Chapter 14: Kinetics

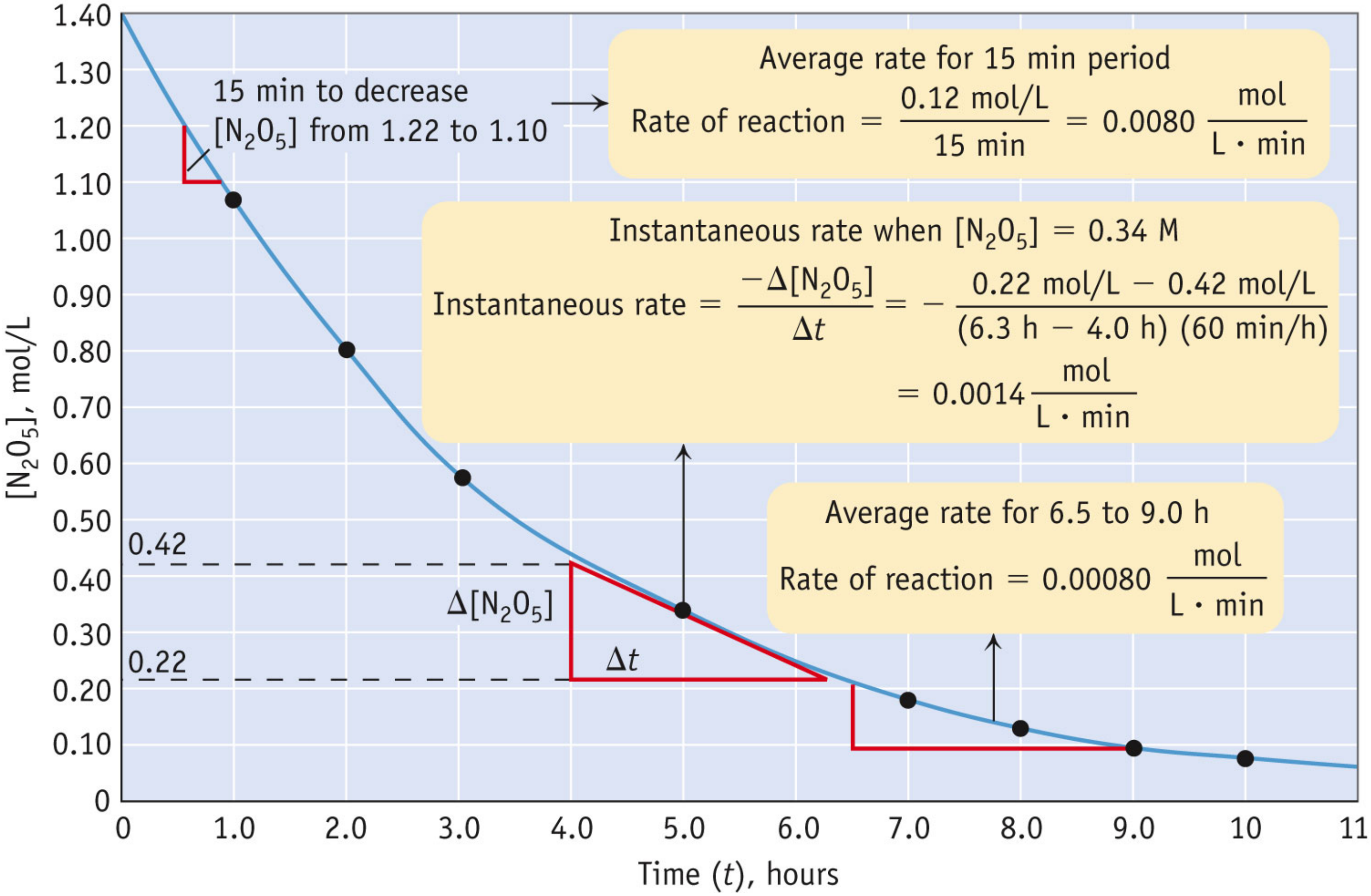
Chapter outline

- Rates of chemical reactions
- Effects of reaction conditions on rates
- Differential rate laws
  - Rate constant and rate equations
  - Method of initial rates
- Integrated rate laws
  - Zero-, first- and second-order reactions
  - Concentration vs. time graphs
- Reaction rates on a particle level
  - Activation energy
  - Arrhenius equation
- Reaction mechanisms

