

Chapter 14. Chemical Kinetics

Common Student Misconceptions

- It is possible for mathematics to get in the way of some students' understanding of the chemistry of this chapter.
- Students often assume that reaction orders may be determined from stoichiometric coefficients.
- Students often confuse intermediates and transition states.
- Students often confuse adsorption and absorption.

Lecture Outline

14.1 Factors that Affect Reaction Rates

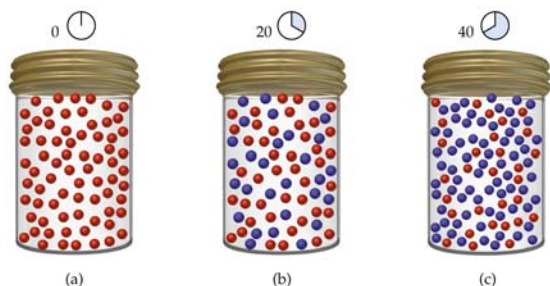
- **Chemical kinetics** = the study of how fast chemical reactions occur.
- Factors which affect rates of reactions:
 - Physical state of the reactants.
 - Concentration of the reactants.
 - Temperature of the reaction.
 - Presence or absence of a catalyst.
- **Goal: to understand chemical reactions at the molecular level.**

14.2 Reaction Rates

- The speed of a reaction is defined as the change that occurs per unit time.
 - It is often determined by measuring the change in concentration of a reactant or product with time.
 - The speed of the chemical reaction is its **reaction rate**.
- For a reaction $A \rightarrow B$

$$\text{Average rate with respect to B} = \frac{\text{Change in the concentration of B}}{\text{Change in time}}$$

- Here the change in the concentration of B is defined as:
$$\Delta [B] = [B] \text{ at final time} - [B] \text{ at initial time}$$



- Illustrate this with an example:
 - Suppose A reacts to form B. Let us begin with 1.00 M A.
 - At $t = 0$ (time zero) there is 1.00 M A and no B present.
 - At $t = 20$ sec, there is 0.54 M A and 0.46 M B.
 - At $t = 40$ sec, there is 0.30 M A and 0.70 M B.

- We can use this information to find the average rate with respect to B:

$$\text{Avg Rate} = \frac{\Delta (\text{Conc B})}{\Delta t} = \frac{(\text{Conc of B at } t = 20\text{s}) - (\text{Conc of B at } t = 0\text{s})}{20\text{s} - 0\text{ min}}$$

$$\text{Avg Rate} = \frac{0.46\text{M} - 0.00\text{ M}}{20\text{s} - 0\text{ s}} = 0.023 \frac{\text{M}}{\text{s}}$$

- For the reaction $A \rightarrow B$ there are two ways of measuring rate:
 - The rate of appearance of product B (i.e., change in moles of B per unit time) as in the preceding example.
 - The rate of disappearance of reactant A (i.e., the change in moles of A per unit time).

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

- Note the negative sign! This reminds us that rate is being expressed in terms of the *disappearance* of a reactant.
- A plot of number of moles versus time shows that as the reactants (A) disappear, the products (B) appear.

Sample Exercise 14.1

For the reaction pictured, calculate the average rate of disappearance of A over the time interval from 20 s to 40 s.

$(1.2 \times 10^{-2} \text{ M/s})$

Practice Exercise 14.1

From the reaction pictured, calculate the average rate of the appearance of B over the time interval from 0 to 40 s.

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

Change of Rate with Time

- In most chemical reactions we will determine the reaction rate by monitoring a change in concentration (of a reactant or product).
 - The most useful unit to use for rate is molarity.
 - Since volume is constant, molarity and moles are directly proportional.
 - Consider the following reaction:

$$\text{C}_4\text{H}_9\text{Cl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{C}_4\text{H}_9\text{OH}_{(aq)} + \text{HCl}_{(aq)}$$
 - We can calculate the average rate in terms of the disappearance of $\text{C}_4\text{H}_9\text{Cl}$.
 - The units for average rate are mol/L's or M/s.
 - The average rate decreases with time.
 - We can plot $[\text{C}_4\text{H}_9\text{Cl}]$ versus time.
 - The rate at any instant in time is called the **instantaneous rate**.
 - It is the slope of the straight line tangent to the curve at that instant.
 - Instantaneous rate is different from average rate.
 - It is the rate at that particular instant in time.
 - For our discussion we will call the "instantaneous rate" the rate, unless otherwise indicated.

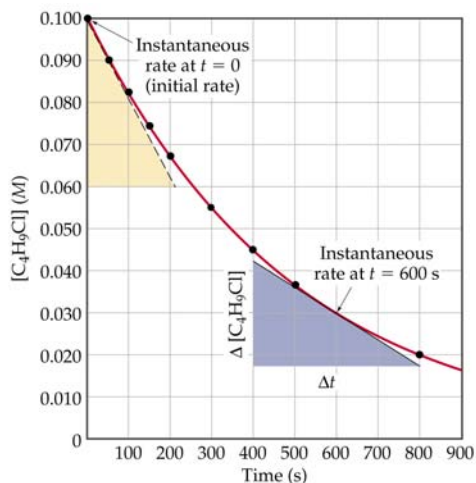


TABLE 14.1 Rate Data for Reaction of C_4H_9Cl with Water

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

Sample Exercise 14.2

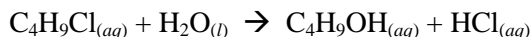
Using the reaction graphed above, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$.
 $(2.0 \times 10^{-4} \text{ M/s})$

Practice Exercise 14.2

For the reaction graphed above, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 300 \text{ s}$.
 $(1.1 \times 10^{-4} \text{ M/s})$

Reaction Rates and Stoichiometry

- For the reaction:



- The rate of appearance of C_4H_9OH must equal the rate of disappearance of C_4H_9Cl .

