

# Section 12.1

## Chemical Reaction Rates



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# Learning Objectives



- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

# Rates



- A **rate** is a measure of how some property varies with time.
- Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time.
- Wage is a rate that represents the amount of money earned by a person working for a given amount of time.
- The **rate of a chemical reaction** is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

# We Can't See Molecules



- Because we can't count the reactants and products directly, we must measure another property that is related to the mass, mols or concentration of the these components.
  - The V, T, and P of gas from a gas evolution reaction.
  - The mass from a precipitation reaction.
  - The absorbance of a colored reactant or product.
  - Conductivity of a conductive reactant or product.
  - NMR, MS, GC-FID, HPLC, ICP-OES, etc.

## Average vs. Instantaneous Rate



- You drive a car to the store ten miles away. It takes you 20 minutes to arrive there.
- Your **average rate** of speed is the distance you traveled divided by the time.

$$\langle v \rangle = \frac{10 \text{ miles}}{20 \text{ minutes}} = 0.5 \frac{\text{mi}}{\text{min}} \text{ or } 30 \frac{\text{mi}}{\text{hr}}$$

- During your trip you weren't always going 30 mph. At any given time your **instantaneous rate** of speed could have been higher or lower.

# Rates of Reactions

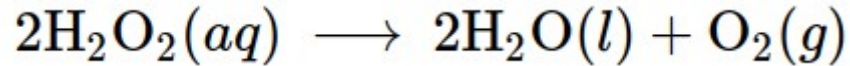


- Reaction rates work the same way.
- The **average rate** is found by dividing the change in concentration by the time this change occurred.
- The **instantaneous rate** may be different at any given moment.
- The instantaneous rate at time zero is called the **initial rate**.
- Calculating initial and instantaneous rates properly requires calculus or sophisticated numerical methods.
  - Approximations can be made using graphical methods or by using very small time intervals.

# Reaction Rate Nomenclature



- The change in species over time is the **rate expression**.



$$\begin{aligned}\text{rate of decomposition of H}_2\text{O}_2 &= - \frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= - \frac{[\text{H}_2\text{O}_2]_{t_2} - [\text{H}_2\text{O}_2]_{t_1}}{t_2 - t_1} \\ &= - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}\end{aligned}$$

# Calculating Rates Numerically



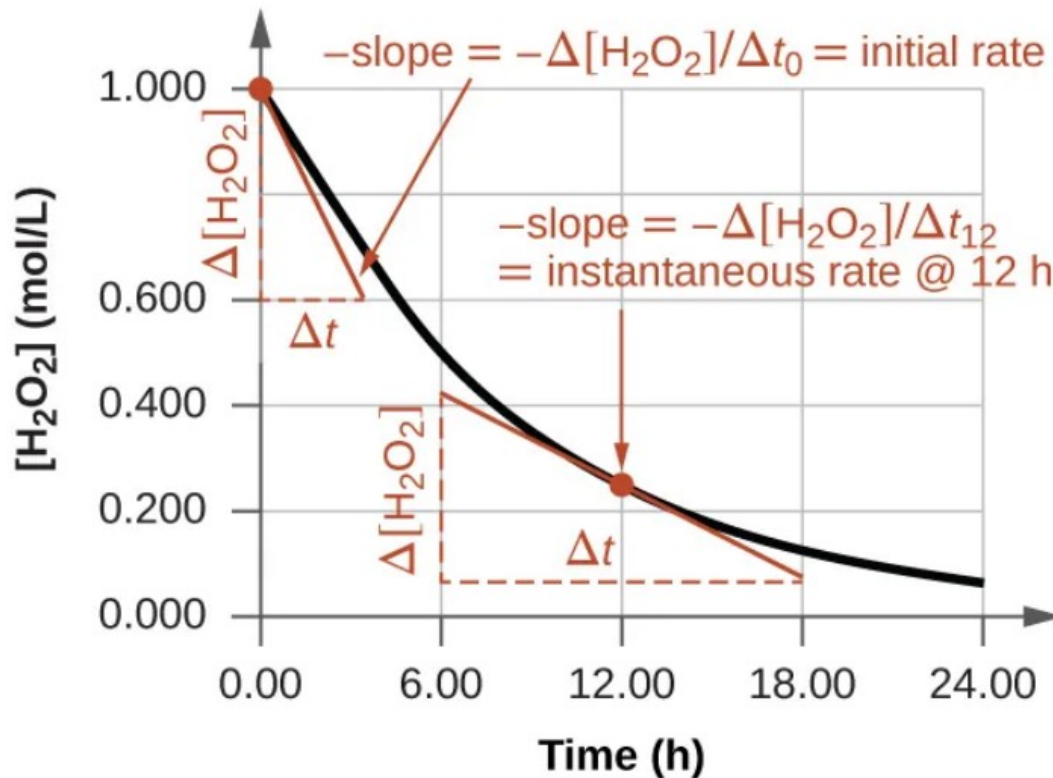
Time (h)	[H <sub>2</sub> O <sub>2</sub> ] (mol L <sup>-1</sup> )	Δ[H <sub>2</sub> O <sub>2</sub> ] (mol L <sup>-1</sup> )	Δt (h)	Rate of Decomposition, (mol L <sup>-1</sup> h <sup>-1</sup> )
0.00	1.000	-0.500	6.00	0.0833
6.00	0.500			
12.00	0.250	-0.250	6.00	0.0417
18.00	0.125			
24.00	0.0625	-0.062	6.00	0.010



