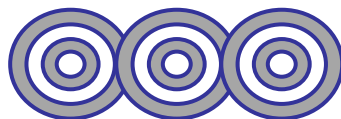




Chemistry, The Central Science, 11th edition
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Chapter 14

Chemical Kinetics

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In **chemical kinetics** we study the **speeds** or **rates** of reactions.

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

Speed is a type of rate. A rate is a change over time. Speed is the rate defined as a change in distance over time. In chemical reaction we're analyzing a change in concentration over time so we don't use the term speed but speed is a type of rate.

14.1

Factors that Affect Reaction Rates

Factors that Affect Reaction Rates

Because **reactions** involve the **breaking** and **forming** of **bonds**, the speeds of reactions depend on the nature of the reactants themselves. Four factors allow us to change the rates at which particular reactions occur:

Physical state of the reactants

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

Concentration of reactants

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

Temperature

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

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.

On a molecular level, reaction rates depend on the **frequency of collisions between molecules**. The greater the frequency of collisions, the greater is the rate of reaction.

For a collision to lead to a reaction, however, it must occur with **sufficient energy** to stretch bonds to a critical length and with **suitable orientation** for new bonds to form in the proper locations.

14.2

Reaction Rates

Reaction Rates

The speed of an event is defined as the change that occurs in a given interval of time: Whenever we talk about speed, we necessarily bring in the notion of time.



Progress of a hypothetical
reaction $A \longrightarrow B$

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

Similarly, the speed of a chemical reaction - its **reaction rate** - is the change in the concentration of reactants or products per unit of time. Thus, the units for reaction rate are usually molarity per second (M/s) – that is the change in concentration (measured in molarity) divided by a time interval (seconds).



1.00 mol A
0 mol B



0.54 mol A
0.46 mol B



0.30 mol A
0.70 mol B

$$\begin{aligned} \text{Average rate of appearance of B} &= \frac{\text{change in concentration of B}}{\text{change in time}} \\ &= \frac{[B] \text{ at } t_2 - [B] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t} \end{aligned}$$

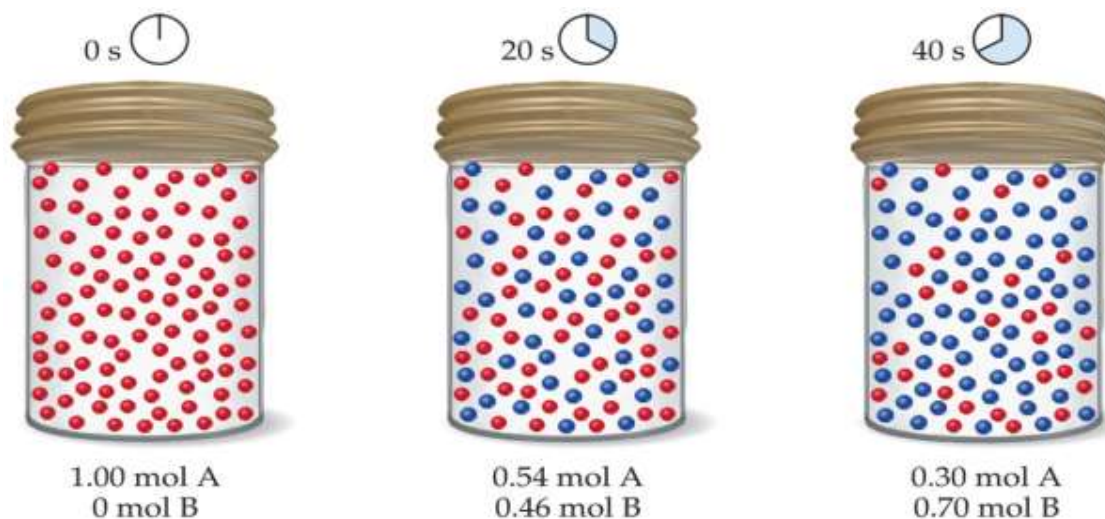
$$\text{Average rate} = \frac{0.46 \text{ M} - 0.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

$$\text{Average rate of disappearance of A} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.54 \text{ M} - 1.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

By convention, rates are always expressed as positive quantities. Because **[A]** is decreasing with time, $\Delta [A]$ is a negative.

Sample Exercise 14.1 Calculating an Average Rate of Reaction



From the data given in the caption of Figure, calculate the average rate at which **A** disappears over the time interval from 20 s to 40 s.

Solution

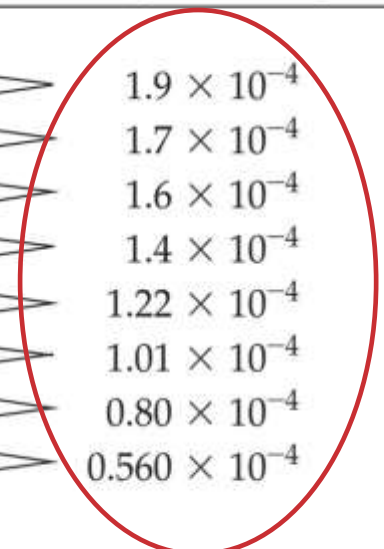
$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30 \text{ M} - 0.54 \text{ M}}{40 \text{ s} - 20 \text{ s}} = 1.2 \times 10^{-2} \text{ M/s}$$

Change of Rate with Time



| Time, $t(\text{s})$ | $[\text{C}_4\text{H}_9\text{Cl}](M)$ |
|---------------------|--------------------------------------|
| 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, **C₄H₉Cl**, was measured at various times.

| Time, t (s) | $[C_4H_9Cl]$ (M) | Average Rate (M/s) |
|---------------|------------------|--|
| 0.0 | 0.1000 |  1.9×10^{-4} 1.7×10^{-4} 1.6×10^{-4} 1.4×10^{-4} 1.22×10^{-4} 1.01×10^{-4} 0.80×10^{-4} 0.560×10^{-4} |
| 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 | |

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

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.

$$\text{average rate} = \frac{\Delta [C_4H_9]}{\Delta t}$$

$$\text{average rate} = \frac{\Delta [C_4H_9]}{\Delta t} = \frac{0.1000 - 0.0905 \text{ M}}{50.0 - 0.0 \text{ s}}$$

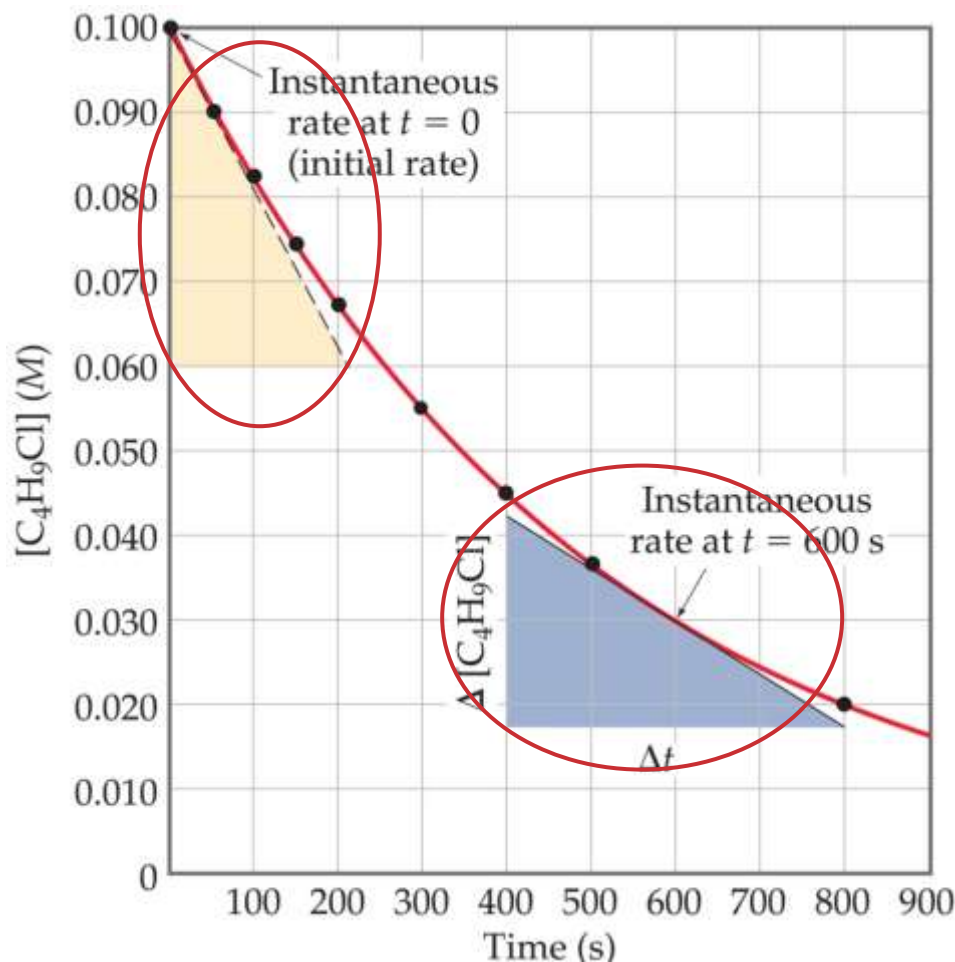
It is typical for rates to decrease as a reaction proceeds, because the concentration of reactants decreases.

