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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.

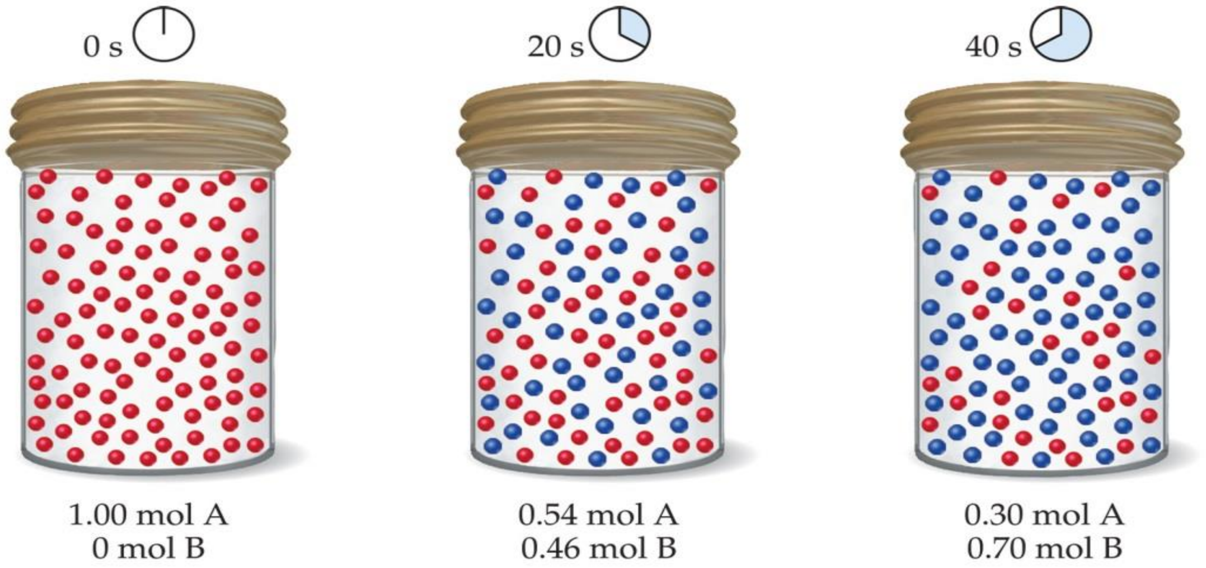
For a collision to lead to a reaction, however, it must occur with **sufficient energy** to stretch bonds to a critical length and with **suitable orientation** for new bonds to form in the proper locations.

14.2

Reaction Rates

Reaction Rates

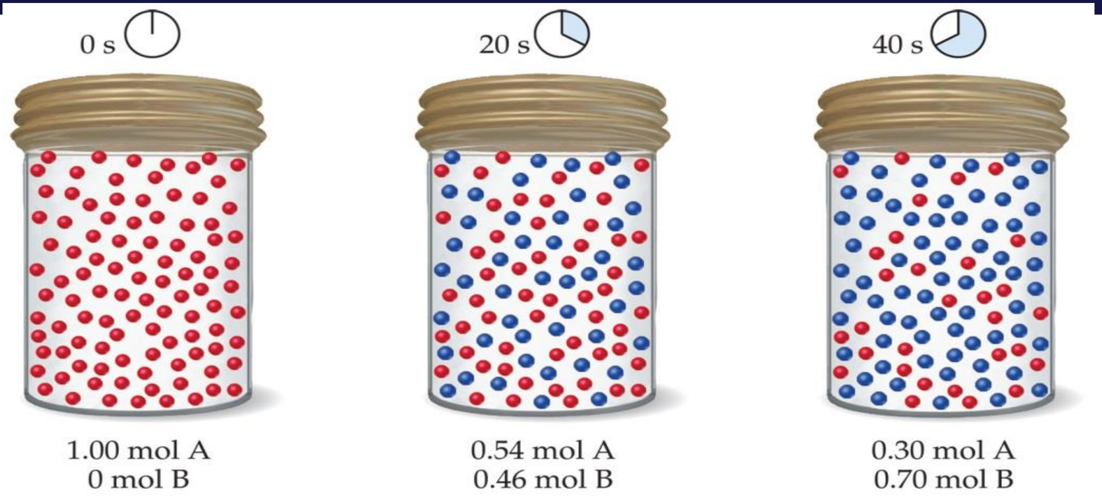
The speed of an event is defined as the change that occurs in a given interval of time: Whenever we talk about speed, we necessarily bring in the notion of time.



Progress of a hypothetical reaction **A** $\longrightarrow$ **B**

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).

$$\mathbf{A} \longrightarrow \mathbf{B}$$



$$\text{Average rate of appearance of B} = \frac{\text{change in concentration of B}}{\text{change in time}}$$

$$= \frac{[\mathrm{B}] \text{ at } t_2 - [\mathrm{B}] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[\mathrm{B}]}{\Delta t}$$

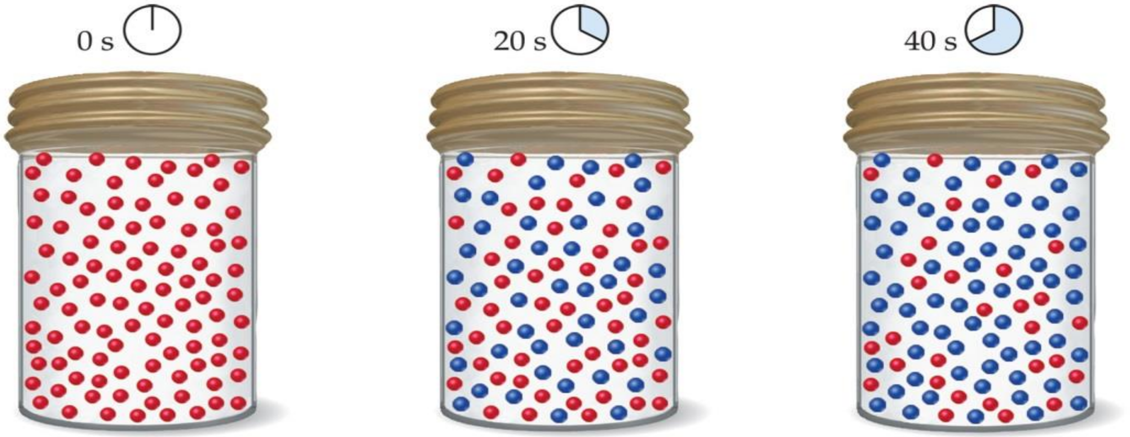
$$\text{Average rate} = \frac{0.46\ M - 0.00\ M}{20\ \mathrm{s} - 0\ \mathrm{s}} = 2.3 \times 10^{-2}\ M/\mathrm{s}$$

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

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

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

Sample Exercise 14.1 Calculating an Average Rate of Reaction



1.00 mol A
0 mol B

0.54 mol A
0.46 mol B

0.30 mol A
0.70 mol B

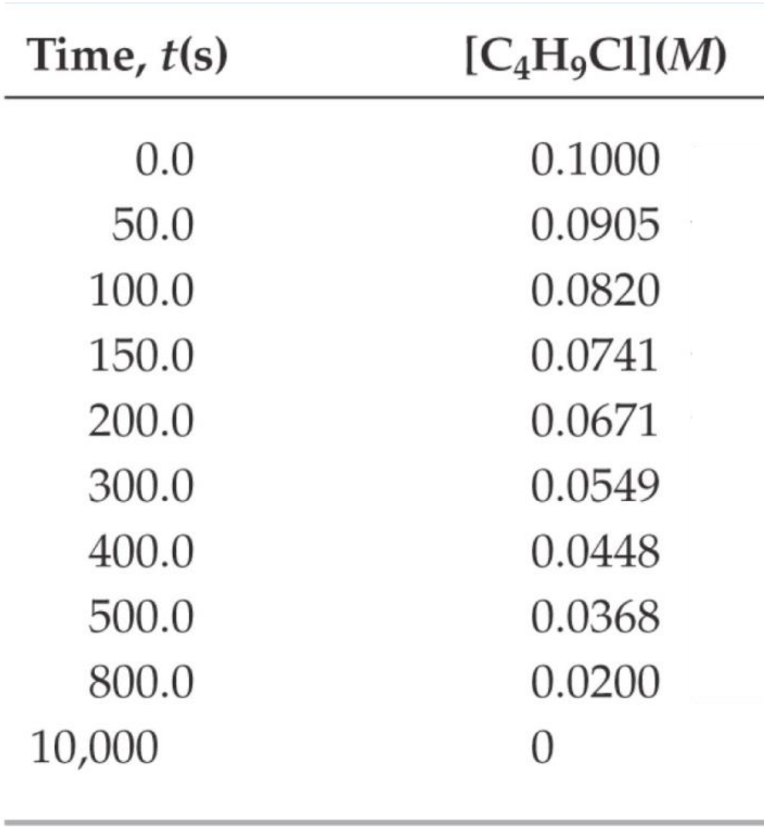
From the data given in the caption of Figure, calculate the average rate at which **A** disappears over the time interval from 20 s to 40 s.

