

Chapter 12 Outline – Chemical Kinetics

The area of chemistry that deals with the rate at which reactions occur is called **chemical kinetics**. One of the goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the **reaction mechanism**.

Reaction Rates

- The reaction rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time. **Rate** = $\Delta[A] \div \Delta t$
- The value of the rate at a particular time (the **instantaneous rate**) can be obtained by computing the slope of a line tangent to the curve at that point.
- Consider the following reaction: $2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$
 - Assume that the rate of reaction was determined by measuring the CO_2 produced and was found to be $2.50 \text{ mol CO}_2 \text{ L}^{-1} \text{ s}^{-1}$. This can be converted to the rates of appearance and disappearance of all of the other species by using the stoichiometric ratio.
 - For example: Calculate the rate of disappearance of O_2 .
 - $\frac{2.50 \text{ mol CO}_2 \text{ L}^{-1} \text{ s}^{-1}}{1} \times \frac{7 \text{ mol O}_2}{4 \text{ mol CO}_2} = 4.38 \text{ mol O}_2 \text{ L}^{-1} \text{ s}^{-1}$
 - You try: Calculate the rate of appearance of water.

Rate Laws: An Introduction

- If we choose to consider conditions where the reverse reaction can be neglected, **the reaction rate will depend only on the concentrations of the reactants**.
- Consider the following reaction: $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$
- For the above reaction the **rate law** is: **Rate** = $k [\text{NO}_2]^n$ where **k**, the proportionality constant, also called the **rate constant** and **n**, the **order of the reactant**. **Both k and n must be determined by experiment; they cannot be written from the balanced equation.**
- The products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.
- A rate law that expresses how the rate depends on the concentration is technically called the **differential rate law**, but it is often simply called the **rate law**.
- The **integrated rate law** expresses how concentrations depend on time.

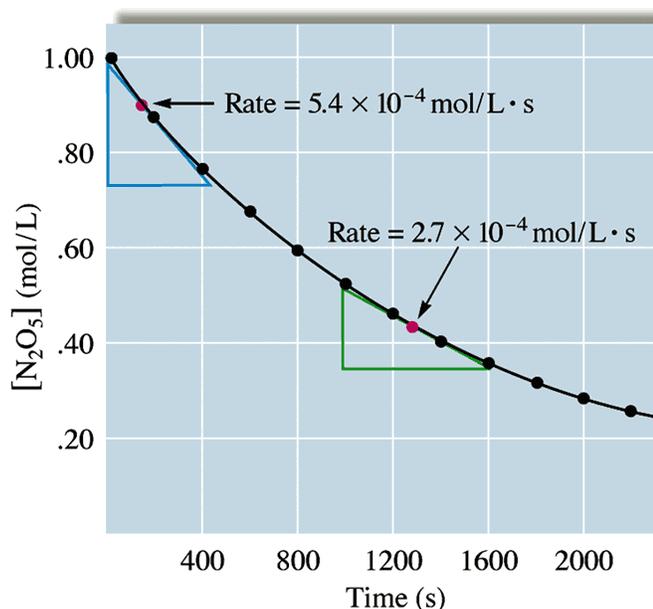
Determining the Form of the Rate Law

- Consider the following reaction:
 $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$
- Data for this reaction is given to the right and plotted below.

TABLE 12.3
Concentration/Time Data for
the Reaction $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow$
 $4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C)

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

- Note from the graph that when $[N_2O_5]$ is halved, the rate is also halved. This means that the rate of this reaction depends on the concentration of N_2O_5 to the **first power**. Thus the reaction is a first order in N_2O_5 .
- Rate = $k[N_2O_5]^1 = k[N_2O_5]$
- One common method for experimentally determining the form of the rate law for a reaction is the **method of initial rates**.
- The initial rate of a reaction is the instantaneous rate determined just after the reaction begins.
- Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run. The results are then compared to see how the initial rate depends on the initial concentrations.