# Graphs are your Friend



- The slope of a tangent line to a point on a time vs. concentration graph is the instantaneous rate.



# Relative Rates of Reactions



- The rate of a reaction may be expressed as the change in concentration of any reactant or product.
- Rate expressions are all related simply to one another according to the reaction stoichiometry.



$$\text{rate} = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

## A Practical Example



- Lets consider the example of the decomposition of ammonia.



- The average rate of the reaction can in terms of nitrogen gas

$$\frac{\Delta \text{mol N}_2}{\Delta t}$$

# Converting Reaction Rates



- Reaction Rates can be converted using Stoichiometric Ratios.

$$\frac{\Delta \text{mol N}_2}{\Delta t} \times \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = - \frac{\Delta \text{mol NH}_3}{\Delta t}$$

$$\frac{\Delta \text{mol N}_2}{\Delta t} = - \frac{1}{2} \frac{\Delta \text{mol NH}_3}{\Delta t}$$

$$\frac{\Delta \text{mol N}_2}{\Delta t} \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = \frac{\Delta \text{mol H}_2}{\Delta t}$$

$$\frac{\Delta \text{mol N}_2}{\Delta t} = \frac{1}{3} \frac{\Delta \text{mol H}_2}{\Delta t}$$

## Mols vs. Concentration



- We can now write the full rate equation for this reaction.

$$\text{rate} = -\frac{1}{2} \frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t} = \frac{1}{3} \frac{\Delta \text{mol H}_2}{\Delta t}$$

- All of these mols occupy the same volume. Therefore we can use concentration and mols interchangeably.

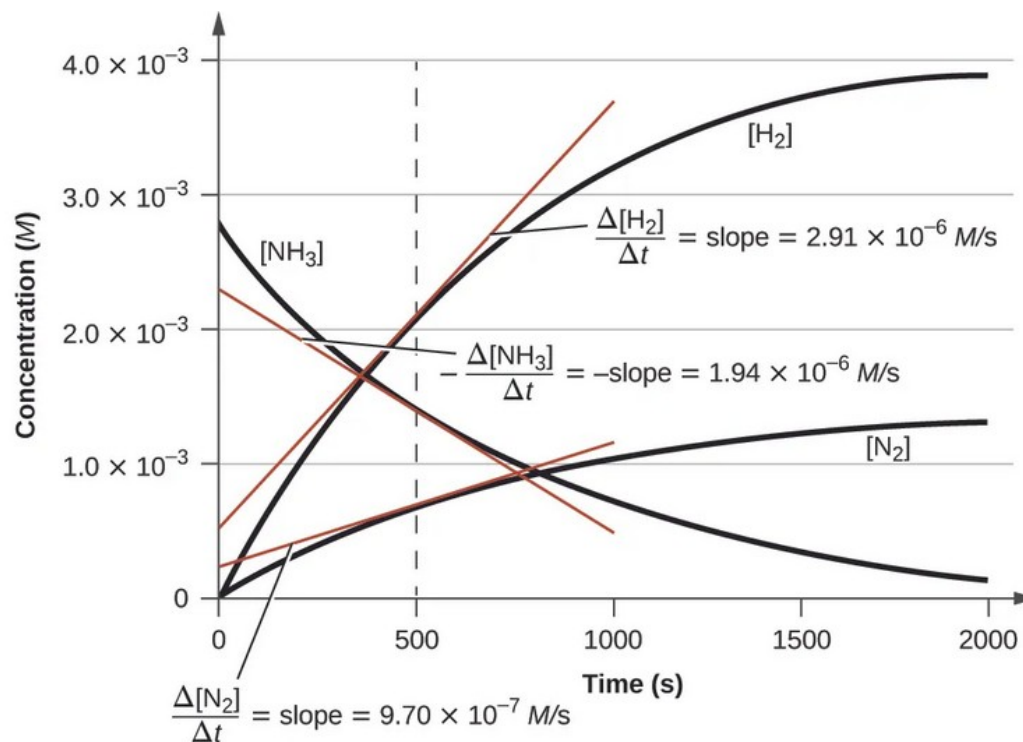
$$\text{rate} = -\frac{1}{2} \frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta [\text{H}_2]}{\Delta t}$$