Solution

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

Change of Rate with Time

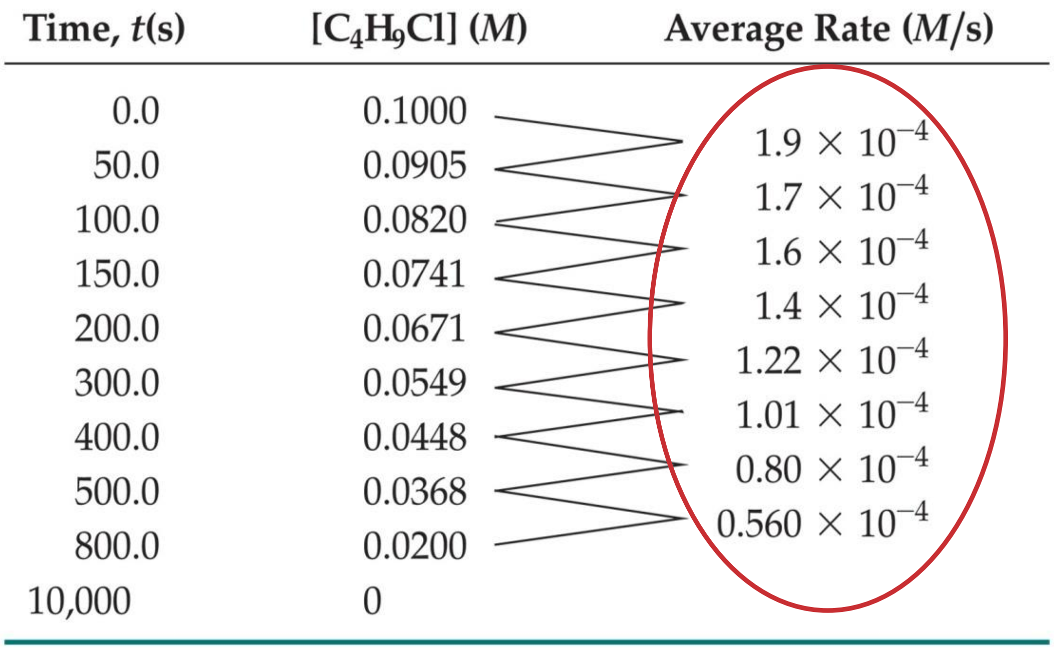
$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$



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

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

The concentration of **C_4H_9Cl** decreases with the time.



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

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

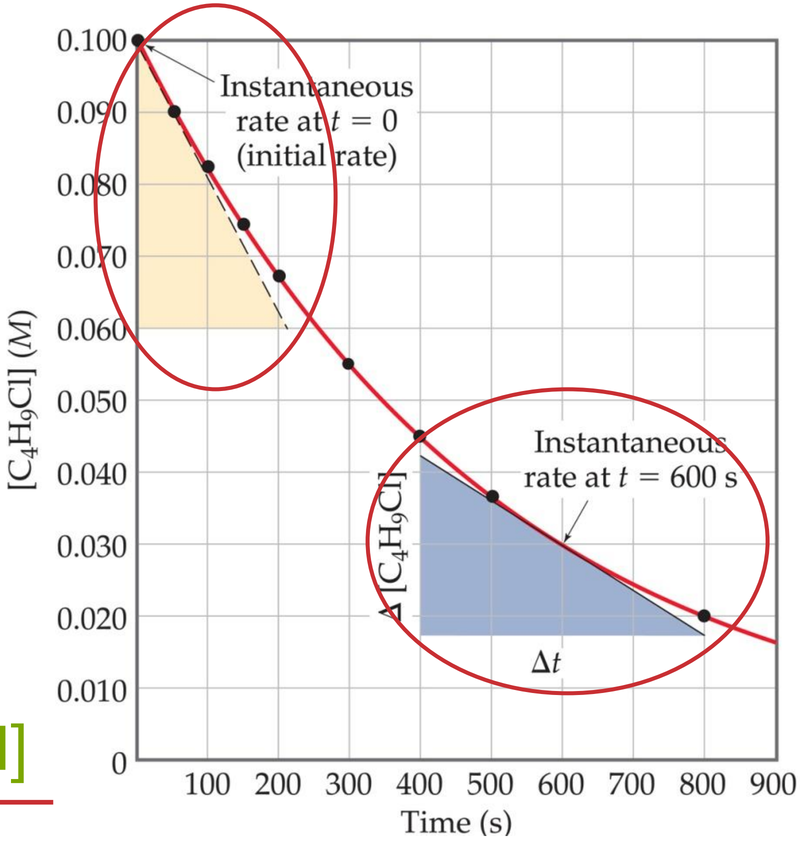
Note that the average rate decreases as the reaction proceeds. This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

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

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

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

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH.



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

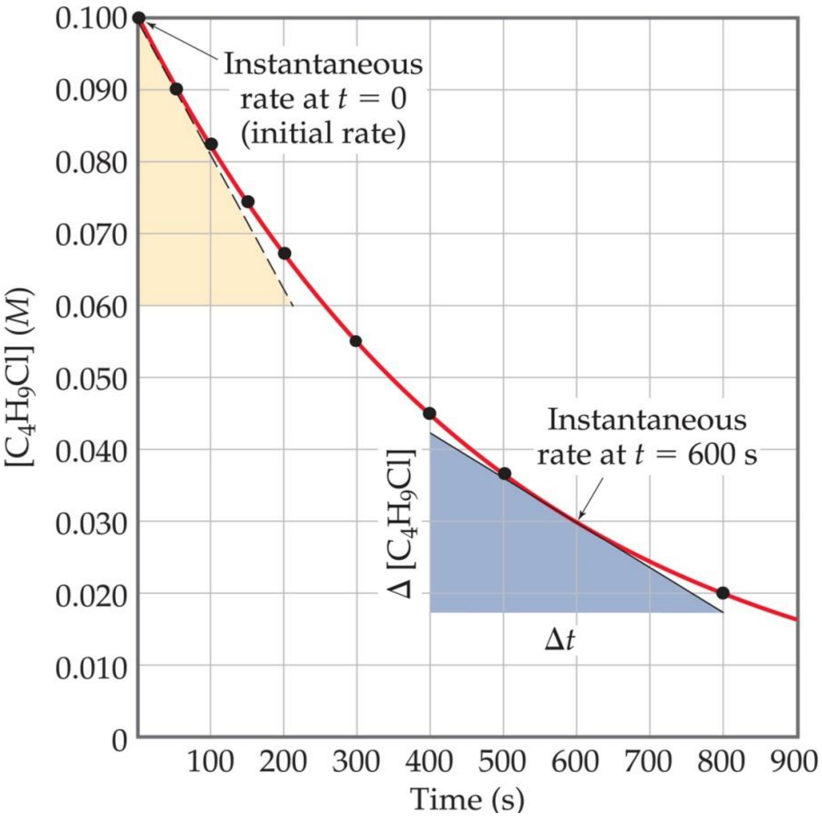
It is typical for rates to decrease as a reaction proceeds, because the concentration of reactants decreases.

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:

$$\text{Instantaneous rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042)\,M}{(800 - 400)\text{s}}$$
$$= 6.3 \times 10^{-5}\ M/\text{s}$$



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

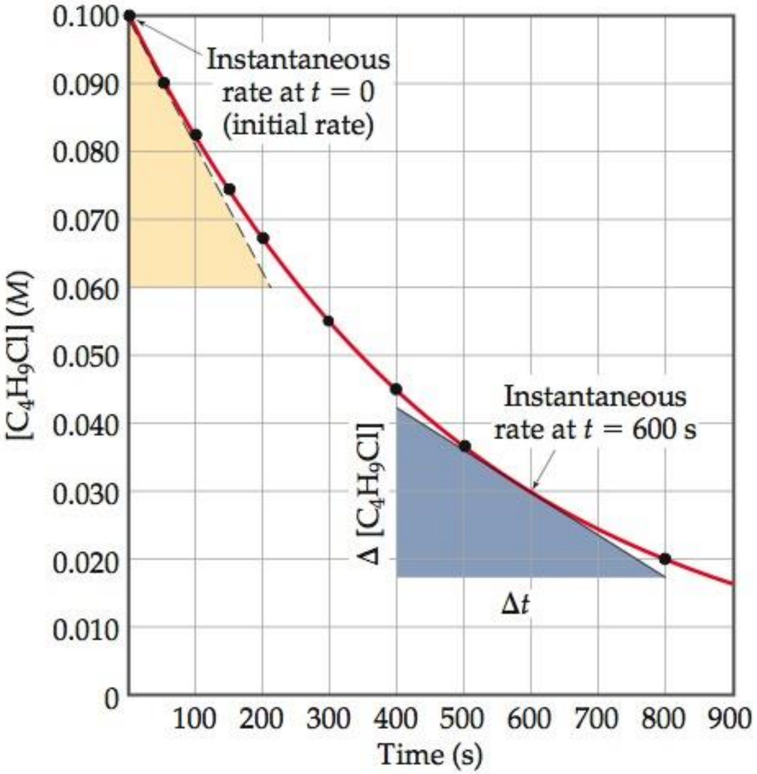
Sample Exercise 14.2 Calculating an Instantaneous Rate of Reaction

Using the Figure, calculate the instantaneous rate of disappearance of C_4H_9Cl 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 $[C_4H_9Cl]$ = 0.100 M to 0.060 M in the time change from 0 s to 210 s. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\ M}{(210 - 0)\ s} = 1.9 \times 10^{-4}\ M/s$$



Practice Exercise

Using the Figure to determine the instantaneous rate of disappearance of C_4H_9Cl at t = 300 s.

