

Chapter 14: *Chemical Kinetics*

Dr. Carlon's Lecture Notes

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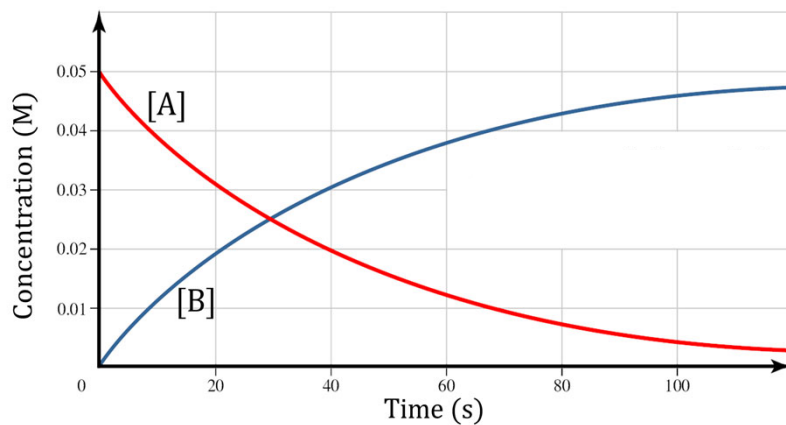
What is a rate?

- A rate refers to the change in an amount of something per a change in time:
 - Speed: miles per hour (mph)
 - Heart rate: beats per minute
- Rates can reflect an increase or decrease.
- The **reaction rate** is defined as the change in concentration of reactants or products per unit time.
 - The rate is a measure of how *fast* a reaction occurs.
 - For any given reaction, the rate will be different as the conditions change.

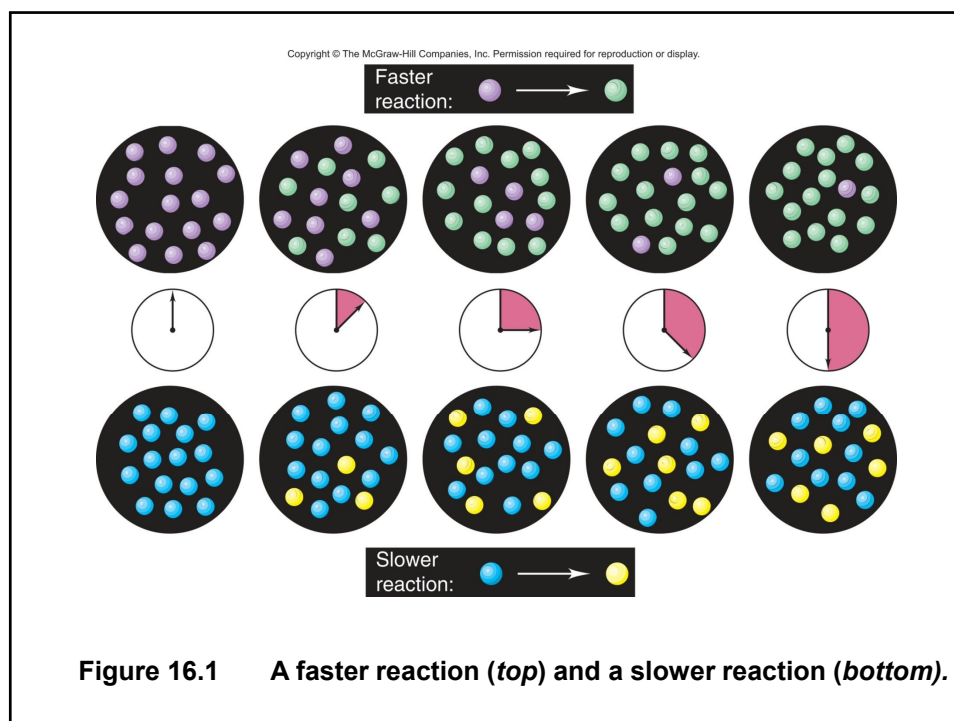
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What is a Reaction Rate?

- Consider a generic reaction:
Reactants \rightarrow Products



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Factors that affect reaction rates

- There are 4 factor which we can control that affects reaction rates:
 1. Concentration of reactants
 2. Physical states
 3. Temperature
 4. Use of a catalyst (Section 16.8)

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Factors that affect reaction rates: Concentration of Reactants

- Atoms/Molecules must collide in order for a reaction to occur (collision theory).
- The more molecules there are, the greater the frequency of collisions, and thus, the higher the reaction rate.

Rate \propto collision frequency \propto concentration

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Factors that affect reaction rates: Physical State

- The physical state determines how easily reactants mix.
 - Homogeneous reactions: all reactants are in the same phase.
 - Heterogeneous reactions: reactants are in different phases.
- Substances must mix in order for the particles to collide.
- The greater the contact surface area, the faster the reaction occurs.

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Factors that affect reaction rates: Temperature

- Temperature affects reaction rate by increasing the frequency and energy of collisions.
 - Frequency:
 - Think back to the Kinetic Molecular Theory of Gases:
 - As T increases, there is a greater distribution of speeds.
 - The most probable speed is directly proportional to T.

Rate \propto collision frequency \propto temperature

- Energy of collisions:
 - Temperature affects the kinetic energy of the molecules.
 - A reaction can only occur if the collision energy is high enough.
 - As T increases, more energetic collisions can occur, thus allowing more molecules to react.

Rate \propto collision energy \propto temperature

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Concept Test

Which of the following statements regarding reaction rates is **incorrect**?

- A. The units can be M/s.
- B. For a given reaction, the rate will always be constant.
- C. It may show an increase or a decrease.
- D. It varies as a function of temperature.

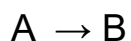
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Expressing the Reaction Rate

- For chemical reactions,

$$\text{Rate} = \frac{\Delta \text{Concentration}}{\Delta \text{time}}$$

- Consider the following chemical reaction:



For A:

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

*Rate of Disappearance
of A*

For B:

$$\text{Rate} = \frac{\Delta [B]}{\Delta \text{time}}$$

*Rate of Appearance
of B*

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Rates of Chemical Reactions

General reaction: $w A + x B \rightarrow y C + z D$

Rate of reaction = Rate of disappearance of reactant

OR

Rate of reaction = Rate of formation of product

$$\begin{aligned}\text{Rate of reaction} &= -1/w \text{ (Rate of disappearance of A)} \\ &= -1/x \text{ (Rate of disappearance of B)} \\ &= 1/y \text{ (Rate of appearance of C)} \\ &= 1/z \text{ (Rate of appearance of D)}\end{aligned}$$

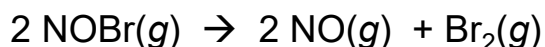
$$\text{Rate} = -\frac{1}{w} \frac{\Delta[A]}{\Delta t} = -\frac{1}{x} \frac{\Delta[B]}{\Delta t} = +\frac{1}{y} \frac{\Delta[C]}{\Delta t} = +\frac{1}{z} \frac{\Delta[D]}{\Delta t}$$

By convention, the reaction rate is always a **positive** number.