- Consider the following reaction: $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

- The table to the right gives initial rates obtained from three experiments involving different initial concentrations of reactants.
- The general form for the rate law for this reaction is:

$$\text{Rate} = k[NH_4^+]^n[NO_2^-]^m$$

- Experiments 1 and 2 are compared because the initial concentration of $[NH_4^+]$ is the same and the initial concentration of NO_2^- is different:

$$\frac{\text{Experiment 2: Rate 2} = 2.70 \times 10^{-7} \text{ mol/L s} = k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m}{\text{Experiment 1: Rate 1} = 1.35 \times 10^{-7} \text{ mol/L s} = k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m}$$

$$2.0 = (2.0)^m$$

$$\mathbf{m = 1}$$

The rate law for this reaction is first order in the reactant NO_2^- .

- A similar analysis of experiments 2 and 3 yield the ratio:

$$\frac{\text{Experiment 3: Rate 3} = 5.40 \times 10^{-7} \text{ mol/L s} = k(0.200 \text{ mol/L})^n(0.010 \text{ mol/L})^m}{\text{Experiment 2: Rate 2} = 2.70 \times 10^{-7} \text{ mol/L s} = k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m}$$

$$2.0 = (2.0)^n$$

$$\mathbf{n = 1}$$

The rate law for this reaction is first order in the reactant NH_4^+ .

- The rate law for this reaction is: **Rate = $k[NH_4^+]^1[NO_2^-]^1$ or Rate = $k[NH_4^+][NO_2^-]$**
- The overall reaction order is the sum of $n + m$. **This reaction is second order overall.**
- The value of the rate constant, k , can now be calculated using the results of any of the three experiments.
- From experiment 1:

$$\begin{aligned} \text{Rate} &= k[NH_4^+][NO_2^-] \\ 1.35 \times 10^{-7} &= k[0.100][0.0050] \\ \mathbf{k} &= \mathbf{2.7 \times 10^{-4} \text{ L/mol s}} \end{aligned}$$

TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L · s)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

- **You try:** The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation: $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$
The results of four experiments are provided below. Using these data, determine the order for all three reactants, the overall reaction order, and the value of the rate constant.

TABLE 12.5 The Results from Four Experiments to Study the Reaction
 $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

The Integrated Rate Law

- The **integrated rate law** expresses how concentrations depend on time.
- We will proceed by first looking at reactions involving a single reactant: $\text{aA} \rightarrow \text{products}$ where the **rate** = $k[\text{A}]^n$
- **First Order Rate Laws:**
 - Consider this reaction: $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$
 - The rate law has been determined to be: $\text{Rate} = k[\text{N}_2\text{O}_5]$
 - Since the rate of this reaction depends on the concentration of N_2O_5 to the first power, it is a first-order reaction. This means that if the concentration of N_2O_5 in a flask were suddenly doubled, the rate of production of NO_2 and O_2 also would double.
 - The **integrated first order rate law is:** $\ln[\text{A}] = -kt + \ln[\text{A}]_0$ or $\ln([\text{A}]_0 / [\text{A}]) = kt$
 - The equation shows how the concentration of A depends on time. If the initial concentration of A and the rate constant k are known, the concentration of A at any time can be calculated.
 - **A reaction is first order in A if the plot of $\ln[\text{A}]$ versus t is a straight line.** If it is not a straight line, it is not a first order in A.
 - **In a first order reaction, k = - slope**

- **For example:** The decomposition of N_2O_5 in the gas phase was studied at constant temperature.

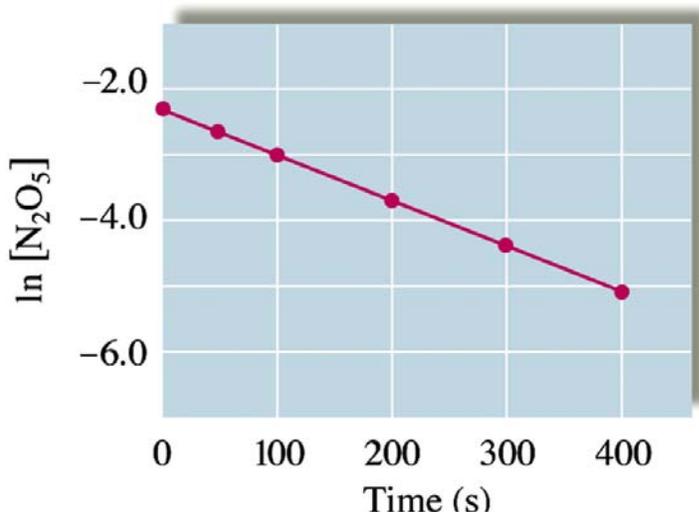


The following results were collected:

Using these data, verify that the rate law is first order in $[\text{N}_2\text{O}_5]$, and calculate the value of the rate constant, where the rate = $-\Delta[\text{N}_2\text{O}_5] / \Delta t$.

