Chemistry, The Central Science, 10th edition AP edition
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Chapter 14: Chemical Kinetics
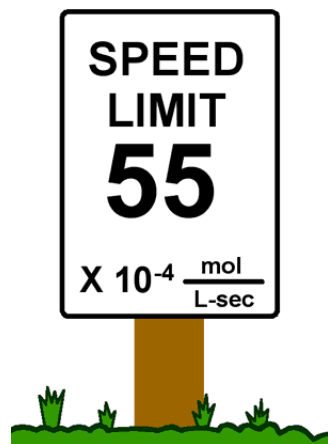
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(ppt modified for our requirements)

Chemical
Kinetics

Kinetics

Studies the rate at which a chemical process occurs.

Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly *how* the reaction occurs).

Resources and Activities

- Textbook - chapter 14 & ppt file
- Online practice quiz
- Lab activities
- POGIL activities
- Chem Guy video lecture series on Chemical Kinetics (several)
  http://www.cosmolearning.com/courses/ap-chemistry-with-chemguy/video-lectures/
- Chemtour videos from Norton & Animations from Glencoe
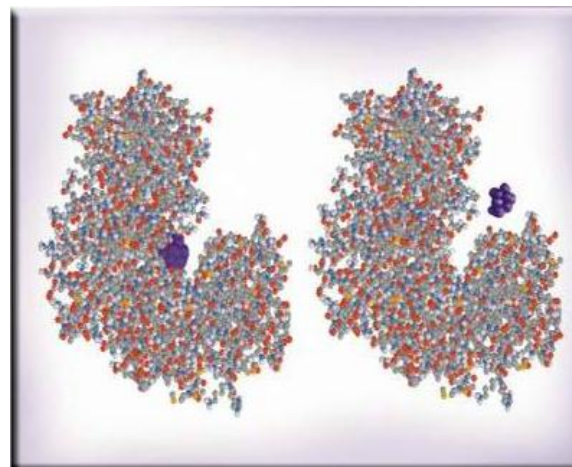
Activities and Problem set for chapter 14   (due date_____)

Lab activities:

- *Kinetics of a reaction (wet lab)*
- Virtual lab (Iodine-Clock expt.)
- http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/kinetics2/iodine_clock.html

POGILS (2) : Chemical Kinetics; Reaction Mechanisms

Online practice quiz ch 14 due by_____

Chapter 14 reading guide and practice problems packet

In class preview and then Independent work - students to view animations & interactive activities (5 in total from Norton) and **write summary notes** on each. These summaries are to be included in your portfolio.

Animations to view in class and at home:
http://www.wwnorton.com/college/chemistry/gilbert2/contents/ch14/studyplan.asp
(Reaction rates, Reaction order, Arrhenius equation, Collision Theory, Reaction mechanisms)

Additional resources to explore (summaries not mandatory)
http://glencoe.mcgraw-hill.com/sites/0023654666/student_view0/chapter13/animations_center.html#
(catalysis, Kinetics simulation)

Outline: Kinetics

Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calc amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with T.
Mechanisms	Link between rate and molecular scale processes.

Chemical Kinetics

Vocabulary terms

Reaction rate

(units $M \cdot s^{-1} \equiv mol \cdot L^{-1} \cdot s^{-1}$)

- Instantaneous rate
- Initial rate (instantaneous rate at t = 0)
- Average rate of reaction
- Rate constant (diff units possible depending on molecularity of reaction)

Reaction orders

- Overall reaction order
- 1st order
- 2nd order

Collision Model/theory

- Activation energy (E_a)
- Activated complex/transition state
- Arrhenius equation

Reaction mechanisms

- ➤ Elementary reactions/processes
- ➤ Molecularity
- ➤ Unimolecular, bimolecular, termolecular

Catalysts

- ➤ Homogeneous & heterogeneous
- ➤ Adsorption vs absorbtion
- ➤ Enzymes, substrates, active sites, lock& key model

Important equations

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D} \qquad \text{Rate} = k\,[\text{A}]^x[\text{B}]^y$$

For a first order reaction A $\rightarrow$ products

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \qquad \ln[\text{A}]_t = -kt + \ln[\text{A}]_0 \qquad \ln\frac{[A]_t}{[A]_0} = -kt$$

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

Because [A] at $t_{1/2}$ is one-half of the original [A], $[\text{A}]_t = \tfrac{1}{2}[\text{A}]_0 = 0.5[\text{A}]_0$

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

Important equations

For a second order reaction A + B $\rightarrow$ products

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$ $$\text{rate} = k\,[A]\,[B]$$ $$\text{rate} = k\,[A]^2$$

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

Half life for second order reaction

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

Important equations (to complete)

Arrhenius equation $\qquad k = A\,e^{-Ea/RT}$

$ln(k) = ln\,A - E_a/RT$

$$ln(k) = -\frac{E_a}{RT} + lnA$$

Chemical Kinetics

Factors That Affect Reaction Rates

- Physical State of the Reactants
  - In order to react, molecules must come in contact with each other.
  - The more homogeneous the mixture of reactants, the faster the molecules can react.

- Concentration of Reactants
  - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

- Temperature
  - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

# Factors That Affect Reaction Rates

- ## Presence of a Catalyst

  - ➤ Catalysts speed up reactions by changing the mechanism of the reaction.

  - ➤ Catalysts are not consumed during the course of the reaction.

Chemical Kinetics

Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).
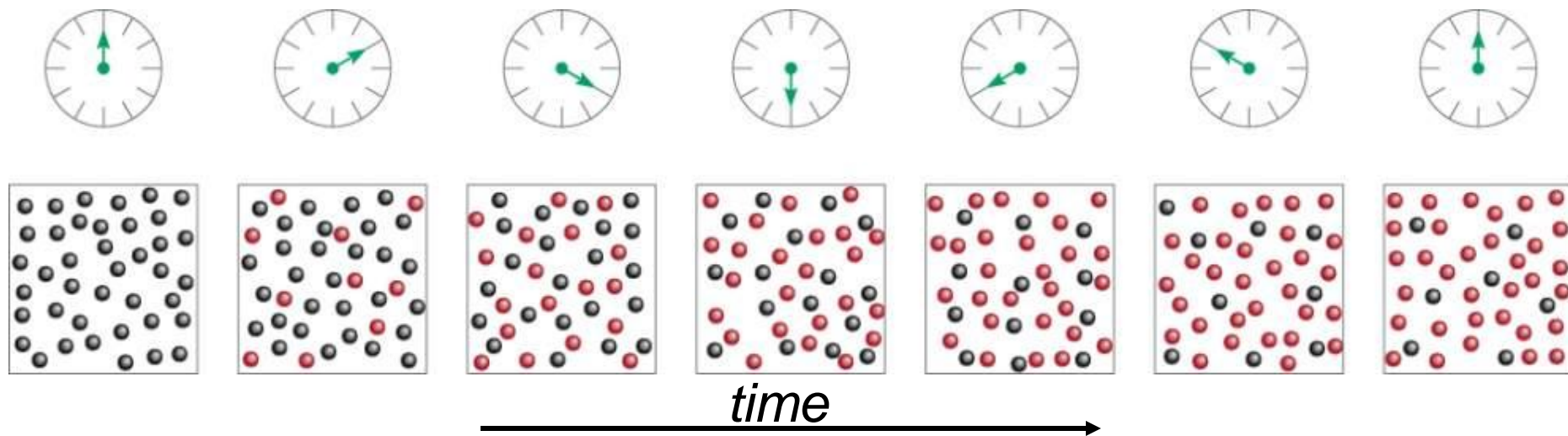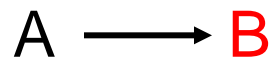
$$A \longrightarrow B$$
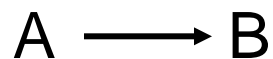
$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt
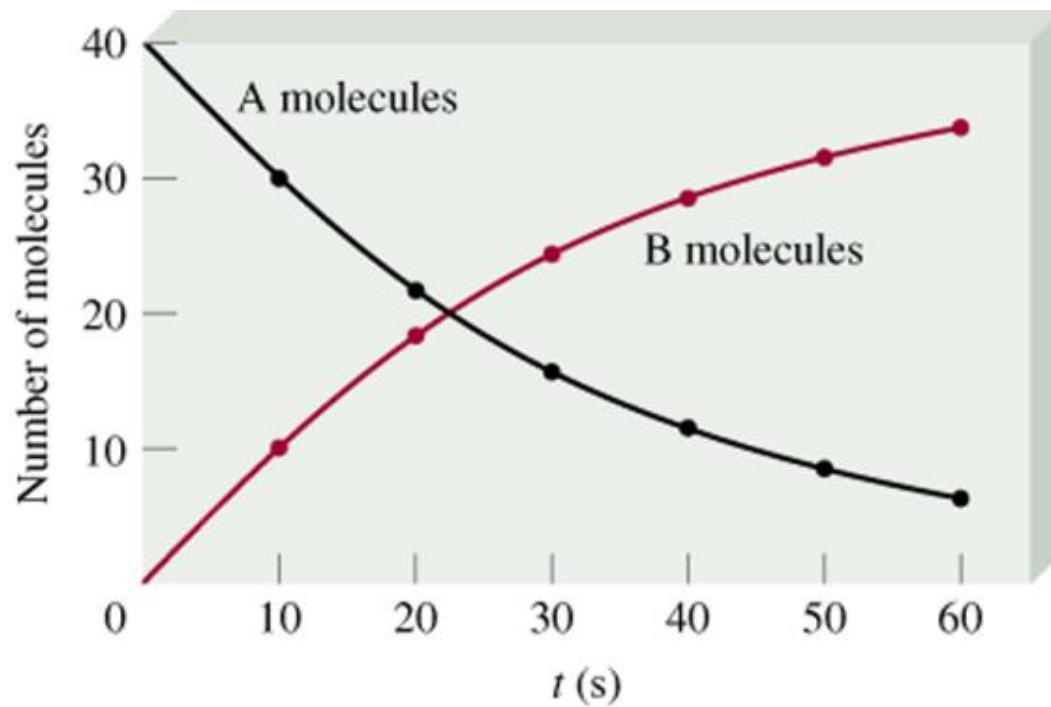
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

A ⟶ B

time

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

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

13.1

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, C_4H_9Cl, was measured at various times.

