

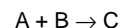
### Chemical Kinetics

Chemical kinetics is concerned with the speeds, or rates of chemical reactions

Chemical kinetics is a subject of broad importance.

- How quickly a medicine can work
- The balance of ozone depletion
- Factors that effect when food will spoil
- Rate at which a fuel burns in an engine
- Fast/slow setting epoxy
- Reaction mechanisms

In order for one chemical species to react with another chemical species they must collide with one another.



In order for "A" and "B" to react, the two must come in contact with each other.

However, collisions must occur with sufficient energy to stretch bonds to a critical length and with suitable orientation.

Factors that Affect Reaction Rates:

- The physical state of the reactants
- The concentrations of the reactants
- The temperature at which the reaction occurs.
- The presence of a catalyst.

- The physical state of the reactants.

Reactants must come together in order to react. The more readily molecules collide with each other, the more rapidly they react.

Homogeneous mixtures (gases or liquids) have good contact between reactants.

Heterogeneous mixtures (gas/liquid or liquid/solid) are limited to the area of contact between the two phase.

- The concentrations of the reactants.

Most chemical reactions proceed faster if the concentration of one or more of the reactants is increased.

Fig. 14.2 p 526

Steel wool burns with difficulty in air with 20% O<sub>2</sub>, but bursts into flames in pure oxygen.

- The temperature at which the reaction occur.

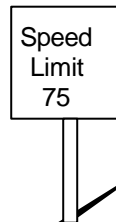
The rates of chemical reactions increase as temperature is increased. Increasing temperature increases the kinetic energies of molecules (see Section 10.7). As molecules move more rapidly, they collide more frequently and also with higher energy.

4. The presence of a catalyst.

Catalysts are agents that increase reaction rates without being used up. They affect the kinds of collisions (the mechanism) that lead to reaction.

**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 have to bring in the notion of time.



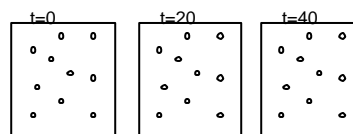
$$\frac{75 \text{ moles}}{\text{sec}}$$

The speed of a chemical reaction (its **reaction rate**) is the change in the concentration of reactants or products per unit time. The units for reaction rates are usually molarity per second (M/s)

A change in concentration divided by a time interval.



Each dot represents 0.1M

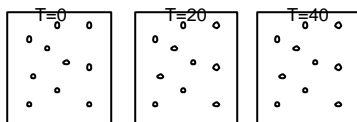


Average rate with respect to B =  $\frac{\text{change in concentration of B}}{\text{change in time}}$   
 $= \frac{[B] \text{ at } t_2 - [B] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$

Average rate =  $\frac{0.4 \text{ M} - 0.0 \text{ M}}{20 \text{ s} - 0.0 \text{ s}} = 2.0 \times 10^{-2} \text{ M/s}$



Each dot represents 0.1M



Average rate with respect to A =  $-\frac{\Delta[A]}{\Delta t}$

Notice the minus sign. By convention, rates are always expressed as positive quantities. Because [A] is decreasing with time,  $\Delta[A]$  is a negative number so the negative sign converts the negative  $\Delta[A]$  to a positive rate.

Average rate =  $-\frac{0.6 \text{ M} - 1.0 \text{ M}}{20 \text{ s} - 0.0 \text{ s}} = 2.0 \times 10^{-2} \text{ M/s}$

**Change of Rate with Time**

Suppose one dumps 0.1 mole of  $C_4H_9Cl$  into a liter of water then measures the concentration of  $C_4H_9Cl$  at various times after time zero.