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Rates of Chemical Reactions

Consider the following reaction:



We can express the rate as:

$$\text{Rate} = -\frac{1}{2} \left(\frac{\Delta [\text{NOBr}]}{\Delta t} \right)$$

$$\text{Rate} = \frac{1}{2} \left(\frac{\Delta [\text{NO}]}{\Delta t} \right)$$

$$\text{Rate} = \frac{1}{1} \left(\frac{\Delta [\text{Br}_2]}{\Delta t} \right)$$

$$\text{Rate} = -\frac{1}{2} (\Delta[\text{NOBr}]/\Delta t) = +\frac{1}{2} (\Delta[\text{NO}]/\Delta t) = +1/1 (\Delta[\text{Br}_2]/\Delta t)$$

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Concept Test

What is the balanced equation that corresponds to the following rate expression?

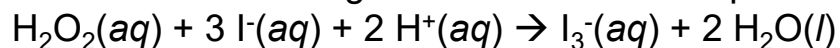
$$\text{Rate} = -\frac{1}{2} (\Delta[\text{J}]/\Delta t) = +\frac{1}{2} (\Delta[\text{N}]/\Delta t) = - (\Delta[\text{K}]/\Delta t)$$

- A. $2\text{J} + \text{K} \rightarrow 2\text{N}$
- B. $2\text{N} \rightarrow 2\text{J} + \text{K}$
- C. $\text{N} \rightarrow \text{J} + 2\text{K}$
- D. $2\text{J} \rightarrow \text{K} + 2\text{N}$

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Example: Rates of Chemical Reactions

Consider the following balanced chemical equation:



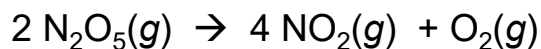
In the first 10 seconds of the reaction, the concentration of I^- dropped from 1 M to 0.868 M.

- A. Calculate the average rate of this reaction in this time interval.
- B. Predict the rate of change in the concentration of H^+ during this time interval.

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Concept Test

Consider the following reaction:



If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of NO_2 ?

- A. $1.7 \times 10^{-6} \text{ M/s}$
- B. $8.4 \times 10^{-7} \text{ M/s}$
- C. $2.1 \times 10^{-7} \text{ M/s}$
- D. $1.1 \times 10^{-7} \text{ M/s}$

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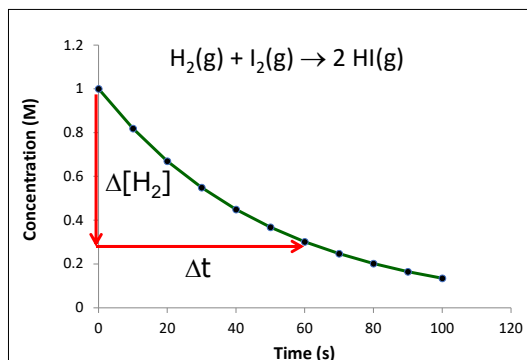
Comments on Reaction Rates

1. Each reaction has a characteristic reaction rate at a specified temperature.
2. Units are molarity/time: M/t , $\text{mol/L} \cdot \text{t}$, etc.
3. The numerical value of the reaction rate is written as a positive value.
 - The rate of change may be negative (eg: rate of disappearance of a reactant).

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Types of Rates

- Reaction rates typically **change** during the course of the reaction (Faster at the beginning and then slow as equilibrium is approached).



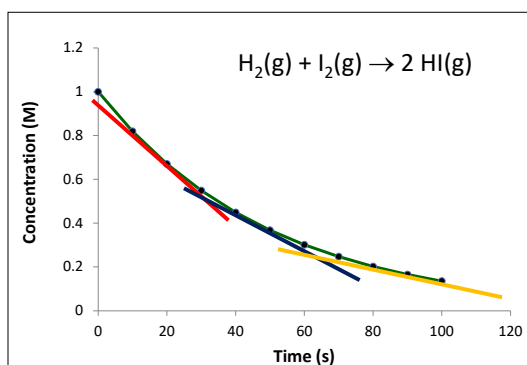
- The **average rate** of the reaction is the change in concentration/change in time:

$$\text{Average reaction rate} = -\Delta[\text{H}_2]/\Delta t$$

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Average vs. Instantaneous Rates

- The **instantaneous rate** of the reaction is the **slope** of the **tangent** line drawn at the time of interest.



- The slope and rate decrease over time as equilibrium is approached.
 - This rate is the important rate of reaction.
- In general, the term reaction rate means instantaneous reaction rate.

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Initial Rates

- The initial rate is the instantaneous rate at the moment the reactants are mixed.
- Found from the slope of the line tangent to the curve at $t = 0$ sec.
- Typically used to find other kinetic parameters.

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Effect of Concentration on Reaction Rate

- The rate of a reaction often depends on the concentration of one or more of the reactants.
 - The **rate law** shows the relationship between the rate of the reaction as a function of concentrations and temperature:

$$wA + xB \rightarrow \text{products}$$

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

$k \equiv$ rate constant (specific for a given reaction at a given T)
 m & $n \equiv$ reaction order
 - The values of m and n are usually integers and determine how the rate depends on the concentrations of the reactants.
- 2 key points to keep in mind:
 - The coefficients in the balanced reactions are not necessarily related in any way to the reaction orders m and n .
 - The component of the rate law must be determined experimentally.

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Reaction Orders

$A \rightarrow \text{products}$

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

$k \equiv \text{rate constant}$

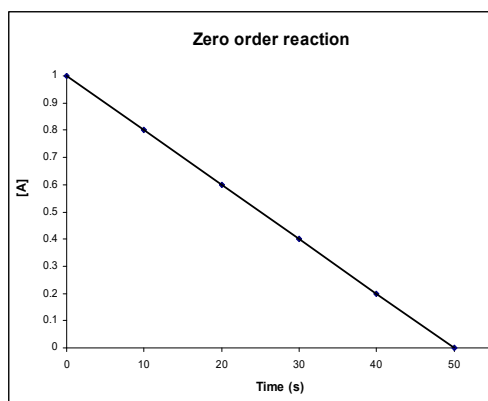
$n \equiv \text{reaction order}$

- $n = 0$ zero order rate is independent of $[A]$
- $n = 1$ first order rate is a to $[A]$
- $n = 2$ second order rate is a $[A]^2$

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Zero Order Reactions

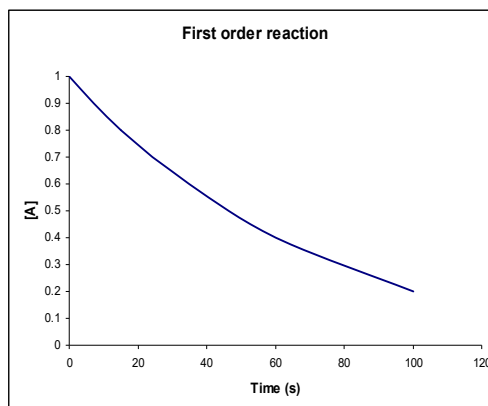
- Zero order reactions:
 - $[A]$ decreases linearly with time.
 - $\text{Rate} = k[A]^0 = k$.
 - Rate is independent of $[A]$.
- Slope is constant.
 - Rate is constant.
- k has units of $M s^{-1}$.
- Zero order reactions occur under conditions where the amount of reactant actually available for a reaction is unaffected by changes in the overall quantity of reactant.
 - Example: Sublimation!



