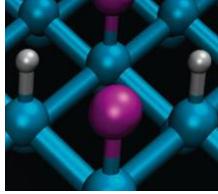


Chapter 11

Chemical Kinetics



Concept of Rate and Rates of Reaction

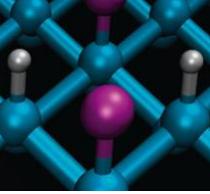


- **Reaction rate** is the ratio of the change in concentration to the elapsed time

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

- Concentration is measured in molarity, or mol L^{-1} , and designated with square brackets, []
- Time is measured in s
- The unit for rate is $\text{mol L}^{-1} \text{s}^{-1}$

Stoichiometry and Rate



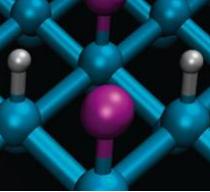
- While measuring the rate of increase in product concentration, the rate of the reaction is a positive number

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

- 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

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

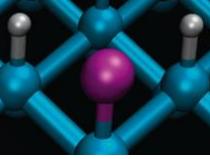
Stoichiometry and Rate



- The change in concentration of the reactant is not equal to the change in concentration of the product
 - To ensure that the same reaction rate is obtained when using either the reactants or the products, the stoichiometric coefficient, v , is included in the denominator of the rate expression

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

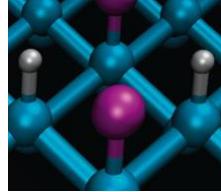
Example Problem 11.1



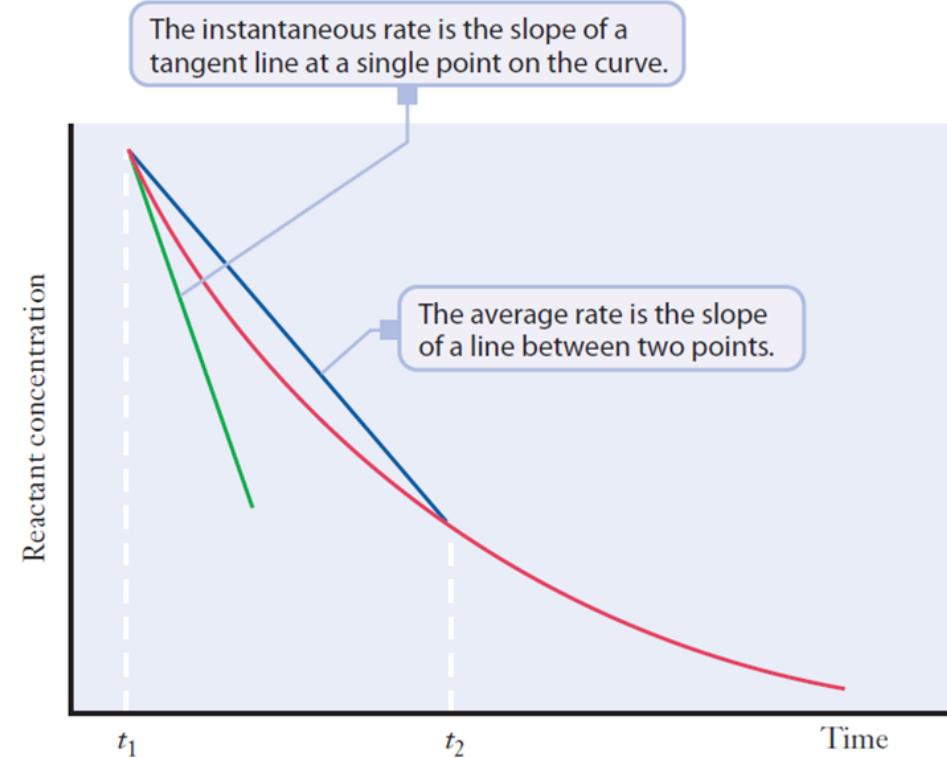
- The production of NO_2 from nitrogen and oxygen, $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$, was studied in an experiment, and the rate of nitrogen consumption was measured as $2.5 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$
 - What was the rate of NO_2 production in this experiment?

$$f 5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

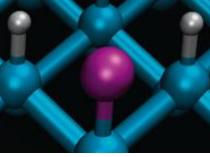
Average Rate and Instantaneous Rate



- 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



The Rate Law

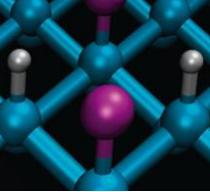


- For a reaction between substances X and Y, the rate of the reaction can be described by an equation of the form:

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

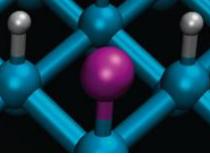
- (*k*) is the **rate constant**
- [X] and [Y] are the reactant concentrations
- m* and *n* are typically either integers or half integers and **must** be determined experimentally

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:
 - Exponent on each reactant is the order with respect to that reactant
 - Sum of the exponents is the **overall order** of the reaction

Example Problem 11.2

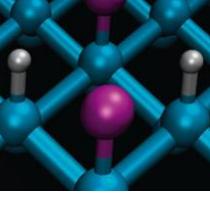


- In the following rate laws, determine the orders with respect to each substance and the overall order of the reaction

- Rate = $k[A]^2[B]$ 3

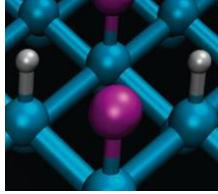
- Rate = $k[A][B]^{1/2}$ 1.5

The Rate Law



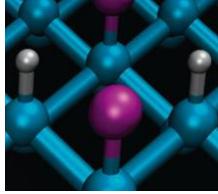
- Rate constant, k , conveys important information about the kinetics of a chemical reaction
 - If the rate constant is small, the reaction is likely to proceed slowly
 - If the rate constant is large, the reaction is likely to proceed quickly
- Value of the rate constant, k , depends on the temperature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

Determination of the Rate Law



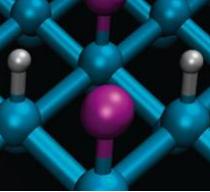
- Rate law can be determined in two ways
 - Measuring the initial rate of the reaction while adjusting the concentrations of various reactants
 - Using a series of graphs to compare data to various possible rate laws

Determination of the Rate Law



- For a reaction with only one reactant, A, the rate of the reaction equals $k[A]^n$
 - Common possible orders with respect to A are 0, 1, and 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 [A] does not change the reaction rate
 - If $n = 1$, doubling [A] doubles the reaction rate
 - If $n = 2$, doubling [A] quadruples the reaction rate

Example Problem 11.3

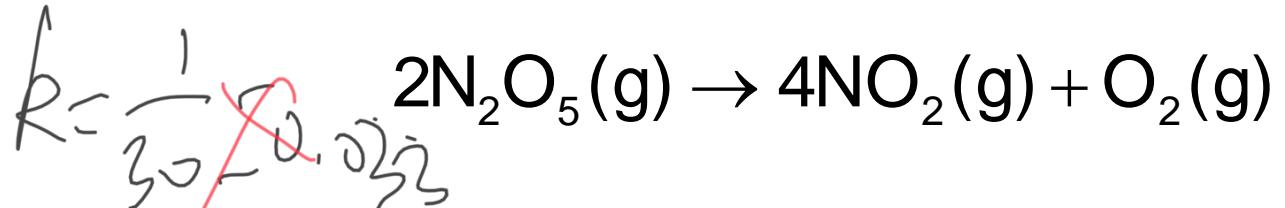


$$r = k [N_2O_5]^2$$

$$\text{Rate} = k [N_2O_5]^1$$
$$k = 0.1$$

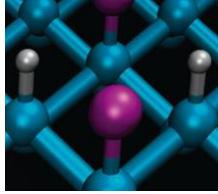
- Consider the following data for the reaction shown:

Experiment	Initial $[N_2O_5]$ (mol L ⁻¹)	Initial Rate of Reaction (mol L ⁻¹ s ⁻¹)
1	3.0×10^{-3}	9.0×10^{-7}
2	9.0×10^{-3} <i>× 3</i>	2.7×10^{-6} <i>× 3</i>



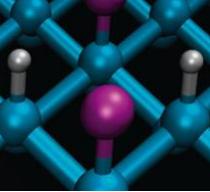
- Determine the rate law and rate constant for this reaction at the temperature of these experiments

Determination of the Rate Law



- For a reaction with two reactants, A and B, the rate of the reaction equals $k[A]^n[B]^m$
 - 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