Answer: 1.1×10^{-4} M/s

Reaction Rates and Stoichiometry

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

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

the ratio of C_4H_9Cl to C_4H_9OH is 1:1.

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

$$H_{2(g)} + I_{2(g)} \longrightarrow 2\ HI_{(g)}$$

Only **1/2 HI** is made for each **H_2** used.

$$rate = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

- To generalize, for the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

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

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 $O_3(g) \rightarrow 3\ O_2(g)$?

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

Solution

(a)

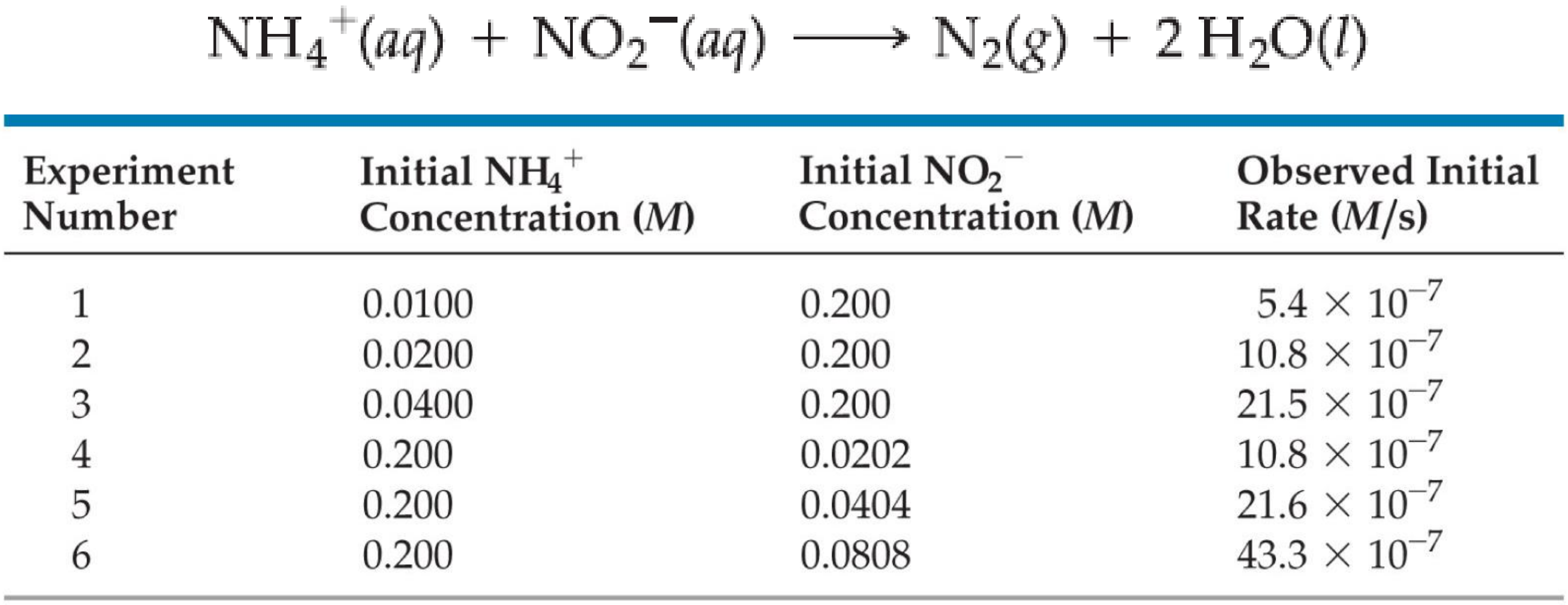
$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

(b)

$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}(6.0 \times 10^{-5}\ M/\mathrm{s}) = 4.0 \times 10^{-5}\ M/\mathrm{s}$$

14.3

The rate Law: the Effect of Concentration on rate



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

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 $[NH_4^+]$ doubles while $[NO_2^-]$ hold constant, the initial rate doubles.

Likewise, when we compare. experiments 5 & 6, we see that when $[NO_2^-]$ doubles while $[NH_4^+]$ hold constant, the initial rate doubles.

If $[NH_4^+]$ is increased by a factor 4 with $[NO_2^-]$ left unchanged (Experiments 1 & 3), the rate changes by a factor of 4, and so forth.

This means

$$\textbf{Rate} \propto [\mathrm{NH_4^+}]$$

$$\textbf{Rate} \propto [\mathrm{NO_2^-}]$$

Therefore,

$$\textbf{Rate} \propto [\mathrm{NH_4^+}]\,[\mathrm{NO_2^-}]$$

which, when written as an equation, becomes

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

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

$$\mathbf{Rate} = \boldsymbol{k}\ [\mathrm{NH_4^+}]\ [\mathrm{NO_2^-}]$$

the reaction is

First-order in $[\mathrm{NH_4^+}]$ and
First-order in $[\mathrm{NO_2^-}]$

$$rate = k\left[NH_4^+\right]^1\left[NO_2^-\right]^1$$

$$\mathbf{Rate} = \boldsymbol{k}\ [\mathrm{NH_4^+}]\ [\mathrm{NO_2^-}]$$

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

For a general reaction,

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

The rate law generally has the form

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

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 $\mathbf{P_A}$ instead of **[A]**.

The rate laws for most reactions have the general form

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

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:

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \qquad \text{Rate} = k[N_2O_5]$$

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g) \qquad \text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \qquad \text{Rate} = k[H_2][I_2]$$

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

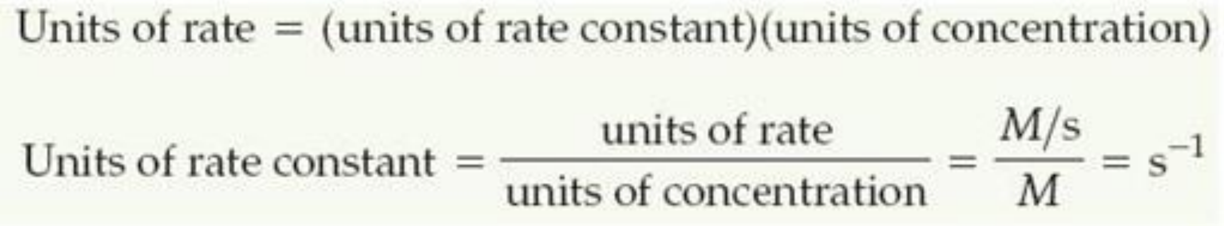
The values of these exponents must be determined **experimentally**. In most rate laws, reaction orders are 0, 1, or 2.

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

Units of Rate Constants

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

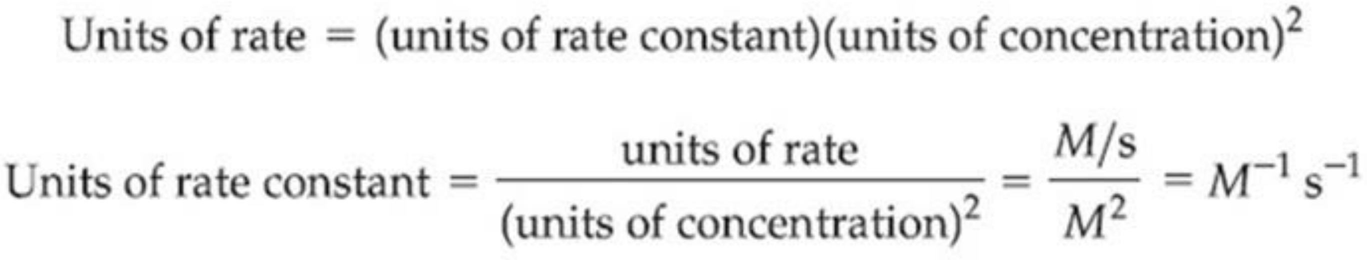
For the first order reactions



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

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

For the second order reactions



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

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

For the zero order reactions

$$\text{Units of rate} = (\text{unit of rate constant})\ (\text{units of concentration})^0$$

Unit of rate constant = units of rate = *M/s*

Using Initial Rates to Determine Rate Laws

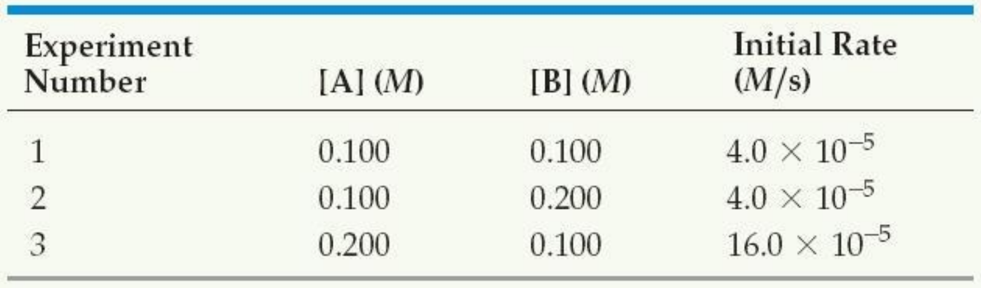
The rate law for any chemical reaction must be determined **experimentally**; it cannot be predicted by merely looking at the chemical equation.