Reaction rate

- Reaction rate = how fast does a reaction proceed
- $Reaction\ rate = \dfrac{change\ in\ concentration}{change\ in\ time}$
- Average rate: change in concentration over a given time interval
- Instantaneous rate: slope of line tangent to concentration vs. time curve at any point in time

Reaction rate



15 min to decrease $[N_2O_5]$ from 1.22 to 1.10

Average rate for 15 min period

$$\text{Rate of reaction} = \frac{0.12\ \text{mol/L}}{15\ \text{min}} = 0.0080\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Instantaneous rate when $[N_2O_5] = 0.34$ M

$$\text{Instantaneous rate} = \frac{-\Delta[N_2O_5]}{\Delta t} = -\frac{0.22\ \text{mol/L} - 0.42\ \text{mol/L}}{(6.3\ \text{h} - 4.0\ \text{h})\ (60\ \text{min/h})}$$

$$= 0.0014\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Average rate for 6.5 to 9.0 h

$$\text{Rate of reaction} = 0.00080\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Reaction rate in stoichiometry

- Consider the decomposition of peroxide
- $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$
- H_2O_2 is disappearing while H_2O and O_2 are formed
- H_2O is formed at twice the rate of O_2
- To make sure that the reaction rate is calculated to be the same, regardless which reactant/product we pick to calculate it:
  - $aA + bB \rightarrow cC + dD$
  - $\boldsymbol{Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta \mathrm{t}} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta \mathrm{t}}}$

Effects of reaction conditions on rate

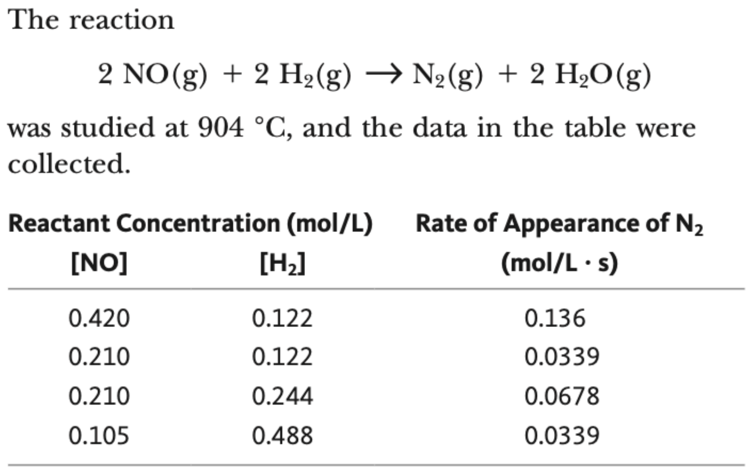
- Increasing **concentration** (of solutes in an aqueous solution) or **pressure** (in a reaction between gas particles) causes the rate of the reaction to increase
  - Exception: zero-order reactions
- Increasing the **surface area** of a solid reactant causes the rate of the reaction to increase
- Increasing **temperature** causes the rate of the reaction to increase
- **Catalysts** are substances that cause an increase in the rate of the reaction without being consumed
  - To understand how catalysts work, we need to study reaction mechanisms

Rate equations (differential rate laws)

- aA + bB → cC + dD
- $\boldsymbol{Rate = k[A]^m[B]^n}$
- k = rate constant (units will depend on the rate equation)
- m, n can only be determined experimentally
  - Usually positive integers, but can be negative integers, fractions or zero
- Order of the reaction = m+n
  - Zero-order: rate = k
  - First-order: rate = k[A]
  - Second-order: rate = $k[A]^2$, rate = k[A][B]

Determining rate equations

- Method of initial rates



The reaction

$$2\ NO(g) + 2\ H_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$$

was studied at 904 °C, and the data in the table were collected.