Chemical Kinetics

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	[C_4H_9Cl] (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{Average rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t}$$

Chemical Kinetics

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	[C_4H_9Cl] (M)	Average Rate (M/s)
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50.0	0.0905	1.9×10^{-4}
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200.0	0.0671	1.4×10^{-4}
300.0	0.0549	1.22×10^{-4}
400.0	0.0448	1.01×10^{-4}
500.0	0.0368	0.80×10^{-4}
800.0	0.0200	0.560×10^{-4}
10,000	0	

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Chemical Kinetics

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.
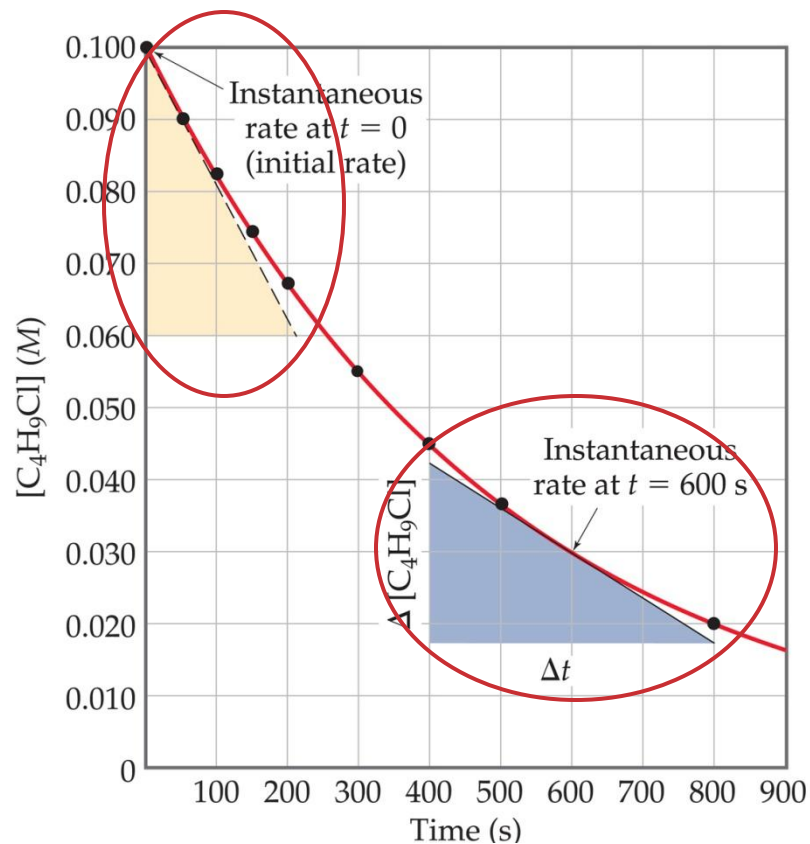

Chemical Kinetics

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$
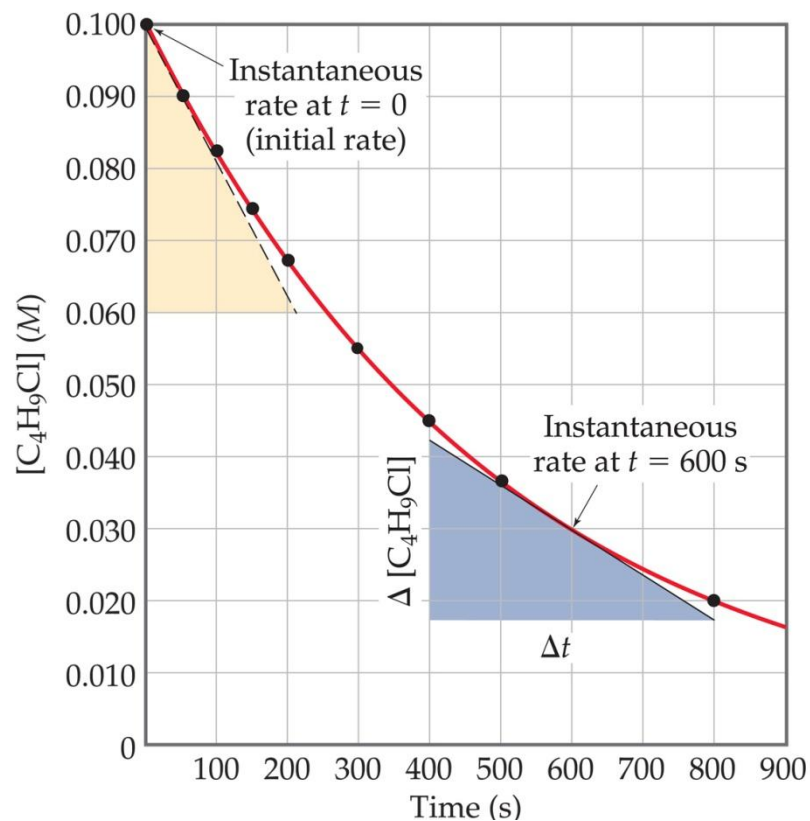
- All reactions slow down over time.

- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the beginning.

Chemical Kinetics

Reaction Rates and Stoichiometry

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.

- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH.
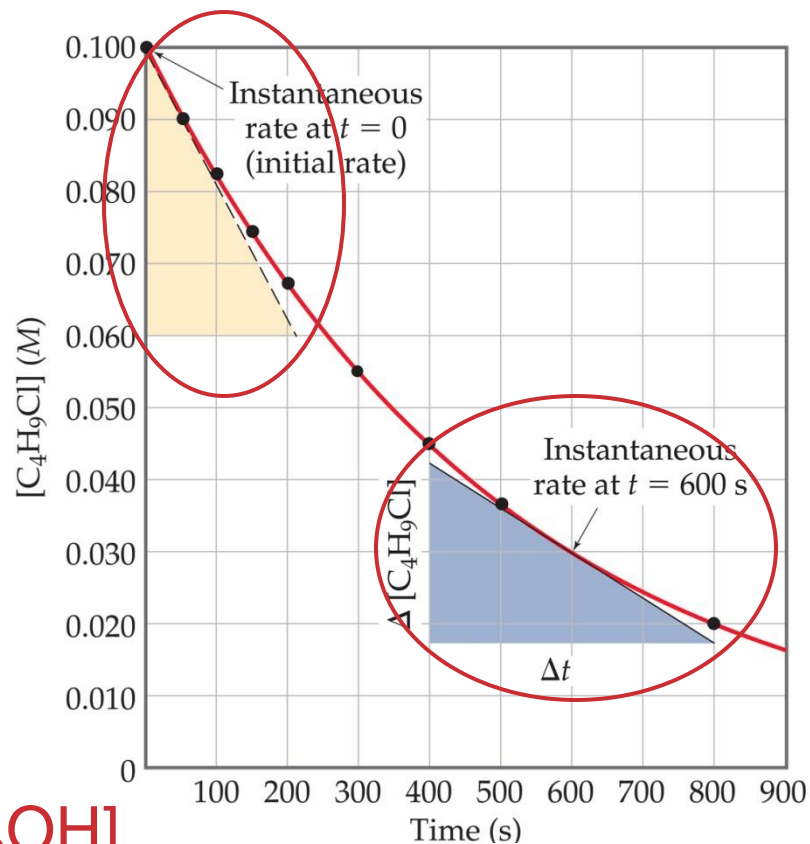
$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Chemical Kinetics

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?

$$2\ HI(g) \longrightarrow H_2(g) + I_2(g)$$

- Therefore,

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Reaction Rates and Stoichiometry

- To generalize, then, for the reaction

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$$

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Concentration and Rate

One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

Comparing Experiments 1 and 2, when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

Likewise, comparing Experiments 5 and 6, when [NO_2^-] doubles, the initial rate doubles.

Chemical Kinetics

Concentration and Rate

- This means

$$\text{Rate} \propto [NH_4^+]$$

$$\text{Rate} \propto [NO_2^-]$$

$$\text{Rate} \propto [NH^+] [NO_2^-]$$

or

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

- This equation is called the rate law, and *k* is the rate constant.

Chemical
Kinetics

Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The exponents tell the order of the reaction with respect to each reactant.
- This reaction is

   First-order in $[NH_4^+]$

   First-order in $[NO_2^-]$

- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is second-order overall.

The Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k\,[A]^x[B]^y$$

reaction is **xth order** in A

reaction is **yth order** in B

reaction is **(x +y)th order overall**

Chemical
Kinetics

13.2

$$F_2\ (g) + 2ClO_2\ (g) \longrightarrow 2FClO_2\ (g)$$
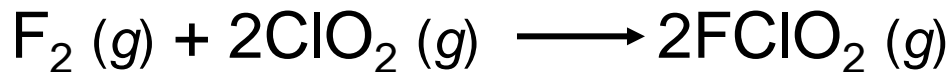
rate $= k\ [F_2]^x[ClO_2]^y$

Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

	$[F_2](M)$	$[ClO_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

Double $[F_2]$ with $[ClO_2]$ constant

Rate doubles

$x = 1$

Quadruple $[ClO_2]$ with $[F_2]$ constant

Rate quadruples

$y = 1$

rate $= k\ [F_2][ClO_2]$

Run #	Initial [A] ($[A]_0$)	Initial [B] ($[B]_0$)	Initial Rate (v_0)
1	1.00 M	1.00 M	1.25×10^{-2} M/s
2	1.00 M	2.00 M	2.5×10^{-2} M/s
3	2.00 M	2.00 M	2.5×10^{-2} M/s

What is the order with respect to A?   0

What is the order with respect to B?   1

What is the overall order of the reaction?   1

Chemical Kinetics

$[NO_{(g)}]$ (mol dm^{-3})	$[Cl_{2(g)}]$ (mol dm^{-3})	Initial Rate (mol dm^{-3} s^{-1})
0.250	0.250	1.43 x 10^{-6}
0.250	0.500	2.86 x 10^{-6}
0.500	0.500	1.14 x 10^{-5}

What is the order with respect to Cl_2?   1

What is the order with respect to NO?   2

What is the overall order of the reaction?

3

Chemical Kinetics

Rate Laws

- Rate laws are **always** determined experimentally.

- Reaction order is **always** defined in terms of reactant (not product) concentrations.

- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

$$F_2\ (g) + 2ClO_2\ (g) \longrightarrow 2FClO_2\ (g)$$
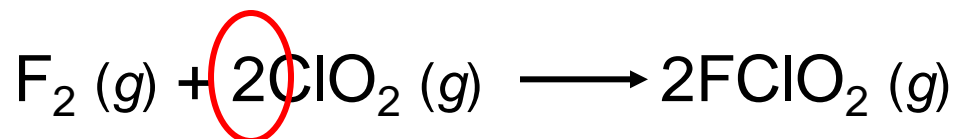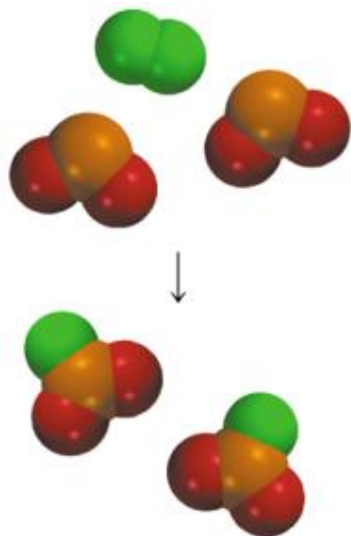
$$\text{rate} = k\,[F_2][ClO_2]^1$$

Determine the rate law and calculate the rate constant for the following reaction from the following data:

$$S_2O_8^{2-} \ (aq) + 3I^- \ (aq) \longrightarrow 2SO_4^{2-} \ (aq) + I_3^- \ (aq)$$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k \, [S_2O_8^{2-}]^x[I^-]^y$$

$y = 1$

$x = 1$

$$\text{rate} = k \, [S_2O_8^{2-}][I^-]$$

Double $[I^-]$, rate doubles (experiment 1 & 2)

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4} \ M/s}{(0.08 \ M)(0.034 \ M)} = 0.08/M \cdot s$$

Chemical Kinetics

13.2

Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process gives us

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

Where

$[A]_0$ is the initial concentration of A.

$[A]_t$ is the concentration of A at some time, t, during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces…

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

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

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

…which is in the form

$$y = mx + b$$

First-Order Processes

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

Therefore, if a reaction is first-order, a plot of ln [A] vs. t will yield a straight line, and the slope of the line will be $-k$.

Chemical
Kinetics

First-Order Reactions (other forms of equations)

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

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

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

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

[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t=0$

[A] vs time

ln[A] vs time

$k = -\text{slope}$

1/ [A] vs time
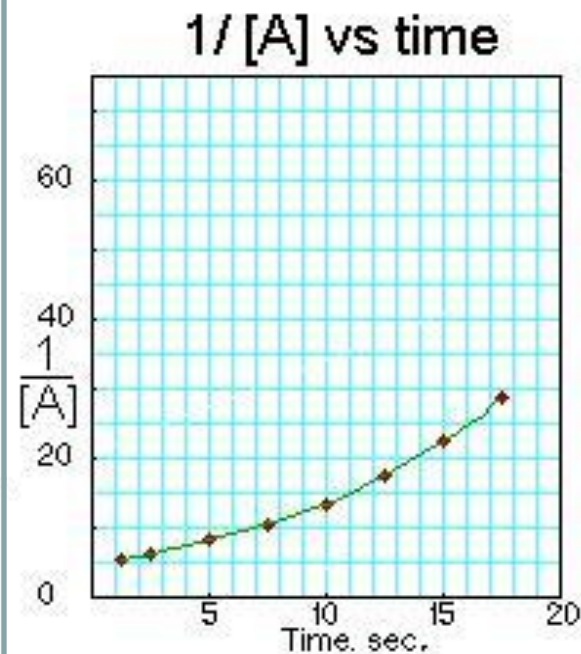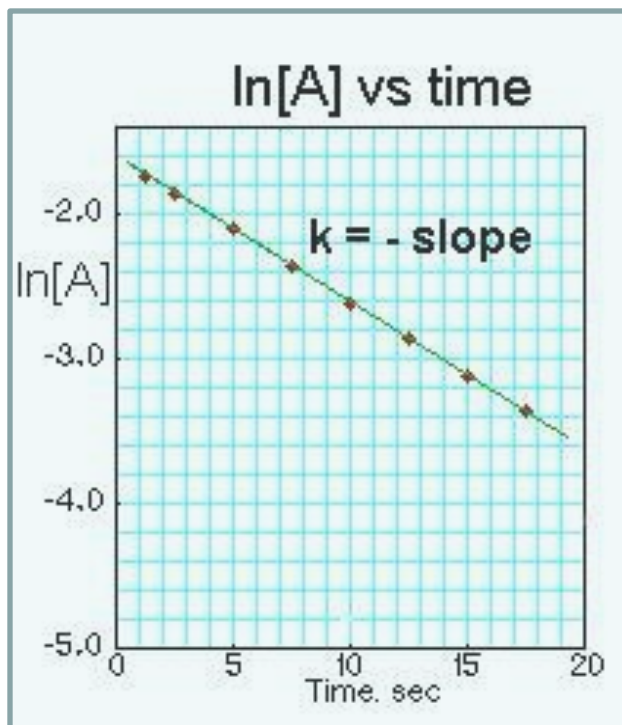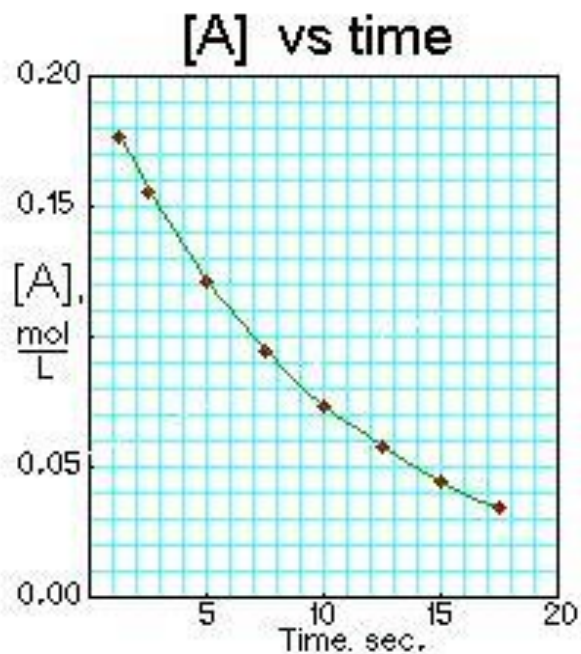
First-Order Processes
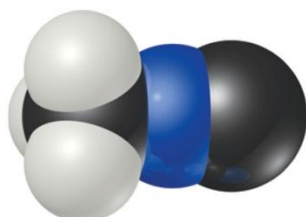
Methyl isonitrile
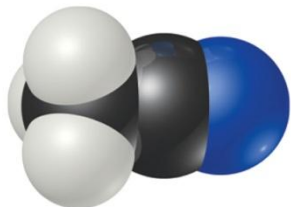
Acetonitrile

Consider the process in which methyl isonitrile is converted to acetonitrile.

$$CH_3NC \longrightarrow CH_3CN$$

Chemical
Kinetics

First-Order Processes

$$CH_3NC \longrightarrow CH_3CN$$

This data was collected for this reaction at 198.9° C.
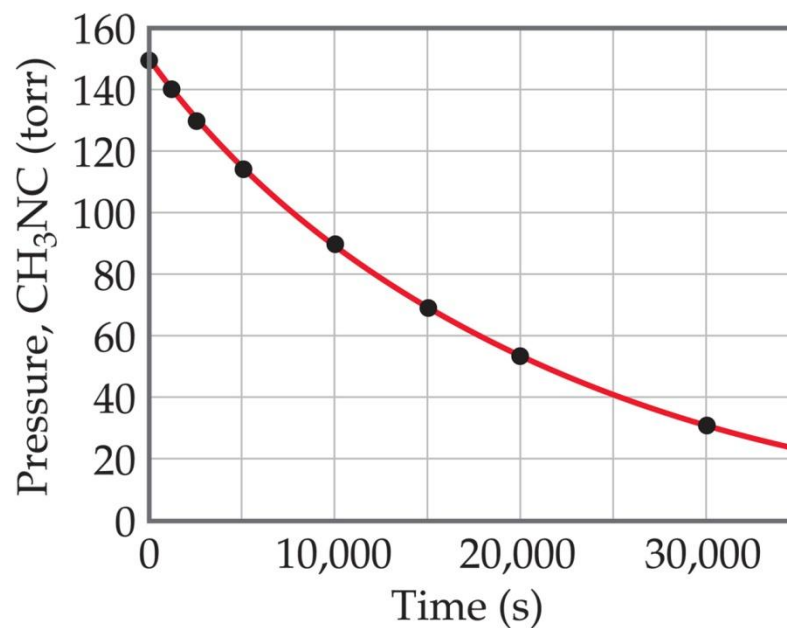
First-Order Processes
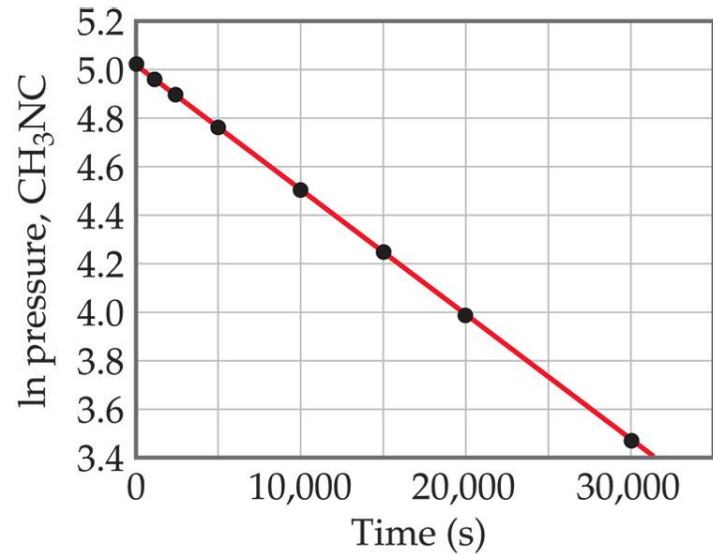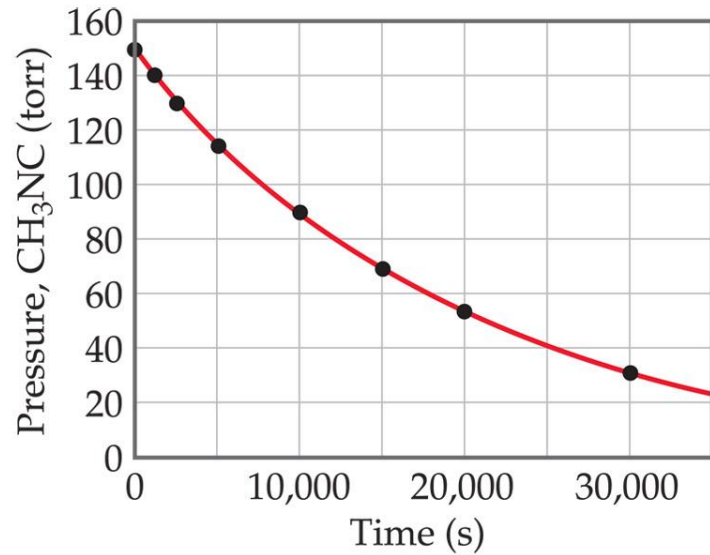
- When ln P is plotted as a function of time, a straight line results.