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 → 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 M and [B] = 0.100 M.

Solution

(a)

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

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

$$n = 0$$

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

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

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

Solution (continued)

Because $2^m = 4$, we conclude that

$$m = 2$$

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

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

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

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

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.

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

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 → B

$$rate = k\left[A\right]$$

Differential form:

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

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

$$-d\left[A\right] = k\left[A\right]dt$$

$$\frac{d\left[A\right]}{\left[A\right]} = -kdt \qquad \int \frac{d\left[A\right]}{\left[A\right]} = -\int kdt$$

Integrated form:

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

The integrated form of first order rate law:

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

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

$[A]_0$ 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…

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

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

$$\boxed{ln\,[A]_t = -kt + ln\,[A]_0}$$

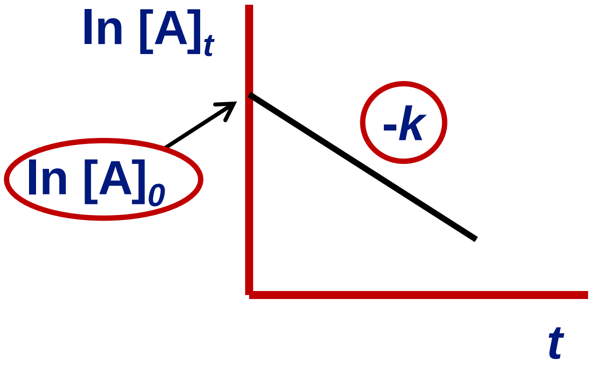
… which is in the form

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

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

If a reaction is first-order, a plot of

$\ln\,[A]_t$ vs. t



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

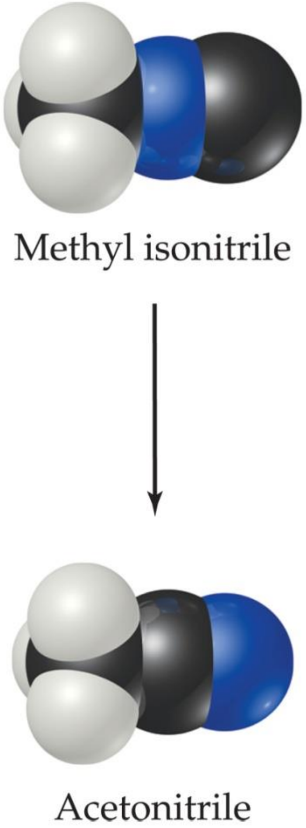
ln $[A]_o$ will be the intercept.

So, use graphs to determine reaction order.

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

$$CH_3NC \longrightarrow CH_3CN$$

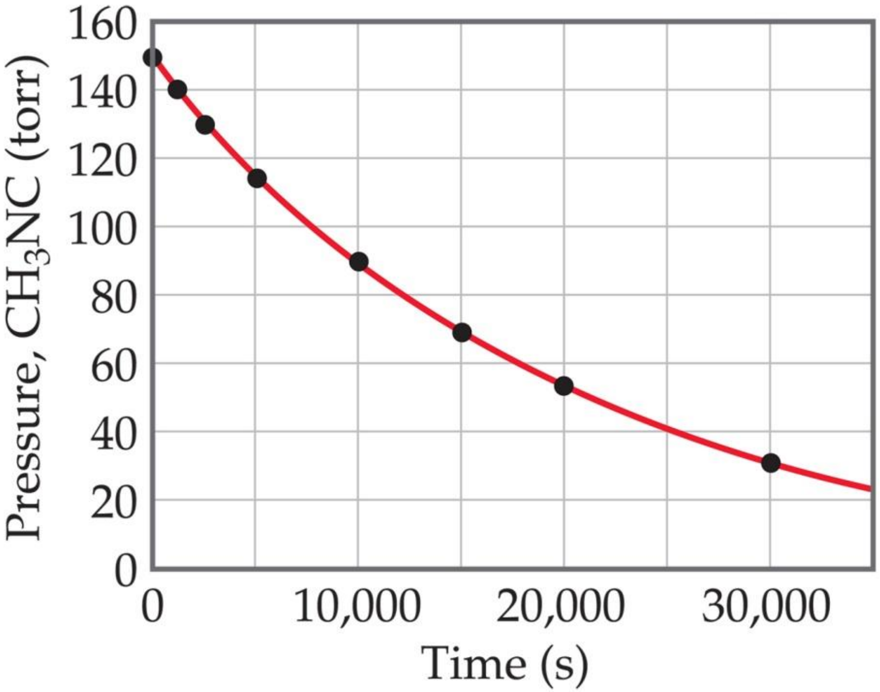
How do we know this is a first order reaction?



Does

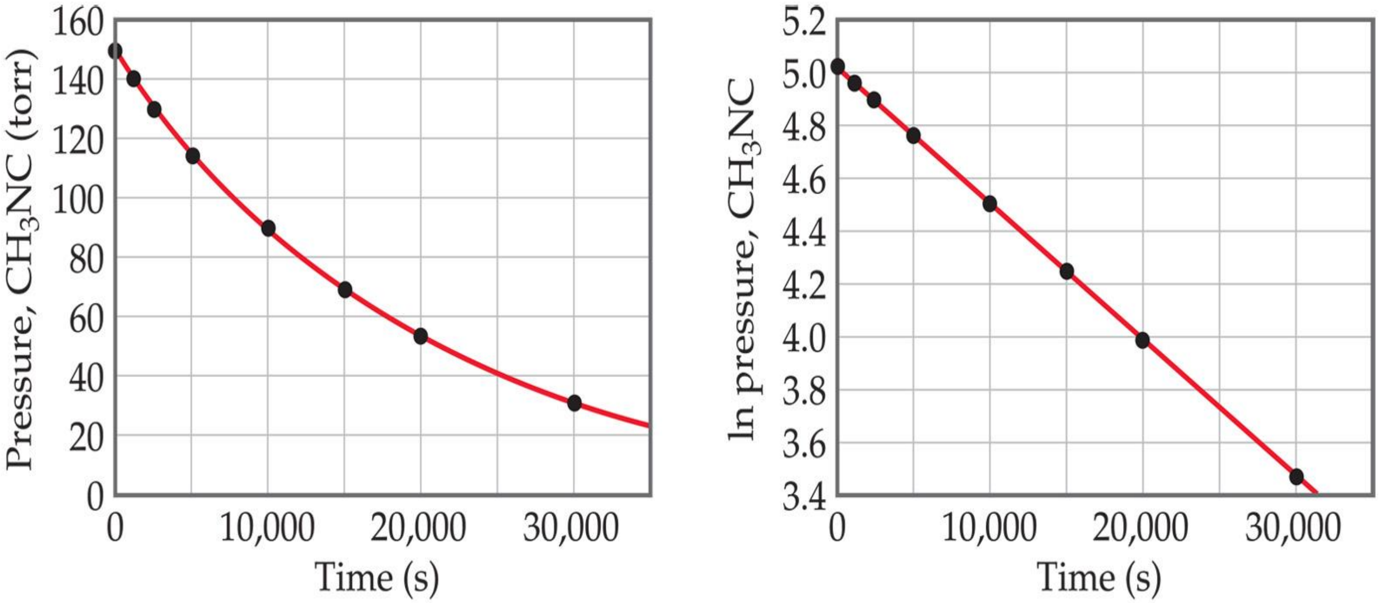
rate=k[CH_3NC]

for all time intervals?



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 CH_3NC with time during the reaction. A plot of natural logarithm of CH_3NC pressure as a function of time. Straight line confirms that the rate law is first order.

$$[A]_t = [A]_0 \, e^{-kt} \qquad ln\,[A]_t = -kt + ln\,[A]_0$$

When **ln *P*** is plotted as a function of ***t***, a straight line results, and hence;

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

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 ^{o}C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0 × 10^{-7} g/cm^3. Assume that the average temperature of the lake is 12 ^{o}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 × 10^{-7} g/cm^3?