Answer: You can verify that the rate law is first order in $[\text{N}_2\text{O}_5]$ by constructing a plot of $\ln[\text{N}_2\text{O}_5]$ versus time. The data and plot is below. The fact that the plot is a straight line confirms that the reaction is a first order in $[\text{N}_2\text{O}_5]$.

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400



$\ln[\text{N}_2\text{O}_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400

To calculate the rate constant we use:

$$k = \text{slope} = -\Delta(\ln[\text{N}_2\text{O}_5]) / \Delta t$$

$$k = [-5.075 - (-2.303)] / 400 - 0$$

$$k = 6.93 \times 10^{-3} \text{ s}^{-1}$$

- **Half-Life of a First-Order Reaction**

- The time required for a reactant to reach half its original concentration is called the half-life of a reactant and is designated symbol $t_{1/2}$. $t_{1/2} = 0.693 / k$
- Example: A certain first order reaction has a half-life of 20.0 minutes. Calculate the rate constant for this reaction. How much time for this reaction to be 75% complete?

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

$$20 = 0.693 / k$$

$$k = 3.47 \times 10^{-2} \text{ min}^{-1}$$

Since 75% is complete, 25% still remains.

$$\ln([A]_0 / [A]) = kt$$

$$\ln(1.0 / 0.25) = (3.47 \times 10^{-2} \text{ min}^{-1})t$$

$$t = 40. \text{ minutes}$$

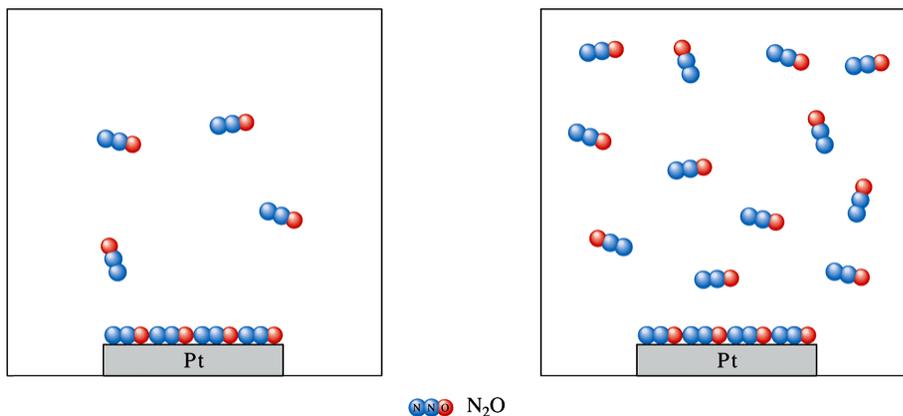
- **Second Order Rate Laws**

- For a general reaction involving a single reactant: $aA \rightarrow \text{products}$ that is second order in A, the rate law is: **Rate = $k[A]^2$**
- The integrated second-order rate law has the form: $1/[A] = kt + 1/[A]_0$
- The expression for the half-life of a second-order reaction: $t_{1/2} = 1 / k[A]_0$
- For a second-order reaction, a plot of $1/[A]$ versus t produces a straight line of slope k .
- For a second-order reaction, $t_{1/2}$ depends on both k and $[A]_0$; for a first order reaction $t_{1/2}$ depends only on k .