- Therefore,

  ➤ The process is first-order.

  ➤ k is the negative slope: 5.1×10^{-5} s^{-1}.

Chemical
Kinetics

The reaction $2A \longrightarrow B$ is first order in A with a rate constant of 2.8×10^{-2} s^{-1} at 80^0C. How long will it take for A to decrease from 0.88 M to 0.14 M ?

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

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

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

$$[A]_0 = 0.88\ M$$

$$[A] = 0.14\ M$$

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.88\ M}{0.14\ M}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ s$$

First-Order Reactions

The **half-life, $t_{1/2}$,** is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

$$t_{1/2} = \frac{\ln \dfrac{\cancel{[A]_0}}{\cancel{[A]_0}/2}}{k} = \frac{\ln 2}{k} = \boxed{\frac{0.693}{k}}$$

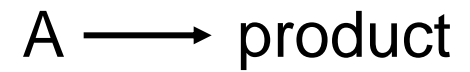What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

units of k (s^{-1})

First-order reaction

$$A \longrightarrow \text{product}$$
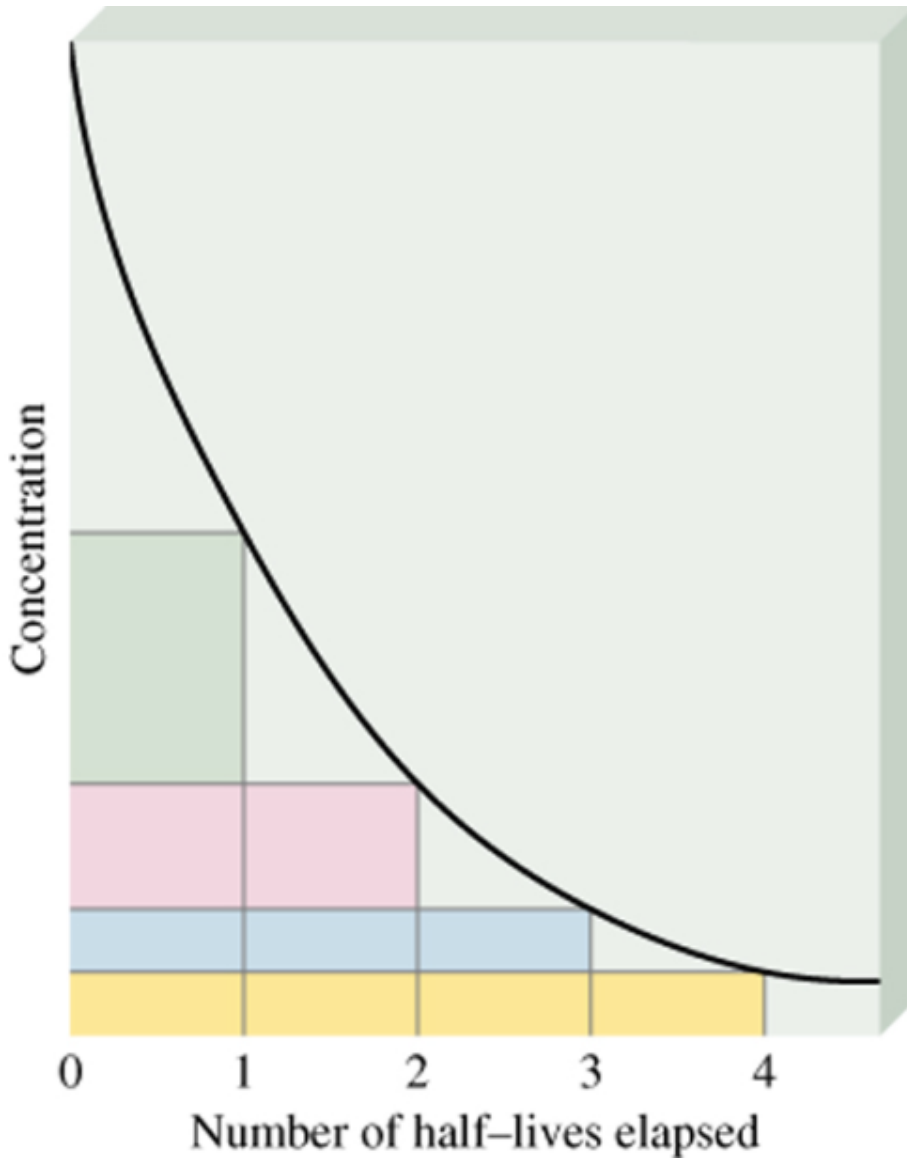
# of half-lives	$[A] = [A]_0/n$
1	2
2	4
3	8
4	16

13.3
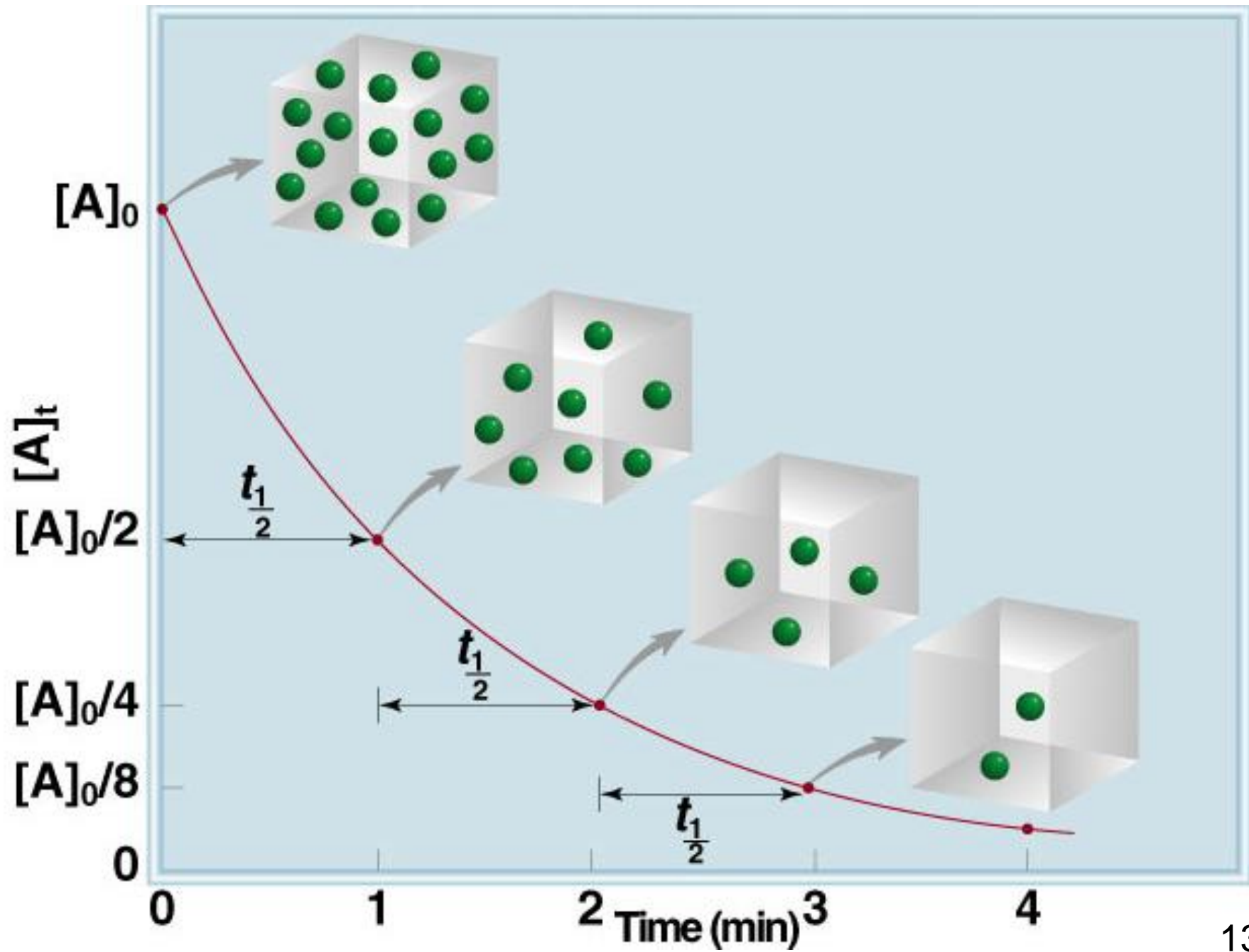
Second-Order Reactions

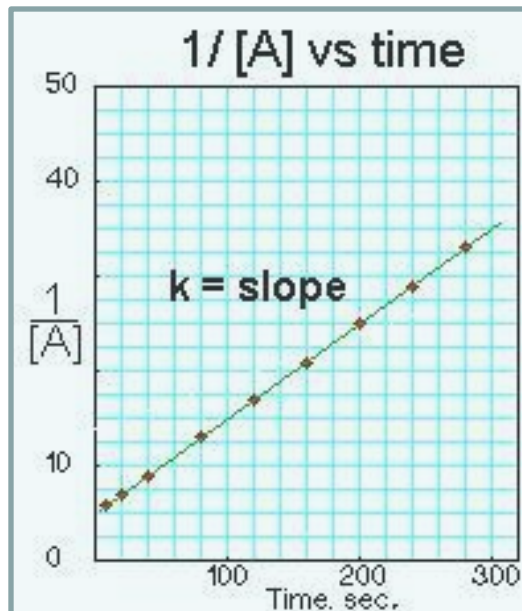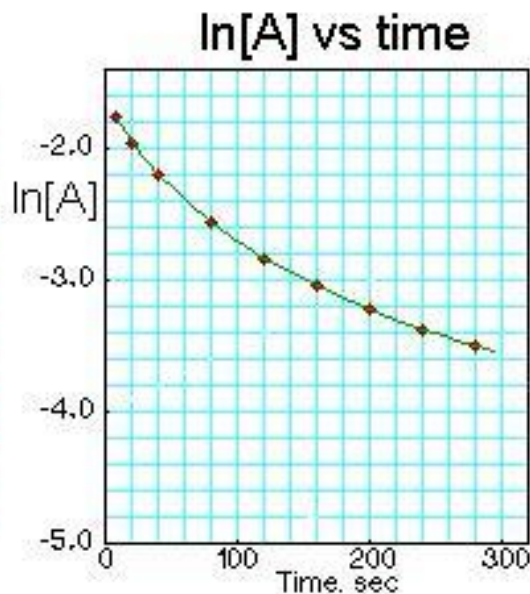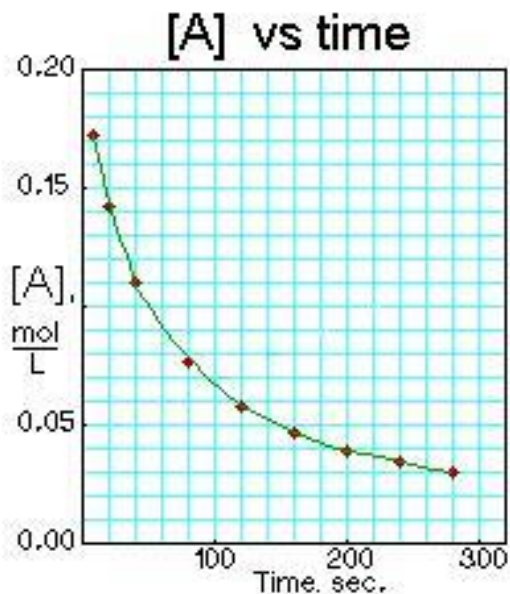$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t=0$

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

Half life for second order

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

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

[A] vs time

ln[A] vs time

1/ [A] vs time

k = slope

13.3

Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A, we get

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

also in the form

$$y = mx + b$$

Second-Order Processes

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

So if a process is second-order in A, a plot of 1/[A] vs. *t* will yield a straight line, and the slope of that line is *k*.