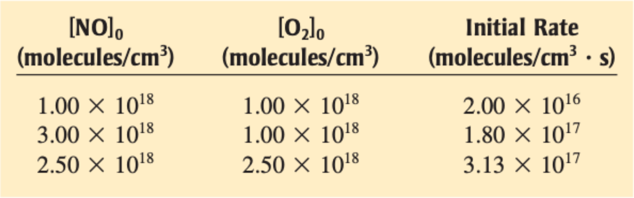
Reactant Concentration (mol/L)		**Rate of Appearance of N_2**
[NO]	**[H_2]**	**(mol/L · s)**
0.420	0.122	0.136
0.210	0.122	0.0339
0.210	0.244	0.0678
0.105	0.488	0.0339

Sample problem

The reaction

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

was studied, and the following data were obtained where rate = $-\frac{\Delta[O_2]}{\Delta t}$



$[NO]_0$ (molecules/cm^3)	$[O_2]_0$ (molecules/cm^3)	Initial Rate (molecules/cm^3 · s)
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

What would be the initial rate for an experiment where $[NO]_0 = 6.21 \times 10^{18}$ molecules/cm^3 and $[O_2]_0 = 7.36 \times 10^{18}$ molecules/cm^3?

Integrated rate laws

- Integrated rate laws: equation produced by integrating differential rare laws
- Useful when it comes to relating time and concentration

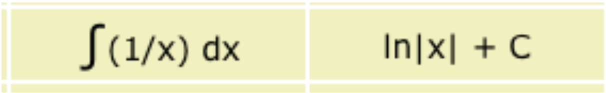
First-order reactions

- Express differential first-order rate law as an infinitesimal change of concentration d[A] in infinitesimally short time dt (=derivative of [A] with respect to time)
- $-\frac{d[A]}{dt} = k[A]$
- Rearrange to have all [A] terms on one side and all t terms on another side
- $-\frac{d[A]}{[A]} = k[dt]$
- Express the equation in integral form
- $-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k\int_0^t dt$

$[A]_0$ = initial concentration. 0 = initial time.

First-order reactions

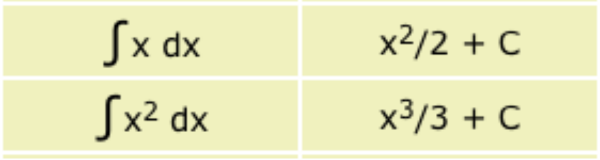
- $-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k\int_0^t dt$
- Integrate the equation
- $-(\ln[A] - \ln[A]_0) = kt$ or $\mathbf{\ln[A] - \ln[A]_0 = -kt}$
- The equation can also be rewritten as:
- $ln\frac{[A]_0}{[A]} = kt$ or $\boldsymbol{ln\frac{[A]}{[A]_0} = -kt}$



$\int (1/x)\,dx$	$\ln\lvert x\rvert + C$

Second-order reactions

- $-\frac{\mathrm{d}[\mathrm{A}]}{dt} = k[A]^2$
- $-\frac{d[A]}{[A]^2} = k[dt]$
- $-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k\int_0^t dt$
- $-[-\frac{1}{[A]} - \left(-\frac{1}{[A]_0}\right)] = kt$ or $\boldsymbol{\frac{1}{[A]} - \frac{1}{[A]_0} = kt}$



$\int x\,dx$	$x^2/2 + C$
$\int x^2\,dx$	$x^3/3 + C$

$\int(x^n)dx \quad = \quad x^{n+1}/(n+1) + c$

Zero-order reactions

- $-\frac{\mathrm{d[A]}}{dt} = k$
- $-d[A] = k[dt]$
- $-\int_{[A]_0}^{[A]} d[A] = k\int_0^t dt$
- $-([A]-[A]_0) = kt$ or $\mathbf{[A]_0 - [A] = kt}$

$$\int_a^b dx = b - a$$

Sample problem

The gas-phase decomposition of HI

$$HI\ (g) \rightarrow \tfrac{1}{2}\ H_2\ (g) + \tfrac{1}{2}\ I_2\ (g)$$

has the rate equation $-\frac{\Delta[\mathrm{HI}]}{dt} = k[HI]^2$, where k = 30. M^{-1} min^{-1} at 443 ˚C. How much time does it take for the concentration of HI to drop from 0.010 M to 0.0050 M at 443 ˚C?