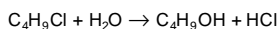
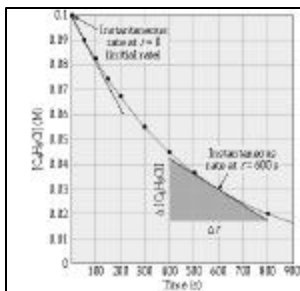


TABLE 14.2 Rate Data for Reaction of  $C_4H_9Cl$  with Water

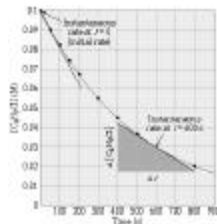
Time, $t$ (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
50.0	0.0905	$1.9 \times 10^{-4}$
100.0	0.0820	$1.7 \times 10^{-4}$
150.0	0.0741	$1.6 \times 10^{-4}$
200.0	0.0671	$1.4 \times 10^{-4}$
300.0	0.0549	$1.22 \times 10^{-4}$
400.0	0.0448	$1.01 \times 10^{-4}$
500.0	0.0368	$0.80 \times 10^{-4}$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



Concentration of butyl chloride as function of time. This plot was made from the first two columns of our data from the last slide.

This graph is particularly useful because it allows us to evaluate the instantaneous rate, the rate at a particular moment in time. The instantaneous rate is determined from the slope of the curve.

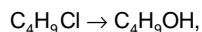
$$\text{Instantaneous rate} = - \frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = - \frac{(0.017 - 0.042)\text{M}}{(800 - 400)\text{s}} = 6.2 \times 10^{-5}\text{M/s}$$



In What follows, the term "rate" means "instantaneous rate," unless indicated otherwise. The instantaneous rate at  $t=0$  is called **initial rate** of the reaction.

### Reaction Rates and Stoichiometry

During our earlier discussion of:

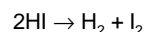


we saw that the stoichiometry requires that the rate of the disappearance of  $\text{C}_4\text{H}_9\text{Cl}$  equals the rate of appearance of  $\text{C}_4\text{H}_9\text{OH}$ .

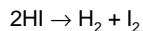
$$\text{Rate} = - \frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta [\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

What happens when the stoichiometric relationships are not one to one?

Consider the decomposition of HI gas:



We can measure the rate of disappearance of HI or the rate of appearance of either  $\text{H}_2$  or  $\text{I}_2$ .

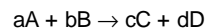


Because 2 mol of HI disappear for each mole of  $\text{H}_2$  or  $\text{I}_2$  produced, the rate of disappearance of HI is twice the rate of appearance of  $\text{H}_2$  or  $\text{I}_2$  produced.

Thus, the rate expression must half the  $\Delta[\text{HI}]$ .

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

In general, for the reaction:

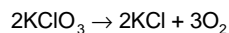


The rate is given by:

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

Sample exercise:

- How is the rate of disappearance of potassium chlorate related to the rate of appearance of oxygen in the following equation:



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

- b) If the rate of appearance of  $\text{O}_2$  is  $4.5 \times 10^{-6} \text{ M/s}$  at a particular instant, what is the value of the rate of disappearance of  $\text{KClO}_3$ ?

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

Got to use this expression

Solve for  $\Delta[\text{KClO}_3]/\Delta t$

$$-\frac{\Delta [\text{KClO}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta [\text{O}_2]}{\Delta t} \quad \text{Plug in the value of } \Delta[\text{O}_2]/\Delta t$$

$$-\frac{\Delta [\text{KClO}_3]}{\Delta t} = \frac{2}{3} (4.5 \times 10^{-6} \text{ M/s}) = 3.0 \times 10^{-6} \text{ M/s}$$

#### The Dependence of Rate on Concentration

Reaction rates diminish as the concentration of reactants diminish. Conversely, rates generally increase when reactant concentrations are increased.

One way of studying the effect of concentration on reaction rates is to determine the way in which the rate at the beginning of a reaction depends on the starting concentrations.

Consider the following reaction:

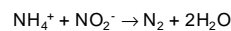
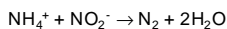


TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial $\text{NH}_4^+$ Concentration (M)	Initial $\text{NO}_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.0600	0.200	$32.3 \times 10^{-7}$
5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$

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5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$

One sees that changing either  $[\text{NH}_4^+]$  or  $[\text{NO}_2^-]$  changes the reaction rate. If one doubles  $[\text{NH}_4^+]$  while holding  $[\text{NO}_2^-]$  constant, the rate doubles. Likewise, when  $[\text{NO}_2^-]$  is similarly varied while is held constant, the rate is affected in the same manner.