# Depicting the Rates Graphically



- The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at  $t = 500$  s.

$$\frac{2.91 \times 10^{-6} \text{ M/s}}{9.70 \times 10^{-7} \text{ M/s}} \approx 3$$



# Section 12.2

## Factors Affecting Reaction Rates



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# Learning Objectives



- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates



# Factors Effecting Reaction Rates



- 1) Chemical properties of the reactants
- 2) State of subdivision, lumps vs. fine particles.
  - Available surface area for reactions to occur.
- 3) Temperature of the reactants
- 4) Concentration of the reactants
- 5) Catalytic activity

# Chemical Nature of Reactants

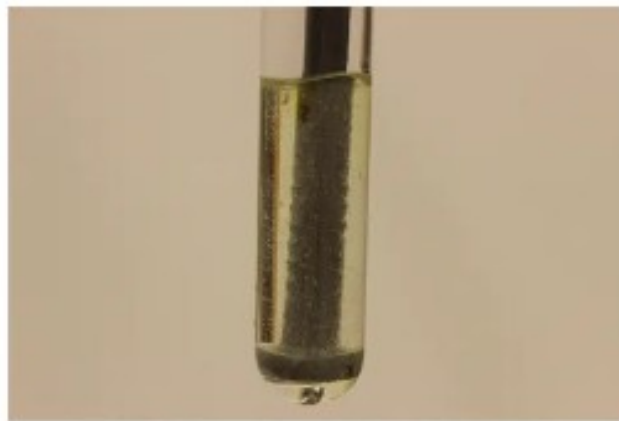
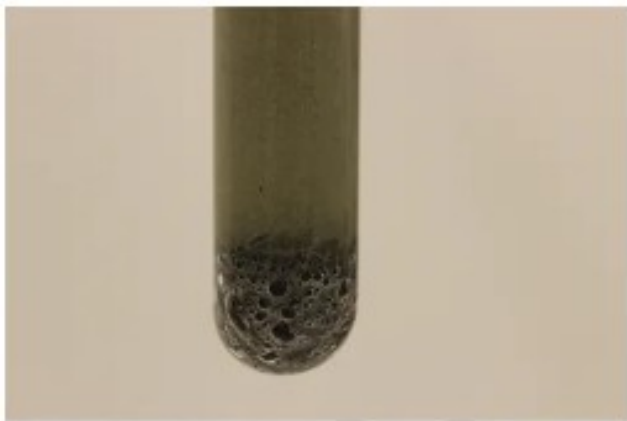


- Reactions that appear similar may have different rates under the same conditions.
- Reactivity of elements tend to be similar within the same group.
  - But rates will vary
- Few conclusions can be drawn from the chemical identity.

# Physical State of Reactants



- A chemical reaction between two or more substances requires contact between the reactants.
- When reactants are in different phases the reaction takes place only at the interface between the phases.



# Temperature of Reactants



- We will learn in a later chapter about the relationship between temperature and spontaneity.
- Most chemical reactions are faster when you increase the temperature.
- This can be justified by considering the increase in atomic collisions that are accompanied by an increase in the average kinetic energy.
- A general rule of thumb, reaction rates are approximately doubled when the temperature is raised by 10 °C.

# Concentrations of Reactants



- Rates usually increase when the concentration of one or more of the reactants increases.
- We will learn more about the dependence of reaction rate on concentration in the next sections.

# Catalysis



- Substances that function to increase the rate of a reaction are called catalysts.
- Catalysts are able to increase reaction rates by providing an alternate reaction pathway that requires less activation energy.

# Section 12.3

## Rate Laws



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# Learning Objectives



- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws



# Rate Laws



- **Rate laws** or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants.



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

- [A] and [B] represent the molar concentrations of reactants, and  $k$  is the **rate constant**, which is specific for a particular reaction at a particular temperature.

# Reaction Order



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

- The exponents  $m$  and  $n$  are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero.
- The **overall reaction order** is the sum of orders for each reactant.

# Reaction Orders Examples



$$\text{rate} = k [\text{H}_2\text{O}_2]$$

- Describes a reaction that is first order in hydrogen peroxide and first order overall.

$$\text{rate} = k [\text{C}_4\text{H}_6]^2$$

- Describes a reaction that is second order in  $\text{C}_4\text{H}_6$  and second order overall.

$$\text{rate} = k [\text{H}^+] [\text{OH}^-]$$

- Describes a reaction that is first order in  $\text{H}^+$ , first order in  $\text{OH}^-$ , and second order overall.

