

Larry Brown  
Tom Holme

www.cengage.com/chemistry/brown

## Chapter 11 Chemical Kinetics

Jacqueline Bennett • SUNY Oneonta

## Chapter Objectives

- Explain the role of **chemical kinetics** in the formation and destruction of ozone in the atmosphere.
- Define the **rate of a chemical reaction** and express the rate in terms of the concentrations of individual reactants or products.
- Use the **method of initial rates** to determine **rate laws** from experimental data.
- Use graphical methods to determine rate laws from experimental data.

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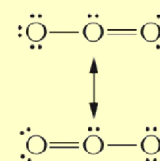
## Chapter Objectives

- Explain the difference between **elementary reactions** and **multistep reactions**.
- Find the rate law predicted for a particular reaction **mechanism**.
- Use a molecular perspective to explain the significance of the terms in the **Arrhenius equation**.
- Calculate the **activation energy** for a reaction from experimental data.
- Explain the role of a **catalyst** in the design of practical chemical reactions.

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## Ozone Depletion

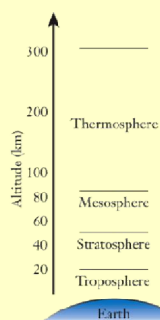
- Ozone is an **allotrope** of oxygen.
- **Tropospheric** ozone is produced by lightning and reactions of various gases from automobile exhaust and industrial processes.
- Tropospheric ozone is considered an air pollutant.
- "Ozone alerts" issued when ozone concentration is above 0.1 ppm.



The two equivalent resonance structures for ozone.

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## Ozone Depletion

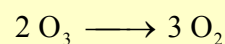


- Several layers of the atmosphere and their altitudes.
- The **ozone layer** is in the **stratosphere** at an altitude of about 30 km.

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## Ozone Depletion

- Ozone decomposes according to the following equation.



- The fact that ozone is highly reactive and cannot exist for long at the earth's surface suggests two important facts:
  - $\text{O}_2$  is the more stable of the two allotropes.
  - For stratospheric ozone to exist, conditions must favor the production of  $\text{O}_3$  to allow a significant concentration of  $\text{O}_3$ .

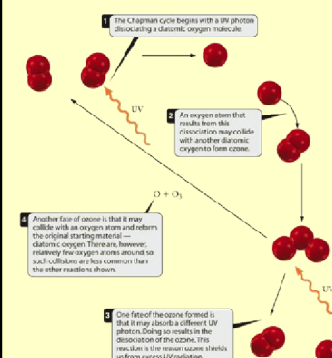
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## Ozone Depletion

- The **Chapman cycle** explains the chemistry behind the formation and destruction of ozone in the stratosphere.
- Ozone is produced in the stratosphere when UV light dissociates a diatomic oxygen molecule and one of the oxygen atoms produced collides with a diatomic oxygen molecule.
- Ozone may be destroyed by:
  - absorbing a different UV photon, dissociating ozone into diatomic oxygen and atomic oxygen.
  - reacting with an oxygen atom and reforming diatomic oxygen molecules.

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## Ozone Depletion



- The Chapman cycle for the formation and destruction of ozone in the stratosphere.

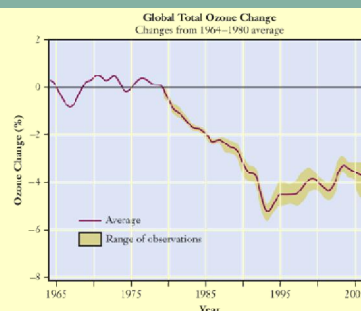
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## Ozone Depletion

- Ozone is a highly reactive, unstable compound.
- For ozone to persist in the stratosphere to form the ozone layer, the rate of ozone production must equal or exceed the rate of ozone depletion.
- There is evidence that the presence of bromine and chlorine in the stratosphere increases the rate of ozone depletion, creating a seasonal ozone hole over Antarctica and North America.

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## Ozone Depletion



- The decrease in the overall levels of atmospheric ozone is clearly shown for the past two decades.

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## Rates of Chemical Reactions

- There are two fundamental issues in chemical kinetics.
  - How is the rate of a reaction defined?
  - How is the rate of a reaction measured?

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## Concept of Rate and Rates of Reaction

- The reaction **rate** is the ratio of the change in concentration to the elapsed time.

$$\text{Rate} = \frac{\text{change in concentration}}{\text{elapsed time}} = \frac{\Delta[\text{substance}]}{\Delta t}$$

- Concentration is measured in M, or mol L<sup>-1</sup>, and designated with square brackets, [ ].
- Time is measured in s.
- The unit for rate is mol L<sup>-1</sup> s<sup>-1</sup>.

