the rate of formation of B decreases and its rate of consumption increases. At this point, the concentration of B starts to decrease. Eventually the concentrations of both A and B drop to near zero as the reaction nears completion.

Part (b) shows a case where Step 2 is somewhat faster than Step 1. In this case, B is consumed more quickly and its concentration does not build up as much as in Part (a).

Part (c) shows a case where Step 2 is much faster than Step 1. In this case, B is consumed almost instantly as it is formed. The concentration of B never rises to an appreciable level and B may never be concentrated enough to observe in an experiment.

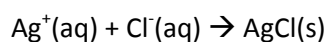
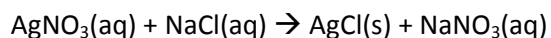
You might wonder, if a case like Part (c) occurs, how would we ever know the intermediate ever existed? In some cases we never do. In other cases, we design experiments to show that the intermediate was present, even if not directly observed. One prime method for this is a “trapping” experiment. If we suspected such an intermediate was present, we add another reagent that we predict will react with the intermediate. If we see the product of that expected reaction, then we have evidence that the intermediate was present. In our simple example,



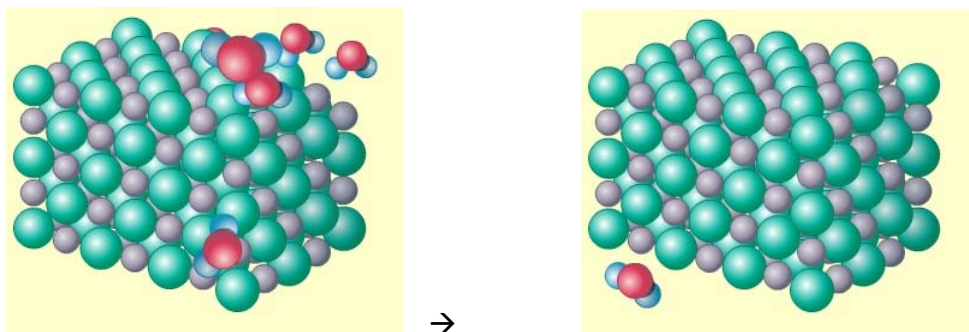
we add reagent D, which intercepts intermediate B before it can form product C. It instead forms product E, which we can observe as it builds up in solution.

Reactions Too Complex to Describe With Mechanisms

Reactions that involve more than one phase are inherently complex and are generally not written as mechanisms. Take for example the formation of solid silver chloride that forms when solutions of silver nitrate and sodium chloride are mixed. The overall reaction and net ionic equations are both simple:



This reaction seems pretty simple. Two ions come together and form a solid. But it is the solid that makes it complex. The solid that forms is huge on the molecular scale, containing billions of ions. Each crystal forms by adding more and more Ag^+ and Cl^- ions.



In the image here, the crystal grows by a few added ions. There is no clear way to write a mechanism for this process. It involves billions of steps and although the general process is always the same, the intermediate crystals involved are different each time the reaction is run.

Vf. Relating Mechanisms to a Reaction's Rate Law

The path a reaction takes has an effect on how rapidly the reaction takes place. The rate of an overall reaction is equal to the rate of that reaction's slowest step, which is called the rate determining step (or sometimes the rate limiting step). A common misperception is that the rate law is directly derived from the reaction equation. This is not true- remove that thought from your mind. The rate law is instead derived directly from the chemical equation of the rate determining step. There are only three types of steps:

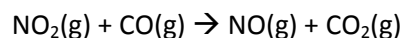
unimolecular	$A \rightarrow D$	Rate = $k[A]$
bimolecular, one reactant	$2 A \rightarrow D$	Rate = $k[A]^2$
bimolecular, two reactants	$A + B \rightarrow D$	Rate = $k[A][B]$

The experimentally determined rate law is one of the most useful tools in trying to determine a mechanism. The process involves three steps:

1. Propose a mechanism, including which step will be rate determining.
2. Predict the rate law using the rate law of the slow step.
3. Measure and compare the experimental rate law to that predicted for the mechanism. If they do not match, then the proposed mechanism is wrong. If they do match, then the proposed mechanism might be correct. But it might not because multiple mechanisms can lead to the same predicted rate law.