Zero-Order Integrated Rate Law



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

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

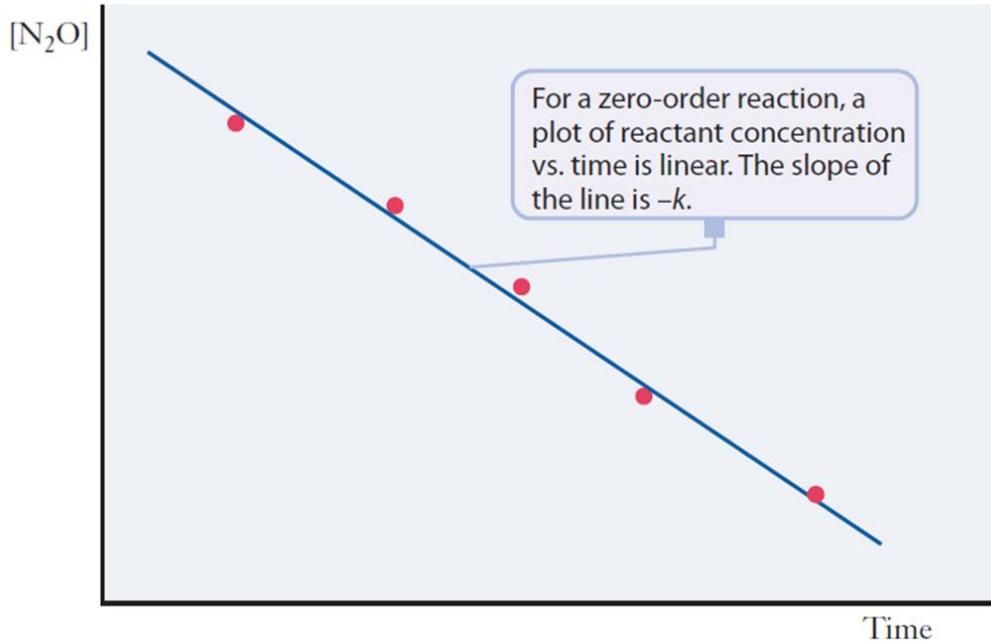
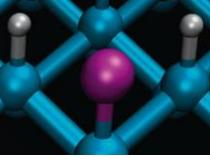
- Zero-order integrated rate law

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

∴

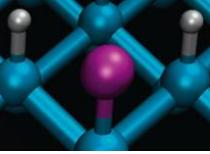
$$[A]_t = [A]_0 - kt$$

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 $-k$

Zero-Order Integrated Rate Law



- Derivation of the zero-order integrated rate law

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

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

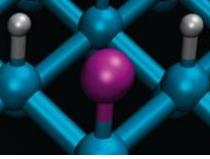
$$-\frac{d[A]}{dt} = k$$

$$d[A] = -kdt$$

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

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

First-Order Integrated Rate Law



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

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

- The first-order integrated rate law

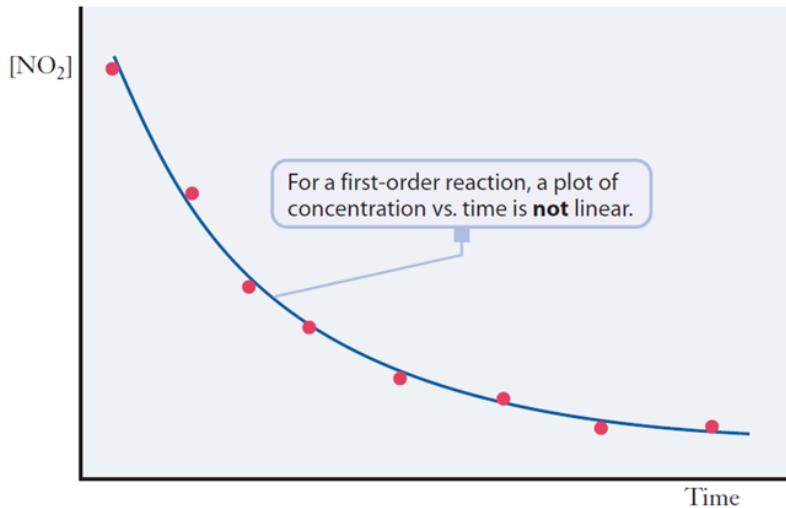
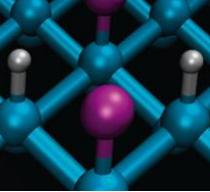
$$-\ln[A] = kt$$

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

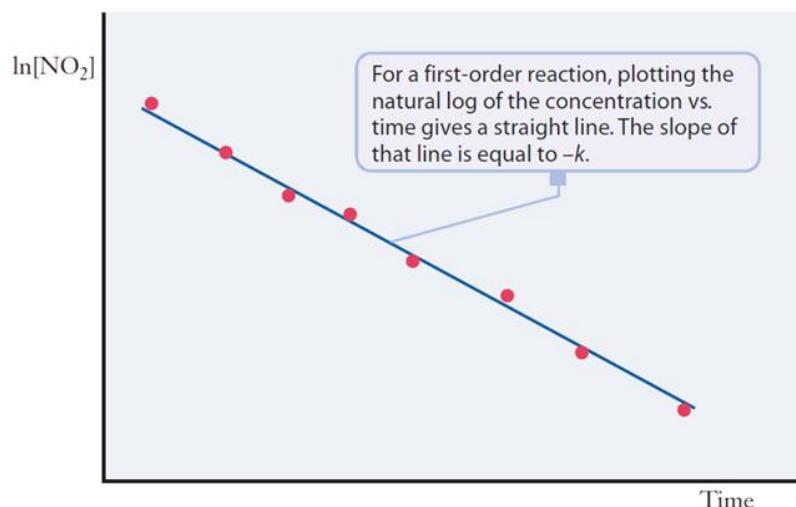
- If a plot of $\ln [A]$ versus time is linear, the overall order is first order and the slope equals $-k$