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.

The reaction slows down with time because the concentration of the reactants decreases.

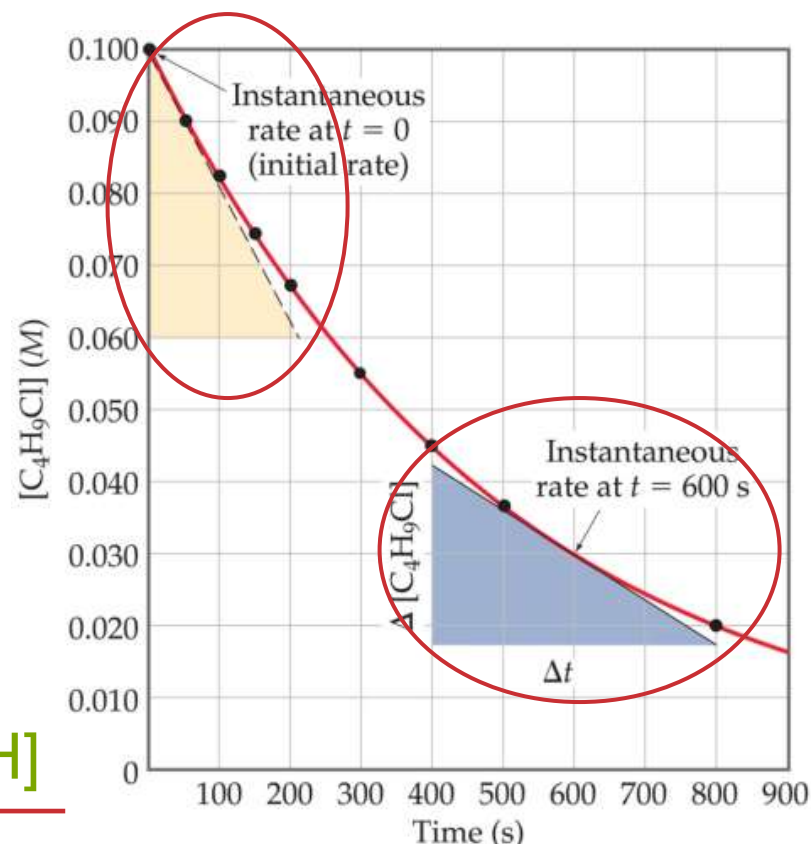
$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$





- 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 $\text{C}_4\text{H}_9\text{OH}$.

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



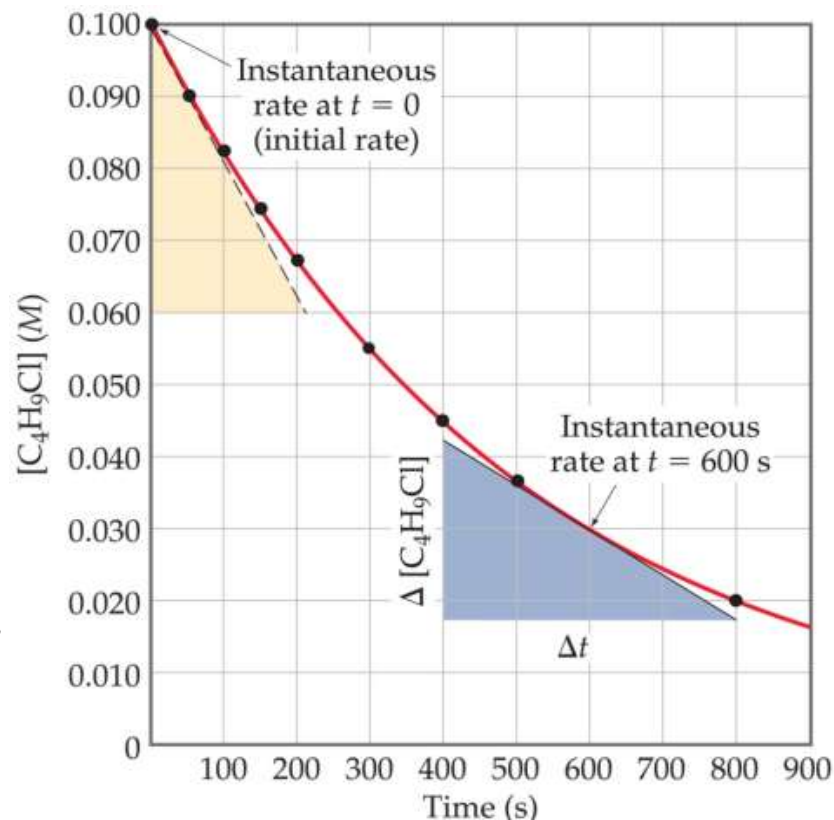
To understand better the difference between average rate and instantaneous rate, imagine that you have just driven 98 mi in 2.0 hr. Your average speed is 49 mi/hr, whereas your instantaneous speed at any moment is the speedometer reading at that time.

Instantaneous Rate

Instantaneous rate is the rate at a particular moment in the reaction. The instantaneous rate is determined from the slope (or tangent) of this curve at the point of interest.

e.g., to determine the instantaneous rate at 600 s, we draw the tangent to the curve at this time, then construct horizontal and vertical lines to form the right triangle. The slope is the ratio of the height of the vertical side to the length of the horizontal side:

$$\begin{aligned}\text{Instantaneous rate} &= -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.017 - 0.042) \text{ M}}{(800 - 400)\text{s}} \\ &= 6.3 \times 10^{-5} \text{ M/s}\end{aligned}$$



The term “rate” means “instantaneous rate”, unless indicated otherwise. The instantaneous rate at $t = 0$ is called the initial rate of the reaction.

Sample Exercise 14.2 Calculating an Instantaneous Rate of Reaction

Using the Figure, calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 0$ (the initial rate).

Solution

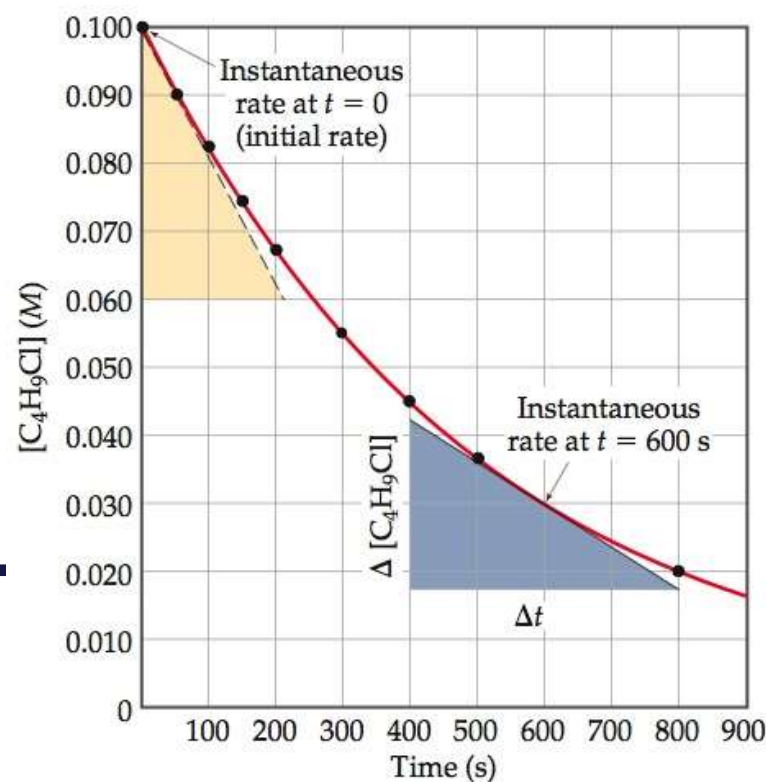
The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (that is, change in molarity over change in time). The straight line falls from $[\text{C}_4\text{H}_9\text{Cl}] = 0.100 \text{ M}$ to 0.060 M in the time change from 0 s to 210 s , as indicated by the tan triangle shown in Figure 14.4. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.060 - 0.100) \text{ M}}{(210 - 0) \text{ s}} = 1.9 \times 10^{-4} \text{ M/s}$$

Practice Exercise

Using the Figure to determine the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 300 \text{ s}$.

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



Reaction Rates and Stoichiometry



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

the ratio of $\text{C}_4\text{H}_9\text{Cl}$ to $\text{C}_4\text{H}_9\text{OH}$ is 1:1.

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



Only **1/2 HI** is made for each **H₂** used.

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

- To generalize, for the reaction



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

Reactants (decrease)

Products (increase)

Sample Exercise 14.3 Relating Rates at Which Products Appear and Reactants Disappear

- (a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$?
- (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, $-\Delta[\text{O}_3]/\Delta t$?

Solution

(a) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

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

(b) Solving the equation from part (a) for the rate at which O_3 disappears, $-\Delta[\text{O}_3]/\Delta t$ we have:

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

14.3

The rate Law: the Effect of Concentration on rate

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

Each reaction has its own equation that gives its rate as a function of reactant concentrations.

this is called its **Rate Law**

To determine the rate law we measure the rate at different starting concentrations.