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## Stoichiometry and Rate

- As a reaction proceeds, the rate of the reaction can be measured by monitoring the concentrations of products and reactants.
- As a reaction proceeds, the concentration of the reactants decreases and the concentration of the products increases.

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## Stoichiometry and Rate

- While measuring the rate of increase in product concentration, the rate of the reaction is a positive number.

$$\text{Rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

- While measuring the rate of decrease in reactant concentration, the change in concentration will have a negative sign.
  - A negative sign is included in the rate statement to obtain a positive value for the rate.

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

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## Stoichiometry and Rate

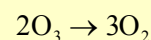
- The change in the concentrations of the product and reactant are not necessarily equal.
- To ensure that the same reaction rate is obtained when using either the reactants or the products, the stoichiometric coefficient,  $\nu$ , is included in the denominator of the rate expression.

$$\text{Rate} = \frac{\Delta[\text{product}]}{\nu_{\text{prod}} \Delta t} = -\frac{\Delta[\text{reactant}]}{\nu_{\text{react}} \Delta t}$$

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## Example Problem 11.1

- The conversion of ozone to oxygen was studied in an experiment and the rate of  $\text{O}_3$  consumption was measured as  $2.5 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ . What was the rate of  $\text{O}_2$  production in this experiment?



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## Average Rate and Instantaneous Rate

- As the concentration of oxygen decreases, the rate of combustion will also decrease.
- When placing a candle in a closed container, the flame will slowly diminish over time as the container's oxygen is consumed. Eventually the flame goes out.



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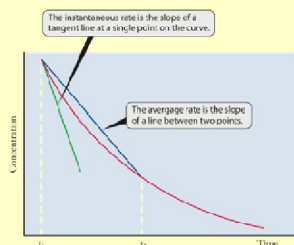
## Average Rate and Instantaneous Rate

- The rate of a reaction can be measured as an average rate and as an instantaneous rate.
  - For the **average rate**, concentration is measured at times separated by a finite difference, and the slope of the line between them gives the rate.
  - The **instantaneous rate** refers to the rate at a single moment, and it is given by the slope of a line tangent to the curve defined by the change in concentration versus time.

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## Average Rate and Instantaneous Rate

- The rates obtained from the average rate and instantaneous rate measurements can be quite different.
- Instantaneous rates are the preferred method for kinetics.
  - The commonly measured rate is the **initial rate**: the instantaneous rate of a reaction just as it begins.



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## Rate Laws and the Concentration Dependence of Rates

- The rate of a chemical reaction depends on a number of factors.
  - One of these factors is the concentration of the reacting species.
- The dependence of reaction rate on concentration often follows relatively simple mathematical relationships.
  - This behavior can be summarized in a mathematical equation known as the rate law.
  - There are two useful forms of the rate law. The first is the **differential rate law**.

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## The Rate Law

- For a reaction between substances X and Y, the rate of the reaction can be described by an equation of the form:

$$\text{Rate} = k[X]^m[Y]^n$$

- $k$  is the rate constant
- $[X]$  and  $[Y]$  are the reactant concentrations
- $m$  and  $n$  are typically either integers or half integers and **must** be determined experimentally.

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## The Rate Law

- The experimentally determined exponents are referred to as the **order of the reaction**.
  - If  $m = 1$ , the reaction is said to be **first order**.
  - If  $m = 2$ , the reaction is said to be **second order**.
  - Exponents greater than 2 are unusual.
- For reactions where the rate depends on more than one reactant concentration:
  - The exponent on each reactant is the order with respect to that reactant.
  - The sum of the exponents is the **overall order** of the reaction.

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## Example Problem 11.2

- In the following rate laws, determine the orders with respect to each substance and the overall order of the reaction.
  - Rate =  $k[A]^2[B]$
  - Rate =  $k[A][B]^{1/2}$

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## The Rate Law

- The **rate constant**,  $k$ , conveys important information about the kinetics of a chemical reaction.
  - If the rate constant is small, the reaction is likely to proceed slowly.
  - If the rate constant is large, the reaction is likely to proceed quickly.
- The value of the rate constant,  $k$ , depends on the temperature and describes temperature dependence of the reaction rate.