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

- What if the stoichiometric relationships are not one-to-one?

- For the reaction:

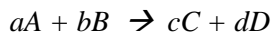


- The rate may be expressed as:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- We can generalize this equation a bit.

- For the reaction:



- The rate may be expressed as:

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

Sample Exercise 14.3

- a) How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation? $2 \text{O}_{3(g)} \rightarrow 3 \text{O}_{2(g)}$

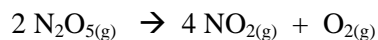
$$\left(-\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t} \right)$$

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

$$(4.0 \times 10^{-5} \text{ M/s})$$

Practice Exercise 14.3

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 ($8.4 \times 10^{-7} \text{ M/s}$)

- b) O_2 ($2.1 \times 10^{-7} \text{ M/s}$)

14.3 Concentration and Rate

- In general, rates:
 - Increase when reactant concentration is increased.
 - Decrease as the concentration of reactants is reduced.
- We often examine the effect of concentration on reaction rate by measuring the way in which reaction rate at the beginning of a reaction depends on starting conditions.

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

- Consider the reaction:

$$\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$$
 - We measure initial reaction rates.
 - The initial rate is the instantaneous rate at time $t = 0$.
 - We find this at various initial concentrations of each reactant.
 - As $[\text{NH}_4^+]$ doubles with $[\text{NO}_2^-]$ constant the rate doubles.
 - We conclude the rate is proportional to $[\text{NH}_4^+]$.
 - As $[\text{NO}_2^-]$ doubles with $[\text{NH}_4^+]$ constant the rate doubles.
 - We conclude that the rate is proportional to $[\text{NO}_2^-]$.
- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.
 - For our example, the rate law is:

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$
 - The proportionality constant k is called the **rate constant**.
 - Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations.

Exponents in the Rate Law

- For a general reaction with rate law:

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n$$
- The exponents m and n are called **reaction orders**.
 - The **overall reaction order** is the sum of the reaction orders.
 - The overall order of reaction is $m + n + \dots$
 - For the reaction:

$$\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$$
 - The reaction is said to be first order in $[\text{NH}_4^+]$, first order in $[\text{NO}_2^-]$, and second order overall.
- Note that reaction orders must be determined experimentally.
 - They do not necessarily correspond to the stoichiometric coefficients in the balanced chemical equation!
 - We commonly encounter reaction orders of 0, 1 or 2.
 - Even fractional or negative values are possible.

Units of Rate Constants

- Units of the rate constant depend on the overall reaction order.
- For example, for a reaction that is second order overall:
- Units of rate are:

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

- Thus the units of the rate constant are:

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

Using Initial Rates to Determine Rate Laws

- To determine the rate law, we observe the effect of changing initial concentrations.
 - If a reaction is zero order in a reactant, changing the initial concentration of that reactant will have no effect on rate (as long as *some* reactant is present).
 - If a reaction is first order, doubling the concentration will cause the rate to double.
 - If a reaction is second order, doubling the concentration will result in a 2^2 increase in rate.
 - Similarly, tripling the concentration results in a 3^2 increase in rate.
 - A reaction is n th order if doubling the concentration causes a 2^n increase in rate.
- Note that the rate, not the rate constant, depends on concentration.
- The rate constant IS affected by temperature and by the presence of a catalyst.

Sample Exercise 14.4 (p. 534)

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

(2 < 1 < 3)

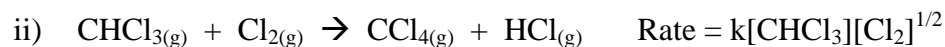
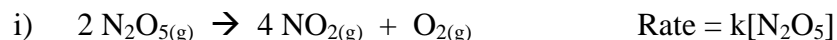
Practice Exercise 14.4 (p. 534)

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

(2 = 3 < 1)

Sample Exercise 14.5 (p. 535)

a) What are the overall reaction orders for the reactions described in the following equations:



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

Practice Exercise 14.5

a) What is the reaction order of the reactant H_2 in Equation (iii)?



(1)

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

($\text{M}^{-1}\text{s}^{-1}$)

Sample Exercise 14.6 (p. 537)

The initial rate of a reaction $\text{A} + \text{B} \rightarrow \text{C}$ 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 ($k[\text{NO}]^2[\text{H}_2]$)

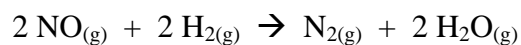
b) the magnitude of the rate constant ($4.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$)

c) the rate of the reaction when $[\text{A}] = 0.050 \text{ M}$ and $[\text{B}] = 0.100 \text{ M}$. ($1.0 \times 10^{-5} \text{ M/s}$)

Sample Exercise 14.6

Practice Exercise 14.6 (p. 537)

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. $(k[\text{NO}]^2[\text{H}_2])$
- b) Calculate the rate constant. $(1.2 \text{ M}^{-1}\text{s}^{-1})$
- c) Calculate the rate when $[\text{NO}] = 0.050 \text{ M}$ and $[\text{H}_2] = 0.150 \text{ M}$. $(4.5 \times 10^{-4} \text{ M/s})$

14.4 The Change of Concentration with Time

- Goal: Convert the rate law into a convenient equation that gives concentration as a function of time.