Solution

(a)

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

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

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

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

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

(b)

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

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

$$= -(-15.02 + 14.51)/1.45\ \text{yr}^{-1} = 0.35\ \text{yr}$$

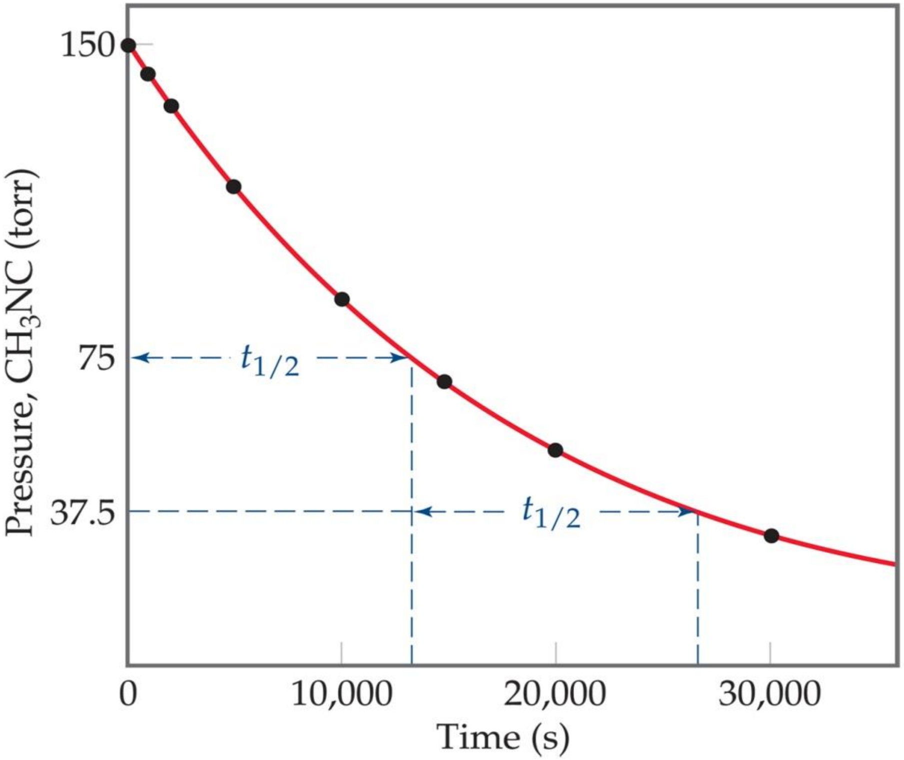
Half-Life (first-order process only)

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 $[A]_0$,

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

The change in concentration over time for the first-order rearrangement of **CH_3NC** 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 ½ in each of a series of regularly spaced time intervals, namely, $t_{1/2}$.



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

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

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

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

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

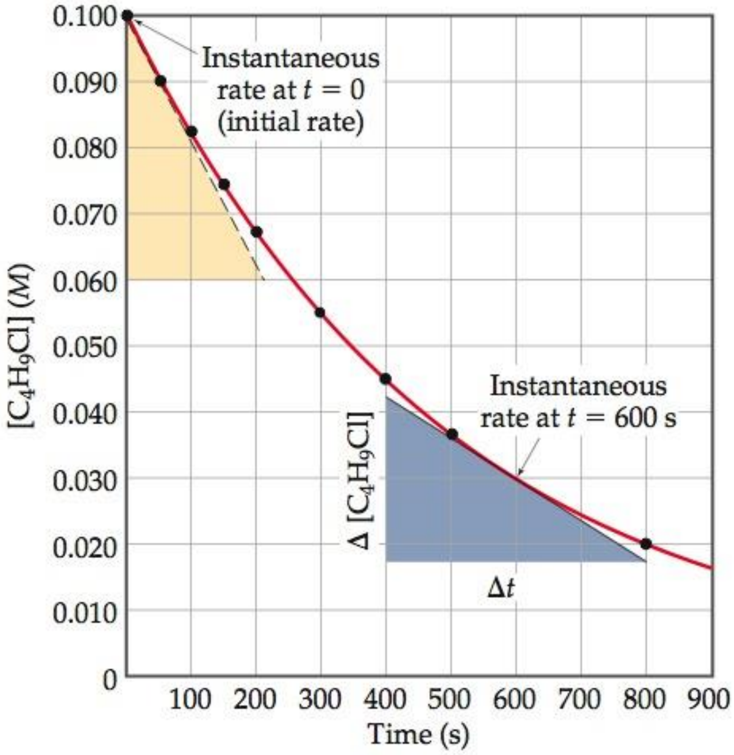
$$t_{1/2} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k}$$

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

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 C_4H_9Cl with water is a first-order reaction. The Figure shows how the concentration of C_4H_9Cl 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 $[C_4H_9Cl]$ is 0.100 M. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ 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

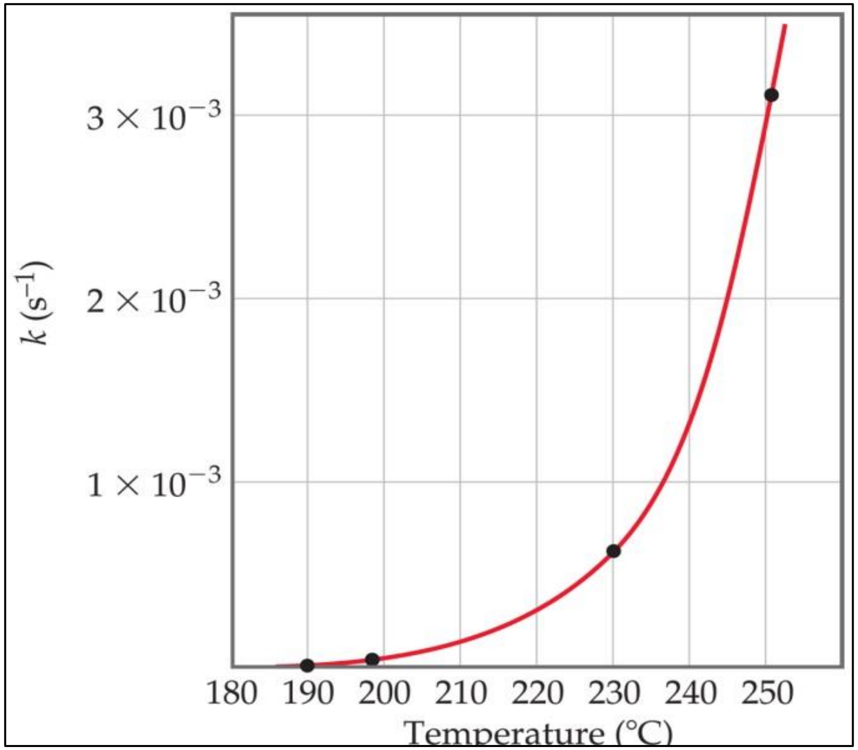
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\ \text{s}} = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

	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	$1 / 2 k [A]_0$

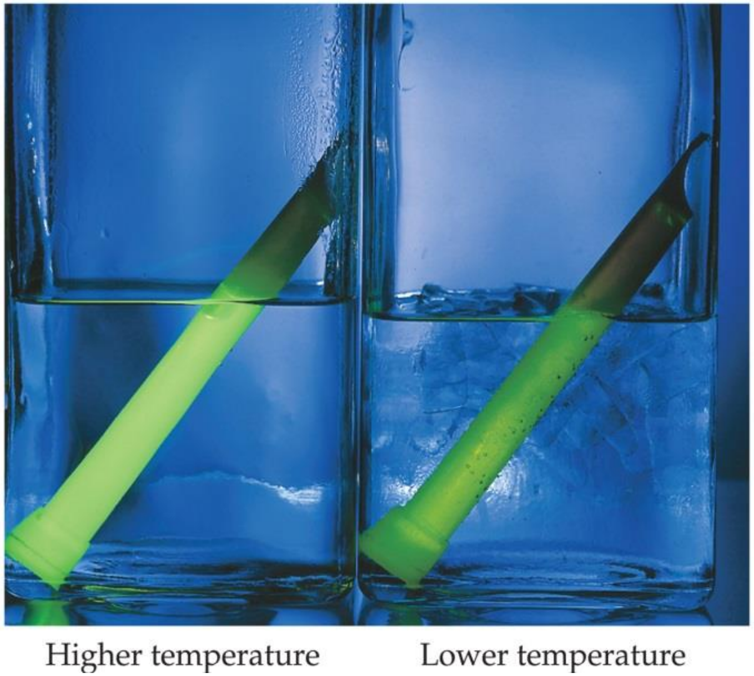
Note:
Zero, second, third (equal and different concentrations)… etc. orders **are not included**.

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).