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First Order Reactions

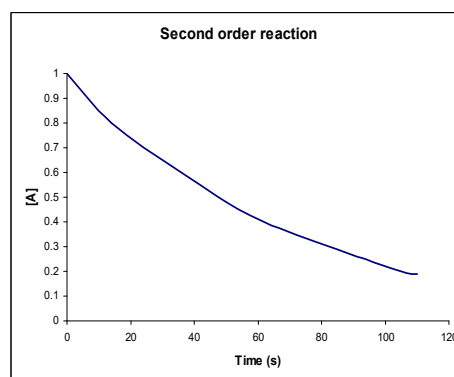
- First order reactions:
 - Rate = $k[A]^1$.
 - Rate is directly proportional to $[A]$.
 - Rate slows down as the reaction proceeds.
- k has units of s^{-1} .



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Second Order Reactions

- Second order reactions:
 - Rate = $k[A]^2$.
 - Rate is proportional to $[A]^2$.
 - Rate is more sensitive to $[A]$.
- k has units of $M^{-1}s^{-1}$



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Concentration, Rate, and Time

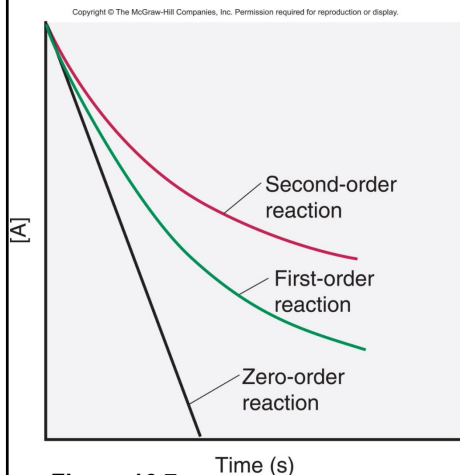


Figure 16.7
Plots of reactant concentration, [A], vs. time for first-, second-, and zero-order reactions.

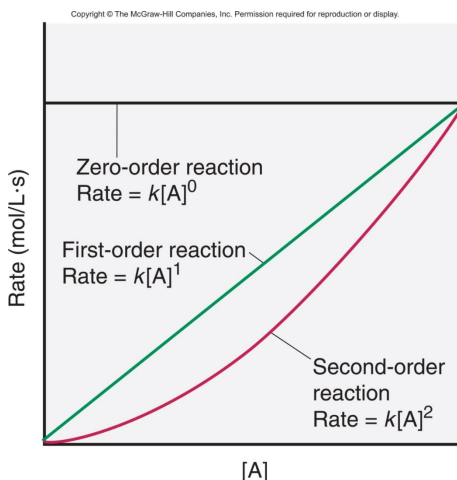
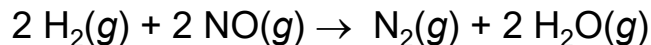


Figure 16.8
Plots of rate vs. reactant concentration, [A], for first-, second-, and zero-order reactions.

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Reaction Order for Multiple Reactants

- When reactions contain 2 or more reactants, the order is specified with respect to each reactant and the overall order.



- Rate laws for any reactions can only be determined from experiments!

$$\text{Rate} = k[\text{H}_2]^1[\text{NO}]^2$$

The reaction is 1st order in H₂ and 2nd order in NO.

The overall reaction is 3rd order.

- If $\text{Rate} = k[\text{A}]^a[\text{B}]^b$ then the overall order is **a+b**.

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Rate Law

- Determined experimentally.
 - Knowing balanced chemical equation isn't enough!
- Establishes a relationship between reactant concentration and rate of the reaction.
 - Overall order of a reaction is the sum of the orders of each reactant.
 - Ex: $\text{Rate} = k[\text{A}]^1[\text{B}]^2 \rightarrow 3^{\text{rd}}$ order reaction.
 - The rate constant is denoted by k .
 - Units change per reaction order.
 - Zero order: M/s
 - First order: $1/\text{s}$
 - Second order: $1/\text{M}\cdot\text{s}$
 - Can determine since the units of rate will always be M/s .

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Concept Test

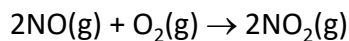
The rate law for $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ is
 $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$.

What are the units of the rate constant?

- A. $1/\text{s}$
- B. $1/\text{M}\cdot\text{s}$
- C. M/s
- D. $1/\text{M}^2\cdot\text{s}$

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Determining the Order of a Reaction



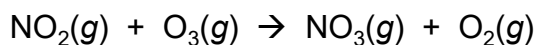
Experiment	[NO]	[O ₂]	Initial Rate (M s ⁻¹)
1	1x10 ⁴	1x10 ⁴	2.8 x 10 ⁻⁶
2	1x10 ⁴	3x10 ⁴	8.4 x 10 ⁻⁶
3	2x10 ⁴	3x10 ⁴	3.5 x 10 ⁻⁵

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[\text{x}]_2}{[\text{x}]_1} \right)^n \quad n = \text{order}$$

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Determining the Order of a Reaction

Using the data provided below, determine the rate law and the rate constant for the following reaction:



<u>Initial [NO₂], M</u>	<u>Initial [O₃], M</u>	<u>Initial rate of formation of O₂(g), M s⁻¹</u>
5.0 x 10 ⁻⁵	1.0 x 10 ⁻⁵	0.022
5.0 x 10 ⁻⁵	2.0 x 10 ⁻⁵	0.044
2.5 x 10 ⁻⁵	2.0 x 10 ⁻⁵	0.022

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Concept Test

Given the data below, what is the correct rate law for the reaction of $2A + 2B \rightarrow C$?