First-Order Reactions

- For a **first-order reaction**, the rate doubles as the concentration of a reactant doubles.
 - Therefore:

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

- Integrating:

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

- We get:

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

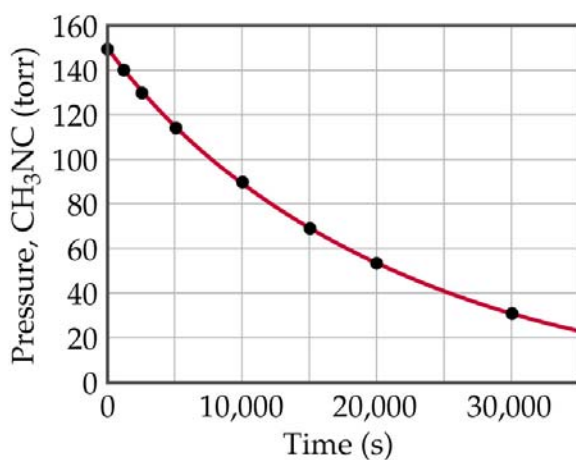
- Rearranging:

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

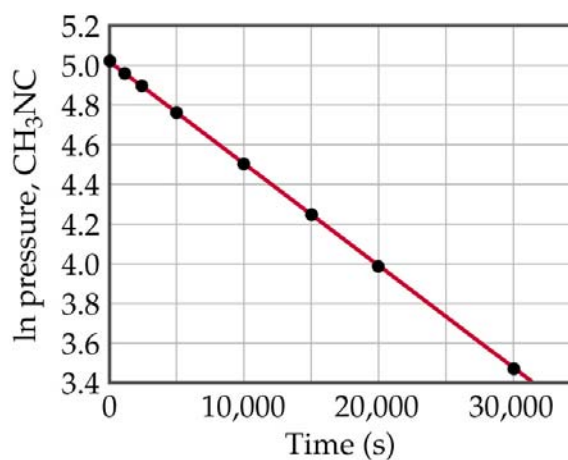
- An alternate form:

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

- A plot of $\ln[A]_t$ versus t is a straight line with slope $-k$ and intercept $\ln[A]_0$.
- Note that in this equation we use the natural logarithm, \ln (log to the base e).



(a)



(b)

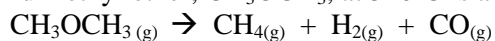
Sample Exercise 14.7 (p. 538)

The first-order rate constant for the decomposition of a certain insecticide in water at 12°C is 1.45 yr^{-1} . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$ of water. 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?
($1.2 \times 10^{-7} \text{ g/cm}^3$)
- b) How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?
(0.35 yr)

Practice Exercise 14.7

The decomposition of dimethyl ether, CH_3OCH_3 , 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 CH_3OCH_3 is 135 torr, what is its partial pressure after 1420 s?

(51 torr)

Second-Order Reactions

- A **second-order reaction** is one whose rate depends on the reactant concentration to the **second power** or on the concentration of two reactants, each raised to the first power.
- For a second-order reaction with just one reactant:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

- Integrating,

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

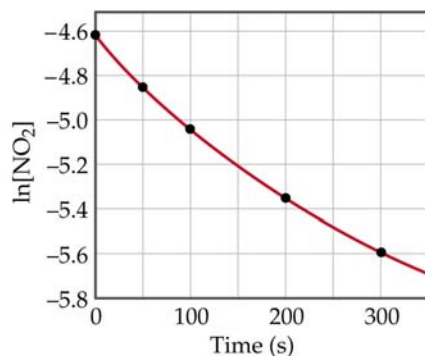
- We get:

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

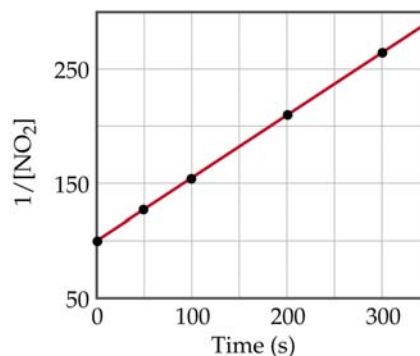
- A plot of $1/[A]_t$ versus t is a straight line with slope k and intercept $1/[A]_0$.
 - For a second order reaction, a plot of $\ln[A]_t$ vs. t is not linear.
- Note that a second-order process can have a rate constant expression of the form:

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

- That is, the reaction is second order overall, but has first order dependence on A and B.



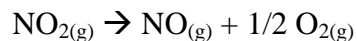
(a)



(b)

Sample Exercise 14.8

The following data were obtained for the gas phase decomposition of nitrogen dioxide at 300°C:



<u>Time (s)</u>	<u>[NO₂] (M)</u>
0.0	.01000
50.0	.00787
100.0	.00649
200.0	.00481
300.0	.00380

Is the reaction first or second order in NO₂? (Hint: use plots above) Explain your answer.

(2nd order)

Practice Exercise 14.8 (p. 540)

Consider again the decomposition of NO_2 discussed above. The reaction is second order in NO_2 with $k = 0.543 \text{ M}^{-1}\text{s}^{-1}$. If the initial concentration of NO_2 in a closed vessel is 0.0500 M , what is the remaining concentration after 0.500 hr ?

$(1.0 \times 10^{-3} \text{ M})$

Half-life

- **Half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half its original value.
 - That is, half life, $t_{1/2}$, is the time taken for $[A]_0$ to reach $\frac{1}{2} [A]_0$.
- Mathematically, the half life of a first-order reaction is:

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

So, for $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$

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

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

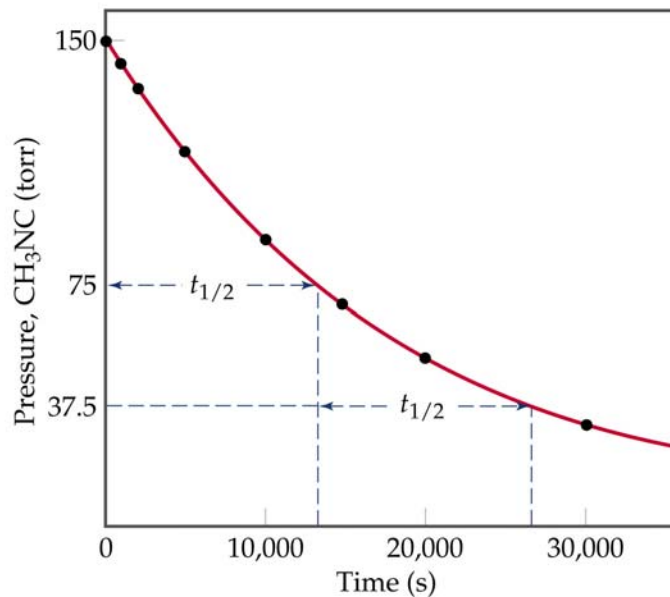
$$\therefore t_{1/2} = -\frac{\ln 1/2}{k} = \frac{0.693}{k}$$

- Note that the half-life of a first-order reaction is independent of the initial concentration of the reactant.