- **Zero-Order Rate Laws**

- Most reactions involving a single reactant show either first-order or second order kinetics. However, sometimes such a reaction can be a zero-order reaction. The rate law is:
Rate = $k[A]^0 = k(1) = k$

- The integrated rate law for a zero-order reaction is: $[A] = -kt + [A]_0$
- The expression for the half-life of a zero-order reaction is: $t_{1/2} = [A]_0 / 2k$
- Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur.
- For example: $2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$ occurs on a hot platinum surface. When the platinum surface is completely covered with N_2O molecules, an increase in the concentration of N_2O has no effect on the rate, since only N_2O molecules on the surface can react. Under these conditions, the rate is a constant because it is controlled by what happens on the platinum surface rather than by the total concentration of N_2O . The diagram below shows this.

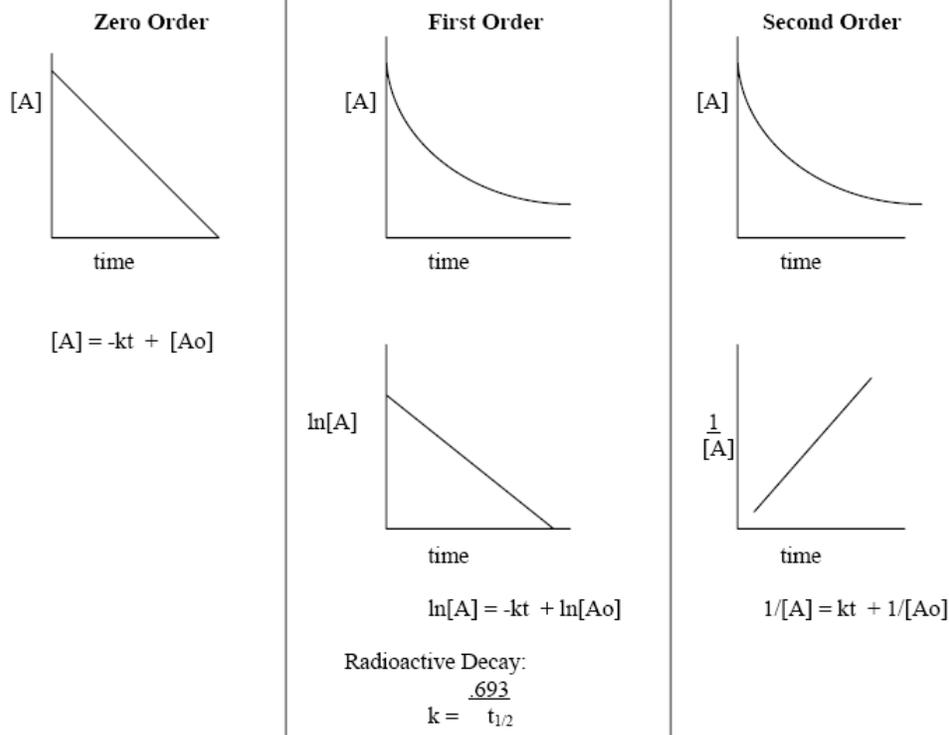
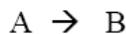


All of this First Order, Second Order and Zero Order stuff is summarized in the table below.

TABLE 12.6 Summary of the Kinetics for Reactions of the Type $a\text{A} \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[\text{A}]$

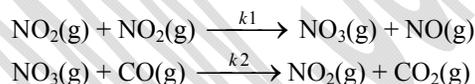
	Order		
	Zero	First	Second
Rate Law:	Rate = k	Rate = $k[\text{A}]$	Rate = $k[\text{A}]^2$
Integrated Rate Law:	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$	$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$
Plot Needed to Give a Straight Line:	$[\text{A}]$ versus t	$\ln[\text{A}]$ versus t	$\frac{1}{[\text{A}]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-life:	$t_{1/2} = \frac{[\text{A}]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[\text{A}]_0}$

I. Order of a Reaction



Reaction Mechanisms

- Most chemical reactions occur by a series of steps called the reaction mechanism.
- A balanced equation does not tell us how the reactants became products.
- Consider the following reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ The rate law for this reaction is known from experiment to be: $\text{Rate} = k[\text{NO}_2]^2$.
- For this reaction between nitrogen dioxide and carbon monoxide, the mechanism is thought to involve the following steps:



Where k_1 and k_2 are the rate constants of the individual reactions. In this reaction NO_3 is an **intermediate**, a species that is neither a reactant nor a product but that is formed and consumed during the reaction sequence.