Chemical Kinetics

Second-Order Processes

The decomposition of NO_2 at 300° C is described by the equation

$$NO_2 \ (g) \longrightarrow NO \ (g) + 1/2 \ O_2 \ (g)$$

and yields data comparable to this:

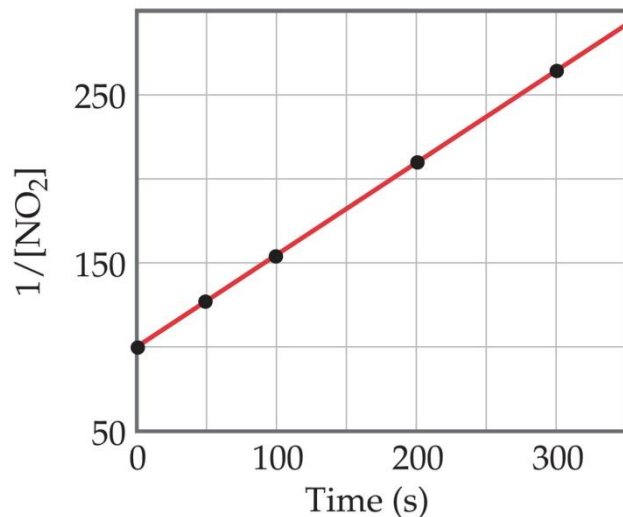| Time (s)	[NO$_2$], M
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Second-Order Processes

- Graphing ln $[NO_2]$ vs. t yields:

- The plot is *not* a straight line, so the process is *not* first-order in [A].
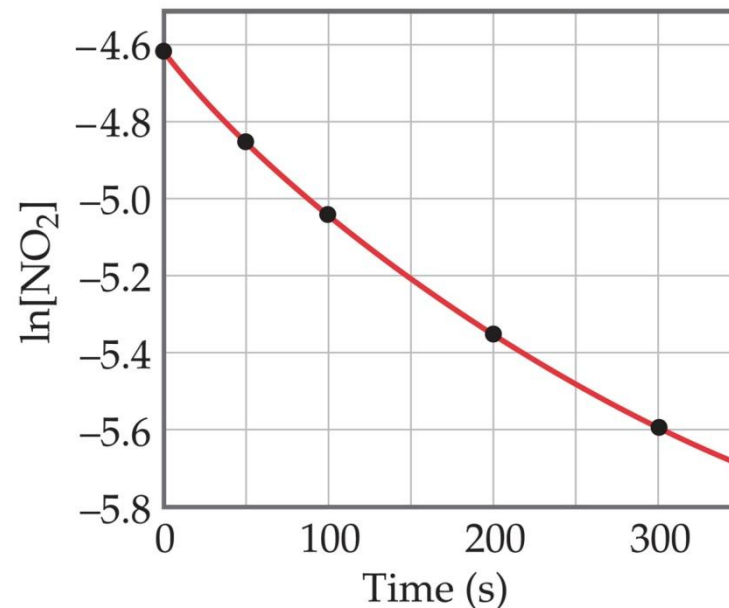
Time (s)	$[NO_2]$, M	ln $[NO_2]$
0.0	0.01000	−4.610
50.0	0.00787	−4.845
100.0	0.00649	−5.038
200.0	0.00481	−5.337
300.0	0.00380	−5.573

Chemical Kinetics

Second-Order Processes

Time (s)	$[NO_2]$, M	$1/[NO_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- Graphing ln $1/[NO_2]$ vs. t, however, gives this plot.

- Because this *is* a straight line, the process is second-order in [A].

Chemical
Kinetics
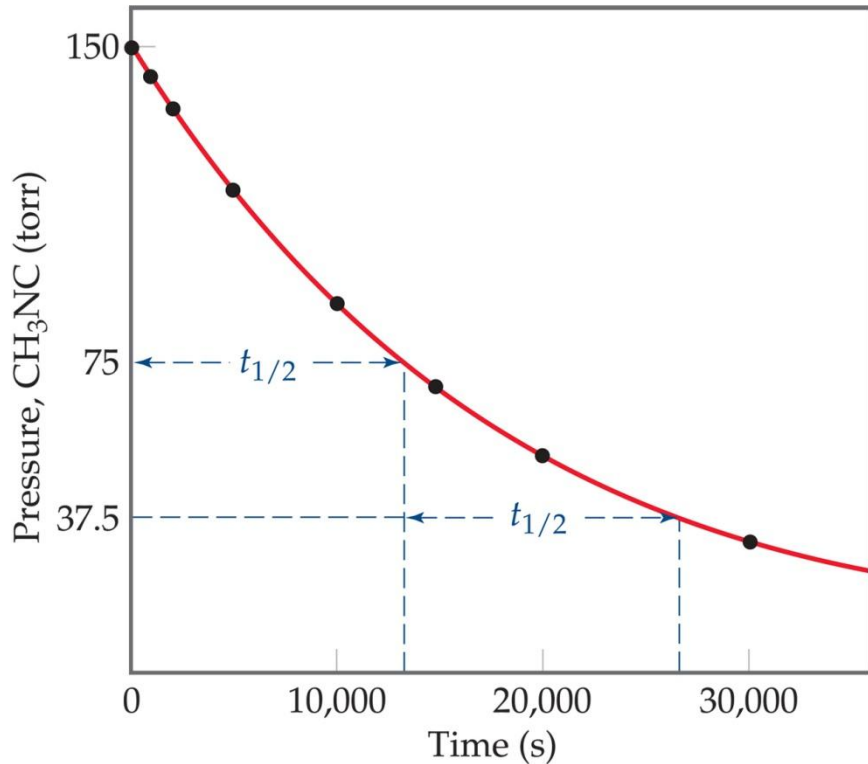
Half-Life

- Half-life is defined as the time required for one-half of a reactant to react.

- Because [A] at $t_{1/2}$ is one-half of the original [A],

$$[A]_t = 0.5 \, [A]_0.$$

Half-Life

For a first-order process, this becomes

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

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

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

NOTE: For a first-order process, the half-life does not depend on $[A]_0$.

Chemical Kinetics

Half-Life

For a second-order process,
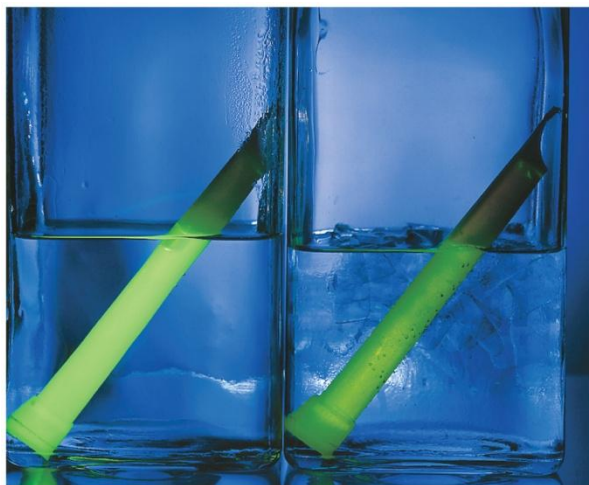
$$\frac{1}{0.5\,[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

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

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

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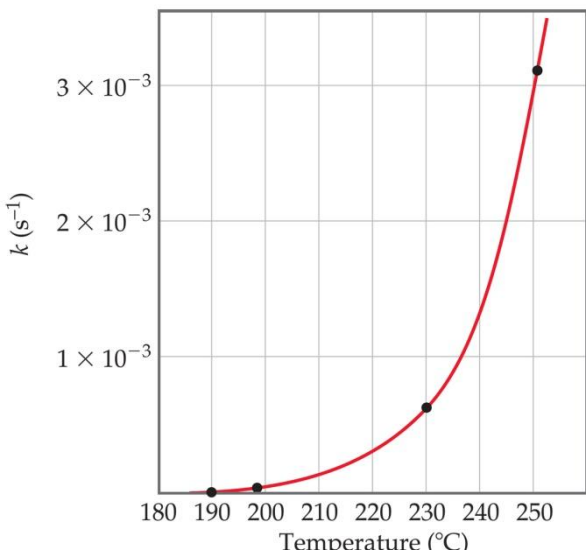
Chemical
Kinetics

Temperature and Rate

Higher temperature   Lower temperature

- Generally, as temperature increases, so does the reaction rate.

- This is because k is temperature dependent.

Chemical Kinetics

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.

- Molecules can only react if they collide with each other.

Chemical Kinetics

The Collision Model

Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.

Before collision   Collision   After collision
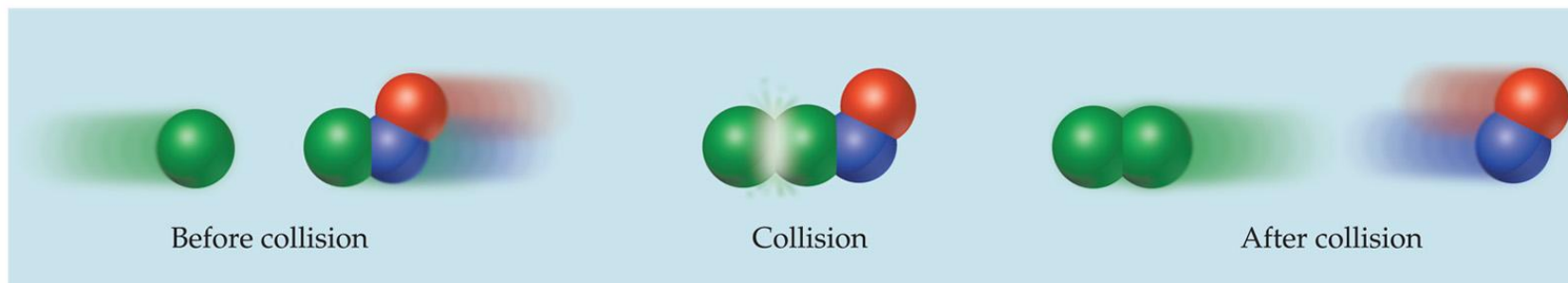
Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the activation energy, E_a.

- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.


Chemical Kinetics

Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.
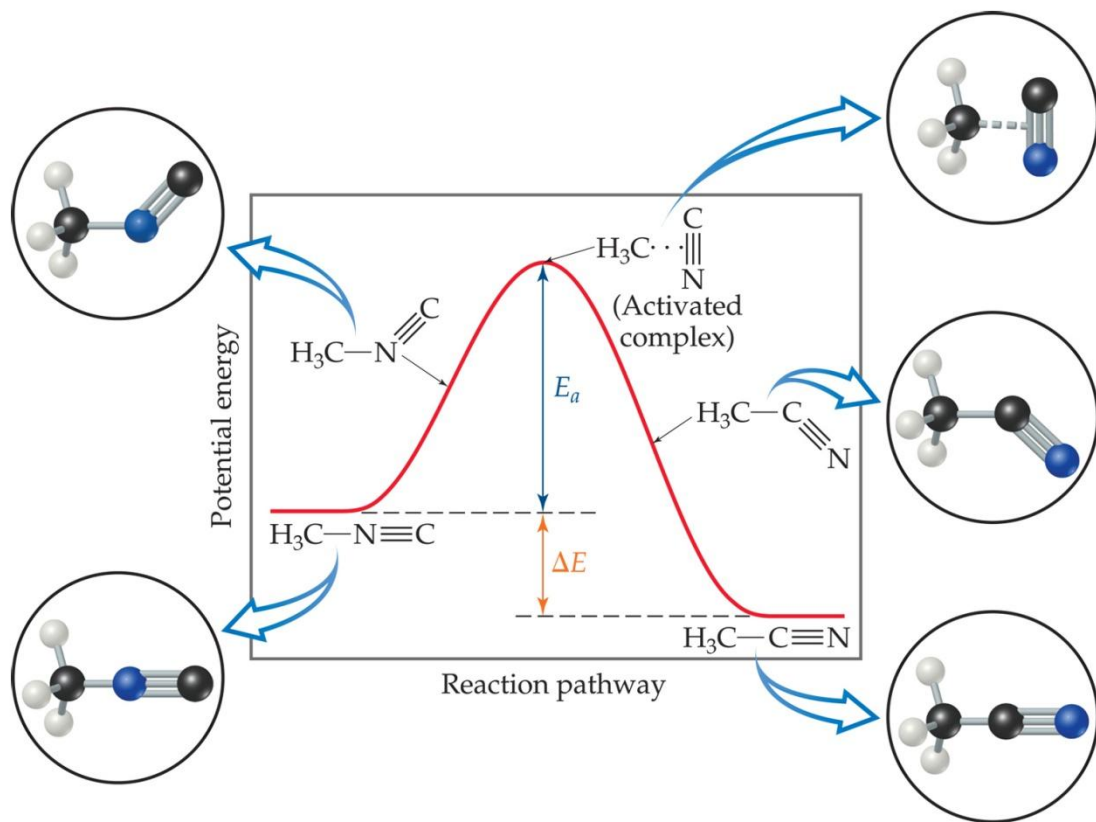
Reaction Coordinate Diagrams

- It shows the energy of the reactants and products (and, therefore, ΔE).

- The high point on the diagram is the transition state.

- The species present at the transition state is called the activated complex.

- The energy gap between the reactants and the activated complex is the activation energy barrier.
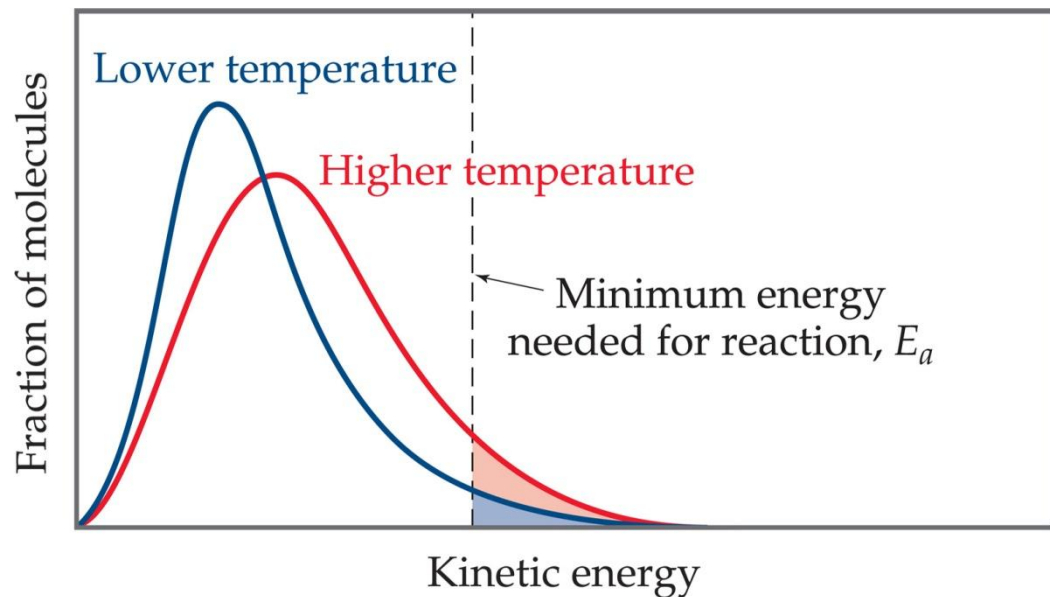

Chemical
Kinetics
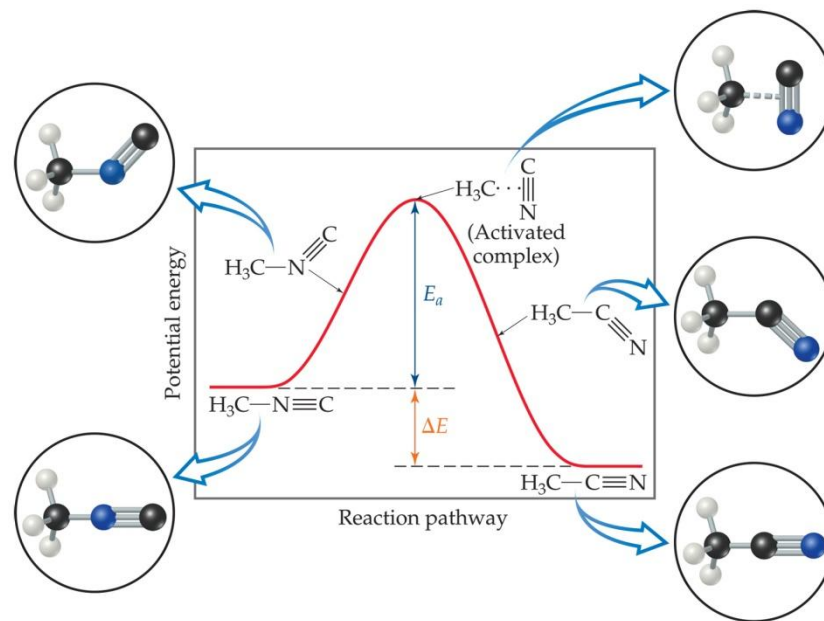
Maxwell–Boltzmann Distributions
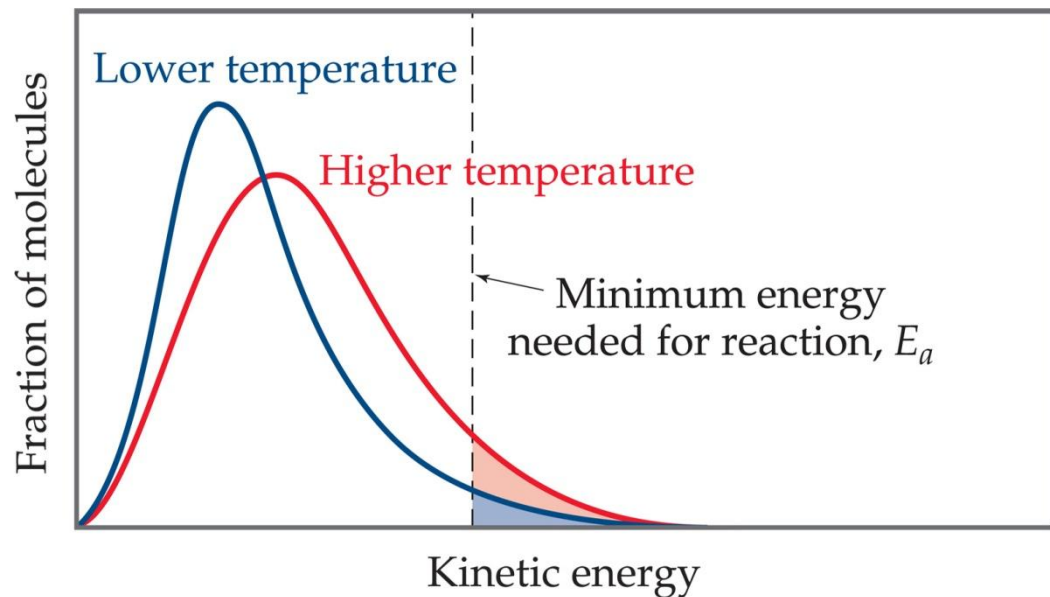
- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.

Chemical Kinetics

Maxwell–Boltzmann Distributions

- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.