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## The Rate Law

- The units for the rate constant,  $k$ , depends on the overall order of the reaction and must be chosen to balance the units in the rate law.
  - The rate has units of  $\text{mol L}^{-1} \text{s}^{-1}$ .
  - The concentration has units of  $\text{mol L}^{-1}$ .
  - The unit of  $k$  for a first order reaction is  $\text{s}^{-1}$ .
  - The unit of  $k$  for a second order reaction is  $\text{L mol}^{-1} \text{s}^{-1}$ .

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## Determination of the Rate Law

- The rate law can be determined two ways:
  - Measuring the initial rate of the reaction while adjusting the concentrations of the various reactants.
  - Using a series of graphs to compare data to various possible rate laws.

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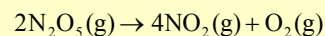
## Determination of the Rate Law

- For a reaction with only one reactant, A, the rate of the reaction is  $\text{rate} = k[\text{A}]^n$ .
- The common possible orders with respect to A are 0, 1, 2.
- If the concentration of A is doubled experimentally, the rate of the reaction will change in a simple and predictable way.
  - If  $n = 0$ , doubling  $[\text{A}]$  does not change the reaction rate.
  - If  $n = 1$ , doubling  $[\text{A}]$  doubles the reaction rate.
  - If  $n = 2$ , doubling  $[\text{A}]$  quadruples the reaction rate.

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## Example Problem 11.3

- Consider the following data for the reaction shown. Determine the rate law and rate constant for this reaction at the temperature of these experiments.



Experiment	Initial $[\text{N}_2\text{O}_5]$ ( $\text{mol L}^{-1}$ )	Initial Rate of Reaction ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	$3.0 \times 10^{-3}$	$9.0 \times 10^{-7}$
2	$9.0 \times 10^{-3}$	$2.7 \times 10^{-6}$

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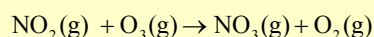
## Determination of the Rate Law

- For a reaction with two reactants, A and B, the rate of the reaction is  $\text{rate} = k[\text{A}]^n[\text{B}]^m$ .
- To separate the influence of one reactant concentration from the other, one reactant concentration is held constant while changing the other to determine its effect on the rate.
- To determine the order with respect to A and B, at least three experiments must be carried out.

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## Example Problem 11.4

- Determine the rate law and rate constant for this reaction.



Experiment	Initial $[\text{NO}_2]$ ( $\text{mol L}^{-1}$ )	Initial $[\text{O}_3]$ ( $\text{mol L}^{-1}$ )	Initial Rate of Reaction ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	$2.3 \times 10^{-5}$	$3.0 \times 10^{-5}$	$1.0 \times 10^{-5}$
2	$4.6 \times 10^{-5}$	$3.0 \times 10^{-5}$	$2.1 \times 10^{-5}$
3	$4.6 \times 10^{-5}$	$6.0 \times 10^{-5}$	$4.2 \times 10^{-5}$

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## Integrated Rate Laws

- Because the concentrations of reactants change over time, the rate law does not let us easily predict the concentrations or rate of a reaction at some later time.
- The **integrated rate law**, derived from the rate law itself, explicitly determines concentration as a function of time.
- The form of the integrated rate law depends on the order of the reaction.

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## Zero-Order Integrated Rate Law

- For a zero-order reaction, the rate law is:

$$\text{rate} = k[A]^0 = k.$$

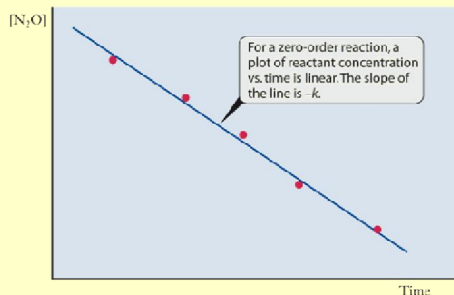
- The zero-order integrated rate law.

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

- If a plot of  $[A]$  versus time is linear, the overall order is zero order and the slope equals  $-k$ .

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## Zero-Order Integrated Rate Law



- A reaction is zero-order if a plot of reactant concentration versus time is linear.
  - The slope of the plot is  $-k$ .

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## Zero-Order Integrated Rate Law

- Derivation of the zero-order integrated rate law

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

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

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

$$d[A] = -kdt$$

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

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

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## First-Order Integrated Rate Law

- For a first-order reaction, the rate law is:

$$\text{rate} = k[A]^1$$

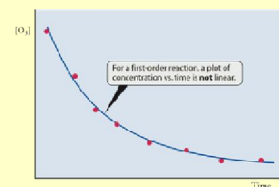
- The first-order integrated rate law.