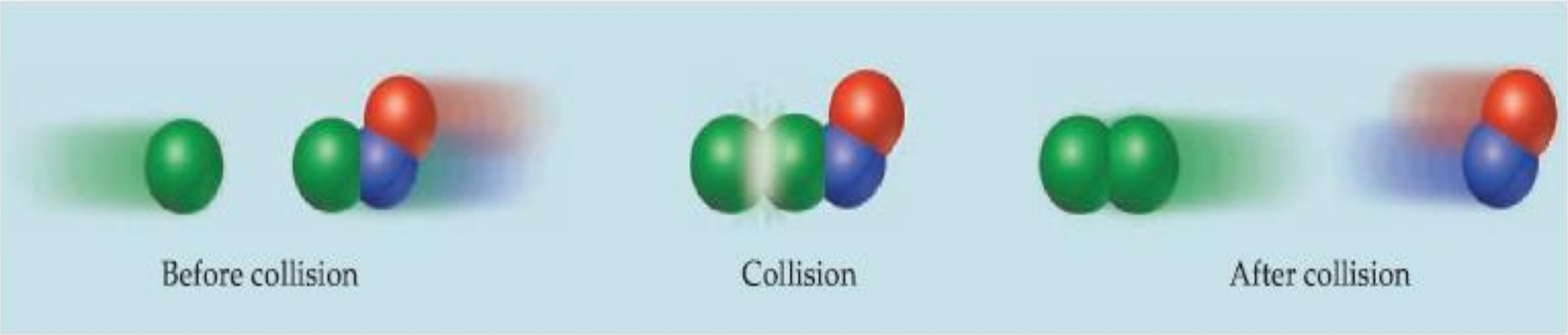


The figure shows the rate constant for this reaction as a function of temperature. The k and hence the rate of the reaction, increases rapidly with temperature, approximately doubling for each 10 °C rise.



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

$$\mathrm{Cl} + \mathrm{NOCl} \longrightarrow \mathrm{NO} + \mathrm{Cl_2}$$

- 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.

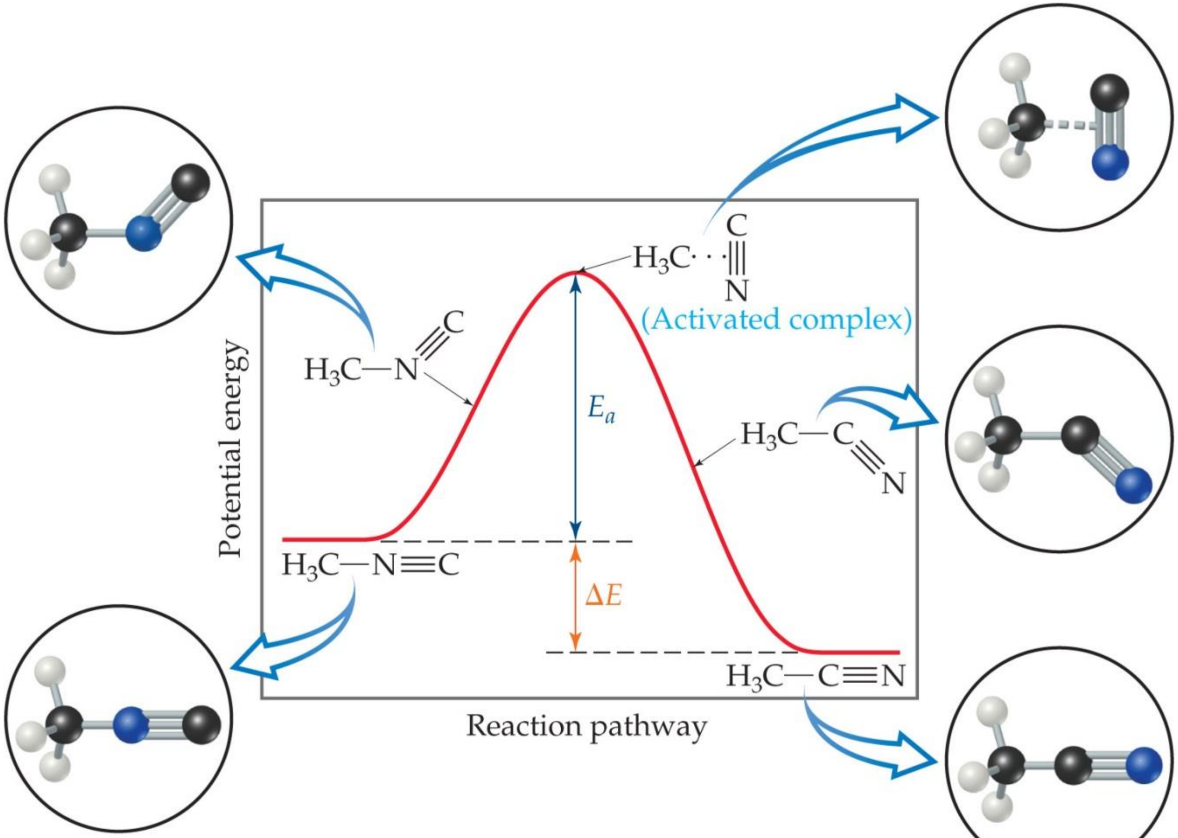
Activation Energy

- 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**.

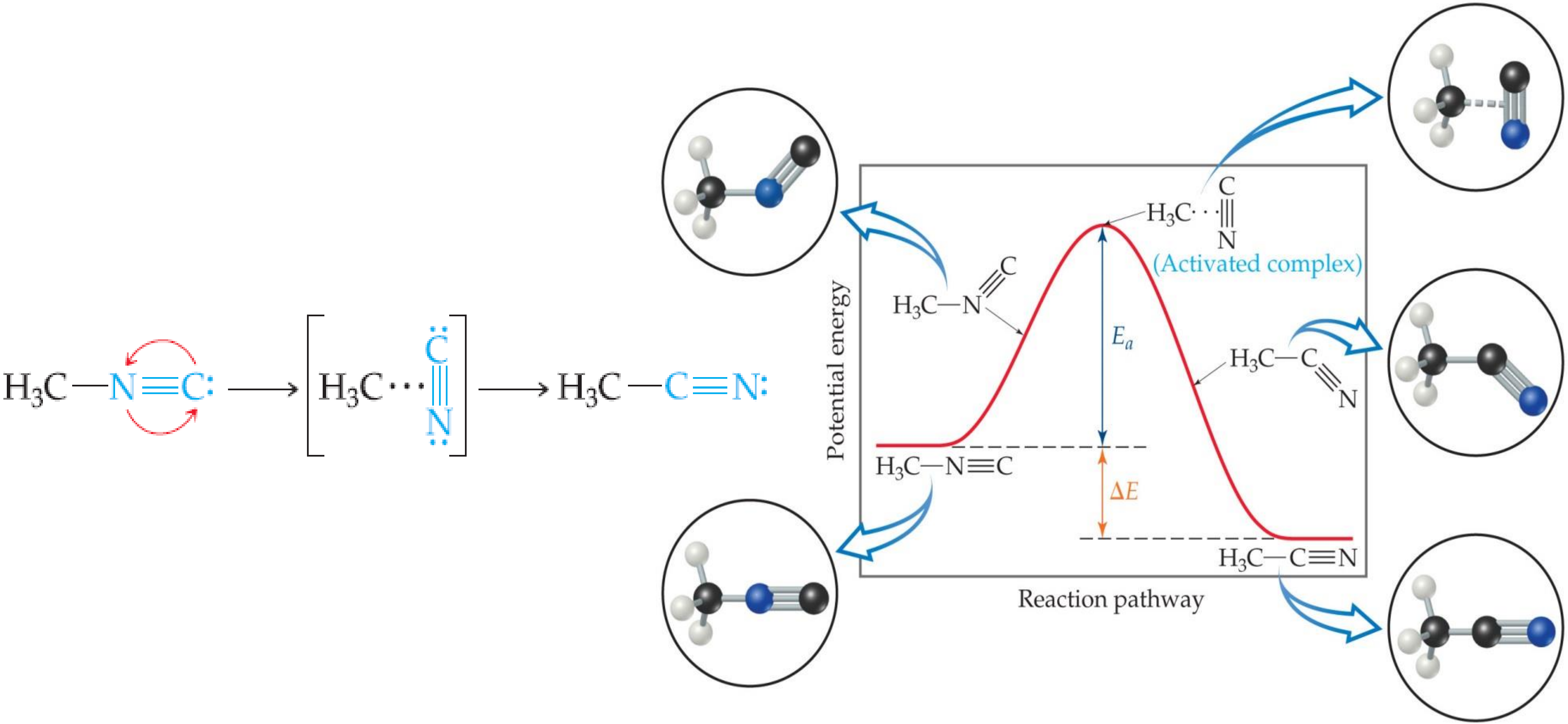
The activation barrier for the reverse reaction is equal to the sum of ΔE and E_a for the forward reaction.

-The diagram shows the energy of the reactants and products (and, therefore, Δ*E*).