Chemical Kinetics

Maxwell–Boltzmann Distributions

- If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.
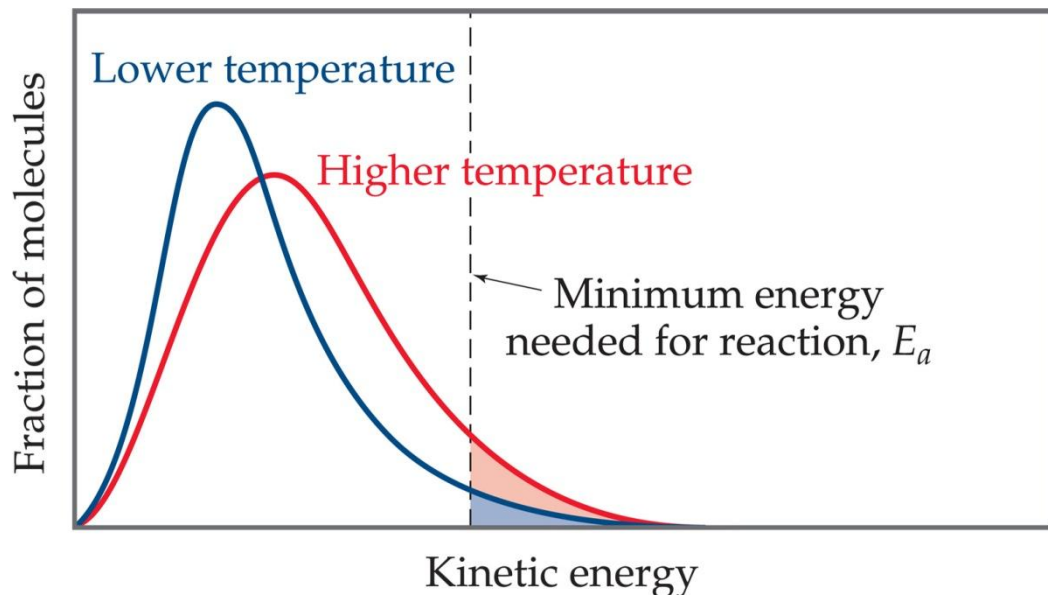
- As a result, the reaction rate increases.
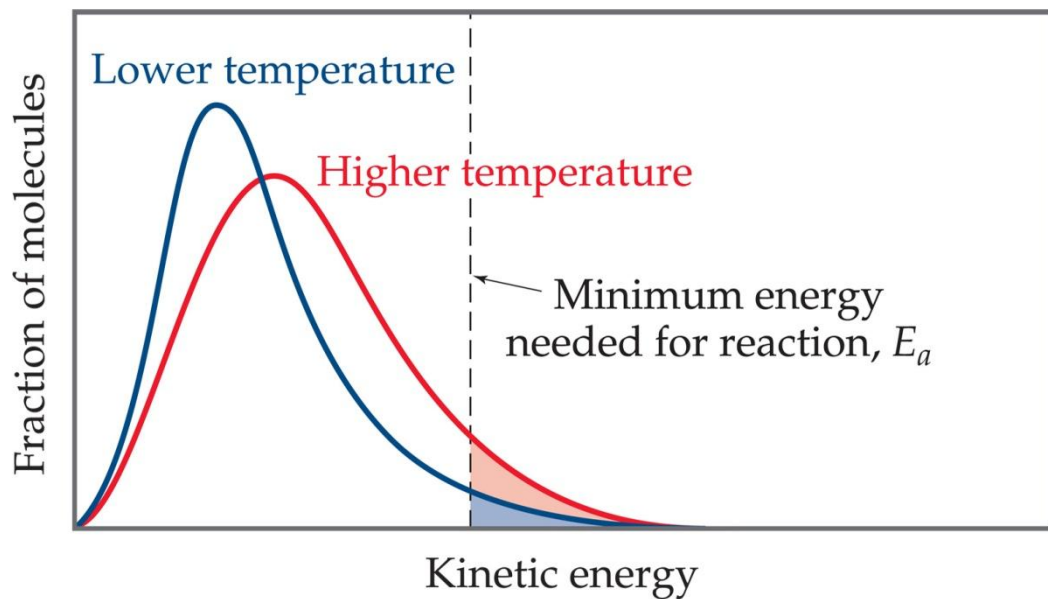

Chemical Kinetics

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{-E_a/RT}$$

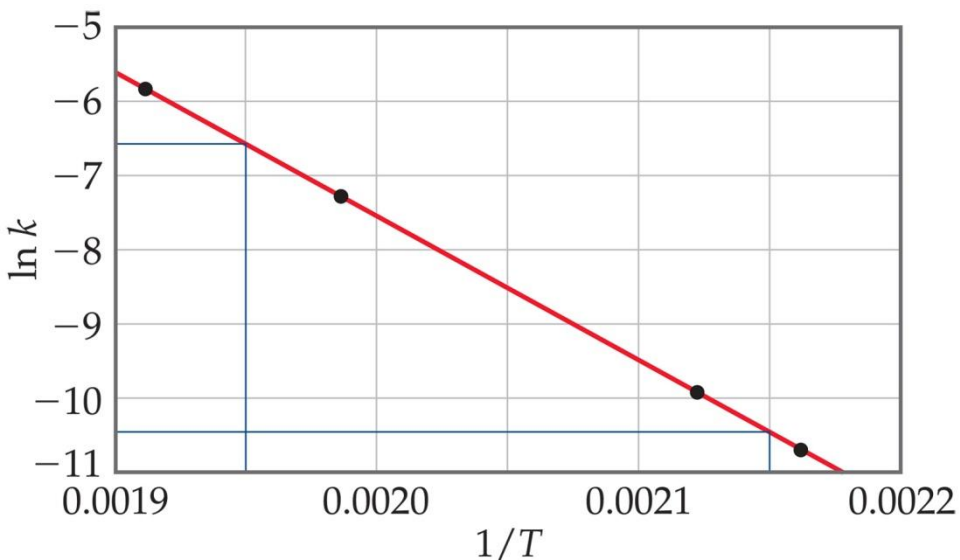where R is the gas constant and T is the Kelvin temperature.

Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

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

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Chemical Kinetics

Arrhenius Equation

Taking the natural logarithm of both sides, the equation becomes

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

$$y \;\; = \;\; mx + b$$

Therefore, if k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of ln k vs. 1/T.

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

Reaction Mechanisms

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	A $\longrightarrow$ products	Rate = $k[A]$
*Bi*molecular	A + A $\longrightarrow$ products	Rate = $k[A]^2$
*Bi*molecular	A + B $\longrightarrow$ products	Rate = $k[A][B]$
*Ter*molecular	A + A + A $\longrightarrow$ products	Rate = $k[A]^3$
*Ter*molecular	A + A + B $\longrightarrow$ products	Rate = $k[A]^2[B]$
*Ter*molecular	A + B + C $\longrightarrow$ products	Rate = $k[A][B][C]$

The molecularity of a process tells how many molecules are involved in the process.
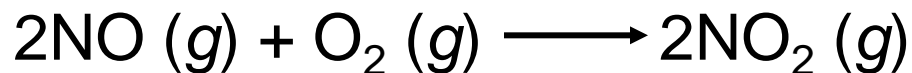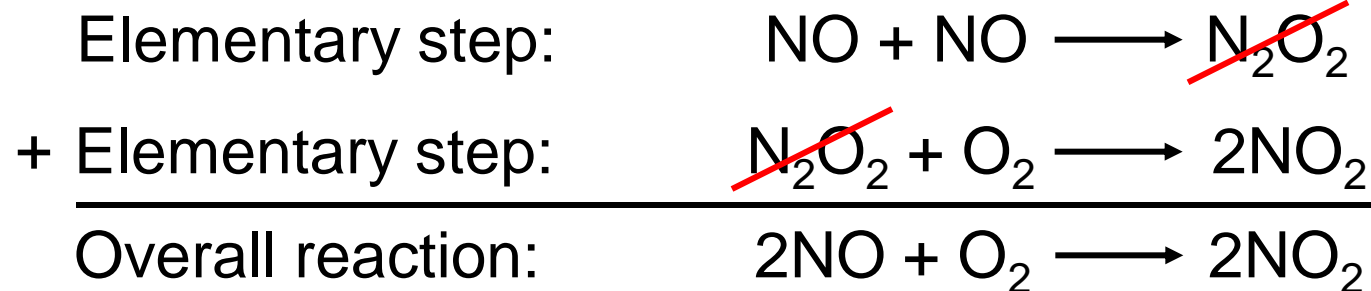
Chemical
Kinetics

Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple **elementary steps** or **elementary reactions.**

The sequence of **elementary steps** that leads to product formation is the **reaction mechanism**.

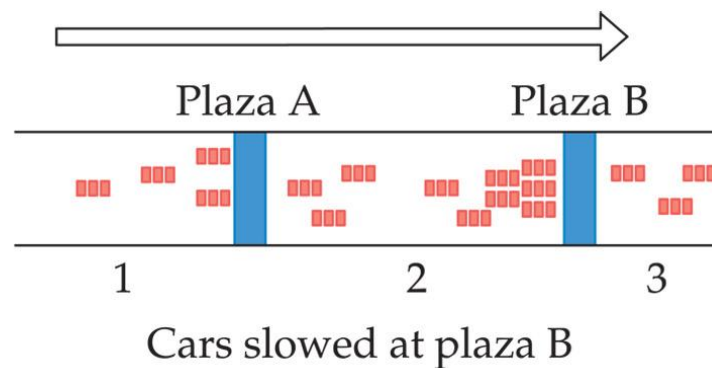$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$$

N_2O_2 is detected during the reaction!

Elementary step:	$NO + NO \longrightarrow N_2O_2$	
+ Elementary step:	$N_2O_2 + O_2 \longrightarrow 2NO_2$	
Overall reaction:	$2NO + O_2 \longrightarrow 2NO_2$	

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Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.

- The overall reaction cannot occur faster than this slowest, rate-determining step.

Cars slowed at plaza A

Cars slowed at plaza B

Chemical Kinetics

Slow Initial Step

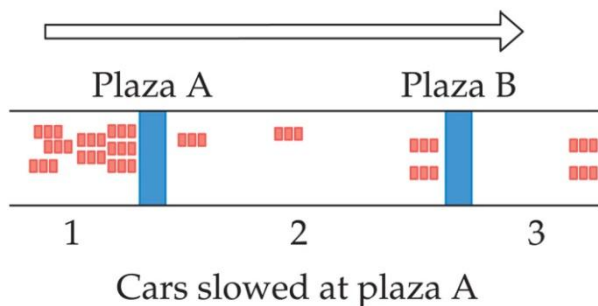$$NO_2 \ (g) + CO \ (g) \longrightarrow NO \ (g) + CO_2 \ (g)$$
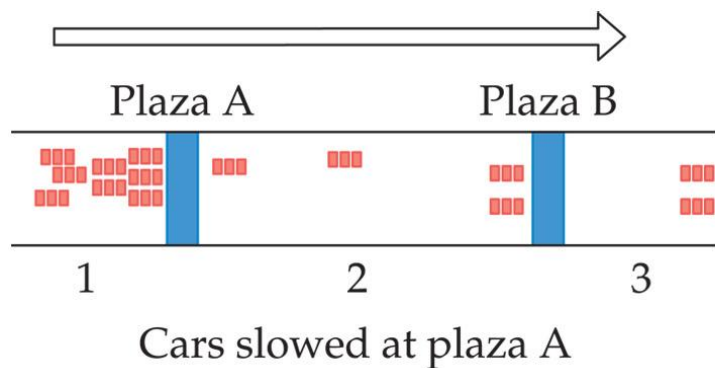
- The rate law for this reaction is found experimentally to be
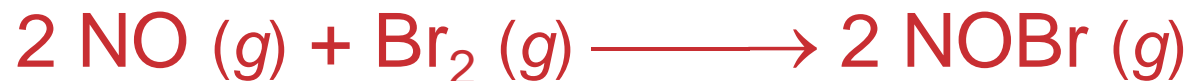
$$\text{Rate} = k \ [NO_2]^2$$

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.