- We can show that the half-life of a second order reaction is:

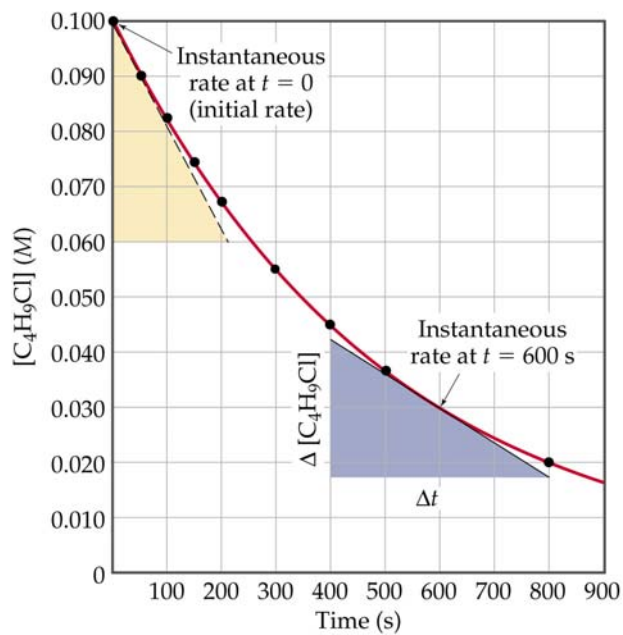
$$t_{1/2} = \frac{1}{k[A]_0}$$

- Note that the half-life of a second-order reaction is **dependent** on the initial concentration of reactant.



Sample Exercise 14.9

From the figure below, estimate the half-life of $\text{C}_4\text{H}_9\text{Cl}$ with water.



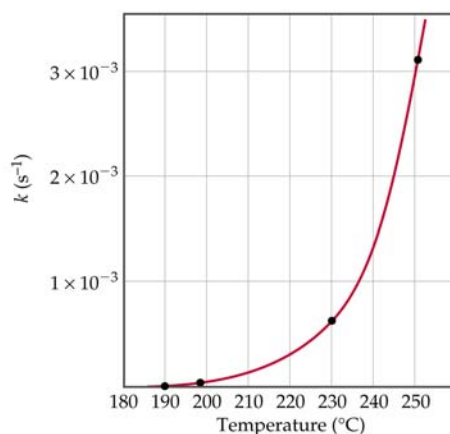
(~340 s)

Practice Exercise 14.9 (p. 542)

Calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7.
(1.02×10^3 s)

14.5 Temperature and Rate

- Most reactions speed up as temperature increases.
- We can illustrate this with chemiluminescent Cyalume® light sticks.
 - A chemiluminescent reaction produces light.
 - Two light sticks are placed in water, one at room temperature and one in ice.
 - The one at room temperature is brighter than the one in ice.
 - Its luminescence also fades more quickly.
 - The chemical reaction responsible for chemiluminescence is dependent on temperature, the higher the temperature, the faster the reaction and the brighter the light.
- As temperature increases, the rate increases.
- How is the relationship between temperature and rate reflected in the rate expression?
 - The rate law has no temperature term in it, so the rate constant must depend on temperature.
- Consider the first-order reaction $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$.
 - As temperature increases from 190°C to 250°C the rate constant increases.
 - The temperature effect is quite dramatic.
 - We see an approximate doubling of the rate with each 10°C increase in temperature.



The Collision Model

- Rates of reactions are affected by **concentration** and **temperature**.
- We need to develop a model that explains this observation.
- An explanation is provided by the **collision model**, based on KMT.
 - In order for molecules to react they must collide.
 - The greater the number of collisions the faster the rate.
 - The more molecules present, the greater the probability of collision and the faster the rate.

Concentration effects:

- Thus reaction rate should \uparrow with an \uparrow in [reactant molecules].

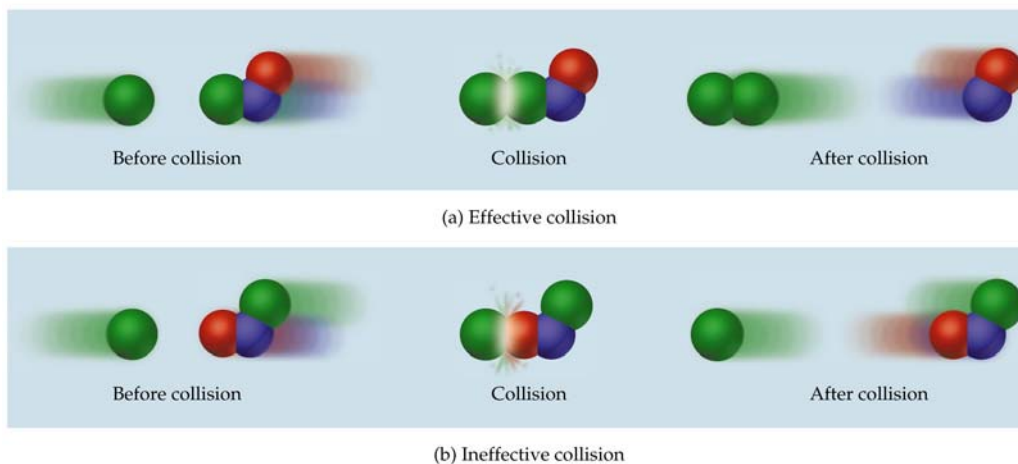
Temperature effects:

- The higher the T, the more E available to the molecules and the more frequently the molecules collide.
 - Thus reaction rate should \uparrow with an \uparrow in T.