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt}$$

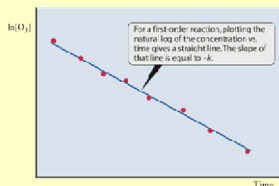
- If a plot of  $\ln [A]$  versus time is linear, the overall order is first order and the slope equals  $-k$ .

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## First-Order Integrated Rate Law



- For a reaction that is first-order, a plot of the reactant concentration versus time is not linear.

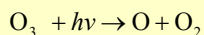


- A reaction is first-order if a plot of the natural log ( $\ln$ ) of the reactant concentration versus time is linear.
  - The slope of the plot is  $-k$ .

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### Example Problem 11.5

- The photodissociation of ozone by ultraviolet light in the upper atmosphere is a first-order reaction with a rate constant of  $1.0 \times 10^{-5} \text{ s}^{-1}$  at 10 km above the planet's surface.



- Consider a laboratory experiment in which a vessel of ozone is exposed to UV radiation at an intensity chosen to mimic the conditions at that altitude. If the initial  $\text{O}_3$  concentration is 5.0 mM, what will the concentration be after 1.0 day?

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### Second-Order Integrated Rate Law

- For a second-order reaction, the rate law is:

$$\text{rate} = k[\text{A}]^2$$

- The second-order integrated rate law.

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

- If a plot of  $1/[\text{A}]$  versus time is linear, the overall order is second order and the slope equals  $k$ .

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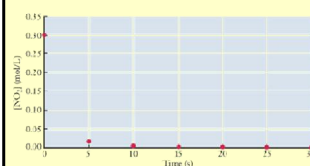
### Example Problem 11.6

- Among the possible fates of  $\text{NO}_2$  in atmospheric chemistry is the decomposition reaction to form  $\text{NO}$  and  $\text{O}_2$ . This reaction was studied at  $37^\circ\text{C}$  by a student, and the following data were obtained. Based on these data, determine the order of this reaction and the rate constant.

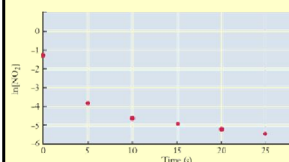
Time (s)	$[\text{NO}_2]$ (mol $\text{L}^{-1}$ )
0.0	0.3000
5.0	0.0197
10.0	0.0100
15.0	0.0070
20.0	0.0052
25.0	0.0041
30.0	0.0035

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### Second-Order Integrated Rate Law



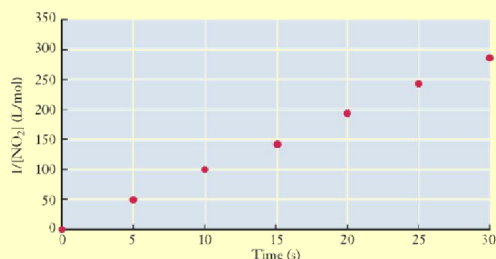
- For a reaction that is second-order, a plot of the concentration versus time is not linear.



- For a reaction that is second-order, a plot of the natural log of the reactant concentration versus time is not linear.

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### Second-Order Integrated Rate Law



- A reaction is second-order if a plot of the reciprocal of reactant concentration versus time is linear.
- The slope of the plot is  $k$ .

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### Half-Life

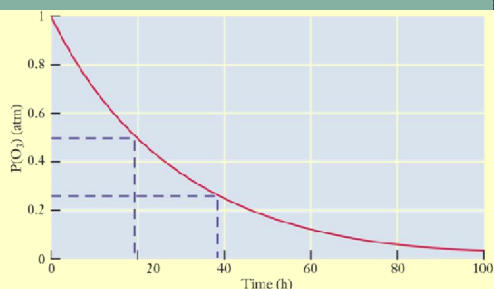
- The **half-life**,  $t_{1/2}$ , of a reactant is the time it takes for its concentration to fall to one-half its original value.
  - When a reaction has proceeded for one half-life, the concentration of the reactant must be  $[\text{A}]_t = 0.5[\text{A}]_0$ .
- Substituting  $[\text{A}]_t = 0.5[\text{A}]_0$  into the first-order integrated rate expression,  $t_{1/2}$  can be evaluated.

$$\ln \frac{0.5[\text{A}]_0}{[\text{A}]_0} = -kt_{1/2} = \ln \frac{1}{2} = \ln 1 - \ln 2 \quad t_{1/2} = \ln \frac{2}{k} = \frac{0.693}{k}$$

- Other half-life equations can be constructed for zero-order and second-order reactions using the same method.