$$k = \frac{\ln[A]}{t}$$

First-Order Integrated Rate Law

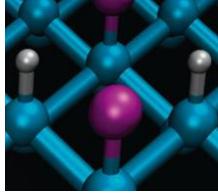


- For a reaction that is first order, a plot of the reactant concentration versus time is **not** linear

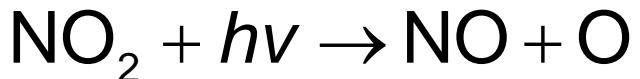


- A reaction is first order if a plot of the natural log, \ln , of the reactant concentration **versus time** is **linear**
 - The slope of the plot is $-k$

Example Problem 11.5



- The photodissociation of NO_2 by ultraviolet wavelengths of sunlight initiates the formation of photochemical smog. It is a first-order reaction with a rate constant of $2.95 \times 10^{-3} \text{ min}^{-1}$ at a given level of light exposure.



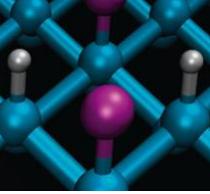
- Consider a laboratory experiment in which a sample of nitrogen dioxide is exposed to UV radiation at an intensity chosen to mimic the conditions for the formation of smog on a summer day. If the initial NO_2 concentration is 7.5 mM, what will the concentration be after 2 days?

$$r = k[A] \Rightarrow \frac{dC_{\text{NO}_2}}{dt} = -k \cdot C_{\text{NO}_2}$$
$$\frac{1}{k} \cdot \frac{1}{C} dC = -dt$$

$$\frac{1}{k} \ln C = -t$$
$$C = e^{kt}$$

$$C_t = C_0 e^{-kt}$$
$$7.5 \times 10^3 \times e^{-2 \times 2.95 \times 10^{-3}}$$
$$1.532 \times 10^{-6} \text{ mol}$$

Second-Order Integrated Rate Law



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

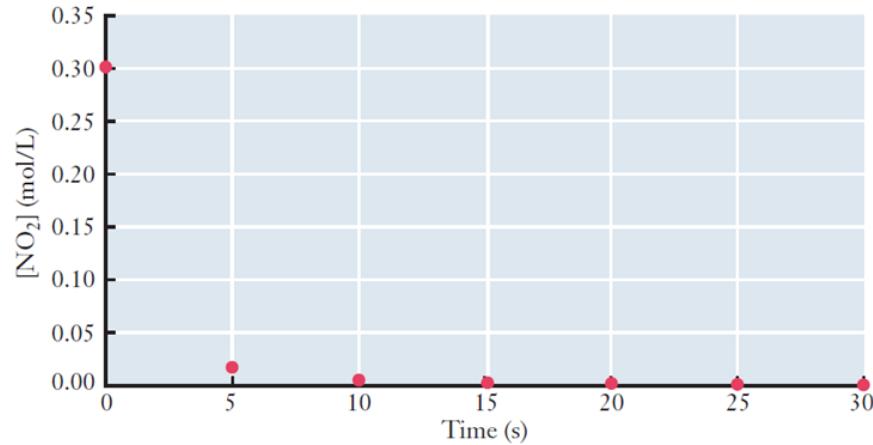
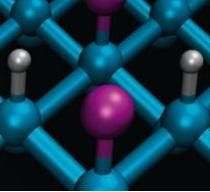
$$\text{rate} = k[A]^2 = \frac{d[A]}{dt}$$
$$kt = \left(-\frac{1}{[A]} \right) \Big|_0^t$$