# Determining $k$ and Reaction Order



- The rate constant,  $k$ , and the reaction orders  $m$  and  $n$  must be determined experimentally
- Observations are made of how the rate of a reaction changes as the concentrations of the reactants are changed.
- The rate constant  $k$  is independent of the reactant concentrations, but it does vary with temperature.

# Method of Initial Rates



- The **method of initial rates** involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations.
- Comparing the measured rates for these trials permits determination of the reaction orders.
- Combining reaction orders with reaction rate data allows us to formulate a rate law.

# Rate Constant Units



- The units of the rate constant depends on the overall reaction order.
- Units can be a complicated as the reaction order can be a fraction.
- In our problems, we will assume the the rate constants have the appropriate units.

# Rate Constant Units



## Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ( $\text{L}^{x-1} \text{mol}^{1-x} \text{s}^{-1}$ )
0 (zero)	$\text{mol L}^{-1} \text{s}^{-1}$
1 (first)	$\text{s}^{-1}$
2 (second)	$\text{L mol}^{-1} \text{s}^{-1}$
3 (third)	$\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$

# Section 12.4

## Integrated Rate Laws



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# Learning Objectives



- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

# Integrated Rate Laws



- The **Integrated Rate Laws** relate the concentration of reactants and time.
- They can be used to determine the amount of reactant or product present after a period of time.
- They can also be used to estimate the time required for a reaction to proceed to a certain extent.
- They are derived using calculus, thus *integrated* ( $\int$ ).

# First-Order Reactions



$$[A]_t = [A]_0 e^{-kt}$$

- Where  $[A]_t$  is the concentration of A at any time t,  $[A]_0$  is the initial concentration of A, and  $k$  is the first-order rate constant.
- For mathematical convenience, this equation may be rearranged to other formats:

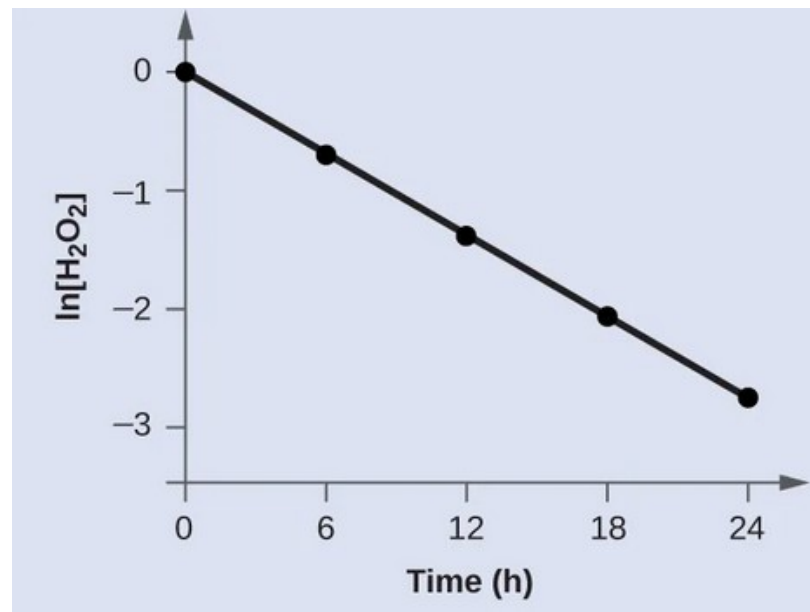
$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \quad \text{or} \quad \ln \left( \frac{[A]_0}{[A]_t} \right) = kt$$

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

# Linear First-Order Integrated Rate Law



- A plot of  $\ln[A]_t$  versus  $t$  for a first-order reaction is a straight line with a slope of  $-k$  and a y-intercept of  $\ln[A]_0$ .
- If a set of rate data are plotted in this fashion but do not result in a straight line, the reaction is not first order in A.



$$\ln[A]_t = (-k)(t) + \ln[A]_0$$

$$y = mx + b$$

## Second-Order Reactions



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

$$y = mx + b$$

- The integrated rate law for second-order reactions has the form of the equation of a straight line:
- A plot of  $1/[A]_t$  versus  $t$  for a second-order reaction is a straight line with a slope of  $k$  and a  $y$ -intercept of  $1/[A]_0$ . If the plot is not a straight line, then the reaction is not second order.

# Zero Order Reactions



- A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s).

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

$$y = mx + b$$

- A plot of  $[A]$  versus  $t$  for a zero-order reaction is a straight line with a slope of  $-k$  and a  $y$ -intercept of  $[A]_0$ .

# Half-Life of Reaction



- The **half-life of a reaction** ( $t_{1/2}$ ) is the time required for one-half of a given amount of reactant to be consumed.
- In each succeeding half-life, half of the remaining concentration of the reactant is consumed.
- The equation for calculating the half life depends on the order of the reaction.