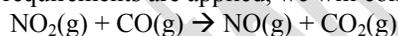
- Each of the steps in this mechanism is called an **elementary step**, a reaction whose rate law can be written from its molecularity.
- **Molecularity** is defined as the number of species that must collide to produce the reaction indicated by that step.
- A reaction involving one molecule is called a **unimolecular step**.
- Reactions involving the collision of two and three species are termed **bimolecular** and **termolecular**, respectively.
- Termolecular reactions are quite rare, because the probability of three molecules colliding simultaneously is very small.
- The chart below puts all these terms in order. We will discuss the possibilities...well I can't really say it will be a discussion. I will talk a lot probably. You can ask me questions.

TABLE 12.7 Examples of Elementary Steps

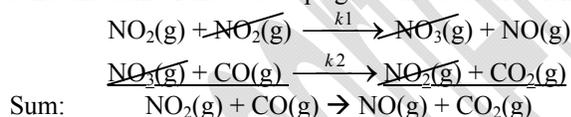
Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	<i>Unimolecular</i>	Rate = $k[A]$
$A + A \rightarrow \text{products}$ ($2A \rightarrow \text{products}$)	<i>Bimolecular</i>	Rate = $k[A]^2$
$A + B \rightarrow \text{products}$	<i>Bimolecular</i>	Rate = $k[A][B]$
$A + A + B \rightarrow \text{products}$ ($2A + B \rightarrow \text{products}$)	<i>Termolecular</i>	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	<i>Termolecular</i>	Rate = $k[A][B][C]$

- Great Discussion!
- A reaction mechanism can now be defined more precisely. It is a series of elementary steps that must satisfy two requirements:
 - The sum of the elementary steps must give the overall balanced equation for the reaction.
 - The mechanism must agree with the experimentally determined law.

- To see how the above requirements are applied, we will consider the reaction from above:



- First note that the sum of the two steps gives the overall balanced equation:



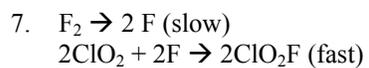
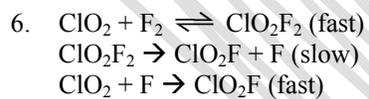
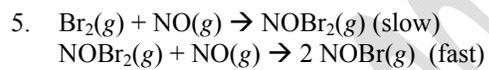
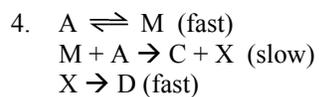
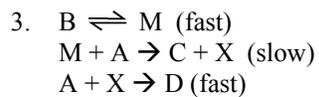
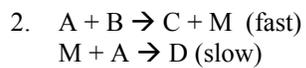
The first requirement is met

- To see whether the mechanism meets the second requirement, we must determine the **rate-determining step**.
- Multi-step reactions often have one step that is much slower than all the others.
- Reactants can only become products as fast as they can get through this slowest step. The overall reaction can be no faster than the slowest, or rate determining, step in the sequence.
- To determine which step is the rate determining step, relates to molecularity and rate order. If it is a second-order reaction, the slow step happens when the first two molecules react. If it is a third order reaction, the slow step occurs when the third molecules reacts with the product of the first two molecules reacting. (Termolecular reactions are rare in one step)
- Since it was determined earlier that this is a second order reaction, the slow step will occur when the first two molecules react. This occurs in the first step. So the first step is the rate-determining step.

You Try: For each of the following reaction mechanisms:

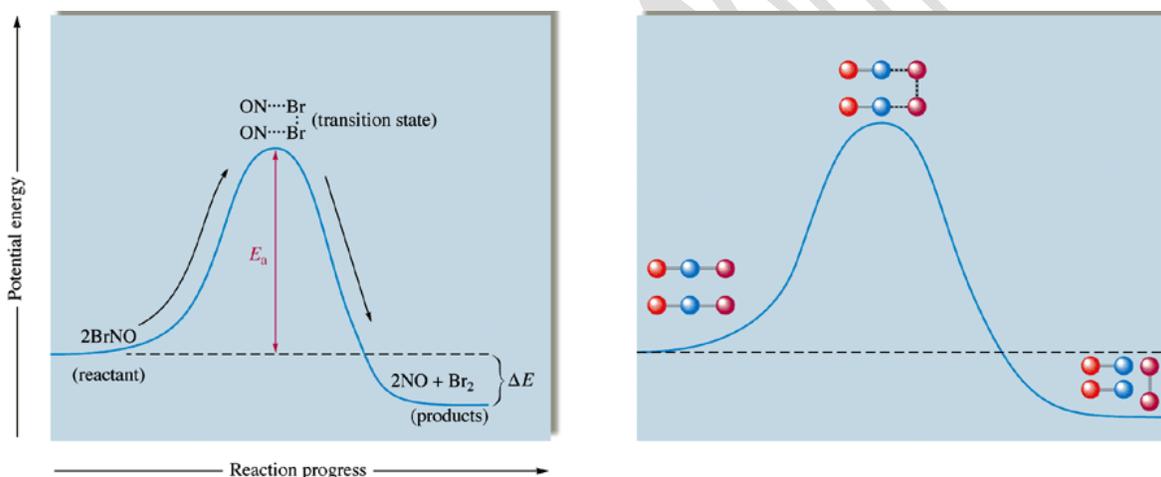
- Write a balanced equation for the overall reaction.
- Identify the intermediates in the reaction. Explain your reasoning.
- Write the rate law for reaction.

- $\text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (fast)
 $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (slow)
 $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (fast)

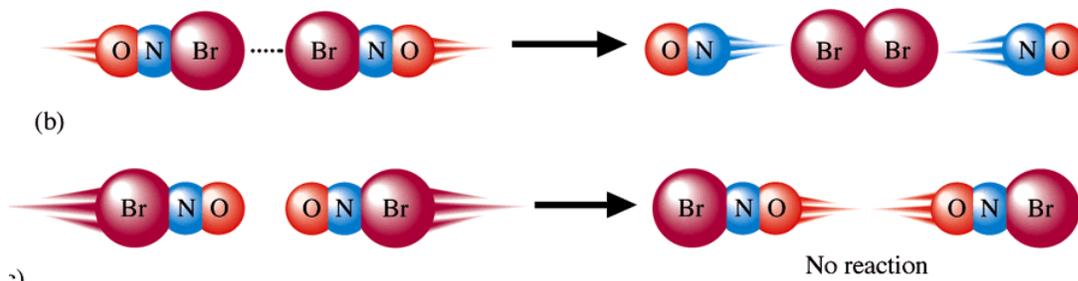


A Model for Chemical Kinetics

- Chemical reactions speed up when the temperature is increased. Experiments have shown that virtually all rate constants show an exponential increase with absolute temperature.
- The **collision model** is built around the central idea that molecules must collide to react.
- The kinetic molecular theory of gases predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecules. This agrees with the observation that reaction rates are greater at higher temperatures qualitatively. However, it is found that the rate of reaction is much smaller than the calculated collision frequency in a collection of gas particles. This means only a fraction of the collisions produces a reaction.
- In 1880 Svante Arrhenius proposed the existence of a *threshold energy*, called **activation energy** that must be overcome by a chemical reaction.
- **Strong bonds between molecules results in high activation energy for a chemical reaction.**
- The arrangement of atoms found at the potential energy “hill,” or barrier, is called the **activated complex**, or **transition state**.
- A certain minimum energy is required for molecules to “get over the hill” so that products can form. This energy is furnished by the energy of the collision.
- Only collisions with energy greater than the activation energy are able to react (get over the barrier).