Concentration-time relationships: first-order

- First-order reactions: **$\ln[A]_0 - \ln[A] = kt$**
- $\ln[A] = -kt + \ln[A]_0$
- Linear relationship between ln[A] and t
- Plotting ln[A] vs. t will yield a straight line (slope = –k)

t(s)	$P \times 10^2$ atm	ln P
0	8.20	−2.50
1000	5.72	−2.86
2000	3.99	−3.22
3000	2.78	−3.58
4000	1.94	−3.94

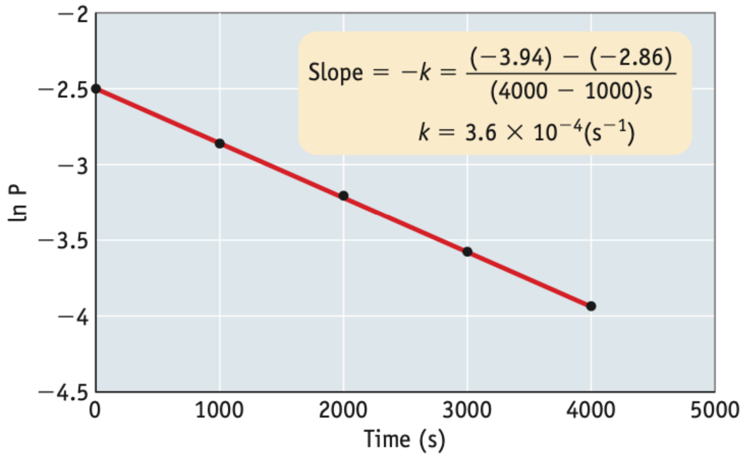


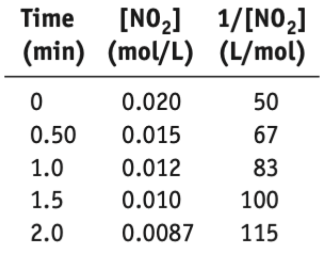
FIGURE 15.6 The decomposition of azomethane, $CH_3N_2CH_3$. If data for the decomposition of azomethane,

$$CH_3N_2CH_3(g) \longrightarrow CH_3CH_3(g) + N_2(g)$$

are plotted as the natural logarithm of the $CH_3N_2CH_3$ pressure versus time, the result is a straight line with a negative slope. This indicates a first-order reaction. The rate constant $k = -$slope.

Concentration-time relationships: second-order

- Second-order reactions: $\mathbf{\frac{1}{[A]} - \frac{1}{[A]_0} = kt}$
- $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
- Linear relationship between 1/[A] and t
- Plotting 1/[A] vs. t will yield a straight line (slope = k)



Time (min)	$[NO_2]$ (mol/L)	$1/[NO_2]$ (L/mol)
0	0.020	50
0.50	0.015	67
1.0	0.012	83
1.5	0.010	100
2.0	0.0087	115