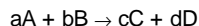
These results indicate that the rate is proportional to  $[\text{NH}_4^+]$  raised to the first power and  $[\text{NO}_2^-]$  raised to the first power.

We can express the overall concentration dependence as follows:

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

The above equation, which show how the rate depends on the concentrations of reactants, is called a **rate law**.

For a general reaction:



The rate law generally has the form:

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

The constant  $k$  in the rate law is called the **rate constant**. The magnitude of  $k$  changes with temperature and therefore determines how temperature affects rate. The exponents  $m$  and  $n$  are typically small whole numbers (0, 1, or 2)

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

If we know the rate law for a reaction and its rate for a set of reactant concentration, we can calculate the value of the rate constant,  $k$ .

Using the values in experiment #1

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

Solving for  $k$  gives:

$$K = \frac{5.4 \times 10^{-7} \text{ M/s}}{(0.0100 \text{ M})(0.200 \text{ M})} = \frac{2.7 \times 10^{-4}}{\text{M s}}$$

Let us verify that  $k$  is a constant using any of the experimental data.

Using the values in experiment #3

$$21.5 \times 10^{-7} \text{ M/s} = k [0.0400][0.200]$$

Solving for  $k$  gives:

$$K = \frac{21.5 \times 10^{-7} \text{ M/s}}{(0.0400 \text{ M})(0.200 \text{ M})} = \frac{2.7 \times 10^{-4}}{\text{M s}}$$

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

Once we have both the rate law and the value of the rate constant for a reaction, we can calculate the rate of reaction for any set of concentrations.

What is the rate of reaction when the concentration of  $[\text{NH}_4^+]$  and  $[\text{NO}_2^-]$  are both 0.100 M?

$$\text{Rate} = \left( \frac{2.7 \times 10^{-4}}{\text{M s}} \right) (0.100 \text{ M})(0.100 \text{ M}) = 2.7 \times 10^{-6} \text{ M/s}$$

### Exponents in the Rate Law

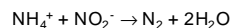
The rate laws for most reactions have the general form:

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

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

For the reaction of  $\text{NH}_4^+$  with  $\text{NO}_2^-$  we found that the exponent of  $[\text{NH}_4^+]$  is one, the rate is first order in  $\text{NH}_4^+$ . The rate is also first order in  $\text{NO}_2^-$ .

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



The exponents in a rate law indicate how the rate is affected by the concentration of each reactant. Doubling the concentration of  $[\text{NH}_4^+]^1$  causes the rate to double ( $[2]^1=2$ ).

Doubling the concentration of  $[\text{NO}_2^-]^1$  makes the rate increase by a factor of 2 as well ( $[2]^1=2$ ).

Because the overall reaction order is second order, doubling both reactants will cause the rate to quadruple.

$$([2]^1 [2]^1 = 4 \text{ which is the same as } [2]^{1+1}=4)$$

If a rate law is second order with respect to a reactant,  $[A]^2$ , then doubling the concentration of that substance will cause the reaction rate to quadruple ( $[2]^2=4$ ).

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

The values of  $m$  and  $n$  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.

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

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

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

Overall reaction order		Units of $k$
1 <sup>st</sup>	$M/s=k[M]^1$	$s^{-1}$
2 <sup>nd</sup>	$M/s=k[M]^2$	$M^{-1} s^{-1}$
3 <sup>rd</sup>	$M/s=k[M]^3$	$M^{-2} s^{-1}$
4 <sup>th</sup>	$M/s=k[M]^4$	$M^{-3} s^{-1}$
0 <sup>th</sup>	$M/s=k[M]^0$	$M s^{-1}$
3/2 <sup>nd</sup>	$M/s=k[M]^{3/2}$	$M^{-1/2} s^{-1}$

### Using Initial Rates to Determine Rate Law

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

If an reaction is zero order in a particular reactant, changing its concentration will have no effect on rate ( $[M]^0=1$ ).