- The second-order integrated rate law

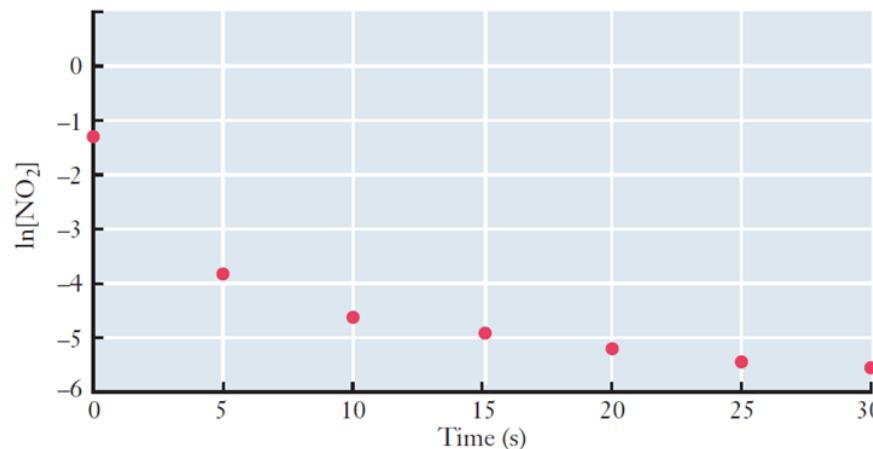
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

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

Second-Order Integrated Rate Law

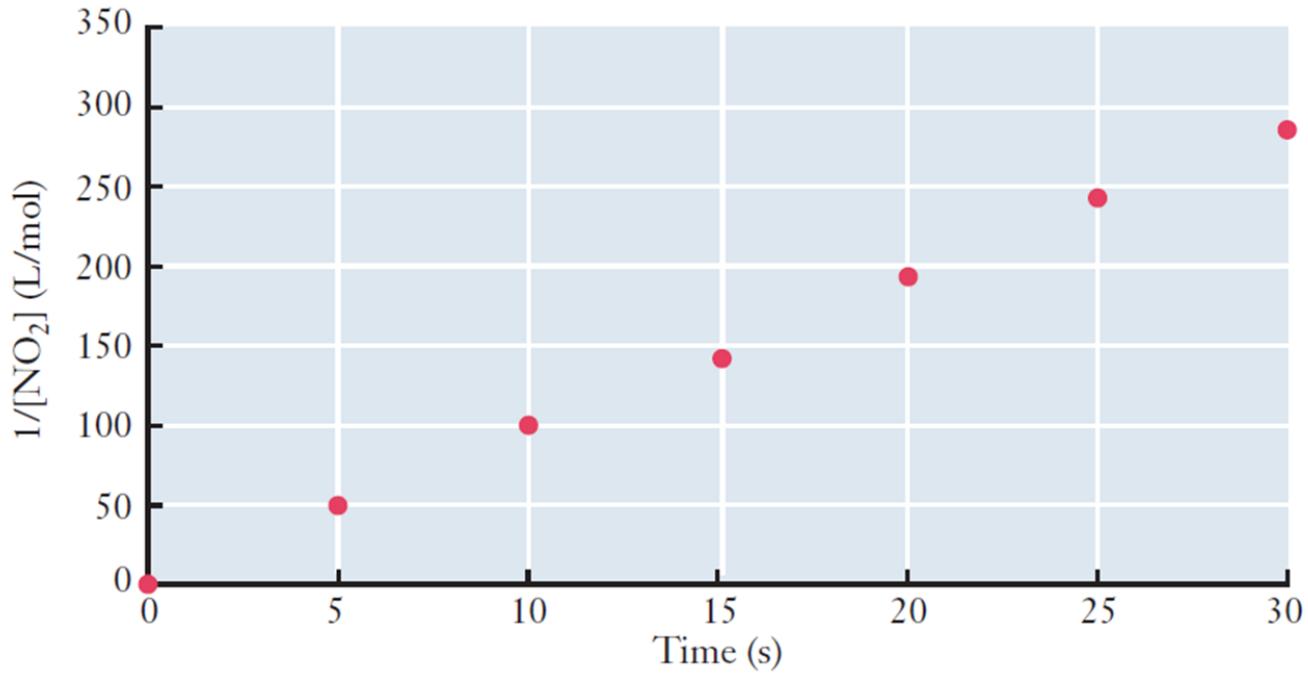
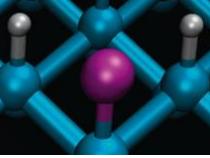


- For a reaction that is second order, a plot of the concentration versus time is not linear



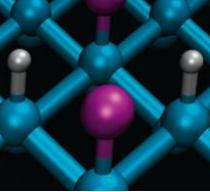
- For a reaction that is second order, a plot of the natural log of the reactant concentration versus time is not linear

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

Half-Life



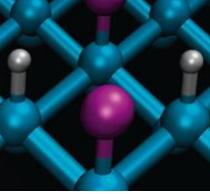
- The **half-life**, $t_{1/2}$, of a reactant is the time it takes for its concentration to fall to one-half its original value
 - When a reaction has proceeded for one half-life, the concentration of the reactant must be $[A] = 0.5[A]_0$
- Substituting $[A]_t = 0.5[A]_0$ into the first-order integrated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

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

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

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

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?