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

If we compare Experiments 1 & 2, we see that when $[\text{NH}_4^+]$ doubles while $[\text{NO}_2^-]$ hold constant, the initial rate doubles. Likewise, when we compare

Experiments 5 & 6, we see that when $[\text{NO}_2^-]$ doubles while $[\text{NH}_4^+]$ hold constant, the initial rate doubles.

If $[\text{NH}_4^+]$ is increased by a factor 4 with $[\text{NO}_2^-]$ left unchanged (Experiments 1 & 3), the rate changes by a factor of 4, and so forth.

This means

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

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

Therefore,

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

which, when written as an equation, becomes

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

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

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

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

the reaction is

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

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

$$\text{rate} = k [\text{NH}_4^+]^1 [\text{NO}_2^-]^1$$

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

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

For a general reaction,



The rate law generally has the form

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

The constant ***k*** in the rate law is called **rate constant**. ***k*** has a specific value for each reaction. The value of ***k*** is determined experimentally. The magnitude of ***k*** changes with temperature and therefore determines how temperature affects rate.

The exponents ***m*** and ***n*** are typically small whole numbers (usually 0, 1, or 2). We will consider these exponents more closely very shortly.

A rate law shows the relationship between the reaction rate and the concentrations of reactants.

For gas-phase reactants use **P_A** instead of **[A]**.

The rate laws for most reactions have the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

The exponents m and n in a rate law are called **reaction orders**.

The **overall reaction order** is the sum of the orders with respect to each reactant in the rate law.

For the **first order** reactions in a reactant $[A]$, changes in the concentration of that reactant will produce proportional changes in the rate. Thus, doubling or tripling the reactant concentration, doubles or triples the rate, and so forth.

If the rate law is **second order** in a particular reactant $[A]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple ($[2]^2 = 4$), whereas tripling the concentration causes the rate to increase ninefold ($[3]^2 = 9$), and so forth.

If a reaction is **zero order** in a particular reactant $[A]^0$, changing its concentration will have no effect on rate, any concentration raised to the power zero equals 1 (catalytic reaction).

The following are some additional examples of rate laws:



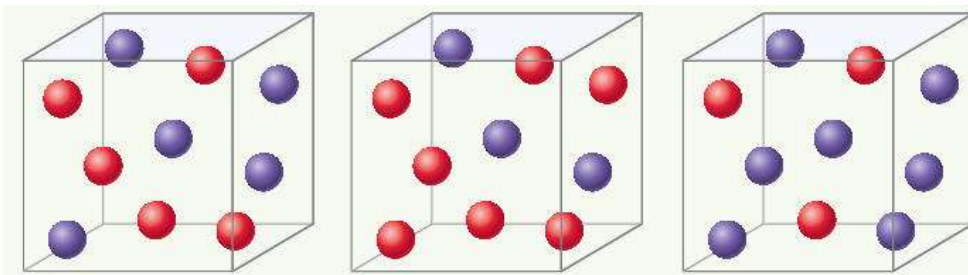
Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case.

The values of these exponents must be determined **experimentally**. In most rate laws, reaction orders are 0, 1, or 2.

However, we also occasionally encounter rate laws in which the reaction order is fractional or even negative.

Sample Exercise 14.4 Relating a Rate Law to the Effect of concentration on Rate

Consider a reaction $A + B \rightarrow C$ for which $R = k[A][B]^2$. 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.



Solution

Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Practice Exercise

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

Answer: $2 = 3 < 1$

Units of Rate Constants

The units of the rate constant depend on the overall reaction order of the rate law.

For the first order reactions

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

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

In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, in our usual units of concentration and time

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{M^2} = M^{-1} s^{-1}$$

Using Initial Rates to Determine Rate Laws

The rate law for any chemical reaction must be determined **experimentally**; it cannot be predicted by merely looking at the chemical equation.

In working with rate laws, it is important to realize that the rate of a reaction depends on concentration, but the rate constant does not.

The rate constant (and hence the reaction rate) is affected by temperature and by the presence of a catalyst.

Sample Exercise 14.6 Determining a Rate Law from Initial Rate Data

The initial rate of a reaction $A + B \rightarrow C$ 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 rate constant, (c) the rate of the reaction when $[A] = 0.050 \text{ M}$ and $[B] = 0.100 \text{ M}$.

Solution

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 1$$

$$1 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{k[0.100 \text{ M}]^m [0.200 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

$$n = 0$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{16.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 4$$

$$4 = \frac{\text{rate 3}}{\text{rate 1}} = \frac{k[0.200 \text{ M}]^m [0.100 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

$$m = 2$$

Solution (continued)

This rate law could be reached in a more formal way by taking the ratio of the rates from two experiments:

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

(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

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

Because [B] is not part of the rate law, it is irrelevant to the rate, if there is at least some B present to react with A.

14.4

**The Change of Concentration
with Time**

The rate laws that we have examined so far enable us to calculate the rate of a reaction from the rate constant and reactant concentrations.

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

These rate laws can also be converted into equations that show the relationship between the concentrations of the reactants or products and time.

Integrated Rate Laws (first-order process only)

Consider a simple 1st order reaction: $A \rightarrow B$

$$rate = k [A]$$

Differential form:

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

How much **A** is left after time, t ? Integrate:

$$-d[A] = k [A] dt$$

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

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

Integrated form:

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

The integrated form of first order rate law:

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

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

$[A]_0$ is the initial concentration of **A** ($t = 0$).

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

Manipulating this equation produces...

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

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

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

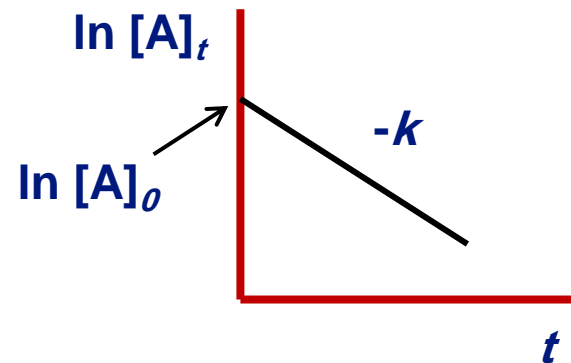
... which is in the form

$$y = mx + b$$

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

If a reaction is first-order, a plot of

$\ln [A]_t$ vs. t



will yield a straight line with a slope of **$-k$** .

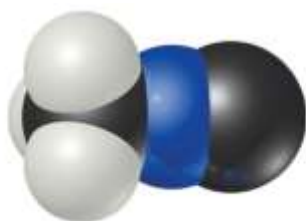
$\ln [A]_0$ will be the intercept.

So, use graphs to determine reaction order.

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



How do we know this is a first order reaction?



Methyl isonitrile

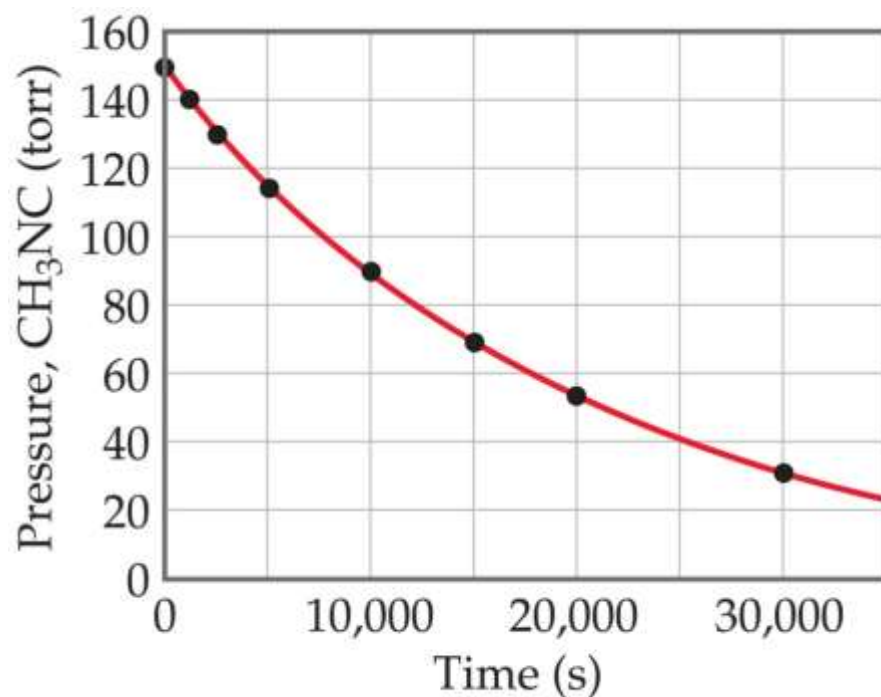


Does
 $\text{rate} = k[\text{CH}_3\text{NC}]$
for all time intervals?