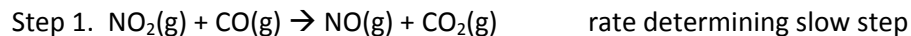
Example 16.

An oxygen-atom transfer reaction occurs between NO_2 and CO .

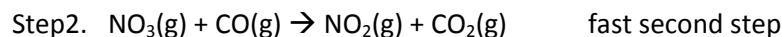


There are two proposed mechanisms:

Mechanism A.



Mechanism B.



The experimentally determined rate law is $\text{rate} = k[\text{NO}_2]^2$.

Which of these two mechanisms is supported by the experimental evidence?

Solution

The rate law predicted for Mechanism A is that for the single step. Because that step has both NO_2 and CO as reactants, the predicted rate law for that step and the overall reaction is:

$$\text{rate} = k[\text{NO}_2][\text{CO}]$$

This does not match the experimental rate law, so this mechanism is wrong.

The rate law predicted for Mechanism B is that for the slow, first step. This step involves two molecules of NO_2 , so the predicted rate law for that step and the overall reaction is:

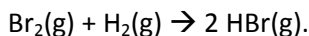
$$\text{rate} = k[\text{NO}_2]^2$$

This does agree with the experimental rate law, so this mechanism is supported but not proved correct.

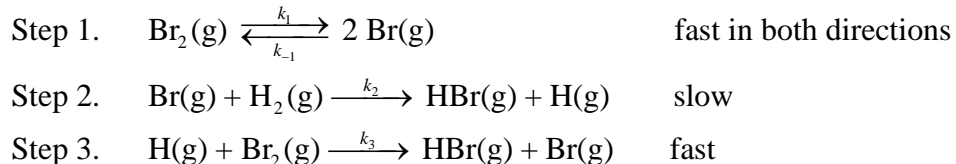
Mechanisms with Reversible Steps

Some reaction steps can react in both the forward and reverse directions. That is, reactants can go to form products, but those products can “back react” to reform the reactants. If both steps are fast, they quickly form an “equilibrium state,” where the rates of the forward and reverse reactions proceed at the same rate.

Bromine and hydrogen react to form hydrogen bromide. The overall reaction is



The proposed mechanism is:



In this mechanism depiction, we write the rate constant for each step along with its reaction arrow. The step number is written as a subscript for each step. The reversible first step is written with a double arrow, with the rate constant for the reverse step being denoted with a minus sign. Note that k_{-1} is not equal to $-k_1$. The -1 just means it's the rate constant for the reverse of step 1.

The rate law for the overall reaction is the rate law for the slow step:

$$\text{Rate} = k_2[\text{Br}][\text{H}_2]$$

However, "Br" is not a reactant and we never know its concentration. In order to obtain the predicted rate law for the overall reaction we need to express the concentration of Br in terms of species we do know. To do this we solve the rate law for Step 1 for [Br]. The key to this is that the reversible Step 1 is "at equilibrium," a state where the forward and reverse reaction *rates* are equal (not the rate constants). So,

$$\begin{aligned}k_1[\text{Br}_2] &= k_{-1}[\text{Br}]^2 \\ [\text{Br}] &= \sqrt{\frac{k_1[\text{Br}_2]}{k_{-1}}} = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Br}_2]^{1/2}\end{aligned}$$

We then insert this solution for [Br] into the rate equation for the slow step 2.

$$\text{Rate} = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]$$

Experimentally, we could not differentiate between the collection of k values and they would collapse into a single, measured rate constant.