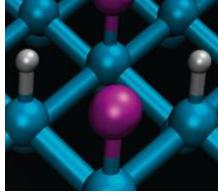


$$R = k \cdot [A]^3$$

$$\frac{1}{[A_0]} - \frac{3}{[A_t]} = kt$$

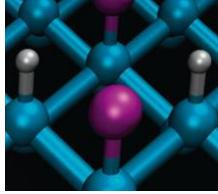
$$t_{1/2} = \frac{1}{k[A_0]}$$

Temperature Effects and Molecules That React



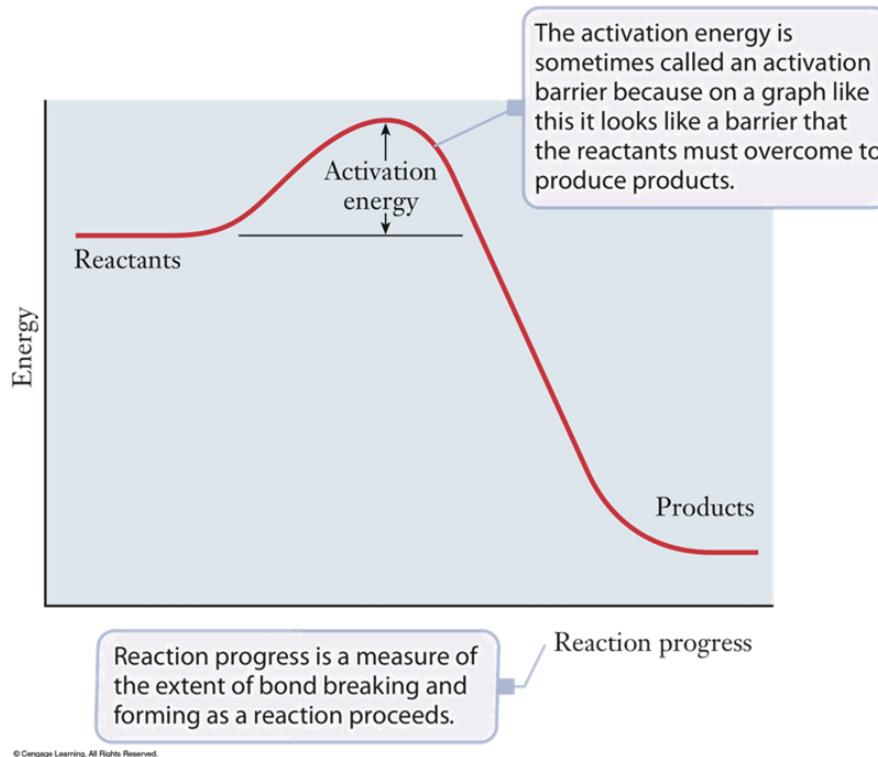
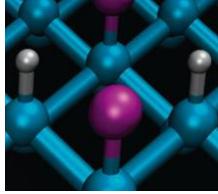
- For two molecules to react, they must first collide
- The collision between reactant molecules must be sufficiently energetic before reaction will occur
- For a given minimum kinetic energy, as temperature increases, the fraction of molecules with the minimum kinetic energy increases and the rate of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

Temperature Effects and Molecules That React



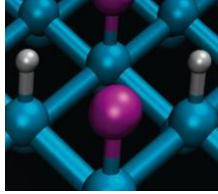
- Activation energy, or activation barrier, is an energy threshold that reactants must overcome to become products
- Collisions of fast-moving particles provide sufficient kinetic energy to overcome the activation barrier
 - The larger the activation energy, the more kinetic energy will be needed
- The activation energy dictates how energetic a collision must be to lead to reaction

Temperature Effects and Molecules That React



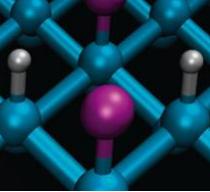
- Graph is a potential energy plot for an exothermic chemical reaction
- To progress from reactants to products, the molecules must collide with enough energy to pass over the activation barrier

Temperature Effects and Molecules That React



- During an effective collision, both bond breaking and bond formation occur
 - As bond rearrangement is occurring, an unstable intermediate species, called an **activated complex** denoted \ddagger , exists in the reaction mixture 10^{-15} s
- 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
- Formation of activated complex and its subsequent decomposition into reaction products depends on both the energy and the geometry of the collision