Experiment	[A]	[B]	Initial Rate (M/s)
1	5	3	0.04
2	5	6	0.04
3	10	3	0.08

- A. Rate = $k[A]$
- B. Rate = $k[B]$
- C. Rate = $k[A][B]$
- D. Rate = $k[A]^2[B]$

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Concept Test

A reaction in which A, B, and C react to form products is first order in A, second order in B, and zero order in C. By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

- A. 2
- B. 4
- C. 6
- D. 8

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Integrated Rate Laws

- Integrated rate laws establish a relationship between the concentrations of the reactants and time
 - Depends on the order of the reaction
- Let's consider a zero-order reaction first
 - Recall, the rate is independent of the concentration of the reactant
 - Ex: $\text{NH}_3(g) \rightarrow \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g)$

$$\text{Rate} = k[\text{NH}_3]^0$$

- Using the definition of rates:

$$\text{Rate} = \frac{-d[\text{NH}_3]}{dt}$$

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Integrated Rate Law: Zeroth Order

Set these equal to each other:

$$k = -d[\text{NH}_3]/dt$$

$$\text{Rearrange: } -d[\text{NH}_3] = k dt$$

$$\text{Integrate from 0 to t: } \int_{[\text{NH}_3]_0}^{[\text{NH}_3]_t} -d[\text{NH}_3] = k \int_0^t dt$$

$$- ([\text{NH}_3]_t - [\text{NH}_3]_0) = k(t - 0)$$

$$0 \text{ order integrated rate equation: } [\text{NH}_3]_0 - [\text{NH}_3]_t = kt$$

$$\text{Rearrange: } [\text{NH}_3]_t = -kt + [\text{NH}_3]_0$$

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Zeroth Order Plots

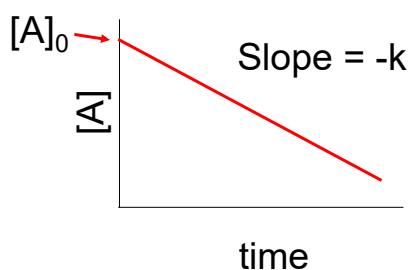
$$[A]_t = -kt + [A]_0$$

$$y = mx + b$$

Plot $[A]$ on the y-axis and time on the x-axis.

Slope = $-k$ and intercept = $[A]_0$

$[A]$ vs. time is linear for 0th Order



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Integrated Rate Law: First Order



This reaction was found to be first order and its rate law is:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

The rate is also equal to the rate of consumption of N_2O_5 :

$$\text{Rate} = \frac{-d[\text{N}_2\text{O}_5]}{dt}$$

Set these equal to each other:

$$k[\text{N}_2\text{O}_5] = -d[\text{N}_2\text{O}_5]/dt$$

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Integrated Rate Law: First Order

$$k[\text{N}_2\text{O}_5] = \frac{-d[\text{N}_2\text{O}_5]}{dt}$$

$$\text{Rearrange: } -d[\text{N}_2\text{O}_5]/[\text{N}_2\text{O}_5] = kdt$$

$$\text{Integrate from 0 to t: } \int_{[\text{N}_2\text{O}_5]_0}^{[\text{N}_2\text{O}_5]_t} \frac{-d[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]} = k \int_0^t dt$$

$$-(\ln[\text{N}_2\text{O}_5]_t - \ln[\text{N}_2\text{O}_5]_0) = k(t - 0)$$

$$1^{\text{st}} \text{ order integrated rate equation: } \ln[\text{N}_2\text{O}_5]_0 - \ln[\text{N}_2\text{O}_5]_t = kt$$

$$\text{Rearrange: } \ln[\text{N}_2\text{O}_5]_t = -kt + \ln[\text{N}_2\text{O}_5]_0$$

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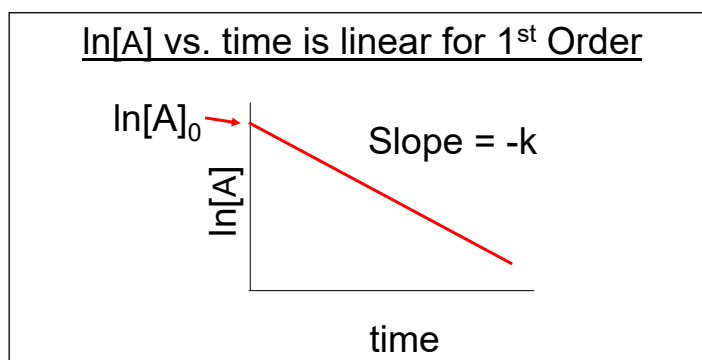
First Order Plots

$$1^{\text{st}} \text{ Order: } \ln[A]_t = -kt + \ln[A]_0$$

$$y = mx + b$$

Plot $\ln[A]$ on the y-axis and time on the x-axis.

Slope = $-k$ and intercept = $\ln[A]_0$



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Half-Life

- First order reactions are very important in nuclear chemistry
- **Half-life ($t_{1/2}$)**: the time required for the reactant concentration to reach half of its initial value
 - The half-life is characteristic of a reaction at a given temperature

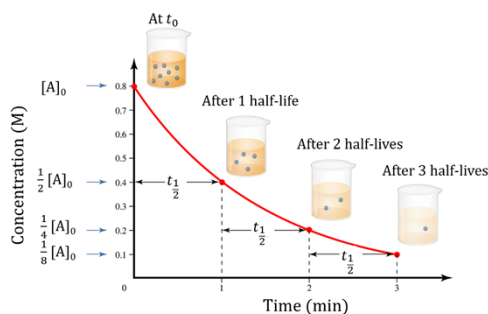


Figure 14.11 Half-Life for a First-Order Reaction

- A first order reaction has a **constant** half life.
- A first order reaction has a half life that is **independent** of the initial concentration.

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Half-Life

$$\text{1st Order: } \ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$\text{Let } t = t_{1/2} \text{ and } [A]_t = \frac{1}{2}[A]_0$$

$$\ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) = kt_{1/2}$$

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

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Concept Test

Radioactive gold-198 has a half-life of 2.7 days. If you begin with a 5.6 mg sample, how much of the sample remains after 1.0 day?

- A. 0.257 mg
- B. 4.33 mg
- C. 0.231 mg
- D. 7.24 mg

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Integrated Rate Law: Second Order

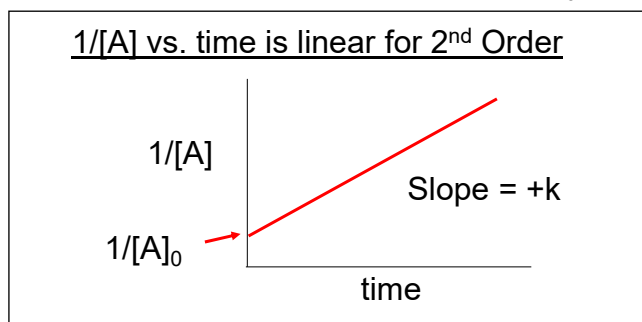
Do the same thing for a second order reaction.