The Orientation Factor

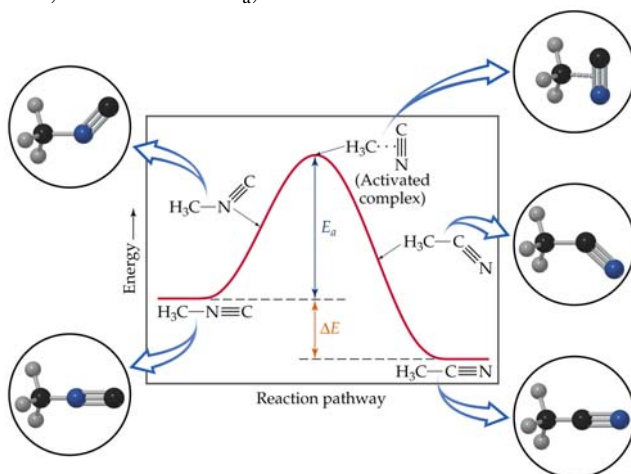
Not all collisions lead to products.

- Only a **small fraction** of collisions lead to products.
- In order for a reaction to occur the reactant molecules must collide in the **correct orientation** and with **enough E** to form products.
- Consider the reaction between Cl and NOCl:
 - If the Cl collides with the Cl of NOCl, the products are Cl_2 and NO.
 - If the Cl collides with the O of NOCl, no products are formed.



Activation Energy

- Arrhenius: Molecules must possess a minimum amount of E to react. Why?
 - In order to form products, bonds must be broken in the reactants.
 - Bond breakage requires E.
 - Molecules moving too slowly, with too little KE, don't react when they collide.
- Activation energy, E_a** , = the minimum E required to initiate a chemical reaction.
 - E_a will vary with the reaction.
- Consider the rearrangement of methyl isonitrile to form acetonitrile:
 - E is required to stretch the bond between the CH_3 group and the $\text{N}\equiv\text{C}$ group to allow the $\text{N}\equiv\text{C}$ to rotate.
 - The C–C bond begins to form.
 - The E associated with the molecule drops.
 - The E barrier between the starting molecule and the highest E state found along the reaction pathway is the E_a .
 - The species at the top of the barrier is called the **activated complex** or **transition state**.
 - The change in E for the reaction is the difference in E between CH_3NC and CH_3CN .
 - ΔE_{rxn} has no effect on reaction rate.
 - The E_a is the difference in energy between reactants, (CH_3NC) and the transition state.
 - The rate depends on the magnitude of the E_a .
 - In general, the lower the E_a , the faster the rate.

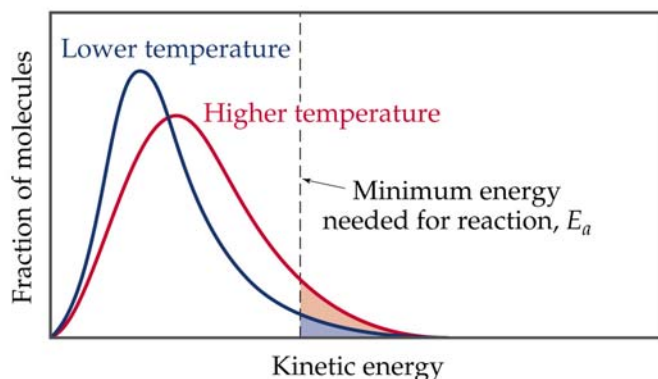


- Notice that if a forward reaction is exothermic ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- How does this relate to temperature?**
 - At any particular T, the molecules present have an average KE associated with the population.
 - In the same distribution, some molecules have less E than the average while others have more than the average value.
 - The fraction of molecules with an energy equal to or greater than E_a is given by:

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

- Molecules that have an $E \geq E_a$ have sufficient E to react.
 - As we \uparrow the T, the fraction of the population that has an $E \geq E_a$ \uparrow .
 - Thus more molecules can react.

Distribution of Kinetic Energies



The Arrhenius Equation

- Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:
 - The number of collisions per unit time.
 - The fraction of collisions that occur with the correct orientation.
 - The fraction of the colliding molecules that have an $E \geq E_a$.

- From these observations Arrhenius developed the **Arrhenius equation**.

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

- Where k is the rate constant, E_a is the activation energy, R is the ideal-gas constant (8.314 J/K·mol) and T is the temperature in K.
- A is called the **frequency factor**.
 - It is related to the frequency of collisions and the probability that a collision will have a favorable orientation.
- Both A and E_a are *specific to a given reaction*.

Determining the Activation Energy

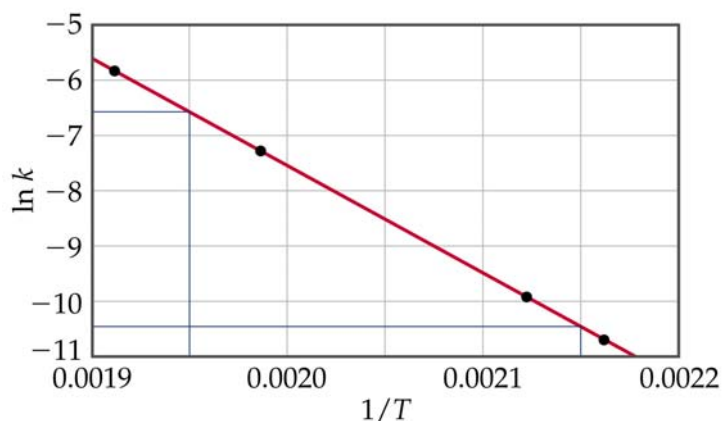
- E_a may be determined experimentally.