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

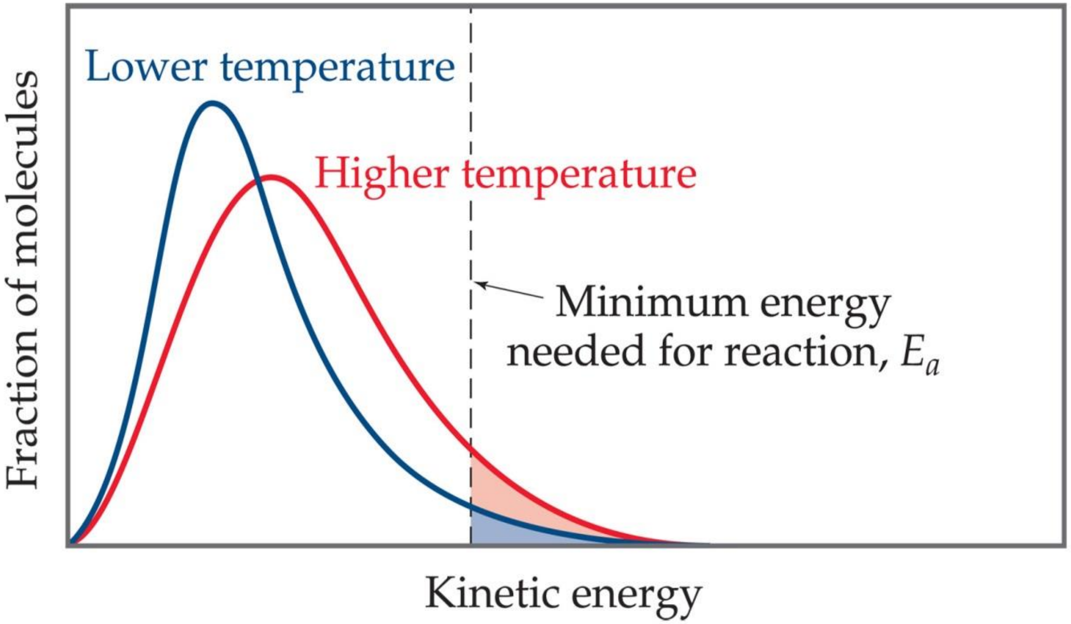
-The particular arrangement of atoms at the top of the barrier is called the activated complex or transition state.

-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**:

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

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. **A** is constant or nearly so as temperature is varied.

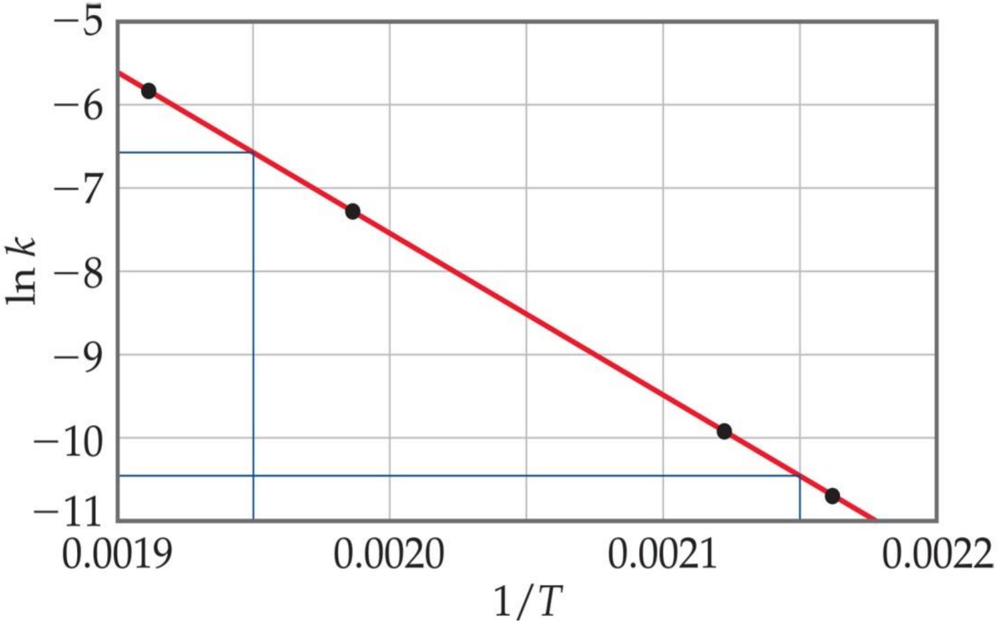
As the magnitude of **E_a** increases, **k** decreases because the fraction of molecules that possess the required energy is smaller. Thus, reaction rates decrease as **E_a** increases.

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

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

$$\Big\Downarrow$$

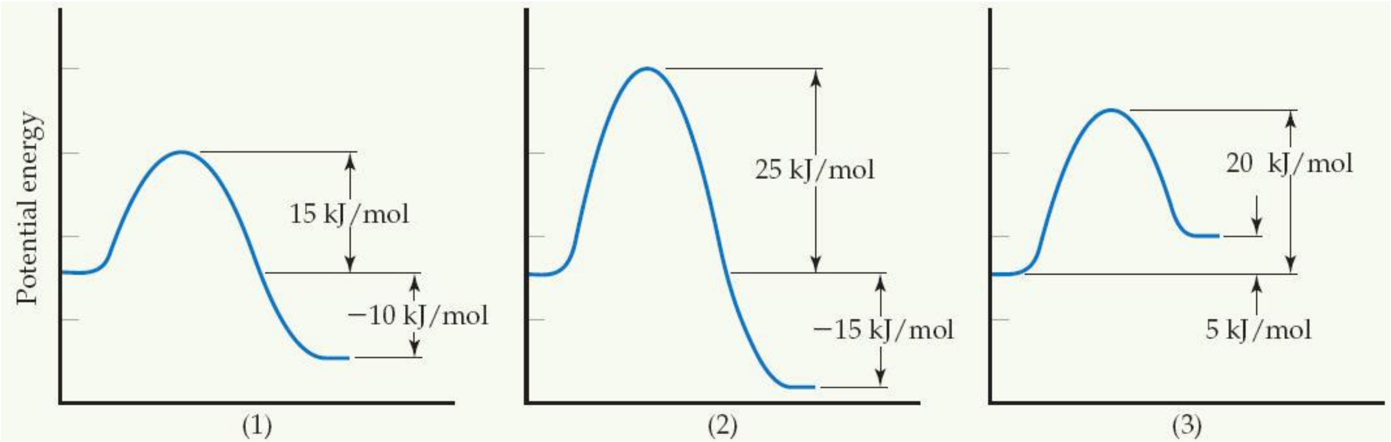
$$\begin{array}{ccccccc} \ln k & = & -\dfrac{E_a}{RT} & + & \ln A \\ \updownarrow & & \updownarrow & & \updownarrow \\ y & = & mx & + & b \end{array}$$



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 non-graphical 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:

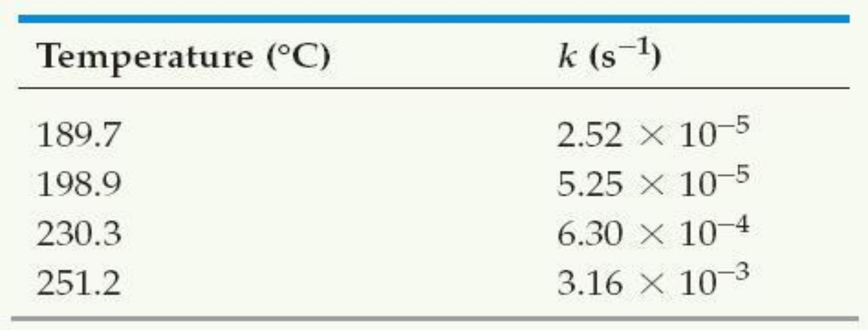
$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

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

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

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 :

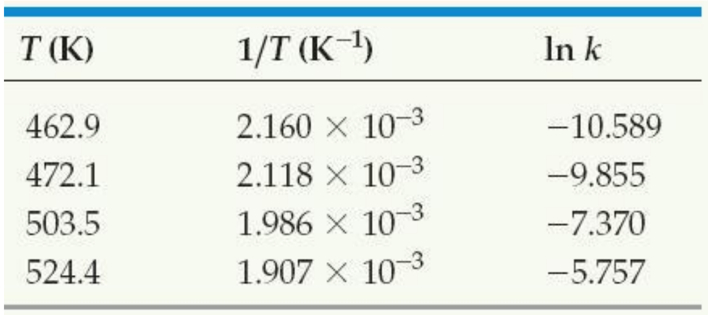


Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

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

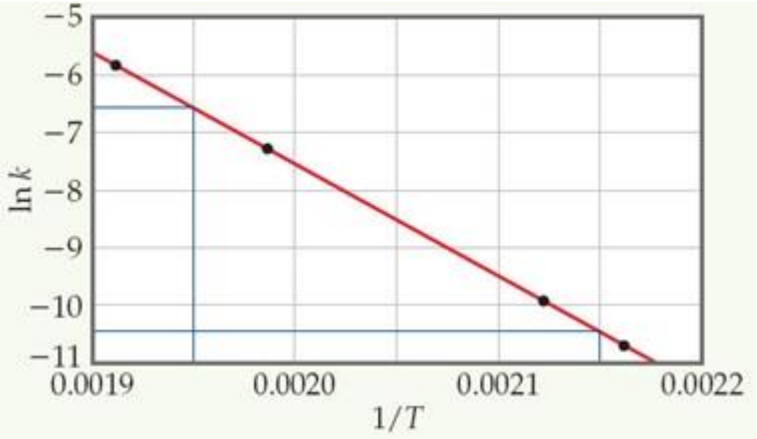
Solution

(a)