Arrhenius Behavior



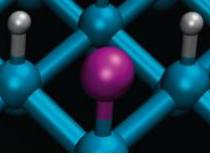
- The Arrhenius equation describes the temperature dependence of the rate constant, k

$$k = A e^{-E_a/RT}$$

$k \propto f(T, E_a)$

- E_a is the activation energy
- R is the universal gas constant
 - The value of R is $8.314 \text{ J mol}^{-1}\text{K}^{-1}$
- T is the temperature
- A is the proportionality constant called the frequency factor or preexponential factor

Arrhenius Behavior

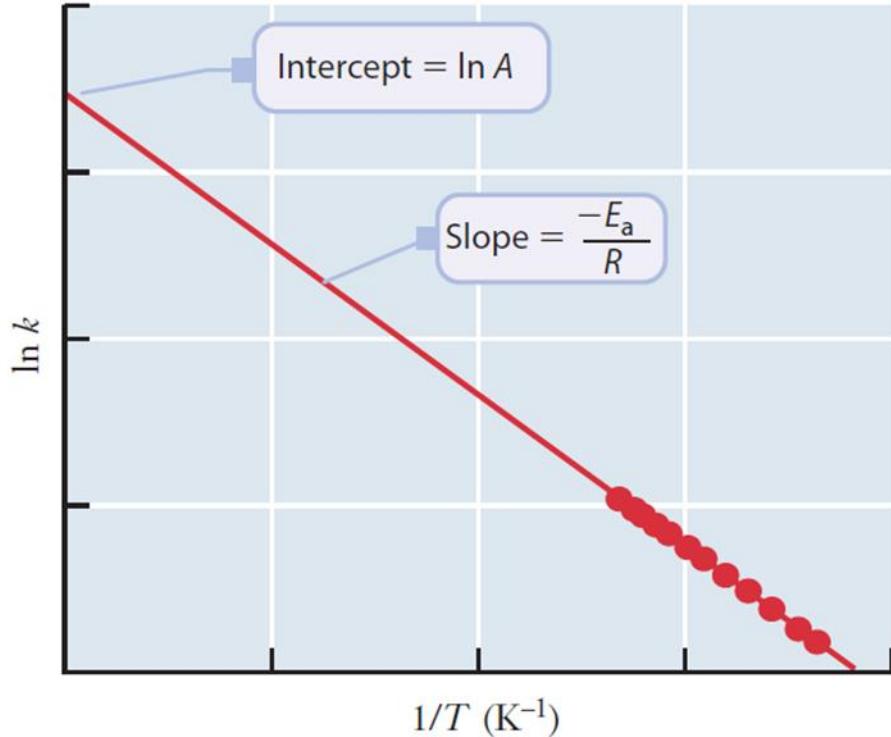
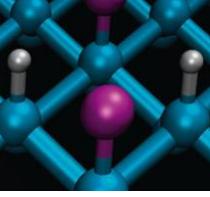


- The Arrhenius equation can be used to experimentally determine the activation energy for a reaction
 - A plot of $\ln k$ versus $1/T$ for a reaction at different temperatures yields a linear plot
 - The slope of the line is $-E_a / R$

$$y = mx + b$$

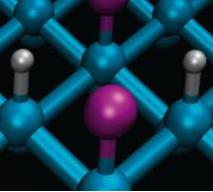
$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

Arrhenius Behavior

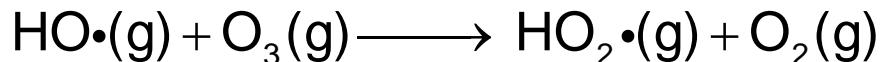


- According to the Arrhenius equation, a plot of $\ln k$ versus $1/T$ should give a straight line, with a slope equal to $-E_a / R$
- Such a plot is frequently used to determine the activation energy of a reaction

Example Problem 11.8



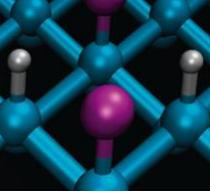
- Once ozone forms in photochemical smog, there are a number of reactions by which it is subsequently destroyed. One such reaction occurs when ozone molecules encounter hydroxyl radicals:



- 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

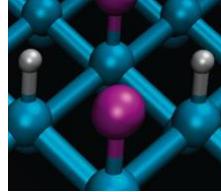
k (mol L ⁻¹ s ⁻¹)	Temperature (K)
1.0×10^7	220
5.1×10^7	340
1.1×10^8	450

Reaction Mechanisms



- A **reaction mechanism** is a collection of one or more molecular steps that account for the way reactants become products
 - A reaction mechanism is composed of a series of individual steps called **elementary steps**
 - The coefficients for reactants in an elementary step provide the exponents in the rate law for that step