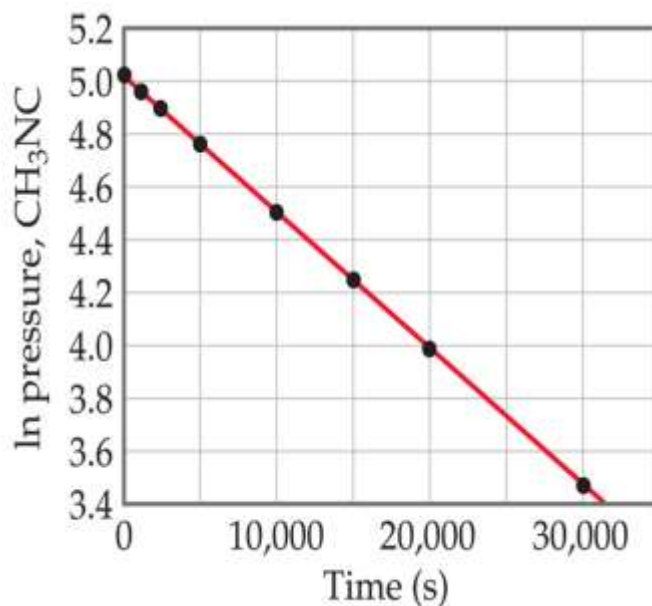
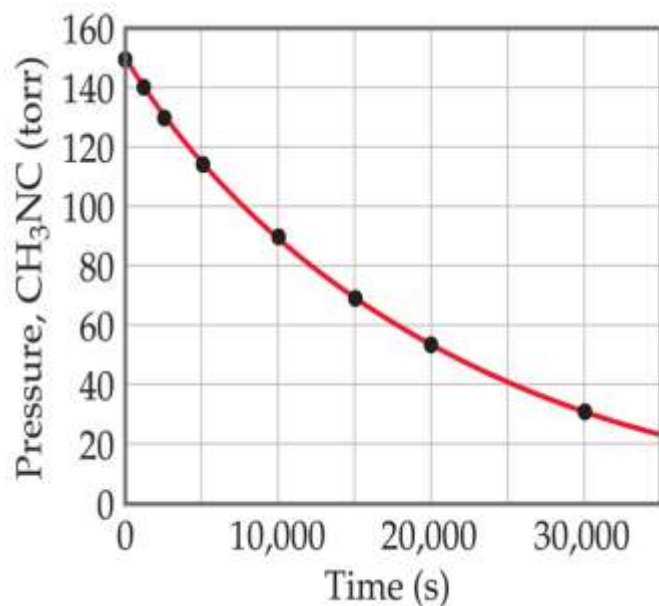


Acetonitrile

The transformation of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) is a first-order reaction. Both are isomers, molecules that have the same atoms arranged differently. This reaction called isomerization reaction.



These data were collected for this reaction at 198.9°C



(a) Variation in the partial pressure of CH₃NC with time during the reaction. A plot of natural logarithm of CH₃NC pressure as a function of time. Straight line confirms that the rate law is first order.

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

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

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

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

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 decrease to $3.0 \times 10^{-7} \text{ g/cm}^3$?

Solution

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

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

We use the \ln function on a calculator to evaluate the second term on the right, giving

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

To obtain $[\text{insecticide}]_{t=1 \text{ yr}}$, we use the inverse natural logarithm, or e^x , function on the calculator:

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

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

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

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

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

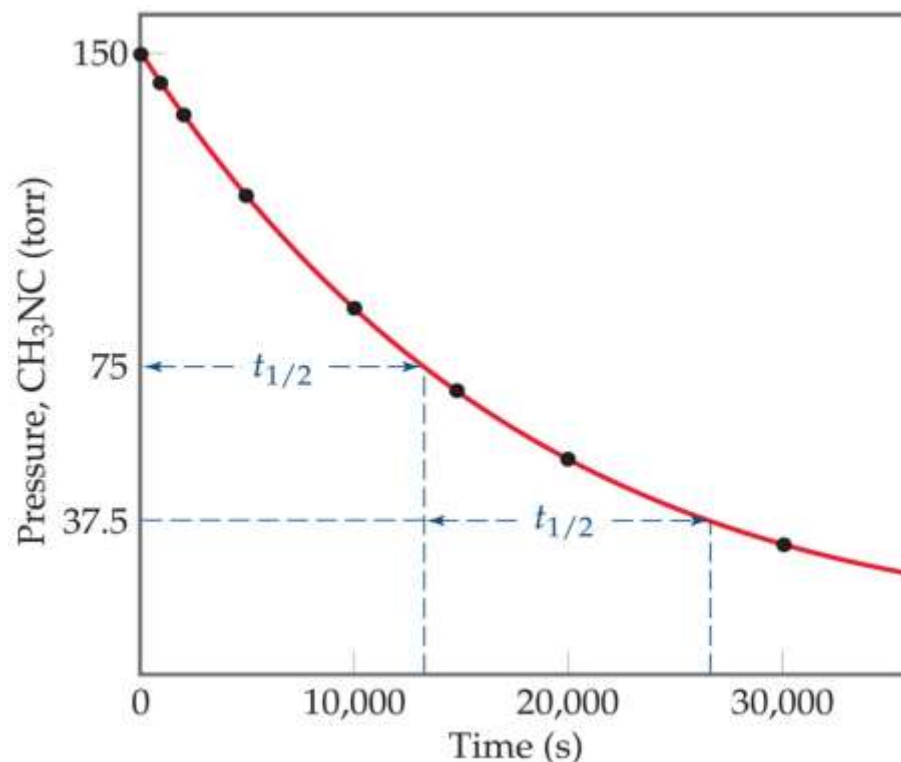
Half-Life (first-order process only)

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

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

The change in concentration over time for the first-order rearrangement of **CH₃NC** at 198.9 °C. The first half-life is shown at 13,600 s (that is 3.78 h). At this time isonitril concentration has decreased to one-half of one half, or one-fourth the original concentration.

In a first-order reaction, the concentration of the reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely, $t_{1/2}$.



Isonitrile shows two successive half-lives of the isomerization reaction.

For a first-order process, set $[A]_t = 0.5 [A]_0$ in integrated rate equation:

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

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

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

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

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

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

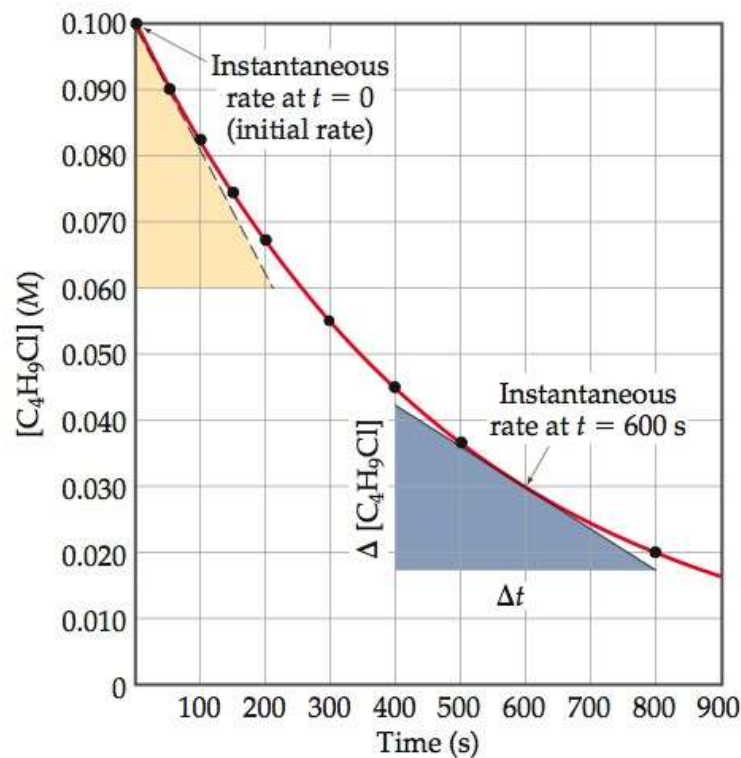
Sample Exercise 14.9 Determining the Half-Life of a First-Order Reaction

The reaction of $\text{C}_4\text{H}_9\text{Cl}$ with water is a first-order reaction. The Figure shows how the concentration of $\text{C}_4\text{H}_9\text{Cl}$ changes with time at a particular temperature. **(a)** From that graph, estimate the half-life for this reaction. **(b)** Use the half-life from (a) to calculate the rate constant.