If an reaction is first order in a particular reactant, changing its concentration will have a proportional change on rate ( $[2]^1=2$ ).

If an reaction is second order in a particular reactant, doubling the concentration the rate increases by a factor of  $[2]^2=4$

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.

Given the data below, determine the rate law expression for the reaction:  $2A + B_2 + C \rightarrow A_2B + BC$

Run	Initial [A]	Initial [B <sub>2</sub> ]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

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

In runs #1 and #3 the initial concentrations of A and C are the same. Thus, any change in the rate would be due to the change in concentration of B<sub>2</sub>. We see that the rate is the same in #1 & #3. Thus, the reaction rate is independent of [B<sub>2</sub>], or  $n=0$

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

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

In runs #1 and #4 involve the same initial concentration of A; thus, the observed change in rate must be due entirely to the changed [C]. So we compare trials 1 and 4 to find y: [C] has been multiplied by a factor of (0.60)/(0.20) = 3. The effect on the rate is that the rate changes by a factor of (7.2)/(2.4) = 3. Thus, y = 1 the rate is first order in [C].

$$\text{Rate} = k [A]^m [B]^n [C]^1$$

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

$$\text{Rate} = k [A]^m [B]^n [C]^1$$

We can use trials #1 and #2 to evaluate m, because [A] is changed, [B] does not matter, and [C] is unaltered. The observed rate change is due only to the changed [A].

[A] has been multiplied by a factor of (0.40)/(0.20) = 2.

The rate has changed by a factor of (9.6)/(2.4) = 4.

We now know that m=2 (2<sup>2</sup>=4). The reaction is second order in [A]

$$\text{Rate} = k [A]^2 [B]^n [C]^1 \quad \text{or} \quad \text{Rate} = k [A]^2 [C]^1$$

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

The rate law could be reached in a more formal way by taking the ratio of the rates from two runs.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{2.4 \text{ M/s}}{2.4 \text{ M/s}} = 1 \quad \text{Using the rate law gives:}$$

$$1 = \frac{k[0.20]^m [0.30]^n [0.20]^y}{k[0.20]^m [0.20]^n [0.20]^y} = (1.5)^n$$

The only way that (1.5)<sup>n</sup>=1 is if n=0

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{7.2 \text{ M/s}}{2.4 \text{ M/s}} = 3$$

$$3 = \frac{\text{rate 4}}{\text{rate 1}} = \frac{k[0.20]^m [0.40]^n [0.60]^y}{k[0.20]^m [0.20]^n [0.20]^y} = (3)^y$$

The only way that (3)<sup>y</sup>=3 is if y=1

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
4	0.20M	0.40M	0.60M	7.2 M/s

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{9.6 \text{ M/s}}{2.4 \text{ M/s}} = 4$$

$$4 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{k[0.40]^m [0.30]^n [0.20]^y}{k[0.20]^m [0.20]^n [0.20]^y} = (2)^m$$

The only way that (2)<sup>m</sup>=4 is if m=2

$$\text{Rate} = k [A]^2 [B]^n [C]^1$$

Run	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20M	0.20M	0.20M	2.4 M/s
2	0.40M	0.30M	0.20M	9.6 M/s
3	0.20M	0.30M	0.20M	2.4 M/s
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a) Now that we know the rate law for this reaction (rate = k [A]<sup>2</sup> [C]<sup>1</sup>), solve for k using any of the runs.

$$K = \frac{7.2 \text{ M/s}}{(0.20 \text{ M})^2 (0.6 \text{ M})} = 30 \text{ M}^{-2} \text{ s}^{-1} = k$$

b) What would be the initial rate of reaction when [A], [B], and [C] = 0.010M?

$$\text{Rate} = (30 \text{ M}^{-2} \text{ s}^{-1})(0.010 \text{ M})^2 (0.010 \text{ M}) = 3.0 \times 10^{-5} \text{ M/s}$$

### The Change of concentration with time

Rate laws can be converted into equations that tell us what the concentrations of the reactants or products are at any time during the course of a reaction.