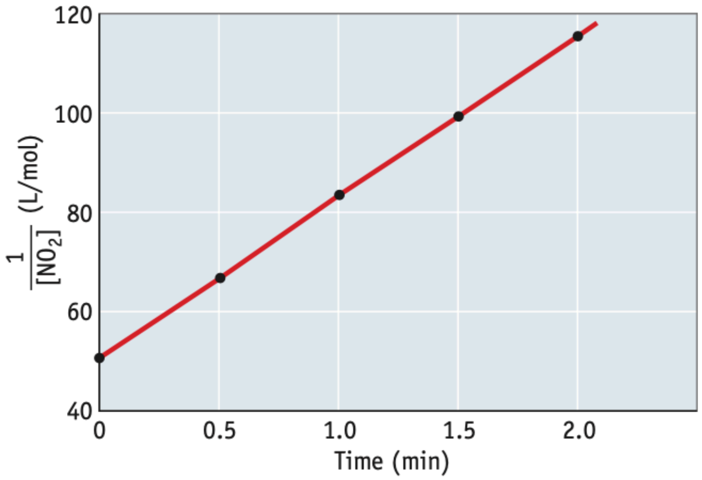


FIGURE 15.7 A second-order reaction. A plot of $1/[NO_2]$ versus time for the decomposition of NO_2,

$$NO_2(g) \longrightarrow NO(g) + \tfrac{1}{2}\, O_2(g)$$

results in a straight line. This confirms this is a second-order reaction. The slope of the line equals the rate constant for this reaction.

Concentration-time relationships: zero-order

- Zero-order reactions:

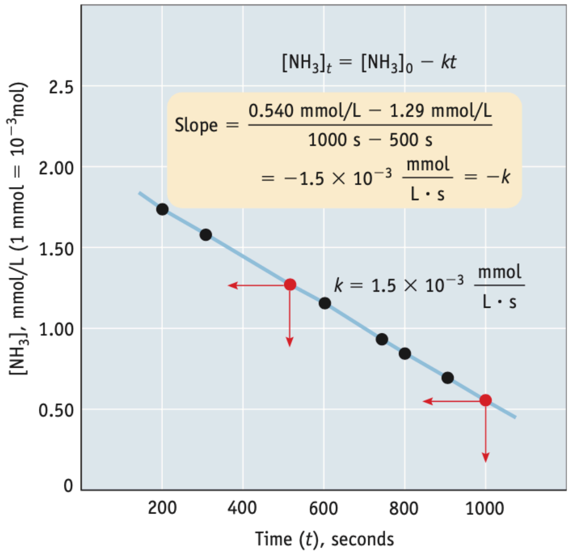
  $[A]_0 - [A] = kt$

- $[A] = -kt + [A]_0$
- Linear relationship between [A] and t
- Plotting [A] vs. t will yield a straight line (slope = –k)

FIGURE 15.8 Plot of a zero-order reaction. A graph of the concentration of ammonia, $[NH_3]_t$, against time for the decomposition of NH_3.

$$NH_3(g) \rightarrow \tfrac{1}{2} N_2(g) + \tfrac{3}{2} H_2(g)$$

on a metal surface at 856 °C is a straight line, indicating that this is a zero-order reaction. The rate constant, k, for this reaction is found from the slope of the line; $k = -\text{slope}$. (The points chosen to calculate the slope are given in red.)



Half-life

- Half-life = time needed for the concentration to decrease to 50% its initial value ½
- Writing expressions for the half-life of first-, second- and zero-order reactions
  - Simple – just substitute $[A]_0/2$ for $[A]$
- First-order: $\ln[A]_0 - \ln[A] = kt$
- $ln[A]_0 - ln\frac{[A]_0}{2} = kt_{½}$
- $\ln 2 = kt_{½}$ or $\boldsymbol{t_{½} = \frac{ln2}{k} = \frac{0.693}{k}}$
- For first-order reactions, half-life is independent of $[A]_0$

Half-life expressions for second-order and zero-order reactions

- Second-order: $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
- $\frac{1}{\frac{[A]_0}{2}} - \frac{1}{[A]_0} = kt_{½}$
- $\frac{1}{[A]_0} = kt_{½}$ or
- $\boldsymbol{t_{½} = \frac{1}{k[A]_0}}$

- Zero-order: $[A]_0 - [A] = kt$
- $[A]_0 - \frac{[A]_0}{2} = kt_{½}$
- $\frac{[A]_0}{2} = kt_{½}$ or
- $\boldsymbol{t_{½} = \frac{[A]_0}{2k}}$