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

- We need to take the natural log of both sides of the Arrhenius equation:
- A graph of $\ln k$ vs $1/T$ will have a slope of $-E_a/R$ and a y-intercept of $\ln A$.

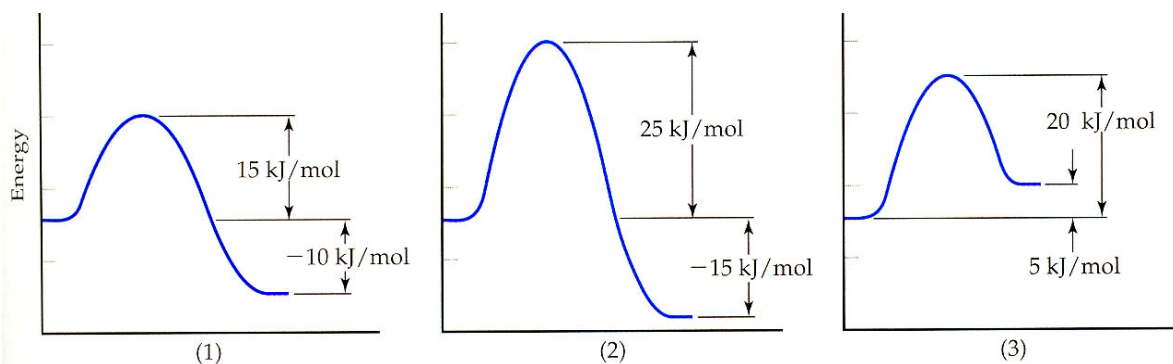
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Alternatively we can use:



Sample Exercise 14.10

Consider a series of reactions having the following energy profiles:



Assuming that all three reactions have nearly the same frequency factors, rank the reactions from slowest to fastest.

((2) < (3) < (1))

Practice Exercise 14.10

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

((2) < (1) < (3))

Sample Exercise 14.11 (p. 548)

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

$T (^{\circ}\text{C})$	$k (\text{s}^{-1})$
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 E_a for the reaction. (160 kJ/mol)
- b) What is the value of the rate constant at 430.0 K? ($1.0 \times 10^{-6} \text{ s}^{-1}$)

Practice Exercise 14.11

Using the data in Sample Exercise 14.11, above, calculate the rate constant for the rearrangement of methyl isonitrile at 280°C.

($2.2 \times 10^{-2} \text{ s}^{-1}$)

14.6 Reaction Mechanisms

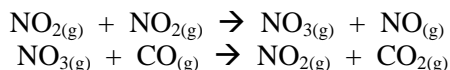
- The balanced chemical equation provides information about substances present at the beginning and end of the reaction.
- The **reaction mechanism** is the process by which the reaction occurs.
- **Mechanisms** provide a picture of which bonds are broken and formed during the course of a reaction.

Elementary Steps

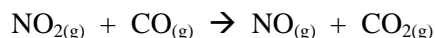
- **Elementary steps** are any processes that occur in a **single step**.
- The number of molecules present in an elementary step is the **molecularity** of that elementary step.
 - **Unimolecular**: one molecule in the elementary step
 - **Bimolecular**: two molecules in the elementary step
 - **Termolecular**: three molecules in the elementary step
 - very uncommon (statistically improbable)

Multistep Mechanisms

Some reactions proceed through > one step:



If we add the above steps, we get the overall reaction:

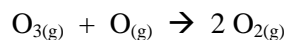
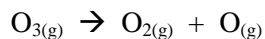


Multistep mechanisms = sequence of elementary steps

- Elementary steps must add to give the balanced chemical equation.
- **Intermediate**: a species which appears in an elementary step which is **not a reactant or product**.
 - **formed in one elementary step and consumed in another.**
 - **not found** in the balanced equation for the overall reaction.

Sample Exercise 14.12 (p. 550)

It has been proposed that the conversion of ozone into O_2 proceeds via two elementary steps:



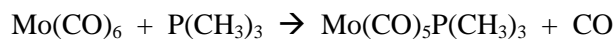
a) Describe the molecularity of each step in this mechanism.

b) Write the equation for the overall reaction.

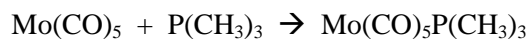
c) Identify the intermediate(s).

Practice Exercise 14.12

For the reaction



the proposed mechanism is



a) Is the proposed mechanism consistent with the equation for the overall reaction?

b) Identify the intermediates.

Rate Laws for Elementary Steps

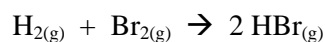
- determine the overall rate law of the reaction
- The rate law of an elementary step is determined by its molecularity:
 - Unimolecular** processes are **first order**.
 - Bimolecular** processes are **second order**.
 - Termolecular** processes are **third order**.

TABLE 14.3 Elementary Steps and Their Rate Laws

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

Sample Exercise 14.13 (p. 551)

If the following reaction occurs in a single elementary step, predict the rate law:



Practice Exercise 14.13

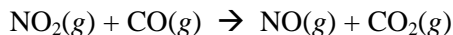
Consider the following reaction: $2 \text{NO}_{(g)} + \text{Br}_{2(g)} \rightarrow 2 \text{NOBr}_{(g)}$.

- Write the rate law for the reaction, assuming it involves a single elementary step.
- Is a single-step mechanism likely for this reaction? Why or why not?

Rate Laws for Multistep Mechanisms

- Most reactions occur by mechanisms with > one elementary step.
- Rate-determining step** (rate-limiting step) of the reaction = the **slowest** of the elementary steps.
 - governs the overall rate law for the overall reaction.