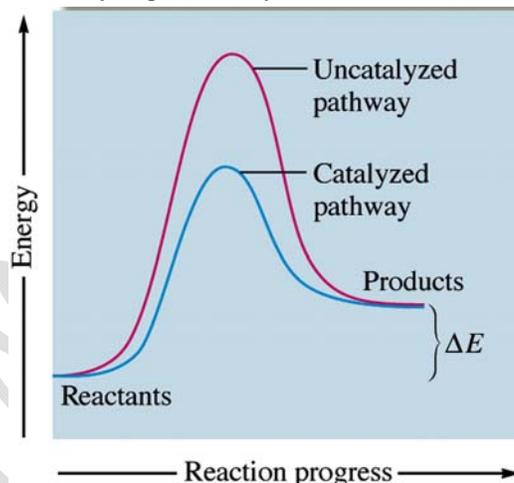
- Experiments show that the observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier. This means that many collisions, even though they have the required energy, still do not produce a reaction. The reason for this is that in some collisions the molecular orientation is not correct for a reaction to occur. (See the diagram to the below. The first reaction occurs but the second reaction does not.



- **To Summarize:** Two requirements must be satisfied for reactants to collide successfully:
 - The collision must involve enough energy to produce the reaction; the collision energy must equal or exceed the activation energy.
 - The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

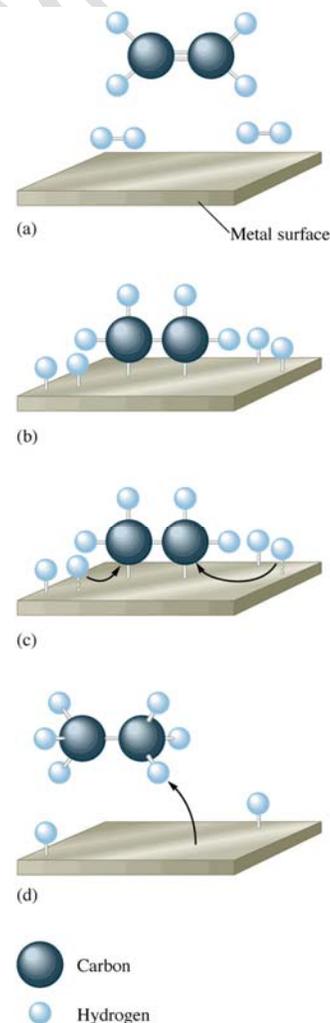
Catalysis

- Although we just saw how increasing the temperature speeds up a reaction, it is not always feasible. For example, living cells can only survive in a rather narrow temperature range, and the human body is designed to operate at an almost constant temperature of 98.6°F. But many of the complex biochemical reactions that take place at this temperature would be too slow at this temperature without intervention. We exist only because our bodies contain many substances called **enzymes**, which increase the rates of these reactions. Almost every biologically important reaction is assisted by a specific enzyme.
- A catalyst is a substance that speeds up a chemical reaction without being consumed itself. Almost all industrial processes involve the use of catalysts.
- Catalysts provide a new pathway for a chemical reaction which has lower activation energy.
- Because the catalyst allows the reaction to occur with a lower activation energy, a much larger fraction of collisions is effective at a given temperature and the reaction rate is increased.
- Catalysts are classified as homogeneous or heterogeneous.
- A homogeneous catalyst is one that is present in the same phase as the reacting molecules.
- A heterogeneous catalyst exists in a different phase as the reacting molecules, usually as a solid.



Heterogeneous Catalysis

- Heterogeneous catalysis most often involves gaseous reactants being adsorbed on the surface of a solid catalyst.
- Adsorption refers to the collection of one substance on the surface of another substance. (Absorption refers to the penetration of one substance into another.)
- Heterogeneous catalysis typically involves four steps:
 - Adsorption and activation of the reactants.
 - Migration of the adsorbed reactants on the surface
 - Reaction of the adsorbed substances
 - Escape, or **desorption**, of the products
- Heterogeneous catalysis is utilized in catalytic converters in automobile exhaust systems. The catalyst promotes the conversion of CO to CO₂, hydrocarbons to CO₂ & H₂O and NO to N₂ to lessen the impact of the exhaust gases. The most effective catalytic materials are transition metal oxides and noble metals such as palladium and platinum.



Homogeneous Catalysis

- A homogeneous catalyst exists in the same phase as the reacting molecules.
- In the troposphere, the part of the atmosphere closest to the earth, nitric oxide catalyzes ozone production. However, in the upper atmosphere it catalyzes the decomposition of ozone. Both these effects are unfortunate environmentally.