Solution

(a) From the graph, we see that the initial value of $[\text{C}_4\text{H}_9\text{Cl}]$ is 0.100 M. The half-life for this first-order reaction is the time required for $[\text{C}_4\text{H}_9\text{Cl}]$ to decrease to 0.050 M, which we can read off the graph. This point occurs at approximately 340 s. **(b)** Solving Equation for k , we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340 \text{ s}} = 2.0 \times 10^{-3} \text{ s}^{-1}$$



| Rate Law | Order | Units of k |
|---|--|-------------------------------|
| $\text{Rate} = k$ | Zero | M s^{-1} |
| $\text{Rate} = k[\text{A}]$ | First order with respect to A First order overall | s^{-1} |
| $\text{Rate} = k[\text{A}]^2$ | Second order with respect to A Second order overall | $\text{M}^{-1} \text{s}^{-1}$ |
| $\text{Rate} = k[\text{A}][\text{B}]$ | First order with respect to A First order with respect to B Second order overall | $\text{M}^{-1} \text{s}^{-1}$ |
| $\text{Rate} = k[\text{A}][\text{B}][\text{C}]$ | First order with respect to A First order with respect to B First order with respect to C Third order overall | $\text{M}^{-2} \text{s}^{-1}$ |

| | Order | | |
|--|-------------------------|----------------------------|---------------------------------|
| | zero | first | second (equal conc.) |
| Overall reaction | $A \longrightarrow B$ | $A \longrightarrow B$ | $2A \longrightarrow B$ |
| Definition of rate | $-\Delta[A] / \Delta t$ | $-\Delta[A] / \Delta t$ | $-\Delta[A] / 2 \Delta t$ |
| Rate law | Rate = k | Rate = k [A] | k [A] ² |
| k unit | M s ⁻¹ | s ⁻¹ | M ⁻¹ s ⁻¹ |
| Integrated rate law | $[A] = -k t + [A]_0$ | $\ln[A] = -k t + \ln[A]_0$ | $1/[A] = k t + 1/[A]_0$ |
| Plot needed to give a straight line | [A] vs. t | ln[A] vs. t | 1 / [A] vs. t |
| Relationship of k to slope of straight line | -k | -k | k |
| Half-life | $[A]_0 / 2 k$ | $\ln 2 / k$ | $1 / 2 k [A]_0$ |

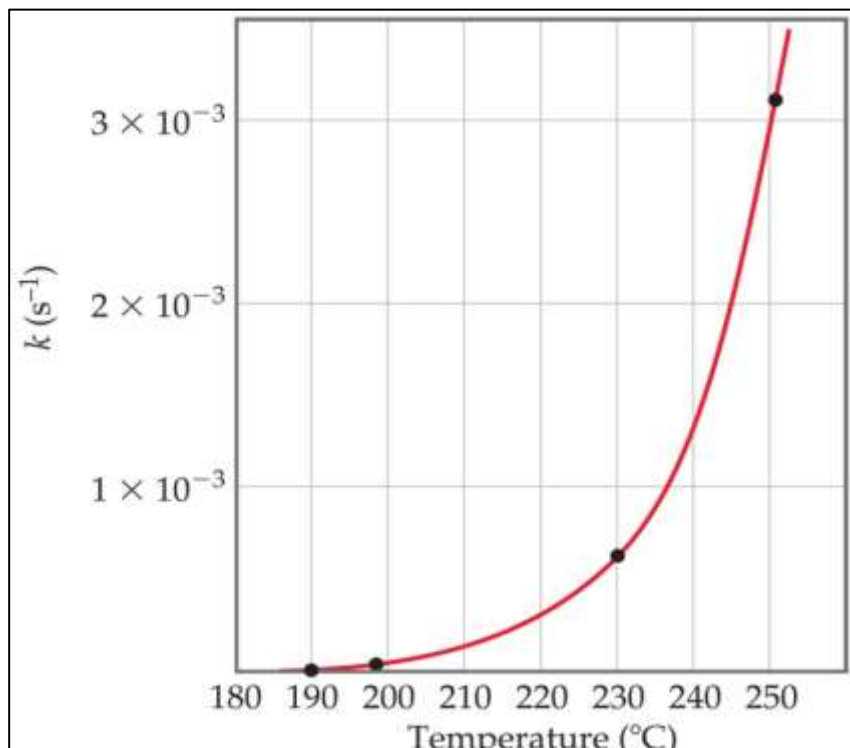
Note:

Zero, second, third (equal and different concentrations)... etc. orders **are not included**.

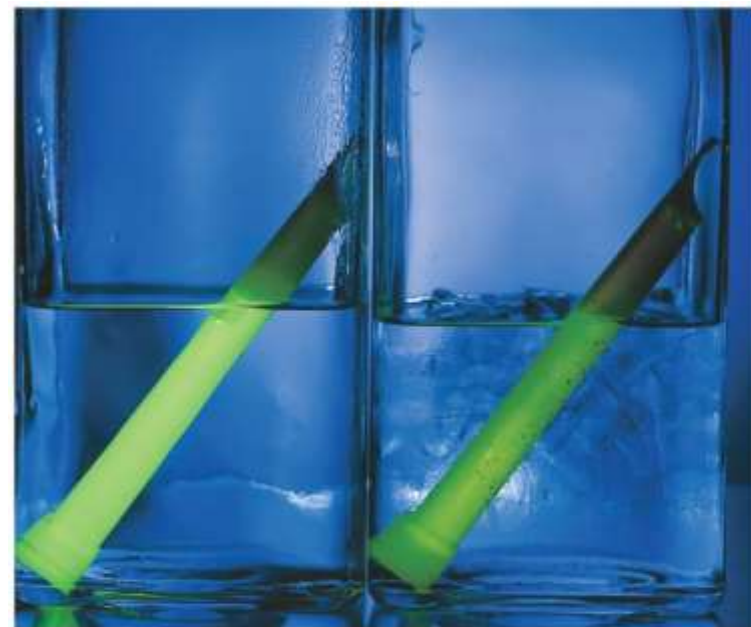
14.5

Temperature and Rate

The rates of most chemical reactions increase as the temperature rises. This due to an increase in the rate constant with increasing temperature; (k is temperature dependent).



The figure shows the rate constant for this reaction as a function of temperature. The k and hence the rate of the reaction, increases rapidly with temperature, approximately doubling for each 10°C rise.

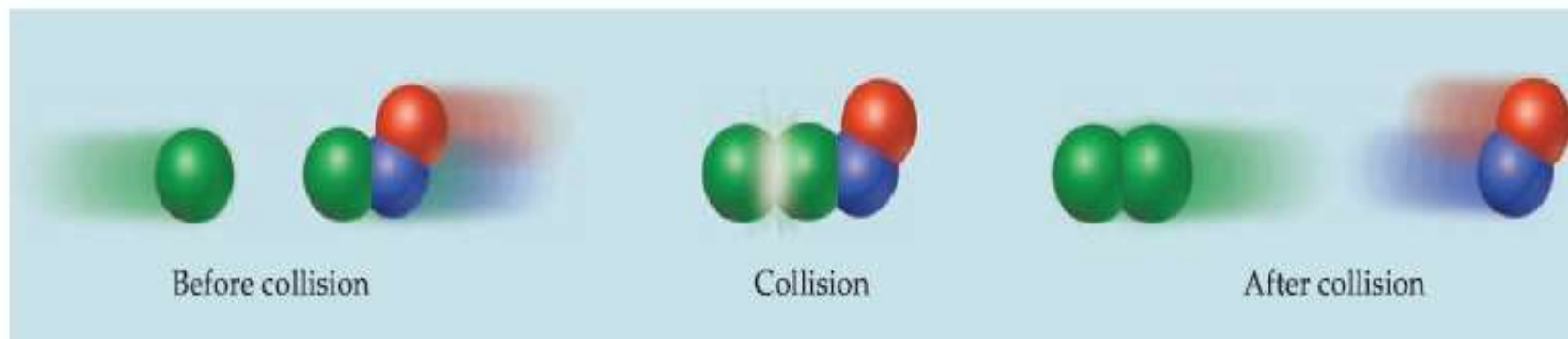


Higher temperature

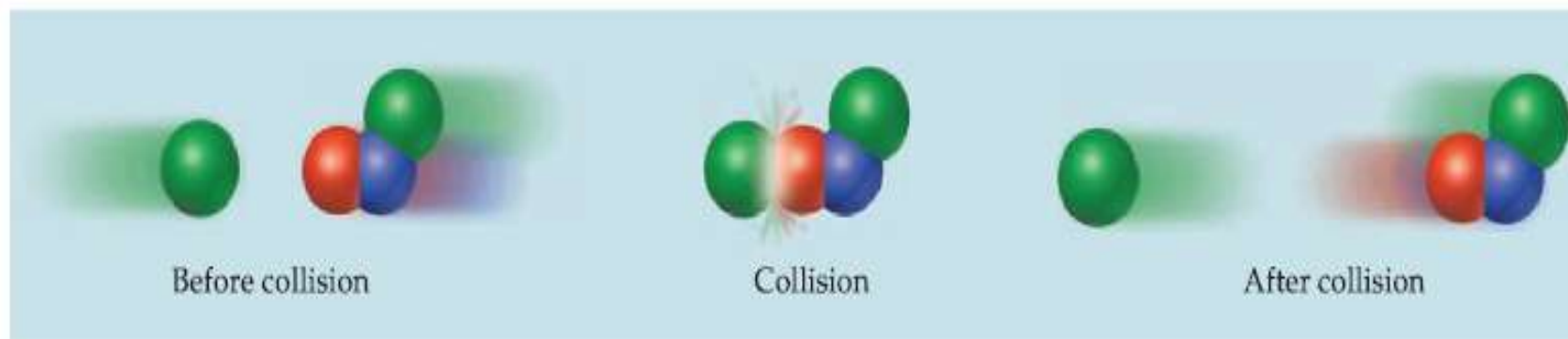
Lower temperature

Temperature affects the rate of the chemiluminescence reaction in Cyalume light sticks. The light stick in hot water glows more brightly than the one in cold water. At higher temperature the reaction is faster.

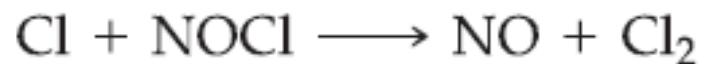
The Collision Model



(a) Effective collision



(b) Ineffective collision



- In a chemical reaction, **bonds** are **broken** and new bonds are **formed**.
- Molecules can only react if they **collide** with each other (molecules must collide to react). The greater the number of collisions, the greater is the reaction rate.
- Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.
- As the **concentration** of reactant molecules increases, the number of collisions increases, leading to an increase in reaction rate.
- Increasing the **temperature** increases molecular speed. Then collide more forcefully (with more energy) and more frequently, increasing reaction rates.