2nd Order: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

$$y = mx + b$$

Plot $1/[A]$ on the y-axis and time on the x-axis.

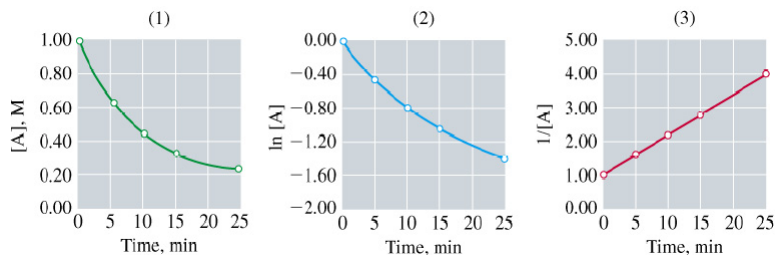
Slope = $+k$ and intercept = $1/[A]_0$



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Concept Test

Suppose you are trying to determine the order of a reaction, $A \rightarrow \text{Products}$. You make the following plots:



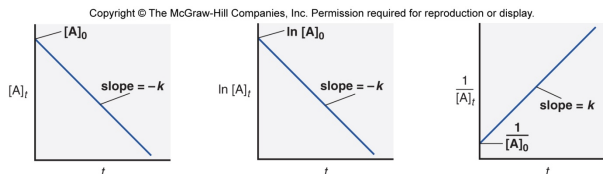
The order of the reaction is:

- A. 0th Order
- B. 1st Order
- C. 2nd Order
- D. Not enough information provided

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Summary of Integrated Rate Laws

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units for k	mol/L · s	1/s	L/mol · s
Half-life	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Plot for straight line	$[A]_t$ vs. t	$\ln[A]_t$ vs. t	$\frac{1}{[A]_t}$ vs. t
Slope, y intercept	$-k, [A]_0$	$-k, \ln[A]_0$	$k, \frac{1}{[A]_0}$



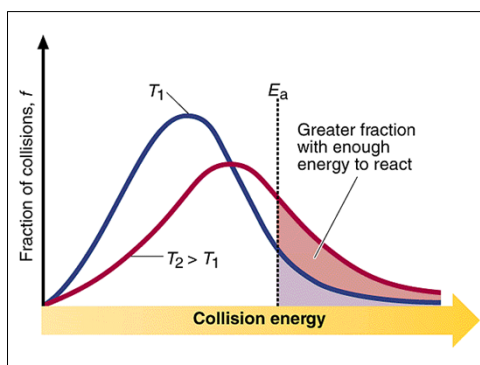
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Effect of Temperature on Reaction Rate

- In general, the rates of chemical reactions are highly sensitive to temperature.
- The rate constant, k , has a temperature parameter embedded in it
 - It's a "constant" when the temperature remains constant
 - An increase in temperature generally results in an increase in k , which in turn, results in a faster rate.
 - Think of thermal energy distribution!
- This happens because of something called **collision theory** – particles must collide in order for a reaction to occur.
 - molecules behave like defective billiard balls

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Thermal Energy Distribution

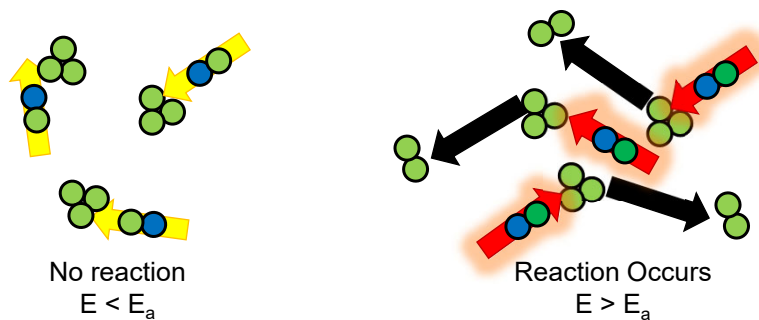


- At any given temperature, atoms and molecules in sample have a range of energies.
- The higher the temperature, the wider the energy distribution, and the greater the average energy.
- The fraction of molecules with enough energy to form products increases with temperature.

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Collision Theory

- The balls bounce apart if they collide at low speed, but when the impact is highly energetic, it leads to a product



E_a is the activation energy

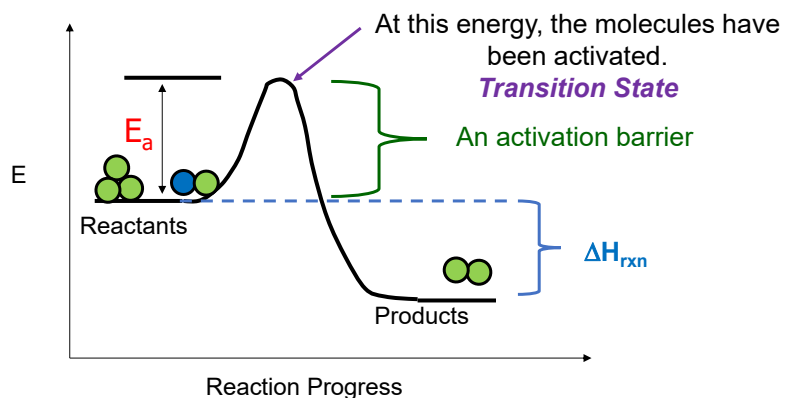
Reactant particles must collide with each other to react.

A chemical reaction occurs only after sufficient energetic collisions between the reactant molecules take place.

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Activation Energy (E_a)

- E_a – the minimum energy needed for the reaction
 - The energy barrier that must be surpassed for the reactants to be transformed into products



Smaller $E_a \rightarrow$ higher the rate (larger k)

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The Arrhenius Equation

- Shows the relationship between the rate constant (k), temperature, and E_a

Arrhenius equation: $k = Ae^{-E_a/RT}$ ($R = 8.314 \text{ J/mol}\cdot\text{K}$)

Frequency factor

Exponential factor

- The **frequency factor** is the number of times that reactants approach the activation barrier per unit time
 - Two parts: orientation factor & collision frequency
- The **exponential factor** is the fraction of approaches that are successful in surmounting the activation barrier and forming products.