- Consider the reaction:



- The experimentally derived rate law is: $\text{Rate} = k[\text{NO}_2]^2$
- We propose a mechanism for the reaction:
 - Step 1: $\text{NO}_2(g) + \text{NO}_2(g) \xrightarrow{k_1} \text{NO}_3(g) + \text{NO}(g)$ **slow step**
 - Step 2: $\text{NO}_3(g) + \text{CO}(g) \xrightarrow{k_2} \text{NO}_2(g) + \text{CO}_2(g)$ fast step
 - Note that NO_3 is an **intermediate**.
- If $k_2 \gg k_1$, then the overall reaction rate will depend on the first step (the **rate-determining step**).
 - $\text{Rate} = k_1[\text{NO}_2]^2$
 - This theoretical rate law is in agreement with the experimental rate law.
→ (but does not prove) our mechanism.

Mechanisms with an Initial Fast Step

- Consider the reaction:

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

- The experimentally determined rate law is:

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

- Consider the following proposed mechanism:

- Step 1: $\text{NO}(g) + \text{Br}_2(g) \xrightleftharpoons[k_{-1}]{k_1} \text{NOBr}_2(g)$ fast step
- Step 2: $\text{NOBr}_2(g) + \text{NO}(g) \xrightarrow{k_2} 2\text{NOBr}(g)$ **slow step**

- The theoretical rate law for this mechanism is based on the rate-determining step, **step 2**:

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

- The rate law should not depend on the **[intermediate]** (intermediates are usually unstable and have low/unknown concentrations.)

→ We need to find a way to remove this term from our rate law.

- We can express the concentration of $[\text{NOBr}_2]$ in terms of NOBr and Br_2 by assuming that there is an **equilibrium** in step 1.
- In a dynamic equilibrium, the **forward rate equals the reverse rate**.
- Therefore, by definition of equilibrium we get:

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

- Rearranging we get:

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

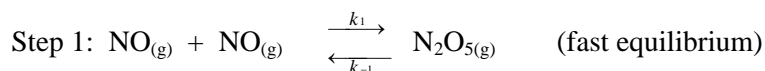
- Therefore, the overall rate law becomes

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

- Note the final rate law is consistent with the experimentally observed rate law.

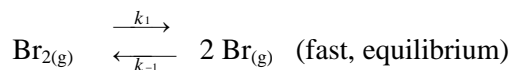
Sample Exercise 14.14

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



Practice Exercise 14.14

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



What is the expression relating the concentration of $\text{Br}_{(\text{g})}$ to that of $\text{Br}_{2(\text{g})}$?

14.7 Catalysis

catalyst = a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.

Two types of catalyst:

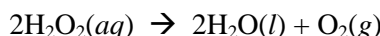
- **Homogeneous**
- **Heterogeneous**

Catalysts are common in the body, in the environment, and in the chemistry lab!

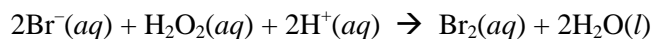
Homogeneous Catalysis

homogeneous catalyst = catalyst that is present in the **same phase** as the reacting molecules.

e.g. Hydrogen peroxide decomposes very slowly in the **absence** of a **catalyst**:



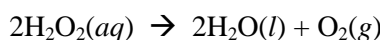
- In the **presence** of bromide ion, the decomposition occurs rapidly in acidic solution:



($\text{Br}_{2(aq)}$ is brown.)



- Br^- is a **catalyst** because it is regenerated at the end of the reaction.
- The net reaction is still:

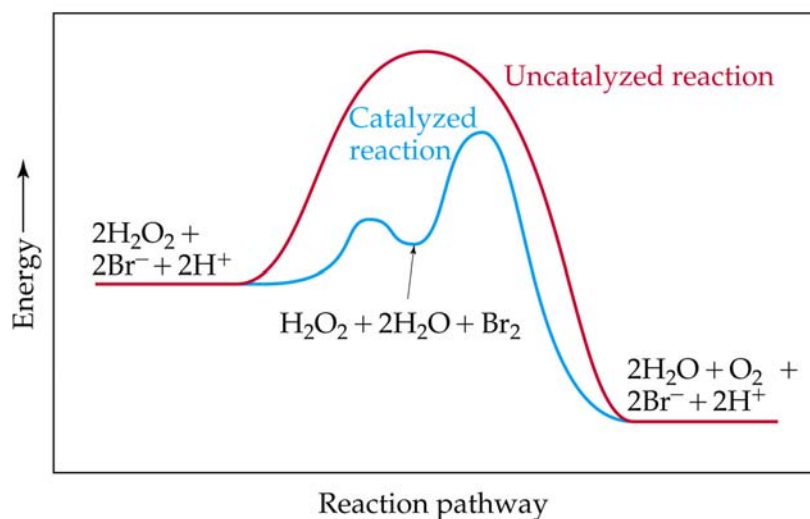


How do catalysts increase reaction rates?

In general, catalysts operate by \square the overall E_a for a reaction.

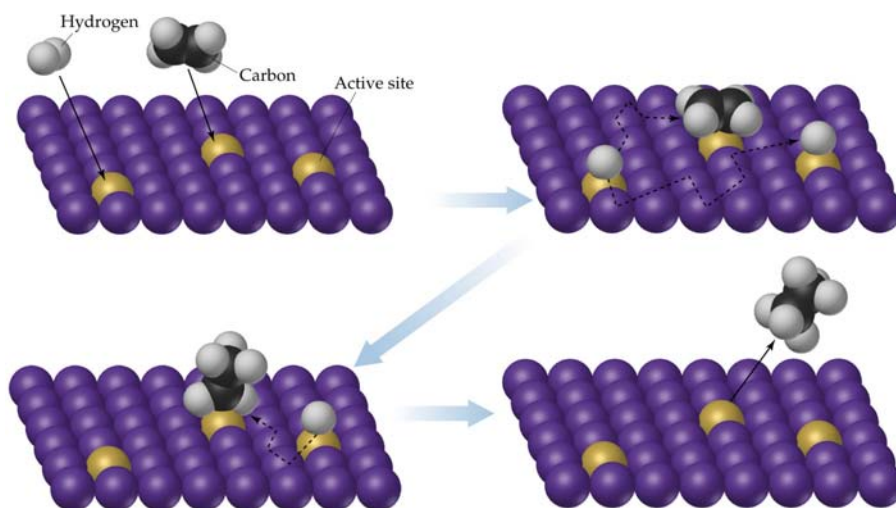
Other ways:

- by \uparrow the number of effective collisions
 $\uparrow k$ by $\uparrow A$ or $\downarrow E_a$ (from the Arrhenius equation)
- A catalyst usually provides a completely different mechanism for the reaction, such as adding new **intermediates** to the reaction.
e.g. In the **absence** of Br^- , H_2O_2 decomposes directly to water and oxygen.
In the **presence** of Br^- , $\text{Br}_{2(aq)}$ is generated as an **intermediate**.
- When a catalyst adds an **intermediate**, the E_a for **both** steps must be **lower** than the E_a for the uncatalyzed reaction.

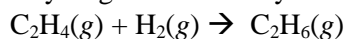


Heterogeneous Catalysis

- A **heterogeneous catalyst** exists in a **different phase** than the reactants.
- e.g. gaseous reactants and products (catalytic converters in cars)
 - Many **industrial** catalysts are **heterogeneous**.
- How do they do their job?
 - The first step is **adsorption** (the binding of reactant molecules to the catalyst surface).
 - **Adsorption** occurs due to the high reactivity of atoms or ions on the surface of the solid.
 - Molecules are adsorbed onto **active sites** on the catalyst surface.
- The number of active sites on a given amount of catalyst depends on several factors such as:
 - The nature of the catalyst.
 - How the catalyst was prepared.
 - How the catalyst was treated prior to use.



- e.g. consider the hydrogenation of ethylene to form ethane:

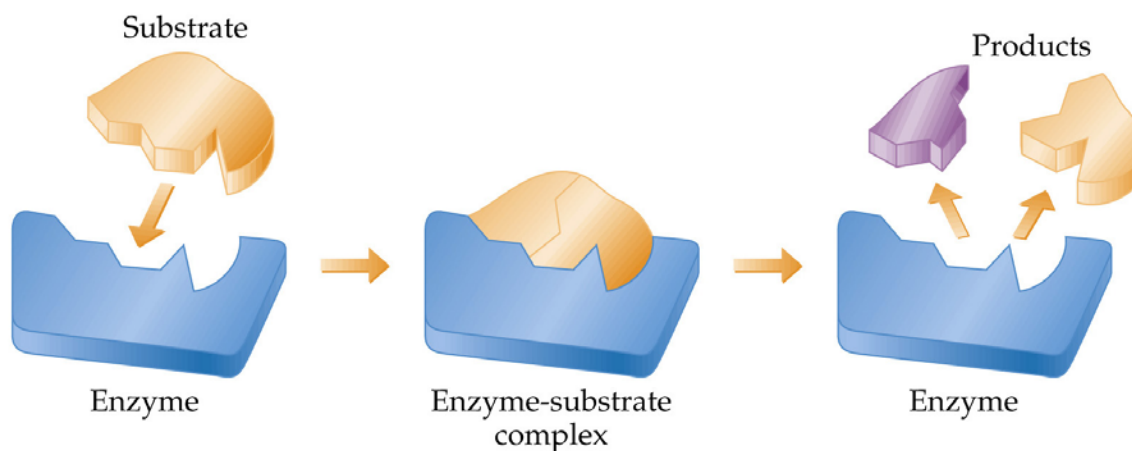


$$\Delta H^\circ = -137 \text{ kJ/mol}$$

- The reaction is **slow** in the absence of a catalyst.
- In the presence of a finely divided metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.
- First, the ethylene and hydrogen molecules are **adsorbed** onto **active sites** on the metal surface.
- The H–H bond breaks and the H atoms migrate about the metal surface.
- When an H atom collides with an ethylene molecule on the surface, the C–C π bond breaks and a C–H σ bond forms.
- An *ethyl group*, C_2H_5 , is weakly bonded to the metal surface with a metal-carbon σ bond.
- When C_2H_6 forms it **desorbs** from the surface.
- When ethylene and hydrogen are **adsorbed** onto a surface, less E is required to break the bonds.
- E_a for the reaction $\downarrow \rightarrow \uparrow$ reaction rate

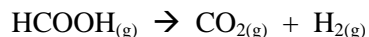
Enzymes

- Enzymes are **biological** catalysts.
- Most enzymes are **protein molecules** with large molecular masses ($10,000$ to 10^6 amu)
- Enzymes have **very specific shapes**.
- Most enzymes catalyze **very specific reactions**.
- Substrates undergo reaction at the **active site** of an enzyme.
- A substrate locks into an enzyme and a fast reaction occurs.
- The products then move away from the enzyme.
- Only substrates that fit into the enzyme lock can be involved in the reaction.
- If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (enzyme inhibitors).
- The number of events (turnover number) catalyzed is large for enzymes (10^3 - 10^7 per second).



Sample Integrative Exercise 14: Putting Concepts Together

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:



The decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 14.28. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.28.

- Estimate the half-life and first-order rate constant for formic acid decomposition.
- What can you conclude from the effect of added ZnO on the decomposition of formic acid?
- The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of k ?
- The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3 , how many moles of gas occupy the reaction chamber at the end of the reaction?
- The standard heat of formation of formic acid vapor is $\Delta H^\circ_f = -378.6 \text{ kJ/mol}$. Calculate ΔH° for the overall reaction. Assuming that the activation energy (E_a) for the reaction is 184 kJ/mol , sketch an approximate energy profile for the reaction, and label E_a , ΔH° , and the transition state.