- This suggests the reaction occurs in two steps.

Chemical Kinetics

Slow Initial Step

- A proposed mechanism for this reaction is

    Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

    Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)

- The NO_3 intermediate is consumed in the second step.

- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.

Plaza A   Plaza B

1   2   3

Cars slowed at plaza A

Fast Initial Step

$$2\ NO\ (g) + Br_2\ (g) \longrightarrow 2\ NOBr\ (g)$$

- The rate law for this reaction is found to be

$$\text{Rate} = k\ [NO]^2\ [Br_2]$$

- Because termolecular processes are rare, this rate law suggests a two-step mechanism.

Chemical Kinetics

Fast Initial Step

- A proposed mechanism is

Step 1: $NO + Br_2 \rightleftharpoons NOBr_2$ (fast)

Step 2: $NOBr_2 + NO \longrightarrow 2\ NOBr$ (slow)

Step 1 includes the forward *and* reverse reactions.

Chemical Kinetics

Fast Initial Step

- The rate of the overall reaction depends upon the rate of the slow step.

- The rate law for that step would be

$$\text{Rate} = k_2 \, [\text{NOBr}_2] \, [\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?

Chemical Kinetics

Fast Initial Step

- NOBr$_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br$_2$
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$\text{Rate}_f = \text{Rate}_r$$

Fast Initial Step

- Because Rate$_f$ = Rate$_r$,

$$k_1 \, [NO] \, [Br_2] = k_{-1} \, [NOBr_2]$$

- Solving for $[NOBr_2]$ gives us

$$\frac{k_1}{k_{-1}} \, [NO] \, [Br_2] = [NOBr_2]$$

Chemical Kinetics
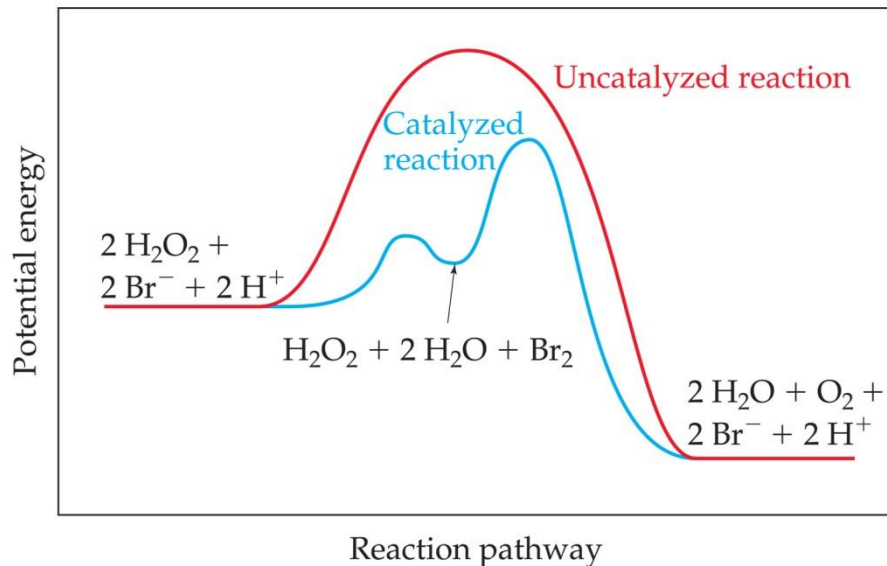
Fast Initial Step

Substituting this expression for [NOBr$_2$] in the rate law for the rate-determining step gives

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} \, [\text{NO}] \, [\text{Br}_2] \, [\text{NO}]$$

$$= k \, [\text{NO}]^2 \, [\text{Br}_2]$$
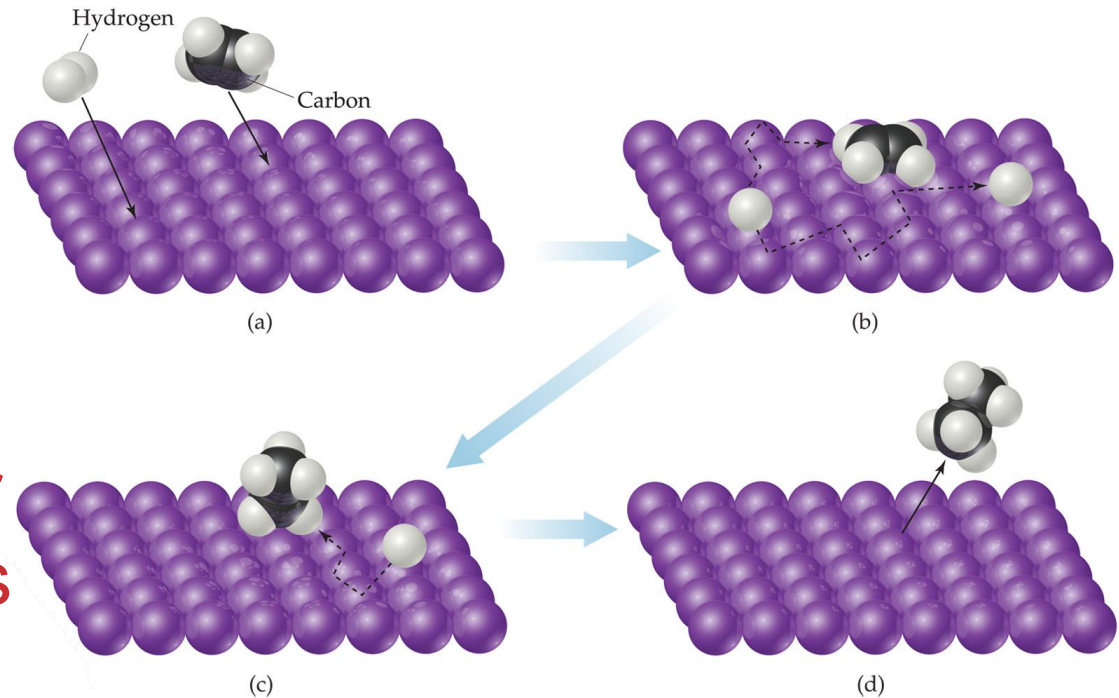
Chemical Kinetics

Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.

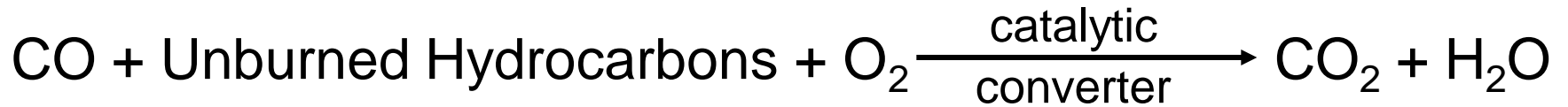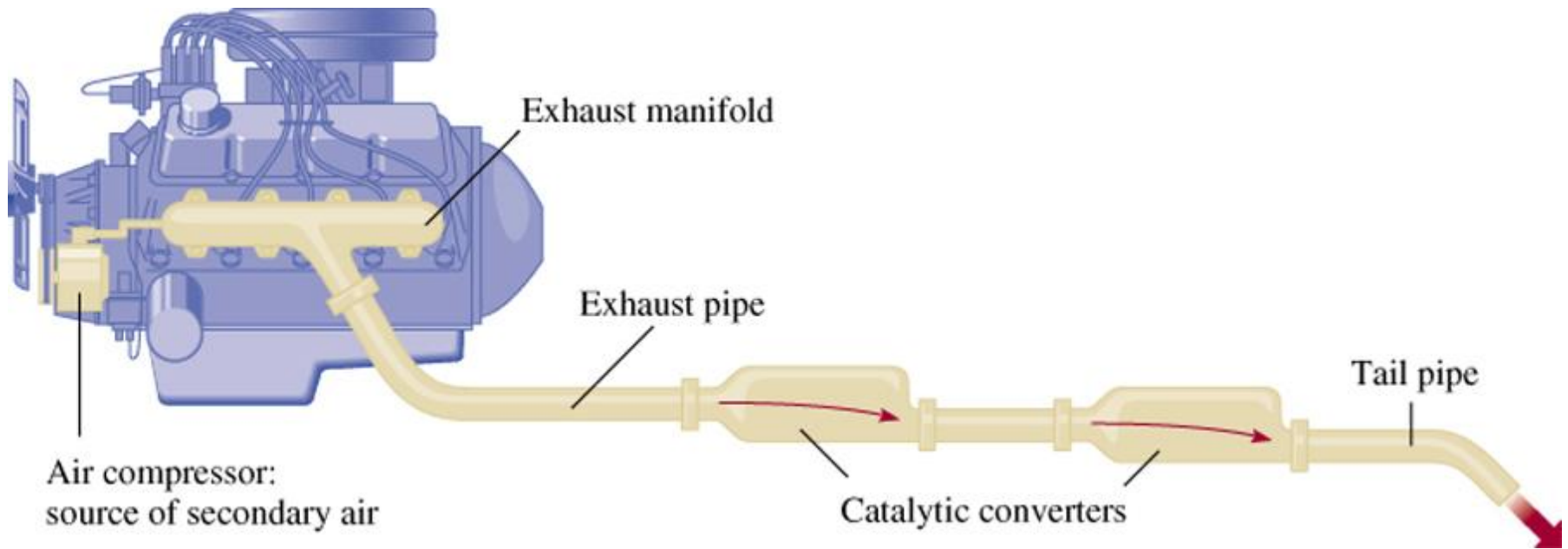- Catalysts change the mechanism by which the process occurs.

Chemical Kinetics

Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.

Chemical Kinetics

Catalytic Converters

Exhaust manifold

Exhaust pipe

Tail pipe

Air compressor:
source of secondary air

Catalytic converters

$$CO + \text{Unburned Hydrocarbons} + O_2 \xrightarrow[\text{converter}]{\text{catalytic}} CO_2 + H_2O$$

$$2NO + 2NO_2 \xrightarrow[\text{converter}]{\text{catalytic}} 2N_2 + 3O_2$$

Chemical
Kinetics

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Enzyme Catalysis

Substrate
+
Enzyme

Enzyme-substrate
complex

Products
+
Enzyme

13.6