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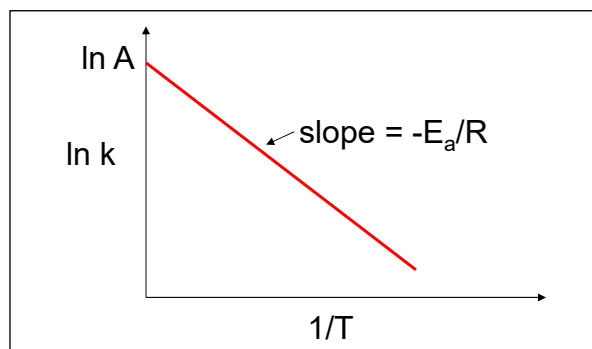
Arrhenius Plots

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

$$\ln k = \ln A - E_a/RT$$

$$y = b + mx$$

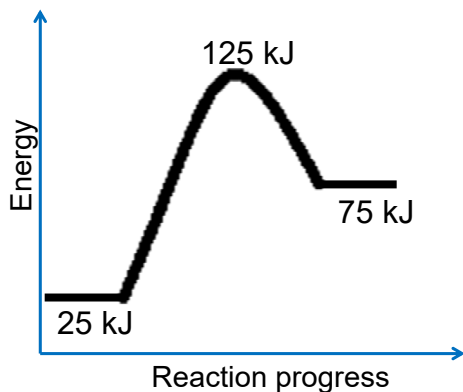
Plot $\ln k$ vs $1/T$ gives straight line with slope $-E_a/R$.



50

Concept Test

What is the activation energy for the following reaction and is it exothermic or endothermic?



- A. 125 kJ exothermic
- B. 100 kJ endothermic
- C. 100 kJ exothermic
- D. 50 kJ endothermic

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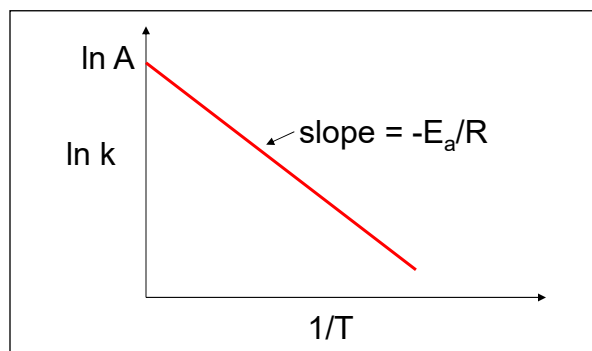
Arrhenius Plots

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

$$\ln k = \ln A - E_a/RT$$

$$y = b + mx$$

Plot $\ln k$ vs $1/T$ gives straight line with slope $-E_a/R$.



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Concept Test

The linear regression of an Arrhenius plot of $\ln k$ vs $1/T$ was $y = -1.00x + 0.693$. What is the activation energy (E_a) for this reaction?

- A. -1.00 kJ/mol
- B. 1.00 kJ/mol
- C. 0.00831 kJ/mol
- D. -0.00831 kJ/mol

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Two-Point form of the Arrhenius Equation

- It is possible to calculate the activation energy if the rate constant at just two different temperatures are known.
 - Useful when either data are limited or plotting capabilities are absent:

$$\ln k_2 = \ln A - (E_a/RT_2)$$

$$\text{---} \ln k_1 = \ln A - (E_a/RT_1)$$

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = -E_a/RT_2 + E_a/RT_1$$

$$\ln \frac{k_2}{k_1} = -(E_a/R)(1/T_2 - 1/T_1)$$

Plug in two sets of data to get E_a

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Using the Two-Point Form of the Arrhenius Equation

Find k_{600K} . Given,

$$k_{500K} = 4.3 \times 10^{-7} \text{ 1/Ms}$$

$$k_{700K} = 6.3 \times 10^{-2} \text{ 1/Ms}$$

$$\text{Arrhenius Equation: } \ln(k_2/k_1) = -(E_a/R)(1/T_2 - 1/T_1)$$

$$\ln(6.3 \times 10^{-2} / 4.3 \times 10^{-7}) = -(E_a/R)(1/700 - 1/500)$$

$$11.89 = -(E_a/8.314 \text{ J/molK})(-5.71 \times 10^{-4})$$

$$E_a = 173 \text{ KJ/mol}$$

$$\ln(k_{600K} / 4.3 \times 10^{-7}) = -(173 \text{ KJ/mol} / 0.008314 \text{ KJ/molK})(1/600 - 1/500)$$

$$k_{600K} = 4.4 \times 10^{-4} \text{ 1/Ms}$$

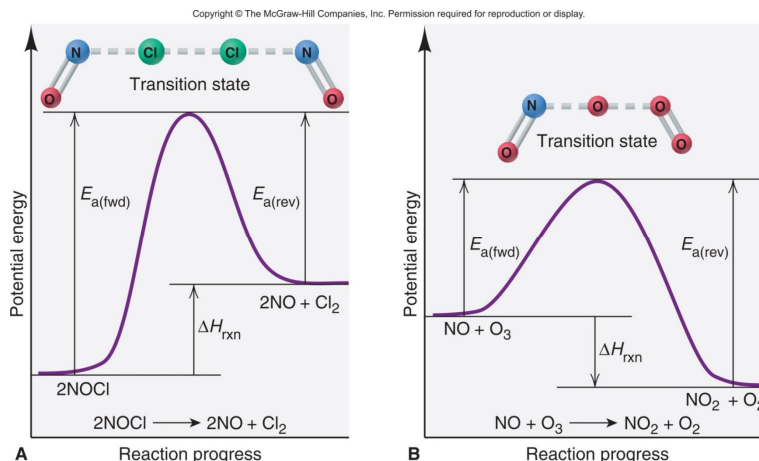
55

Transition State

- To get from the reactant to the product, the molecule must go through an activated complex or **transition state** – unstable species that contains **partial bonds**.
 - It is a transitional species partway between reactants and products.
 - Transition states cannot be isolated.
- The transition state exists at the point of maximum potential energy.
 - The energy required to form the transition state is the activation energy.
- Redefine E_a – the energy needed to reach the transition state.
 - The higher the E_a , the slower the reaction rate (at a given temperature).
 - The E_a determines the rate of a reaction!

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Figure 16.21 Reaction energy diagrams and possible transition states for two reactions.



The reaction must first go uphill to reach the activated complex because energy is required to initially weaken the bonds and allow the new product to form

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Reaction Mechanisms

- Most chemical reactions occur through several steps, not in a single step.
- Consider the following reaction:

$$\text{H}_2(g) + 2 \text{ICl}(g) \rightarrow 2 \text{HCl}(g) + \text{I}_2(g)$$
 - This is actually the overall reaction, not the series of individual steps by which the reaction occurs.
 - The overall equation shows only the substances present at the beginning of a reaction and the substances formed by the reaction.
 - It does NOT show the intermediate steps that are involved.
- A **reaction mechanism** is a series of individual chemical steps by which the overall chemical reaction occurs.