We will only consider first order reactions for a reaction of the type  $A \rightarrow \text{products}$ .

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

By using calculus and integrating, the following is obtained:

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

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

The above equation can be used in several ways. Given any three quantities, we can solve for the fourth;  $k$ ,  $t$ ,  $[A]_0$ , and  $[A]_t$ .

These equations can be used, to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time required for a given fraction of a sample to react, or (3) the time required for a reactant concentration to fall to a certain level.

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

The thermal decomposition of dinitrogen pentoxide ( $\text{N}_2\text{O}_{5(g)} \rightarrow 2\text{NO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$ ) is a first-order reaction. The rate constant for the reaction is  $5.1 \times 10^{-4} \text{ s}^{-1}$  at 318K. If the initial amount of  $\text{N}_2\text{O}_{5(g)}$  is 4.500 moles, how much would be left after 5 minutes?

$$\ln[A]_t = -(300 \text{ s}) 5.1 \times 10^{-4} \text{ s}^{-1} + \ln[4.500 \text{ mol}]_0$$

$$\ln[A]_t = -0.153 + 1.504077$$

$$\ln[A]_t = 1.351077397$$

$$[A]_{t=300\text{s}} = e^{1.351077397}$$

$$[A] = 3.862 \text{ moles left}$$

### Half-life

The half-life of a reaction,  $t_{1/2}$ , is the time required for the concentration of a reactant to drop to one half of its initial value,  $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ .

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

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

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

$$t_{1/2} = -\frac{\ln \frac{1}{2}}{k} \quad t_{1/2} = \frac{0.6932}{k}$$

The thermal decomposition of dinitrogen pentoxide ( $\text{N}_2\text{O}_{5(g)} \rightarrow 2\text{NO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$ ) is a first-order reaction. The rate constant for the reaction is  $5.1 \times 10^{-4} \text{ s}^{-1}$  at 318K. What is the half-life of this process?

$$t_{1/2} = \frac{0.6932}{k}$$

$$t_{1/2} = \frac{0.6932}{5.1 \times 10^{-4} \text{ s}^{-1}}$$

$$t_{1/2} = 1359 \text{ seconds or 23 min}$$

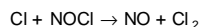
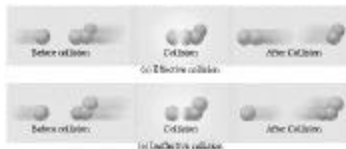
### The Collision Model

Reaction rates are affected both by the concentrations of reactants and by temperature. How can we explain these effects at the molecular level? The collision model of chemical kinetics, which is based on the kinetic-molecular theory (10.7) The central idea of the collision model is that molecules must collide to react. The greater the number of collisions occurring per second, the greater the reaction rate.

For reaction to occur, though, more is required than simply a collision. For most reactions, only a tiny fraction of the collisions leads to reaction. Only about 1 in every  $10^{13}$  collisions produces a reaction.

### The Orientation Factor

In most reactions, molecules must be oriented in a certain way during collisions in order for a reaction to occur. The relative orientations of the molecules during their collisions determine whether the atoms are suitably positioned to form new bonds.



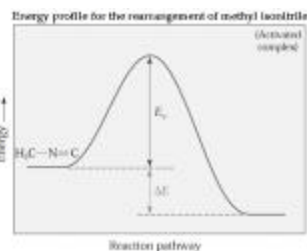
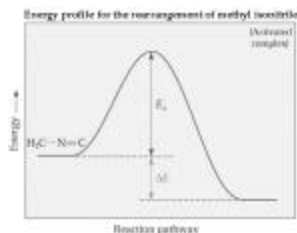
The reaction will take place only if the collision brings Cl atoms together to form  $\text{Cl}_2$ .