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## Half-Life



- Ozone pressure as a function of time in an experiment designed to model the destruction of ozone in the stratosphere.
  - The ozone pressure falls by a factor of 0.5 every 19 hours.
  - Thus,  $t_{1/2}$  is 19 hours.

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## Example Problem 11.7

- The rate constant,  $k$ , for the thermal decomposition of ozone in the dark at 25°C is just  $3 \times 10^{-26} \text{ s}^{-1}$ . What is the half-life of ozone under these conditions?

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## Temperature and Kinetics

- There is a temperature dependence for the rate of reaction.
  - The rate of reaction decreases as the temperature of the reaction is decreased.

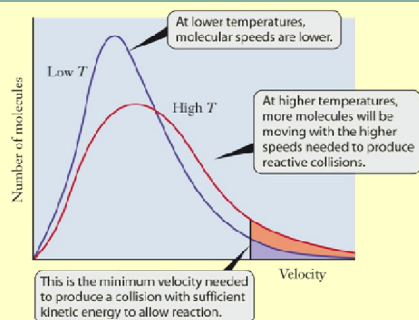
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## Temperature Effects on Molecules That React

- For two molecules to react, they must first collide.
- The collision between reactant molecules must be sufficiently energetic before reaction will occur.
- For a given minimum kinetic energy, as temperature increases, the fraction of molecules with the minimum kinetic energy increases and the rate of reaction increases.

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## Temperature Effects on Molecules That React



- The Maxwell-Boltzmann molecular speed distributions at two temperatures.

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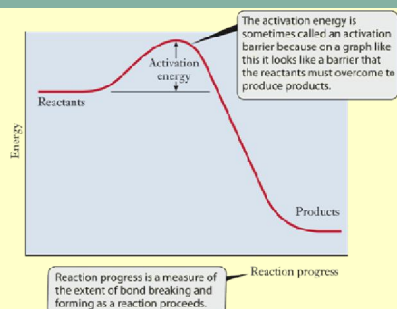
## Temperature Effects on Molecules That React

- Activation energy** or activation barrier is an energy threshold reactants must overcome to become products.
- Collisions of fast-moving particles provide sufficient kinetic energy to overcome the activation barrier.
  - The larger the activation energy, the more kinetic energy will be needed.

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### Temperature Effects on Molecules That React



- Potential energy plot for an exothermic chemical reaction. To progress from reactants to products, the molecules must collide with enough energy to pass over the activation barrier.

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### Temperature Effects on Molecules That React

- Collision geometry plays an important role in determining if collisions between fast-moving molecules are effective.
  - Collisions with improper geometry but sufficient kinetic energy are ineffective collisions.
- During an effective collision, both bond breaking and bond formation is occurring.
  - As bond rearrangement is occurring, an unstable intermediate species, called the **activated complex** and designated by  $\ddagger$ , exists in the reaction mixture.

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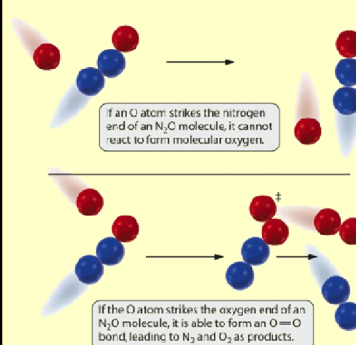
### Temperature Effects on Molecules That React

- The activated complex represents the highest energy point along the route from reactants to products.
  - The activated complex is highly unstable and has a lifetime as short as  $10^{-15}$  s.
- The activated complex decomposes into the products to complete the reaction.

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### Temperature Effects on Molecules That React

- Geometric factors can also be important in determining whether a molecular collision is reactive. For the oxygen atom to react with  $N_2O$ , it must strike the oxygen end of the molecule.



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### Arrhenius Behavior

- The **Arrhenius equation** describes the temperature dependence of the rate constant,  $k$ .