## First-Order Half Life



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

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

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

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

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



## Second-Order Half Life



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

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

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

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

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

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

# Zero-Order Half Life



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

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

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

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

# Summary



	Zero-Order	First-Order	Second-Order
rate law	rate = $k$	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M s^{-1}$	$s^{-1}$	$M^{-1} s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. $t$	$\ln[A]$ vs. $t$	$\frac{1}{[A]}$ vs. $t$
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = \text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

# Section 12.5

## Collision Theory



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# Learning Objectives



- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

# Collision Theory

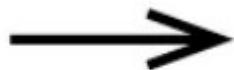


- Collision Theory is based on the following postulates:
  - 1) The rate of a reaction is proportional to the rate of reactant collisions:

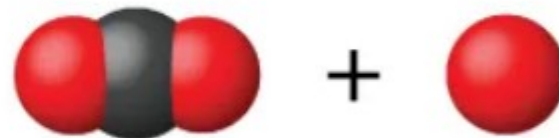
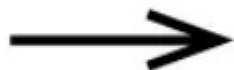
$$\text{reaction rate} \propto \frac{\# \text{ collisions}}{\text{time}}$$

- 2) The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
- 3) The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds.

# Orientation Matters



No reaction



More CO<sub>2</sub> formation

# Transition States



- In addition to a proper orientation, the collision must also occur with sufficient energy.
- When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**.
- These unstable intermediates are difficult to detect but strong evidence has been gathered to confirm their existence.



# Collisions and Concentration



- Most reaction rates increase as concentrations increase.
- Increasing the concentration increases the density of molecules.
- With more molecules packed tighter together the probability of a collision increases.
- This assumes that the molecules have adequate kinetic energy (temperature) to react.

# Activation Energy

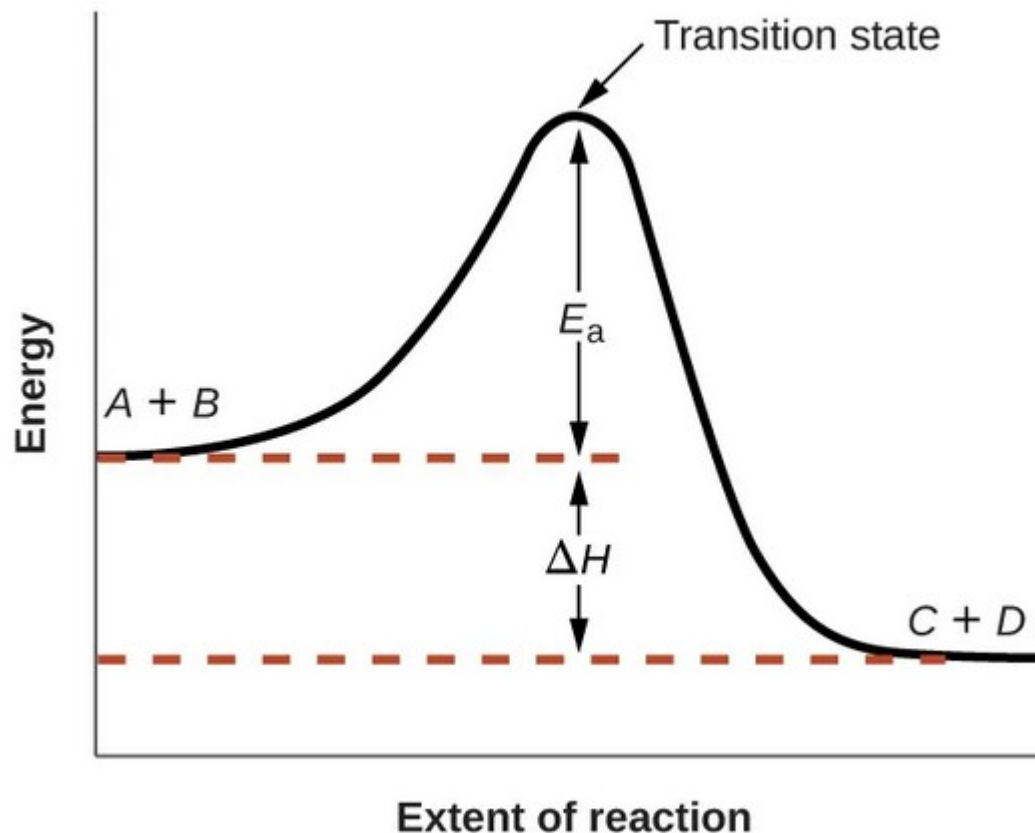


- The minimum energy necessary to form a product during a collision between reactants is called the **activation energy ( $E_a$ )**.
- If the average kinetic energy of the molecules is larger than the activation energy, the reaction will proceed quickly.
- If the average kinetic energy is lower than the activation energy, the reaction will proceed slowly.