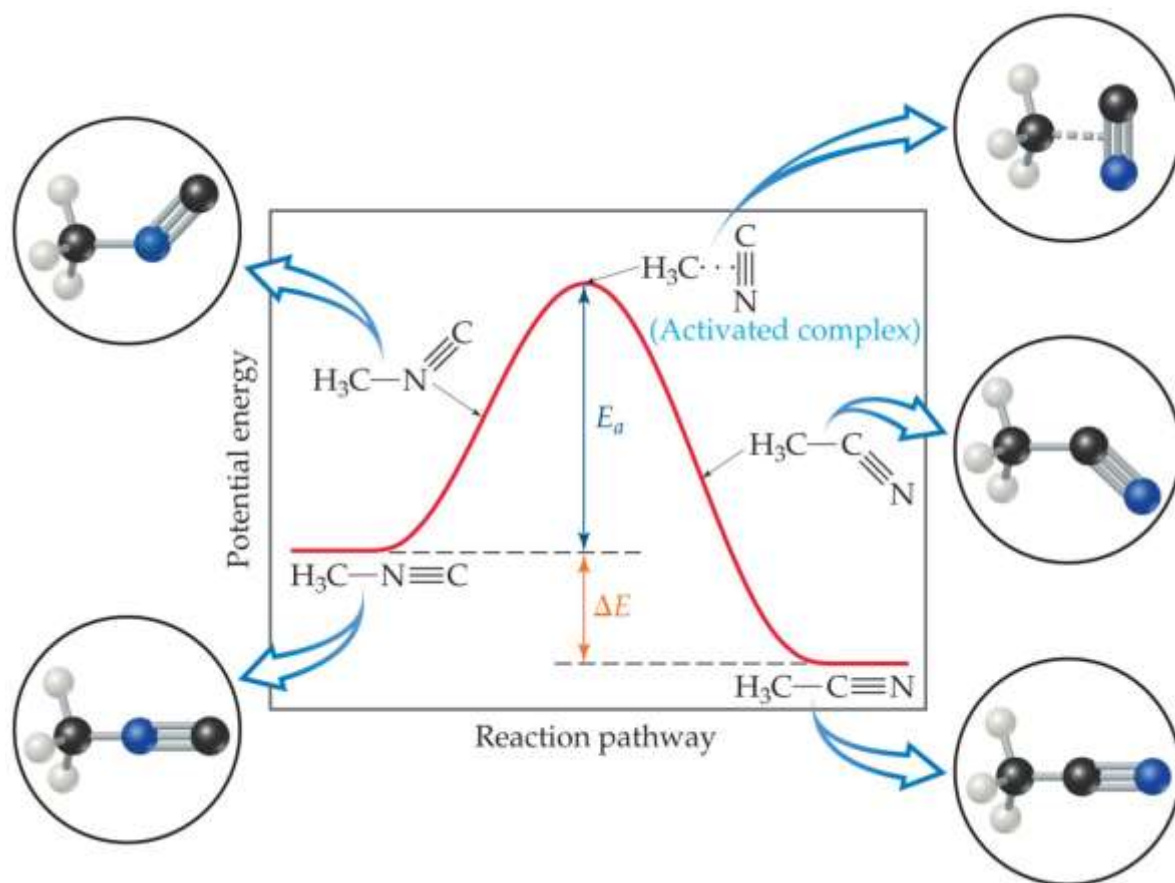
Activation Energy

- There is a minimum amount of energy required for reaction: the **activation energy**, E_a .
- The value of E_a varies from reaction to reaction.
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.



Reaction Coordinate Diagrams

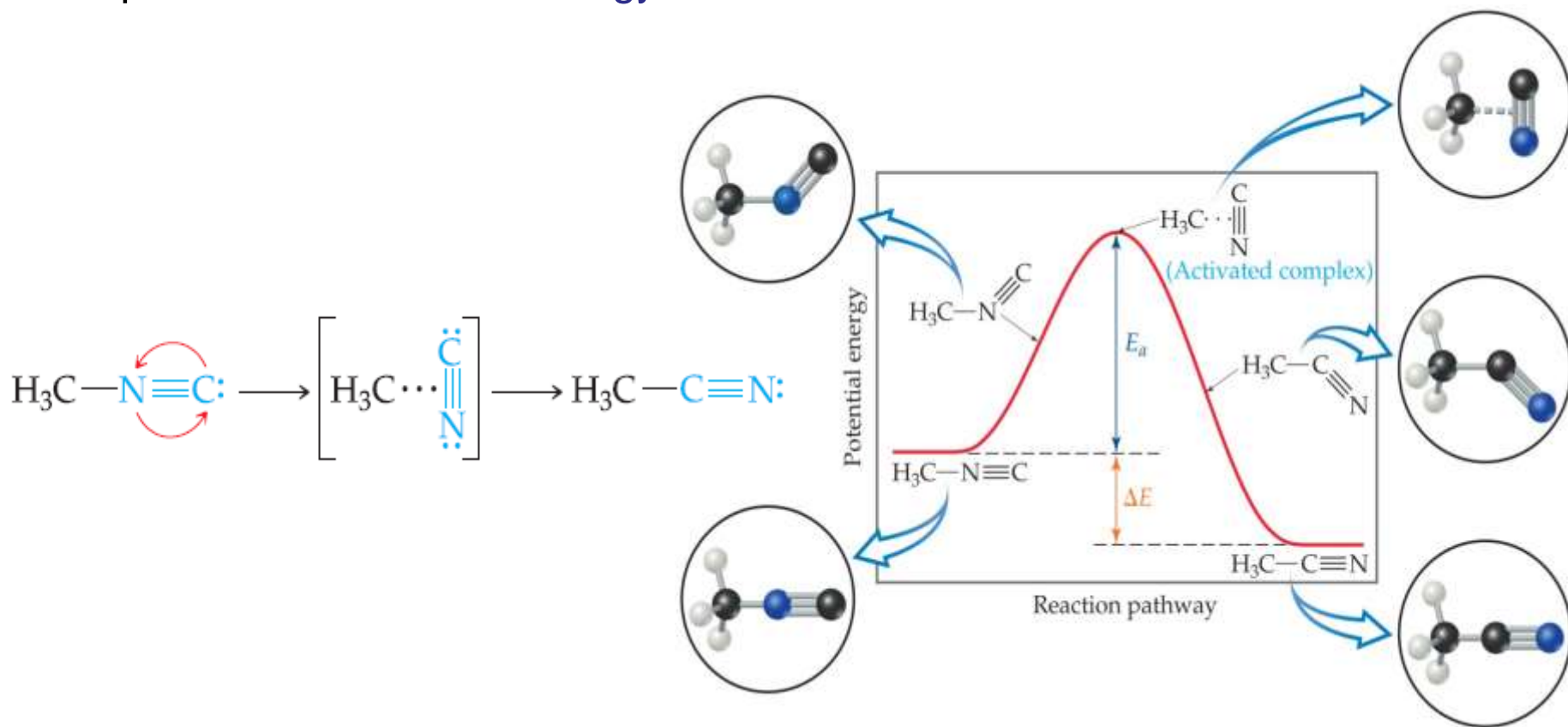
It is helpful to visualize energy changes throughout a process on a **reaction coordinate diagram** like this one for the rearrangement of methyl isonitrile.



The energy change for the reaction, ΔE , has no effect on the rate of the reaction. The rate depends on the magnitude of E_a ; generally, **the lower E_a is the faster the reaction**. The activation barrier for the reverse reaction is equal to the sum of ΔE and E_a for the forward reaction.

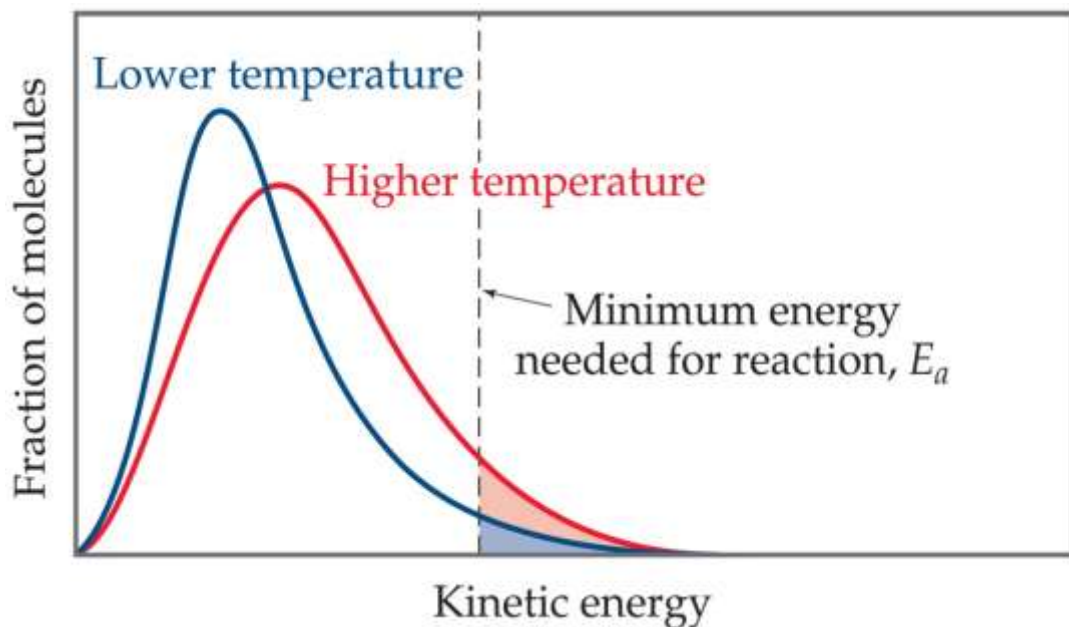
Energy profile for isonitrile isomerization (reaction pathway or progress of reaction). The isonitrile molecule must surmount the activation energy barrier before it can form product, acetonitrile.