Elementary Steps and Reaction Mechanisms



- Only three types of elementary steps may occur
 - **Unimolecular** steps have one reactant
 - **Bimolecular** steps have two reactants
 - **Termolecular** steps have three reactants
 - Reactions involving the collision of three reactants are uncommon

Elementary Steps and Reaction Mechanisms

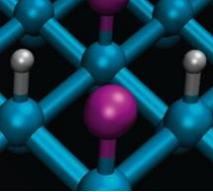
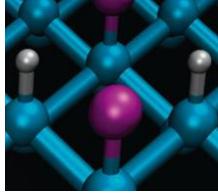


Table 11.2 Types of elementary reactions

Summary of molecularity of elementary reactions

Type of Elementary Reaction	Molecularity	Rate Law
$A \rightarrow \text{products}$	Unimolecular	$\text{Rate} = k[A]$
$A + B \rightarrow \text{products}$	Bimolecular	$\text{Rate} = k[A][B]$
$2 A \rightarrow \text{products}$		$\text{Rate} = k[A]^2$
$A + B + C \rightarrow \text{products}$	Termolecular	$\text{Rate} = k[A][B][C]$
$2 A + B \rightarrow \text{products}$		$\text{Rate} = k[A]^2[B]$
$A + B + C + D \rightarrow \text{products}$	Not observed	

Elementary Steps and Reaction Mechanisms

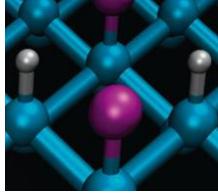


- Two important characteristics of a reaction mechanism are:
 - Chemical species generated in one step and consumed in a later step is called a **reactive intermediate**, such as the NO_3 shown below

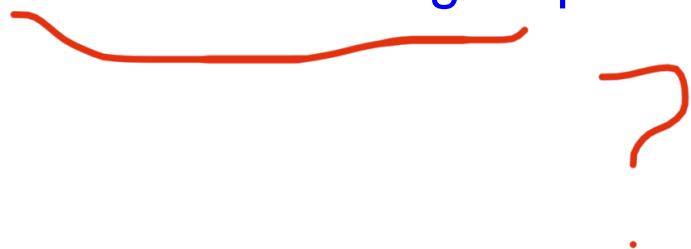


- When the steps of the mechanism are properly summed, they give the observed stoichiometry of the overall reaction

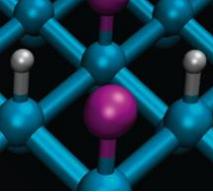
Mechanisms and Rate: The Rate-Determining Step



- For a reaction mechanism, the rate law for each fundamental step is determined using the coefficients for the reactants in the elementary steps as the orders
 - The rate law derived from the mechanism must equal the experimentally determined rate law
- The rate of one elementary step in a mechanism is slower than the others
 - This slow step is the **rate-determining step** and dictates the rate of the overall reaction

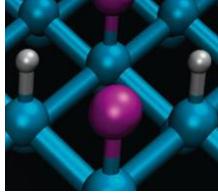


Catalysis



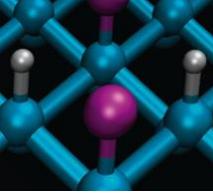
- Process in which a reaction is influenced by the presence of substances that are neither reactants nor products in the overall equation
 - **Catalyst** is a substance that increases the rate of a reaction but is neither created nor destroyed in the process
- Three properties of a catalyst are:
 - They are not part of the reaction stoichiometry
 - They are not consumed by the reaction
 - They increase the rate of the net reaction

Homogeneous Catalysts



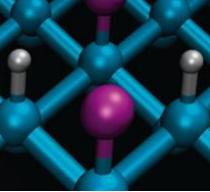
- Catalysts that are in the same phase as the reacting substances
- Example: Catalytic destruction of ozone in stratosphere involves reaction between gases there
 - Chlorine atoms serve as a catalyst for ozone depletion because they:
 - Are not part of the reaction stoichiometry
 - Are not consumed by the reaction
 - Increase the rate of the net reaction

Heterogeneous Catalysts



- Catalysts that are in a different phase from the reacting species
- Steps found in most examples of heterogeneous catalysis
 - Reactive species adsorb, or stick, onto the surface of the catalyst
 - Species migrate on the surface until they encounter each other
 - Reaction takes place on the surface
 - Products desorb from the catalyst surface

Molecular Perspective of Catalysis



- Catalysts increase the rate of reaction by providing a new reaction pathway that lowers the activation energy
 - When a catalyst is introduced, the amount of energy needed decreases, and a larger fraction of molecules have speeds that are high enough to provide the needed energy