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Reaction Mechanisms

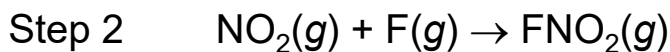
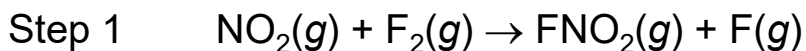
- The proposed mechanism for the reaction between H_2 and ICl contains two steps:
 Step 1: $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HI}(\text{g}) + \text{HCl}(\text{g})$
 Step 2: $\text{HI}(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{I}_2(\text{g})$

 Net: $\text{H}_2(\text{g}) + 2 \text{ICl}(\text{g}) \rightarrow 2 \text{HCl}(\text{g}) + \text{I}_2(\text{g})$
- Each step in a reaction mechanism is called an **elementary step**.
 - These cannot be broken down into simple steps.
 - They occur as they are written.
- The individual steps in the mechanism must add to give the overall reaction.
 - HI is called the **reaction intermediate** – forms in one elementary step and is consumed in another.

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Concept Test

What is the reaction intermediate in the following reaction mechanism?



- A. NO_2
- B. F_2
- C. F
- D. FNO_2

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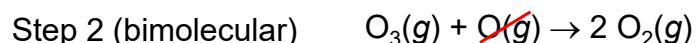
Rate Laws for Elementary Steps

- Elementary steps are characterized by their **molecularity** – the number of reactant particles involved in the step:
 - $A \rightarrow \text{Products}$ Unimolecular
 - $A + A \rightarrow \text{Products}$ Bimolecular
 - $A + B \rightarrow \text{Products}$ Bimolecular
 - $A + B + C \rightarrow \text{Products}$ Termolecular (very rare)
- The rate law for an elementary step **CAN** be deduced from the balanced chemical equation.
 - In elementary steps, the collision of reactant particles is proportional to the product of the concentrations of those particles.

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Rate Laws for Elementary Steps

- Consider the destruction of ozone:



$\text{O}(g)$ is the
reaction
intermediate

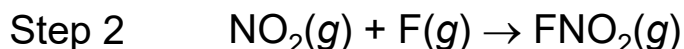
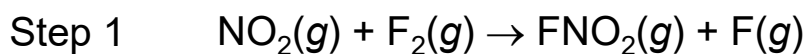


- Notice that the **order** of an elementary step is the same as its **molecularity** (number of reactant molecules).
- Remember, we don't know the order of an overall reaction unless we do an experiment.

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Concept Test

What is the rate law for step 1 of the following mechanism?



- A. Rate = $k[\text{NO}_2][\text{F}_2]$
- B. Rate = $k[\text{NO}_2]$
- C. Rate = $k[\text{F}_2]$
- D. The rate law cannot be determined without experimental data.

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Rate-Determining Steps

- In most chemical reactions, one of the elementary steps is much slower than the others.
 - Called the *rate-determining step*.
 - This step limits the overall rate of the reaction and therefore, determines the rate law for the overall reaction.
- Example: $\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$
 - Step 1: $\text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g)$ k_1 , slow
 - Step 2: $\text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g)$ k_2 , fast
- Step 1 is the rate-determining step (bimolecular)

Rate of step 1 = $k_1[\text{NO}_2]^2$
- Thus, the **overall** order of the reaction should follow this same 2nd-order rate equation.

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Intermediate in a Rate-Determining Step

- What if the rate determining step involves an intermediate?
- Example: $2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$
 - Step 1: $2 \text{NO}(\text{g}) \leftrightarrow \text{N}_2\text{O}_2(\text{g})$ k_1, k_{-1} , Fast
 - Step 2: $\text{H}_2(\text{g}) + \text{N}_2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{N}_2\text{O}(\text{g})$ k_2 , Slow
 - Step 3: $\text{N}_2\text{O}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ k_3 , Fast
- Step 2 is the rate-determining step (bimolecular)

$$\text{Rate of step 2} = k_2[\text{H}_2][\text{N}_2\text{O}_2]$$

But N_2O_2 is a reaction intermediate

Problem: The rate expression involves a reactant we can't measure...so, now what?

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Intermediate in a Rate-Determining Step

- Solution: Express the concentration of the intermediate in terms of the reactants of the overall equation
- Since the first step reaches equilibrium, the rate of the forward reaction in the first step equals the rate of the reverse reaction:

$$\text{Rate}(\text{forward}) = \text{Rate}(\text{backward})$$

The rate of the forward reaction is given by

$$\text{Rate} = k_1[\text{NO}]^2$$

The rate of the reverse reaction is given by

$$\text{Rate} = k_{-1}[\text{N}_2\text{O}_2]$$

- Since these two rates are equal at equilibrium, we can set them equal to one another and solve for $[\text{N}_2\text{O}_2]$

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

$$[\text{N}_2\text{O}_2] = k_1/k_{-1} [\text{NO}]^2$$

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Intermediate in a Rate-Determining Step

- Now, substitute in this expression into our original rate law from the rate determining step:

$$\text{Rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2] \quad (\text{From Step 2})$$

$$[\text{N}_2\text{O}_2] = k_1/k_{-1} [\text{NO}]^2$$

$$\text{Rate} = k_2 (k_1/k_{-1}) [\text{H}_2][\text{NO}]^2$$

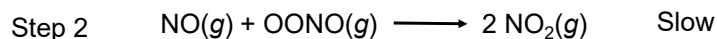
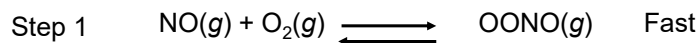
$$\text{Rate} = \underbrace{k}_{} [\text{H}_2][\text{NO}]^2$$

$$k_2 (k_1/k_{-1})$$

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Concept Test

Consider the following elementary steps for the overall reaction: $2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$



What is the correct rate law for the rate determining step?

- A. $\text{Rate} = k[\text{NO}][\text{O}_2]$
- B. $\text{Rate} = k[\text{OONO}]$
- C. $\text{Rate} = k[\text{NO}][\text{OONO}]$
- D. $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$

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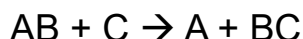
Summary of Reaction Mechanisms

- For a proposed reaction mechanism to be valid, the elementary steps in the mechanism must sum to the overall reaction.
- The rate law predicted by the reaction mechanism must be consistent with the experimentally observed rate law.
- The rate law is determined by the rate-determining step (RDS); if the RDS contains an intermediate, it must be expressed in terms of the reactants in the overall reaction.

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Concept Test

The experimentally determined rate law for the following reaction was observed to be second order in AB and zero order in C:



Which mechanism is valid for this reaction?