The diagram shows the energy of the reactants and products (and, therefore, ΔE). The high point on the diagram is the transition state. The particular arrangement of atoms at the top of the barrier is called the **activated complex** or **transition state**. The energy gap between the reactants and the activated complex is the activation **energy barrier**.



Maxwell–Boltzmann Distributions

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



- At any temperature there is a wide distribution of kinetic energies.
- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules (greater fraction of the molecules) has higher energy (greater than E_a).
- As a result, the reaction rate increases.

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

This fraction of molecules can be found through the expression

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

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

Arrhenius Equation

Svante Arrhenius noted that for most reactions, the increase in rate with increasing temperature is nonlinear. Arrhenius developed a mathematical relationship between k and E_a :

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

where k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/mol-K), and T is the absolute temperature. A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction. A is constant or nearly so as temperature is varied.

As the magnitude of E_a increases, k decreases because the fraction of molecules that possess the required energy is smaller. Thus, reaction rates decrease as E_a increases.

Taking the natural logarithm of both sides, the equation becomes:

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



$$\ln k = -\frac{E_a}{RT} + \ln A$$



y

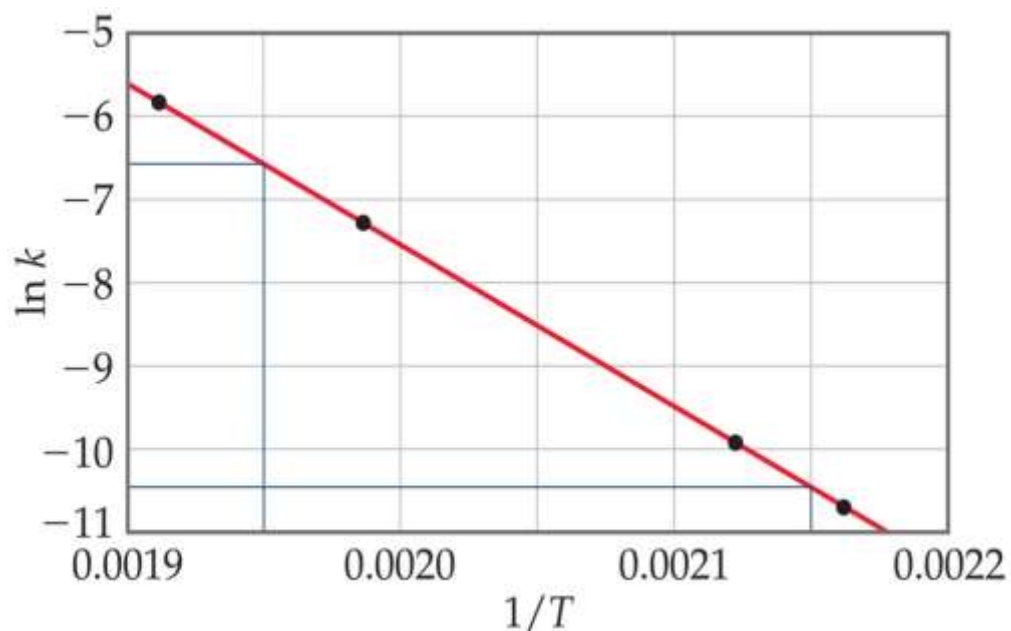


mx



b

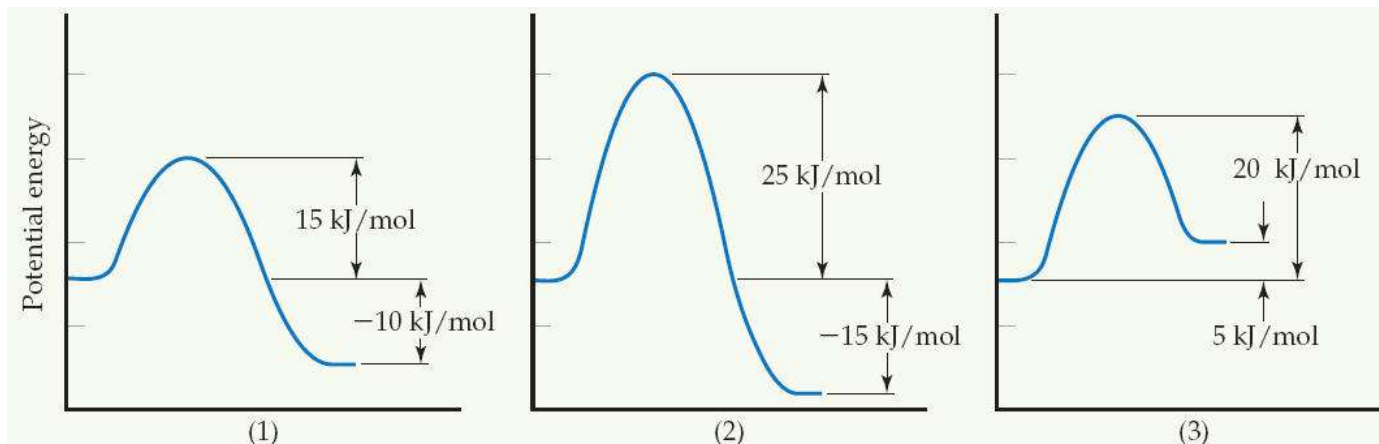
$$y = mx + b$$



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

Sample Exercise 14.10 Relating Energy Profiles to Activation Energies and Speed of Reaction

Consider a series of reactions having the following energy profiles:



Rank the reactions from slowest to fastest assuming that they have nearly the same frequency factors.

Solution

The lower the activation energy, the faster the reaction. The value of ΔE does not affect the rate. Hence the order is (2) < (3) < (1).

Practice Exercise

Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest.

Answer: (2) < (1) < (3) because E_a values are 40, 25, and 15 kJ/mol , respectively

We can evaluate E_a in a nongraphical way if we know the rate constant of a reaction at two or more temperatures.

Suppose that at two different temperatures, T_1 and T_2 , a reaction has rate constants k_1 and k_2 . For each condition, we have:

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

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

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

Sample Exercise 14.11 Determining the Energy of Activation

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures :

| Temperature (°C) | k (s ⁻¹) |
|------------------|------------------------|
| 189.7 | 2.52×10^{-5} |
| 198.9 | 5.25×10^{-5} |
| 230.3 | 6.30×10^{-4} |
| 251.2 | 3.16×10^{-3} |

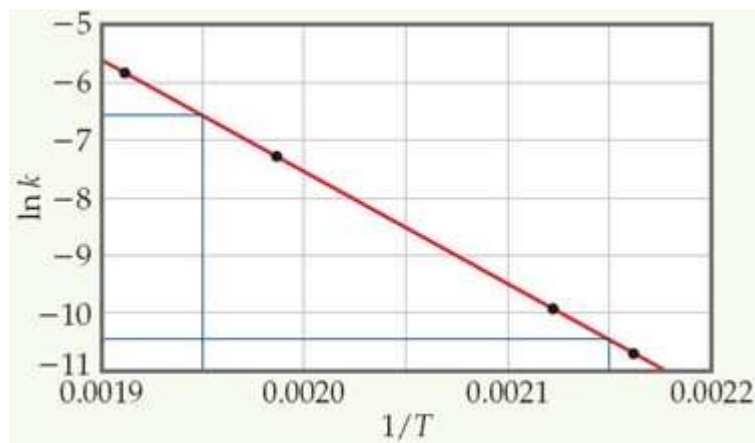
(a) From these data, calculate the activation energy for the reaction. **(b)** What is the value of the rate constant at 430.0 K?

Solution

(a) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the table shown at the right:

A graph of $\ln k$ versus $1/T$ results in a straight line.

| T (K) | $1/T$ (K ⁻¹) | $\ln k$ |
|---------|--------------------------|---------|
| 462.9 | 2.160×10^{-3} | -10.589 |
| 472.1 | 2.118×10^{-3} | -9.855 |
| 503.5 | 1.986×10^{-3} | -7.370 |
| 524.4 | 1.907×10^{-3} | -5.757 |



Graphical determination of activation energy. The natural logarithm of the k for the rearrangement of isonitrile is plotted as a function of $1/T$. The linear relationship is predicted by Arrhenius equation giving a slope equal to $-E_a/R$.