### Activation Energy

In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy in order to react.

If molecules are moving too slowly, with too little kinetic energy, they merely bounce off one another without reacting. In order to react, colliding molecules must have a total kinetic energy equal to or greater than some minimum value. The minimum energy required to initiate a chemical reaction is called the **activation energy**,  $E_a$ .

As an example, the rearrangement of methyl isonitrile to acetonitrile, we might imagine pass through an intermediate state in which the  $\text{N}=\text{C}$  portion of the molecule is sitting sideways.



The energy difference between that of the starting molecules and the highest energy along the reaction pathway is the **activation energy**,  $E_a$ . The particular arrangement of atoms at the top of the barrier is called the **activated complex** or **transition state**.

### The Arrhenius Equation

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear. He found that most reaction-rate data obeyed an equation based on three factors (1) the fraction of molecules possessing an energy of  $E_a$  or greater, (2) the number of collisions occurring per second, and (3) the fraction of collisions that have the appropriate orientation. These three factors are incorporated into the **Arrhenius equation**:

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

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

$k$  is the rate constant,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature. The **frequency factor**,  $A$ , is constant, or nearly so, as the temperature is varied. It is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction.

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.

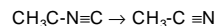
### Reaction Mechanisms

A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those produced as the reaction proceeds. It provides no information about how the reaction occurs. The process by which a reaction occurs is called the **reaction mechanism**.

At the most sophisticated level, a reaction mechanism will describe in great detail the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.

### Elementary Steps

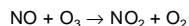
Collisions between molecules methyl isocyanide can provide the energy to allow the  $\text{CH}_3\text{CNC}$  to rearrange



This process occurs in a single event and is called an **elementary step**.

The number of molecules that participated as reactants in an elementary step defines the molecularity of the step. If a single molecule is involved, the reaction is **unimolecular**.

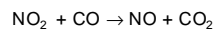
Elementary steps involving the collision of two reactant molecules are bimolecular. The reaction between NO and  $\text{O}_3$  is **bimolecular**.



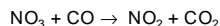
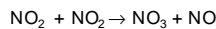
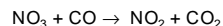
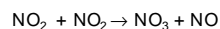
Elementary steps involving the simultaneous collision of three molecules are **termolecular**. Termolecular steps are far less probable than unimolecular or bimolecular processes and are rarely encountered.

### Multistep Mechanisms

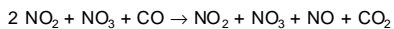
A balanced chemical equation often occurs by a multistep mechanism, which consists of a sequence of elementary steps. Consider the reaction of  $\text{NO}_2$  with CO:



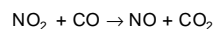
This reaction appears to proceed in two elementary steps, each of which is bimolecular.



The elementary steps in a multistep mechanism must always add to give the chemical equation of the overall process.



Simplifying this equation by eliminating substances that appear on both sides of the arrow yields:



Because  $\text{NO}_3$  is formed in one elementary step and consumed in the next it is called an **intermediate**.

### Rate Laws for Elementary Steps

Every reaction is made up of a series of one or more elementary steps, and the rate laws and relative speeds of these steps will dictate the overall rate law.

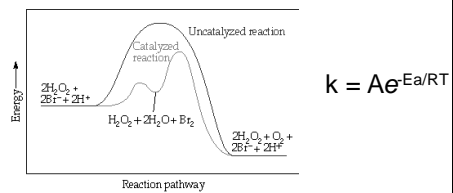
Kinetics can lead us to reaction mechanisms that are consistent with those observed experimentally.

TABLE 14.4 Elementary Steps and Their Rate Laws

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

## Catalysis

A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process.



On the basis of the Arrhenius equation, the rate constant ( $k$ ) is determined by the activation energy ( $E_a$ ) and the frequency factor ( $A$ ). A catalyst may affect the rate of reaction by altering the value of either  $E_a$  or  $A$ .