# Reaction Diagrams



- **Reaction Diagrams** are used to visualize the energetics of a reaction.



# The Arrhenius Equation



- The **Arrhenius equation** relates the activation energy and the rate constant,  $k$ , for many chemical reactions:

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

- $R$  is the ideal gas constant,  $8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
- $T$  is temperature in Kelvin
- $E_a$  is the activation energy in joules per mole
- $e$  is the constant 2.7183
- $A$  is a constant called the **frequency factor**

# Frequency Factor

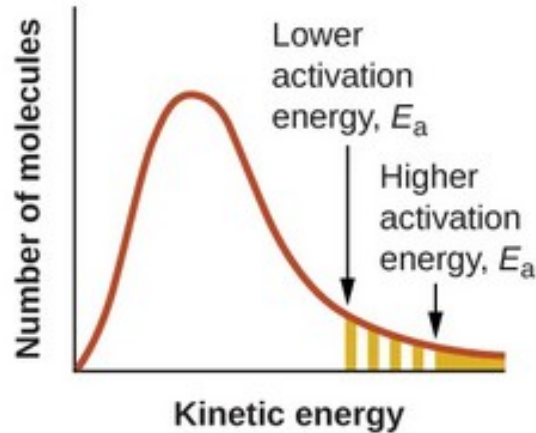


- The frequency factor is related to the frequency of collisions and the orientation of the reacting molecules.
- It reflects how well the reaction conditions favor properly oriented collisions between reactant molecules.
- An increased probability of effectively oriented collisions results in larger values for  $A$  and faster reaction rates.

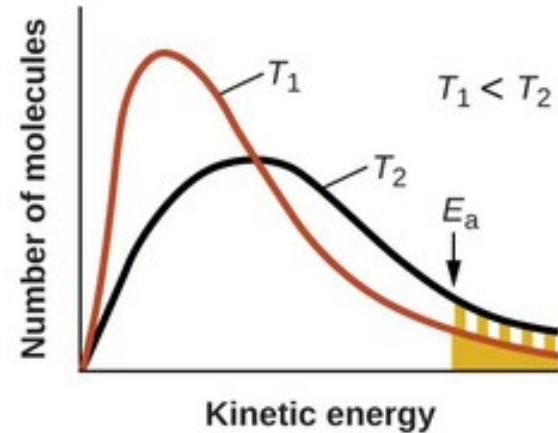
# Temperature and Activation Energy



- The exponential term of the Arrhenius Equation describes the effect of temperature on reaction rate.
- Higher temperature means a greater fraction of molecules possess sufficient energy ( $RT$ ) to overcome the activation barrier ( $E_a$ ).



(a)



(b)

# Linearizing the Arrhenius Equation

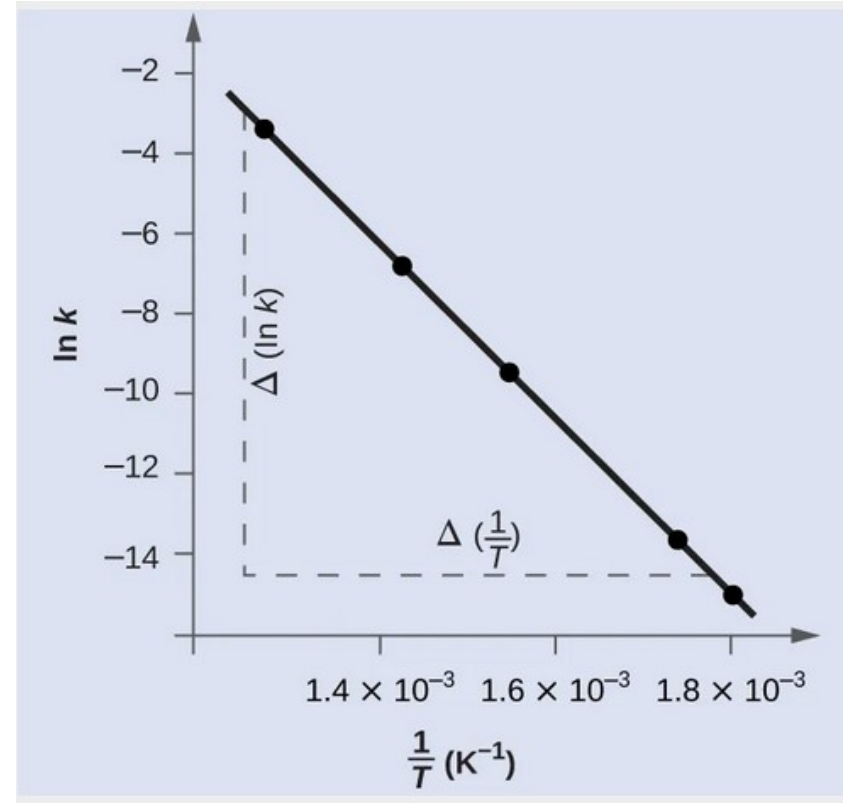


- Arrhenius equation can be rewritten to have a linear form:

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

$$y = mx + b$$

- A plot of  $\ln(k)$  versus  $1/T$  is linear with a slope equal to  $-E_a/R$  and a y-intercept equal to  $\ln(A)$ .