Solution (continued)

The slope of the line is obtained by choosing two well-separated points, as shown, and using the coordinates of each:

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1} . Thus, the overall units for the slope are K . The slope equals $-E_a/R$. We use the value for the molar gas constant R in units of $J/mol\cdot K$ (Table 10.2). We thus obtain

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

$$\text{Slope} = -\frac{E_a}{R}$$

$$\begin{aligned} E_a &= -(\text{slope})(R) = -(-1.9 \times 10^4 K) \left(8.314 \frac{J}{mol \cdot K} \right) \left(\frac{1 kJ}{1000 J} \right) \\ &= 1.6 \times 10^2 kJ/mol = 160 kJ/mol \end{aligned}$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.17.

(b) To determine the rate constant, k_1 , at $T_1 = 430.0$ K, we can use Equation 14.21 with $E_a = 160$ kJ/mol, and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5} s^{-1}$ and $T_2 = 462.9$ K:

$$\ln\left(\frac{k_1}{2.52 \times 10^{-5} s^{-1}}\right) = \left(\frac{160 kJ/mol}{8.314 J/mol \cdot K}\right) \left(\frac{1}{462.9 K} - \frac{1}{430.0 K}\right) \left(\frac{1000 J}{1 kJ}\right) = -3.18$$

Thus,

$$\begin{aligned} \frac{k_1}{2.52 \times 10^{-5} s^{-1}} &= e^{-3.18} = 4.15 \times 10^{-2} \\ k_1 &= (4.15 \times 10^{-2})(2.52 \times 10^{-5} s^{-1}) = 1.0 \times 10^{-6} s^{-1} \end{aligned}$$

Note that the units of k_1 are the same as those of k_2 .

Practice Exercise

Using the data in the above Sample Exercise, calculate the rate constant for the rearrangement of methyl isonitrile at $280^\circ C$.

Answer: $2.2 \times 10^{-2} s^{-1}$



Q & A



The rate of a chemical reaction is affected by:

- a. the concentration of the reactants
- b. the temperature of the reaction
- c. the presence of a catalyst
- d. all of the above

As a chemical reaction proceeds, the rate of the reaction tends to:

- a. increase
- b. decrease
- c. remain constant
- d. oscillate

The time needed for half of the reactant to be consumed is called the _____ of the reaction.

- a. midpoint
- b. equivalence point
- c. half-rate
- d. half-life

The half-life of a first-order reaction is equal to _____, where k is the rate constant.

a. $0.693/k$

b. $0.693k$

c. $k/2$

d. $2k$

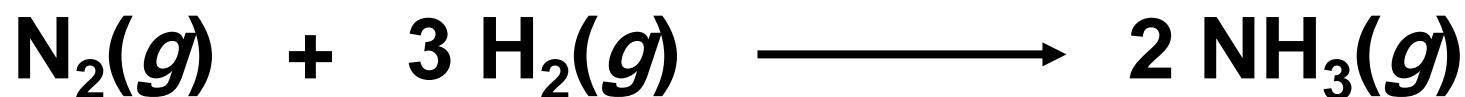
The minimum energy a collision between molecules must have to produce the products is called the _____ energy.

- a. initiation
- b. internal
- c. external
- d. activation

The rate-determining step is the _____ step in a reaction mechanism.

- a. first
- b. last
- c. fastest
- d. slowest

Which expression correctly states the rate of reaction?



1. $\text{rate} = \frac{-\Delta 3[\text{H}_2]}{\Delta t}$

2. $\text{rate} = \frac{-\Delta[\text{H}_2]}{\Delta t}$

3. $\text{rate} = \frac{+\Delta[\text{N}_2]}{\Delta t}$

4. $\text{rate} = \frac{+\Delta[\text{NH}_3]}{2\Delta t}$

5. $\text{rate} = \frac{+\Delta 2[\text{NH}_3]}{\Delta t}$

What is the rate law for the reaction?

A + 2 B \longrightarrow products

- Rate = $k[A][B]^2$
- Rate = $k[A][B]$
- Rate = $k[A]^2[B]$
- **Rate = $k[A]$**
- Rate = $k[B]$

| [A] | [B] | Initial Rate <i>M/s</i> |
|------|------|-------------------------|
| 0.10 | 0.10 | 1.0×10^{-4} |
| 0.10 | 0.20 | 1.0×10^{-4} |
| 0.20 | 0.20 | 2.0×10^{-4} |

What is the rate law for the reaction?

$$2 \text{ A} + \text{ B} \longrightarrow \text{ products}$$

- Rate = $k[\text{A}][\text{B}]^2$
- Rate = $k[\text{A}][\text{B}]$
- Rate = $k[\text{A}]^2[\text{B}]$
- Rate = $k[\text{A}]^2[\text{B}]^4$
- Rate = $k[\text{B}]$

| [A] | [B] | Initial Rate M/s |
|------|------|----------------------|
| 0.10 | 0.10 | 1.0×10^{-4} |
| 0.10 | 0.20 | 4.0×10^{-4} |
| 0.20 | 0.20 | 8.0×10^{-4} |

What are the units of the rate constant for a reaction with a rate law of:

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

- M s
- M² s
- M⁻¹ s⁻¹
- M⁻¹ s⁻²
- M⁻² s⁻¹

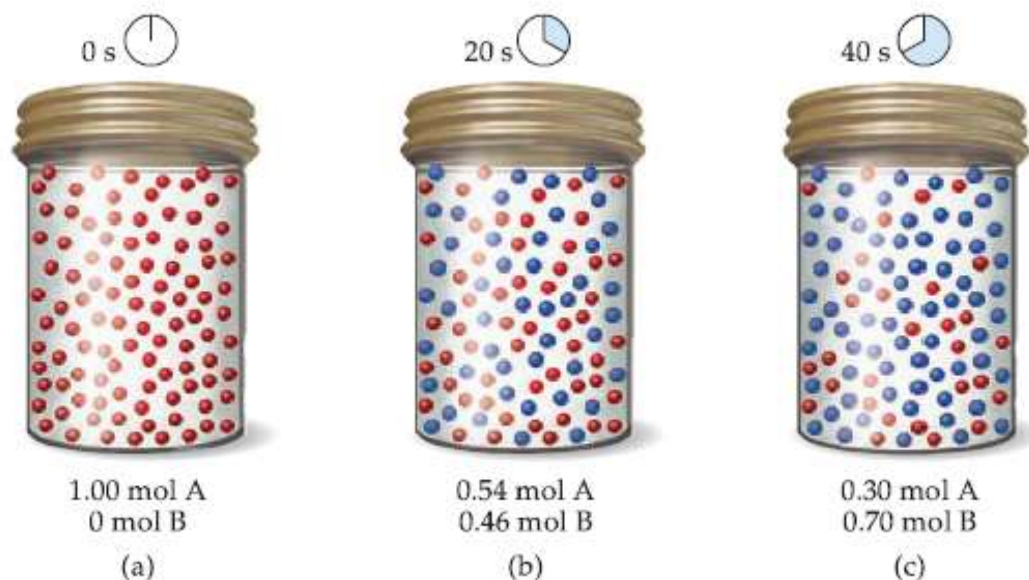
If $t_{1/2} = 500$ s for a first-order reaction, how long will it take for the concentration of a reactant to decrease to $1/8$ of its original value?

- $2 \times 500 = 1000$ s
- $3 \times 500 = 1500$ s
- $4 \times 500 = 2000$ s
- $5 \times 500 = 2500$ s
- $8 \times 500 = 4000$ s

For the reaction pictured in the Figure to calculate the average rate of appearance of B over the time interval from 0 to 40 s.

Answer:

$$1.8 \times 10^{-2} \text{ M/s}$$



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 ?

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

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



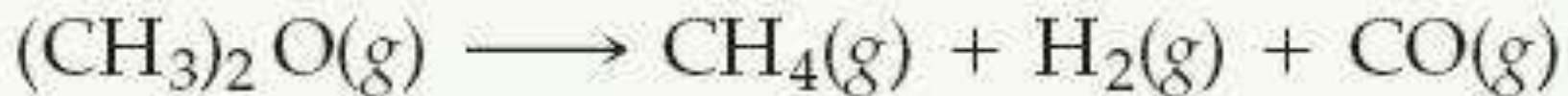
| Experiment Number | [NO] (M) | [H ₂] (M) | Initial Rate (M/s) |
|-------------------|----------|-----------------------|-----------------------|
| 1 | 0.10 | 0.10 | 1.23×10^{-3} |
| 2 | 0.10 | 0.20 | 2.46×10^{-3} |
| 3 | 0.20 | 0.10 | 4.92×10^{-3} |

(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

Answers: (a) $\text{rate} = k[\text{NO}]^2[\text{H}_2]$;

(b) $k = 1.2 \text{ M}^{-2} \text{ s}^{-1}$; (c) $\text{rate} = 4.5 \times 10^{-4} \text{ M/s}$

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 pressure after 1420 s?

Answer: 51 torr

(a) Calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. **(b)** How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Answer: (a) $0.478 \text{ yr} = 1.51 \times 10^7 \text{ s}$;

(b) it takes two half-lives, $2(0.478 \text{ yr}) = 0.956 \text{ yr}$