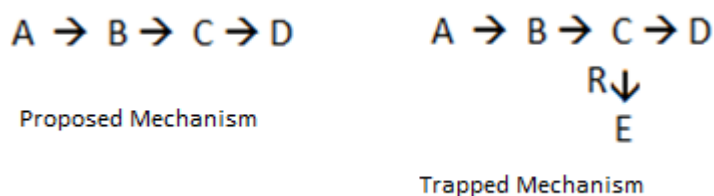
$$\text{Rate} = k[\text{Br}_2]^{1/2}[\text{H}_2]$$

The overall reaction order is 3/2.

Vg. Advanced Methods for Determining Mechanisms

A large part of the chemist's work is determining the pathway by which a reaction occurs. If you're lucky- and you're usually not- some easy experiments can help determine a mechanism. If not, more advanced methods are employed. Some common methods are described below.

1. Reaction to the experimental rate law. This was described in the previous section.
2. Detection of an intermediate. This was described in Section Vd. Detection is usually done spectroscopically, by observing absorption of radiation in the UV, VIS, or IR regions. Sometimes NMR spectroscopy is used. The main obstruction to detecting intermediates is that they are unstable and tend to react quickly. That's why they are intermediates. But, sometimes they stick around awhile and you can see them.
3. Trapping experiments. These experiments are used to chemically detect intermediates by having the intermediate react with a secondary reagent to produce an identifiable product. That is, you design an experiment to hijack an intermediate and cut off the rest of the mechanism under study.



In the reaction diagrams above, the proposed mechanism involves three steps, with formation of two intermediates, B and C. In the trapped mechanism, a reagent R is added to siphon off intermediate C. If addition of R leads to formation of E and of less D, that supports the proposed mechanism. If no E is observed and D is still formed, that means the proposed mechanism is wrong. This all assumes you are sure the trapping reaction ($C + R \rightarrow E$) both occurs and occurs faster than conversion of $C \rightarrow D$. But you can know that with reasonable certainty, so it's ok.

4. Isotopic labeling. In this type of experiment, one of the reactants is synthesized containing a particular minor isotope of one of the reacting atoms. You can then track where that isotopically labeled atom ends up in the products. In oxidation reactions involving metal oxides, it is unclear whether the oxygen that is added to the species oxidized comes from the metal oxide, or just from water in solution.

To determine this, the metal oxide can be synthesized using the rare isotope ^{18}O , in a solution where the water contains almost all ^{16}O . If the product contains ^{18}O , you know it comes from the metal oxide. If it contains ^{16}O , you know it comes from the water. To be sure this experiment is valid, you need to make sure the metal oxide and water do not exchange O atoms.

Vh. Catalysis

Catalysis is the technique of using a catalyst to influence the rate of a reaction. Catalysts serve one of two functions: making reactions faster or making them more “selective.” In either case, the catalyst provides an alternative mechanistic pathway for the reaction, which changes the activation energy and changes the rate.

Increasing Reaction Rate.

Earlier, we saw the mechanism of the I⁻ ion-catalyzed decomposition of H₂O₂. The reaction can be observed to occur over a short period once an iodide is added. However, H₂O₂ can also decompose all on its own, thank you very much. If you have an unopened bottle of hydrogen peroxide that has been on the shelf for a few months, pay attention when you first open it—there will often be a swoosh of air escaping. This is due to the build up of O₂ gas that has formed in the decomposition over time.

Figure 14.10 shows a reaction coordinate diagram for this reaction, both with a catalyst present, and without one. The lower activation energy in the catalyzed case leads to a faster reaction.

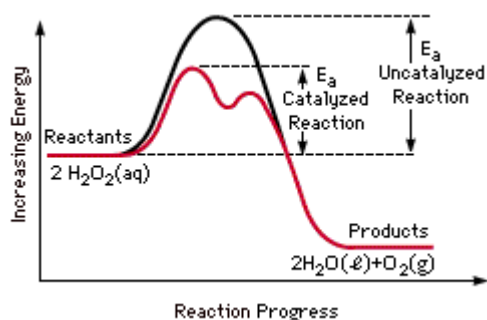


Figure 14.10 Reaction Coordinate diagrams for the uncatalyzed and the catalyzed decomposition of hydrogen peroxide.