# Section 12.6

## Reaction Mechanism



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# Learning Objectives



- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

# Reaction Mechanisms



- Reactions often involve two or more distinct reactions taking place in sequence.
- The **reaction mechanism** (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.
- Each of the steps in a reaction mechanism is an **elementary reaction**.

# Considering Elementary Reactions

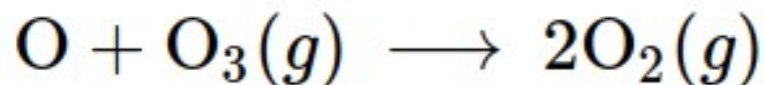
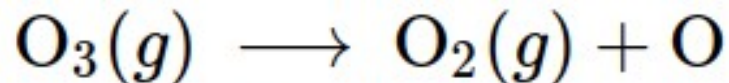


- Elementary reactions are explicit representations of the chemical change taking place.
- They depict only the bond-breaking and/or making events depicted to yield the product(s).
- The rate law for an elementary reaction may be derived directly.
- This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

# Elementary Reactions



- The decomposition of ozone has two elementary steps.



- They sum to yield the overall equation for this reaction.



- The oxygen atom produced in the first step of this mechanism is consumed in the second step. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

# Unimolecular Elementary Reactions



- The **molecularity** of an elementary reaction is the number of reactant entities (atoms, molecules, or ions).
- A **unimolecular reaction** involves the reaction of a single reactant entities to produce one or more molecules of product:



- The rate law for a unimolecular reaction is first order:

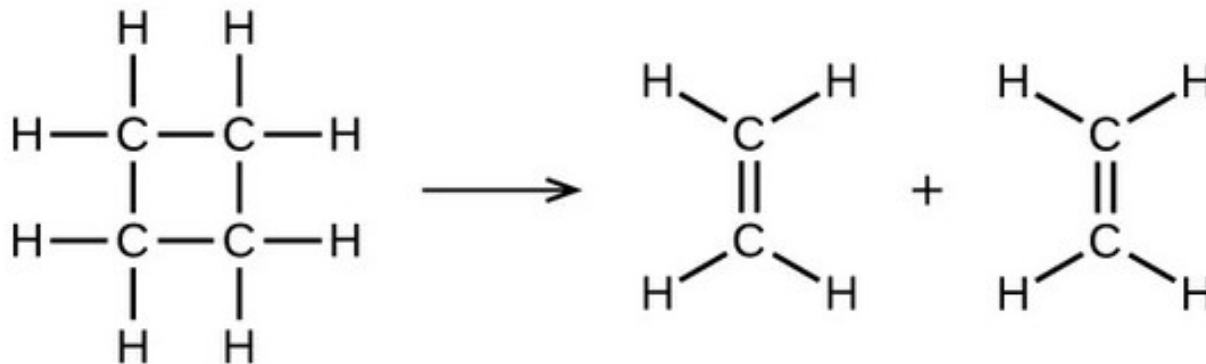
$$\text{rate} = k[A]$$

- A Unimolecular equation can be an elementary equation or an overall equation.

## Unimolecular Equation Example



- The gas-phase decomposition of cyclobutane,  $C_4H_8$ , to ethylene,  $C_2H_4$ , is an example of a unimolecular equation that is both an elementary and overall equation:

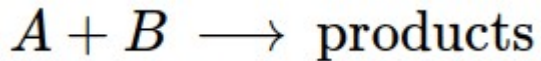


$$\text{rate} = - \frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8]$$

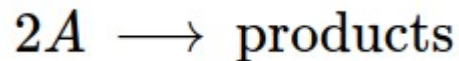
# Bimolecular Elementary Reactions



- A **bimolecular reaction** involves two reactant entities:



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



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

- Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction.

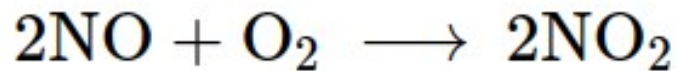


$$\text{rate} = k [\text{NO}_2][\text{CO}]$$

# Termolecular Elementary Reactions



- Although very rare there are some documented termolecular reactions involving the simultaneous collision of three molecules.