- A. Step 1: $\text{AB} + \text{AB} \rightarrow \text{AB}_2 + \text{A}$ k_1 , Slow
 Step 2: $\text{AB}_2 + \text{C} \rightarrow \text{AB} + \text{BC}$ k_2 , Fast
- B. Step 1: $\text{AB} + \text{B} \rightarrow \text{AB}_2$ k_1 , Slow
 Step 2: $\text{AB}_2 + 2 \text{C} \rightarrow 2 \text{BC} + \text{A}$ k_2 , Fast
- C. Both (A) and (B) are valid reaction mechanisms
- D. Neither (A) nor (B) are valid reaction mechanisms

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Catalysis

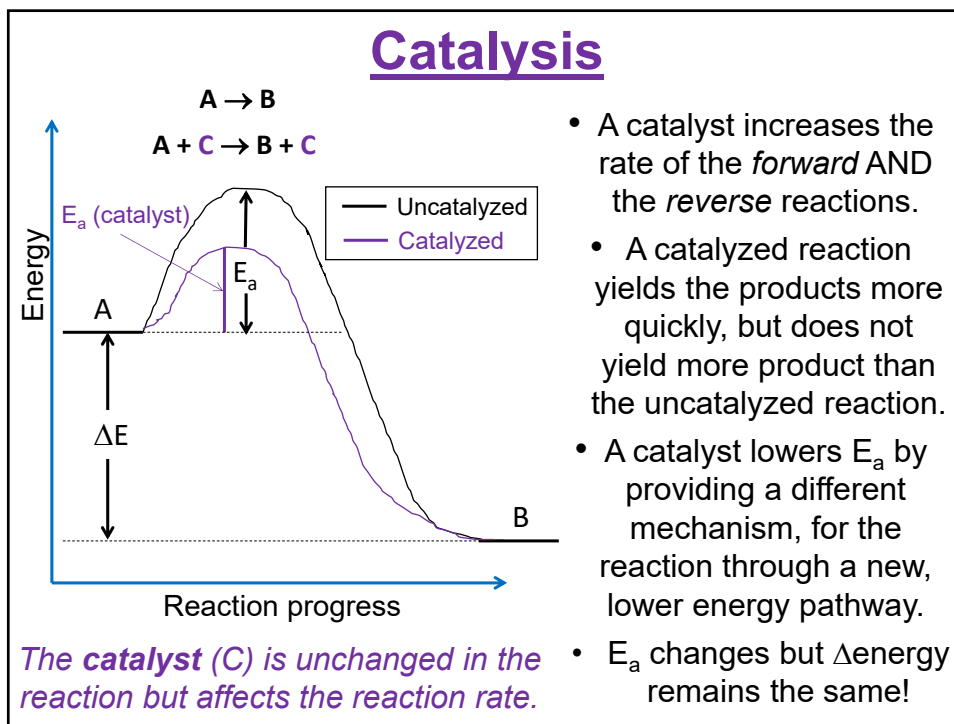
- We know that the rate of reaction can be increased by increasing temperature.
 - Think back to Arrhenius's equation: $k = Ae^{-(E_a/RT)}$
- It is possible to increase the reaction rate without increasing the temperature.
 - Use of a **catalyst** – substance that increases the rate without being consumed in the reaction.
 - Generally, very small quantities of it is required.
- Catalysts work in general by *lowering* the activation energy of a reaction.
 - This makes the rate constant larger.
 - Increases the rate.

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Catalysis

- Catalysts provide an alternative pathway for the reaction to occur, one with a lower activation energy, which speeds up the reaction.
- This alternative pathway follows a different set of elementary steps.
- Catalysts are not consumed by reactions. Rather, they are reactants in one elementary step and are produced in another elementary step.

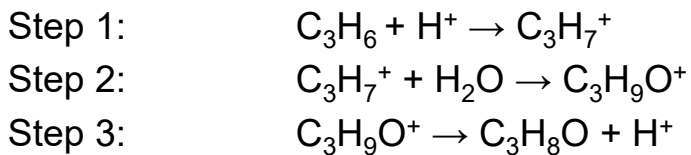
72



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Catalysis Example

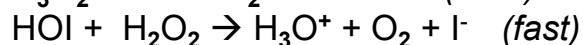
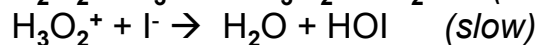
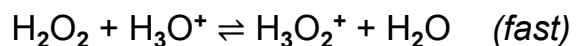
Use the elementary reactions below for the hydration of propene, C_3H_6 , to a) write the balanced overall reaction and b) to identify any intermediates and catalysts.



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Concept Test

Consider the following reaction mechanism:



How many catalysts are in this mechanism?

- A. 0
- B. 1
- C. 2
- D. 3

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Information from Shapes of Energy Diagrams

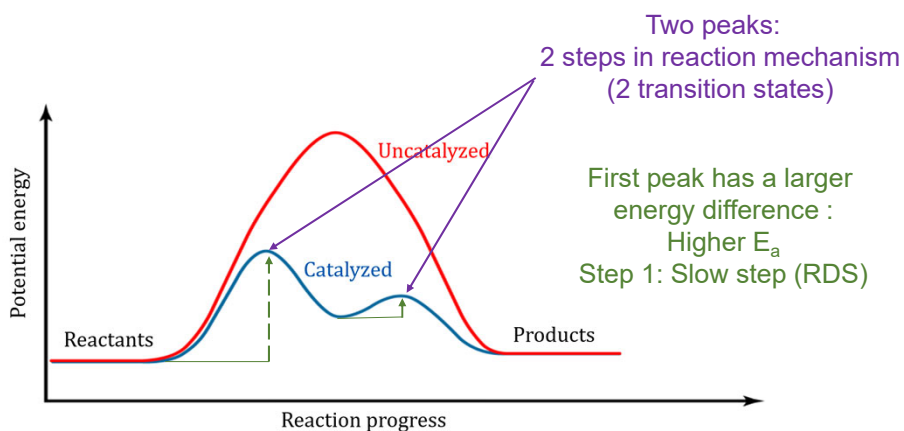


Figure 14.21

Activation Energy of Catalyzed Reaction Compared to Uncatalyzed Reaction

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Information from Shapes of Energy Diagrams

- The number of peaks indicate the number of steps in the proposed reaction mechanism (and hence, the number of transition states)
- The peak with the higher difference in energy has the higher activation energy barrier
 - This will correspond to the RDS

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Types of Catalysts

- **Homogeneous catalyst:** exist in the same phase as the reactants.
- **Heterogeneous catalyst:** exist in a different phase as the reactants.
 - Usually, the catalyst is a solid surface; reactants are gases or in solution.
- Examples:
 - Rh(s) used in catalytic converters for car exhaust systems.
 - Converts: $2 \text{ CO} + 2 \text{ NO} \rightarrow \text{CO}_2 + \text{N}_2$
 - Enzymes are biological catalysts
 - A given enzyme catalyzes one specific reaction, no (or few) others.
 - Highly **efficient**: increase rate by much more than inorganic catalysts .

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Importance of Catalysis

- All metabolic reactions are catalyzed by a class of proteins called enzymes.
- Most industrial processes involve catalysis.
- Many consumer products also include catalysts.