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

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



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)

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

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

$$E_a = -(\text{slope})(R) = -(-1.9 \times 10^4\ K)\left(8.314\frac{\text{J}}{\text{mol-K}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= 1.6 \times 10^2\ \text{kJ/mol} = 160\ \text{kJ/mol}$$

(b)

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

$$\frac{k_1}{2.52 \times 10^{-5}\ \text{s}^{-1}} = e^{-3.18} = 4.15 \times 10^{-2}$$

$$k_1 = (4.15 \times 10^{-2})(2.52 \times 10^{-5}\ \text{s}^{-1}) = 1.0 \times 10^{-6}\ \text{s}^{-1}$$

Practice Exercise

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

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

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. 0.693*k*
c. *k*/2
d. 2*k*

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

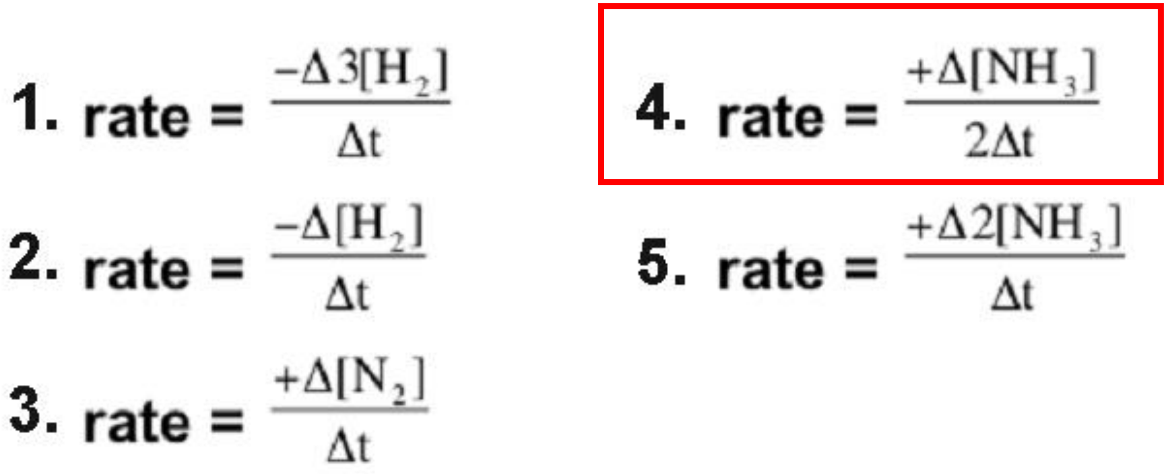
a. initiation
b. internal
c. external
d. activation

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?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$



1. rate = $\frac{-\Delta 3[H_2]}{\Delta t}$
2. rate = $\frac{-\Delta[H_2]}{\Delta t}$
3. rate = $\frac{+\Delta[N_2]}{\Delta t}$
4. rate = $\boxed{\frac{+\Delta[NH_3]}{2\Delta t}}$
5. rate = $\frac{+\Delta 2[NH_3]}{\Delta t}$

What is the rate law for the reaction?

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

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

[A]	**[B]**	**Initial Rate *M*/s**
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? $2\,A + B \longrightarrow \text{products}$

- Rate = $k[A][B]^2$
- Rate = $k[A][B]$
- Rate = $k[A]^2[B]$
- Rate = $k[A]^2[B]^4$
- Rate = $k[B]$

[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:

$$\textbf{Rate} = \boldsymbol{k}\,\textbf{[A][B]}$$

- $M\ s$
- $M^2\ s$
- $M^{-1}\ s^{-1}$
- $M^{-1}\ s^{-2}$
- $M^{-2}\ s^{-1}$

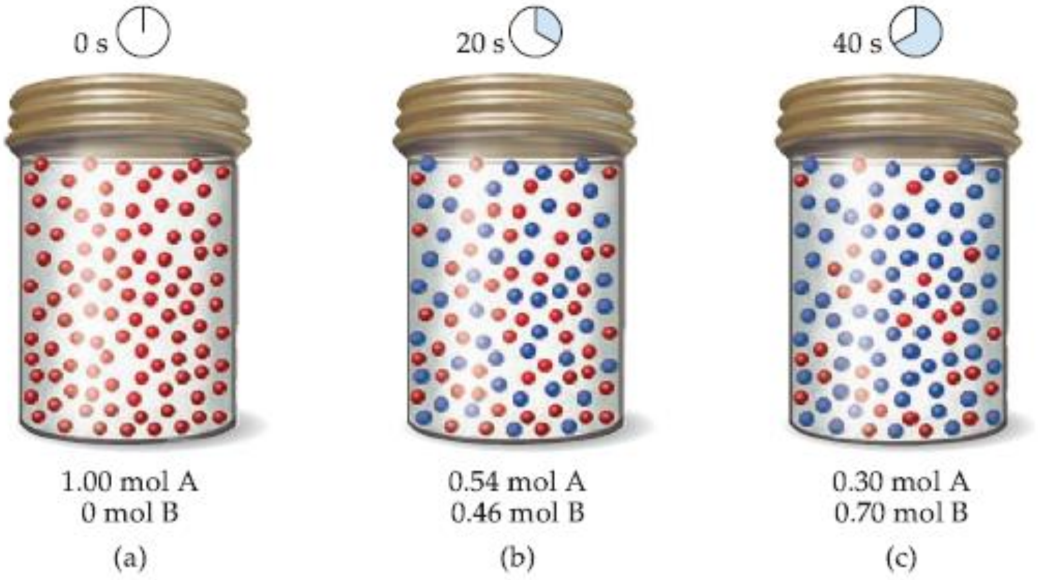
If $t_{1/2}$ = 500 s for a first-order reaction, how long will it take for the concentration of a reactant to decrease to 1/8 of its original value?

- 2 x 500 = 1000 s
- 3 x 500 = 1500 s
- 4 x 500 = 2000 s
- 5 x 500 = 2500 s
- 8 x 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:

1.8×10^{-2} M/s



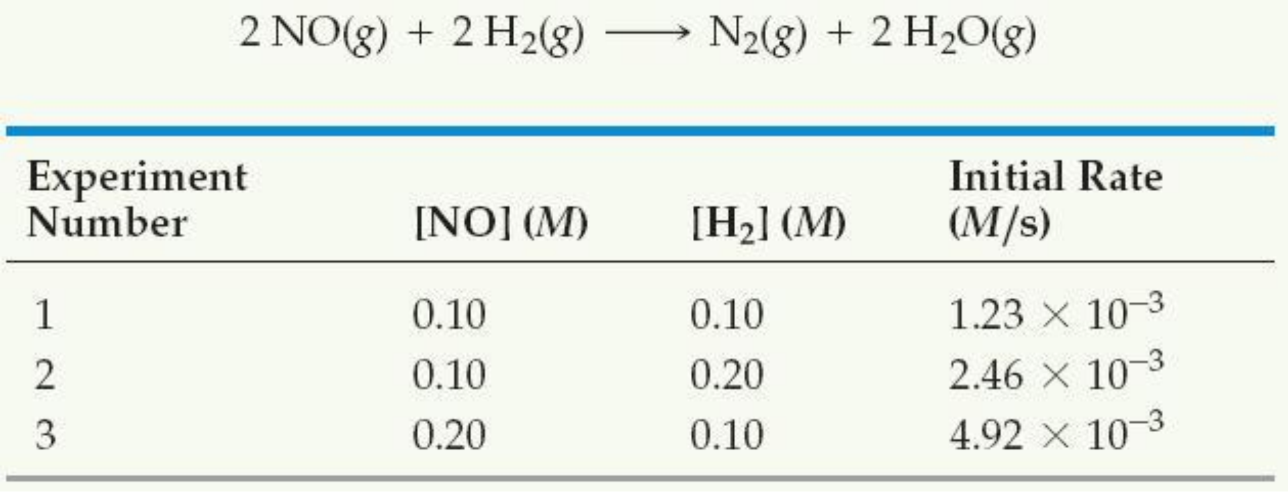
The decomposition of N_2O_5 proceeds according to the following equation:

$$\mathbf{2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)}$$

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

Answer: (a) 8.4×10^{-7} M/s,
(b) 2.1×10^{-7} M/s

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



$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

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 $[H_2] = 0.150$ M

Answers: (a) rate = $k[NO]^2[H_2]$;
(b) $k = 1.2\ M^{-2}\ s^{-1}$; **(c)** rate = 4.5×10^{-4} M/s

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510 °C is a first-order process with a rate constant of
$6.8 \times 10^{-4}\ s^{-1}$:

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ 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 yr = 1.51×10^7 s;
(b) it takes two half-lives, 2(0.478 yr) = 0.956 yr


Thank You!