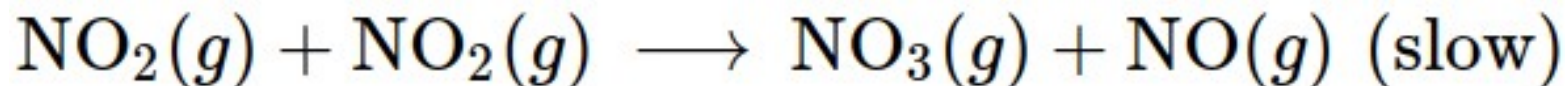
$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$



## The Slowest Step



- It's often the case that one step in a multistep reaction mechanism is significantly slower than the others.
- The slowest step is called the **rate-limiting step** (or rate-determining step) of the reaction.
- The rate of the overall reaction will be determined by the slowest step.



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

# Section 12.7

## Catalysis



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# Learning Objectives

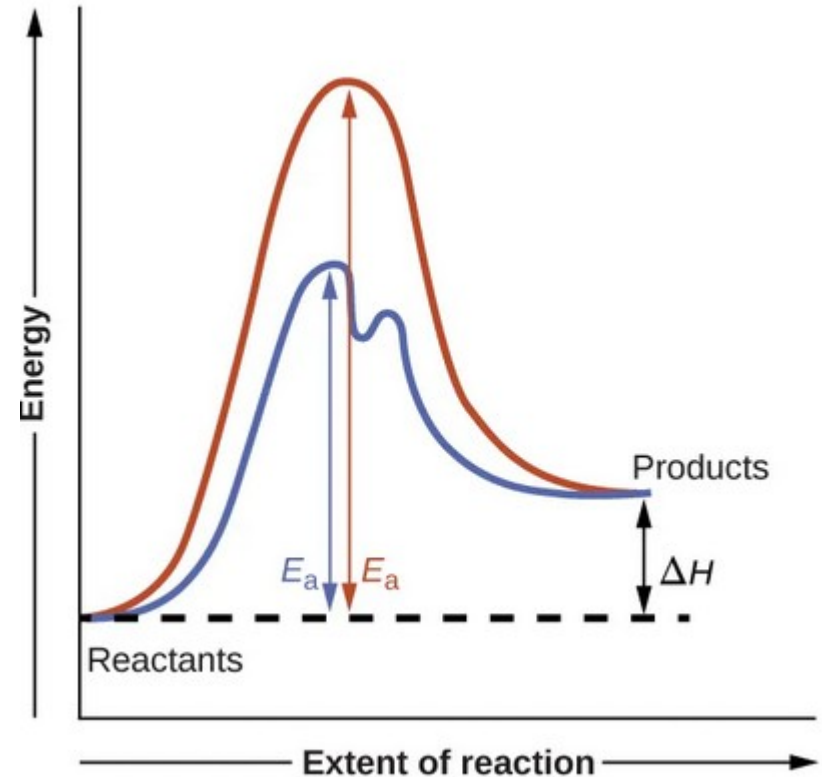


- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

# Catalysts



- A **catalyst** is a substance that can increase the reaction rate without being consumed in the reaction.
- Catalyzed reactions will have alternate reaction mechanism with a lower activation energy.



# Homogeneous Catalysts



- A **homogeneous catalyst** is present in the same phase as the reactants.
- It interacts with a reactant to form an intermediate substance
- The intermediate decomposes or reacts with another reactant to regenerate the original catalyst and form product.

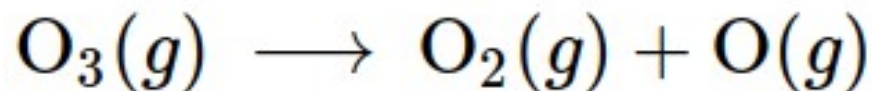
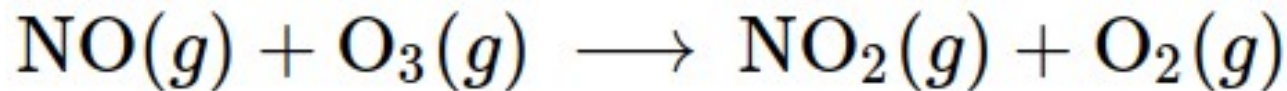
# Homogeneous Catalyst Example



- Uncatalyzed Reaction



- Catalyzed Reaction



# Heterogeneous Catalysts



- A **heterogeneous catalyst** is a catalyst that is present in a different phase (usually a solid) than the reactants.
- They typically provide a surface able to distort and align the reactants.
  - 1) Adsorption of the reactant(s) onto the surface of the catalyst
  - 2) Activation of the adsorbed reactant(s)
  - 3) Reaction of the adsorbed reactant(s)
  - 4) Desorption of product(s) from the surface of the catalyst

## Picturing the Process



- Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol.