Increasing Selectivity

We lie to you. You’ve suspected it. We tend to write chemical reactions as if they will occur as written and go all the way to completion. Oftentimes, though, reactions are messy. One form of the messiness is that a set of reactants can often undergo different reactions to form different sets of products. That’s bad. You always want one set of products because it is difficult and expensive to purify the products of a mixed reaction. These multiple reactions occur when both mechanistic pathways have similar activation energies. Selectivity is a measure of how much the reaction creates one set of products over another. (Up till now we have been assuming all reactions are perfectly selective.)

A catalyst can increase selectivity by changing the pathway of one reaction path and not the other. When this happens, the reaction to form one set of products will increase while the other stays slow. The reaction prefers the faster-formed products and is more selective. Figure 14.11 shows reaction coordinate diagrams representing how this works.

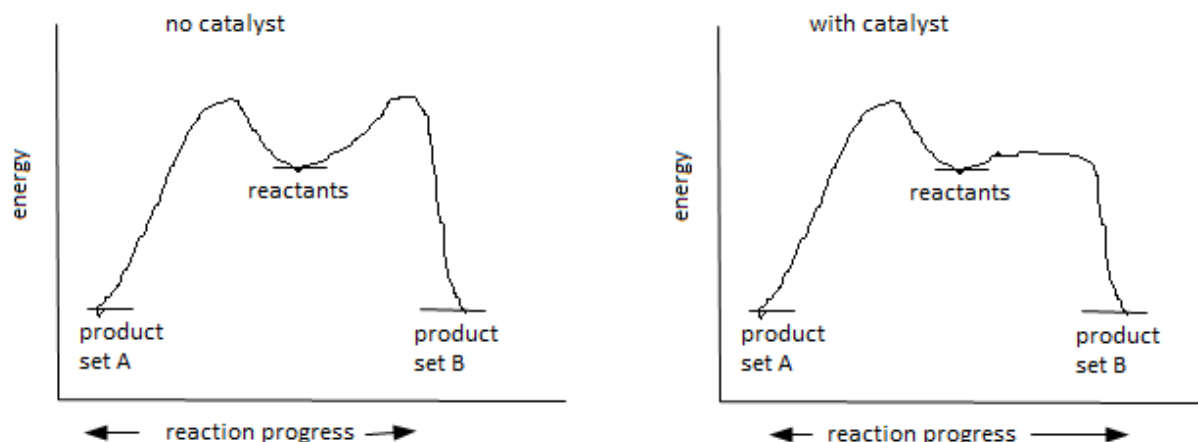


Figure 14.11 Reaction Coordinate diagrams showing the progress for two simultaneous reactions that occur from a single set of reactants. The two sets of products (A and B) are shown to either side of the reactants, which are in the center of the diagram.

In the uncatalyzed case, the two reactions have similar activation energies and proceed at close to the same rate, forming significant quantities of products for both cases. Addition of the catalyst decreases the activation energy for formation of product set B, but not product set A. In this case, formation of B is much faster than formation of A, so the reaction is selective for formation of B.

Types of Catalysts

Catalysts are generally homogeneous or heterogeneous. Homogeneous catalysts are soluble compounds that are added to solutions along with the reactants. These have the advantage of being chemically modified to a great degree. Chemists are very good at synthesizing small molecules and can generally create small, soluble compounds that act in very specific ways. Homogeneous catalysts are good at modifying reactions in a highly selective way. The main disadvantage of homogeneous catalysts is that they must be removed from solution when the reaction is complete. That is, once the products are formed, they are still mixed with the catalyst and the two must be separated. This is often expensive.

Heterogeneous catalysts are solids that serve as a reactive surface upon which reactants in either the gas or solution phase can react. These have advantages and disadvantages that are opposite from homogeneous catalysts. They are easy to separate from the reaction products: just filter off the solid. They are, however, much more difficult to modify. Because of these differences, homogeneous catalysts are more often used for reactions in which great selectivity is needed; heterogeneous catalysts are needed where selectivity is not an issue.