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

- $E_a$  is the activation energy,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $A$  is the proportionality constant called the **frequency factor** or **preexponential factor**.
  - $R$  is  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

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### Arrhenius Behavior

- The Arrhenius equation can be used to experimentally determine the activation energy for a reaction.
  - A plot of  $\ln k$  versus  $1/T$  for a reaction at different temperatures yields a linear plot. The slope of the line equals  $-E_a/R$ .

$$y = mx + b$$

$$\ln k = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

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### Arrhenius Behavior

- According to the Arrhenius equation, a plot of  $\ln k$  vs.  $1/T$  should give a straight line, with a slope equal to  $-E_a/R$ . Such a plot is frequently used to determine the activation energy of a reaction.

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### Example Problem 11.8

- In the troposphere, ozone can be converted to  $O_2$  by the following reaction with hydrogen oxide radicals:
 
$$HO \bullet (g) + O_3 (g) \longrightarrow HO_2 \bullet (g) + O_2 (g)$$
- The following values for the rate constant,  $k$ , for this reaction were measured in experiments at various temperatures.
  - Does this reaction display Arrhenius behavior?
  - Estimate the activation energy from these data.

$k$ (mol L <sup>-1</sup> s <sup>-1</sup> )	Temperature (K)
$1.0 \times 10^7$	220
$5.1 \times 10^7$	340
$1.1 \times 10^8$	450

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### Arrhenius Behavior

- The connection between temperature, collision energy, and reaction rate.

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### Tropospheric Ozone

- Ozone is a major lung irritant in the troposphere and a major constituent of photochemical smog.
- The kinetics of ozone production in the troposphere differs substantially from the stratosphere.

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### Tropospheric Ozone

- The formation of ozone in smog requires several steps.
  - Production of  $NO_2$  in the high temperature environment of automobile engines.
  - The  $NO_2$  absorbs sunlight and dissociates.

$$NO_2 + h\nu \longrightarrow NO + O$$

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### Tropospheric Ozone

- The atomic oxygen reacts with diatomic oxygen and species M to form ozone.
 
$$O + O_2 + M \longrightarrow O_3 + M$$
  - Species M removes excess energy from ozone as it forms, else ozone would decompose immediately.
- The ozone that forms can be quickly consumed by reaction with NO.
 
$$O_3 + NO \longrightarrow NO_2 + O_2$$
  - If NO were removed from the troposphere, ozone *could* accumulate in the troposphere.

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## Tropospheric Ozone

Table 11.2

Rate constants for some reactions in atmospheric chemistry (Data adapted from NBS technical Note 866, "Chemical Kinetic and Photochemical Data for Modeling Atmospheric Chemistry," U.S. Department of Commerce, National Bureau of Standards, 1975.)

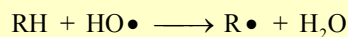
Reaction (at 300 K unless indicated)	Rate Constant
$O + O_2 + M \rightarrow O_3 + M$	$5.0 \times 10^5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
$O_3 + NO \rightarrow NO_2 + O_2$	$1.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$
$O_3 + NO_2 \rightarrow NO_3 + O_2$	$3.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
$O_3 + OH \rightarrow OOH + O_2$	$4.8 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$
$O_3 + Cl \rightarrow OCl + O_2$	$1.1 \times 10^{16} \text{ L mol}^{-1} \text{ s}^{-1}$
$O + N_2O \rightarrow N_2 + O_2$ (1200 K)	$8.1 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$
$NO + CH_3O_2 \rightarrow CH_3O + NO_2$	$3.8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$
$ClO + ClO \rightarrow Cl_2 + O_2$	$1.4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$

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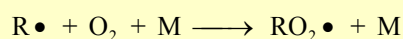
- Rate constants for some reactions in atmospheric chemistry.

## Tropospheric Ozone

- NO can be removed from the troposphere by reacting with volatile organic compounds (VOCs).
  - VOCs react with OH radicals to produce organic radicals.



- The organic radical reacts with diatomic oxygen and species M to produce **alkylperoxy radical**.



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## Tropospheric Ozone

Table 11.3

Examples of volatile organic chemicals and their sources

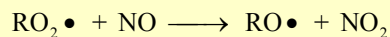
VOC	Source
Petroleum distillates (pentane, hexane, benzene)	Gasoline spills and evaporation
Terpenes	Emitted from live plants (e.g., odors of trees)
Alcohols and aldehydes	Solvents (for paint thinners, etc)
Plasticizers	Outgassing from new rugs, upholstery, electronic equipment

- Examples of volatile organic chemicals and their sources.

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## Tropospheric Ozone

- Alkylperoxy radical reacts with tropospheric NO to produce a new radical and NO<sub>2</sub>.
  - Removal of NO from the troposphere allows the ozone concentration to increase.



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