Sample problem

Sucrose, $C_{12}H_{22}O_{11}$, decomposes to fructose and glucose in acid solution with the rate law

$$\text{Rate} = k[C_{12}H_{22}O_{11}] \qquad k = 0.216\ \text{h}^{-1} \text{ at } 25\ ^\circ\text{C}$$

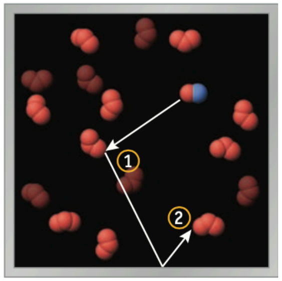
1. What is the half-life of $C_{12}H_{22}O_{11}$ at this temperature?
2. What amount of time is required for 87.5% of the initial concentration of $C_{12}H_{22}O_{11}$ to decompose?

Sample problem

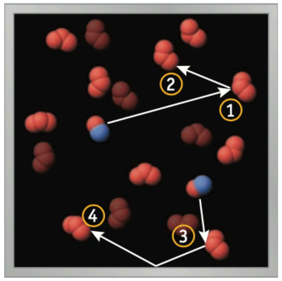
Radioactive decay is a first-order process. Radioactive radon-222 gas (^{222}Rn) occurs naturally as a product of uranium decay. The half-life of ^{222}Rn is 3.8 days. Suppose a flask originally contained 4.0×10^{13} atoms of ^{222}Rn. How many atoms of ^{222}Rn will remain after one month (30. days)?

Collision theory of reaction rates

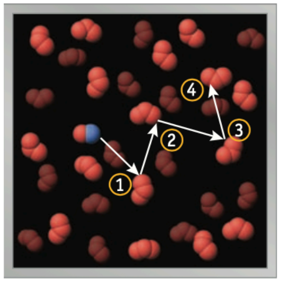
- To really understand reaction rates, we must look at the particle level
- In order to react, the particles must
  - Collide with each other
  - Collide with sufficient energy
  - Collide with proper orientation



(a) 1 NO : 16 O_3 — *2 hits/second.*
A single NO molecule, moving among sixteen O_3 molecules, is shown colliding with two of them per second.



(b) 2 NO : 16 O_3 — *4 hits/second.*
If two NO molecules move among 16 O_3 molecules, we would predict that four NO—O_3 collisions would occur per second.

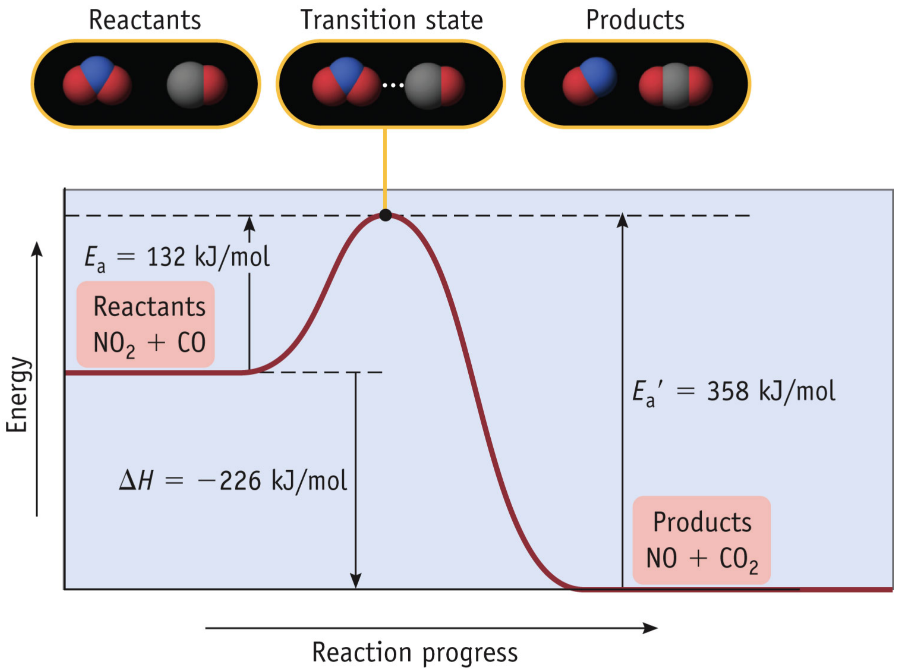


(c) 1 NO : 32 O_3 — *4 hits/second.*
If the number of O_3 molecules is doubled (to 32), the frequency of NO—O_3 collisions is also doubled, to four per second.

$$\text{NO (g)} + O_3\text{ (g)} \rightarrow NO_2\text{ (g)} + O_2\text{ (g)}$$

Activation energy, E_a

- The energy barrier that needs to be overcome for the reaction to happen
  - Recall that to break bonds we need to supply energy
  - High E_a = slow rate (fewer particles will possess sufficient energy)
  - Low E_a = fast rate

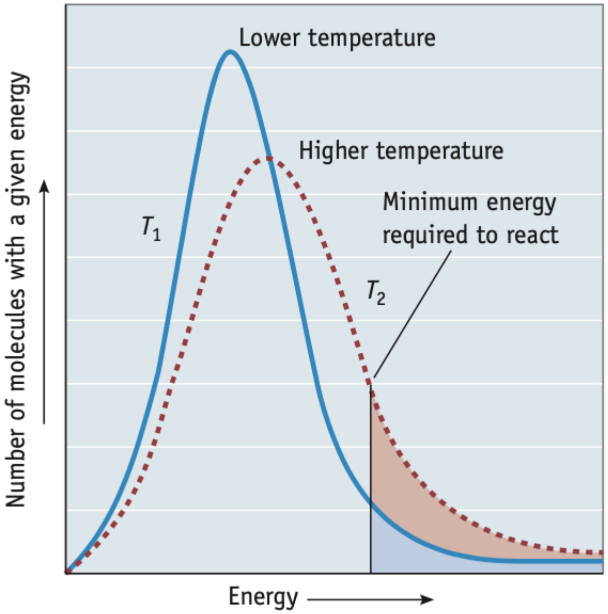


Reaction coordinate

$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$

Effect of temperature on rate

- As T goes up, average kinetic energy of the particles goes up
- More particles possess sufficient energy to overcome the energy barrier
- Rate increases

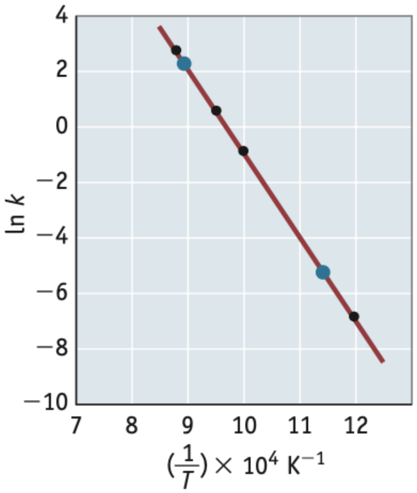


Arrhenius equation

- $\boldsymbol{k = Ae^{\frac{-E_a}{RT}}}$
- k = rate constant
- E_a = activation energy (J/mol)
- R = gas constant (8.314 J K^{-1} mol^{-1})
- T = temperature (K)
- A = frequency factor
  - Reaction specific
  - Related to fraction of collisions with proper orientation

Arrhenius plot

- $k = Ae^{\frac{-E_a}{RT}}$ can be rewritten as
- $lnk = -\left(\frac{E_a}{R}\right)\frac{1}{T} + lnA$
- Linear relationship
- Allows us to calculate E_a if we know the values of rate constants at various temperatures
  - Plot lnk vs. 1/T; slope = $-\frac{E_a}{R}$
- Algebraic form: $lnk_2 - lnk_1 = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$

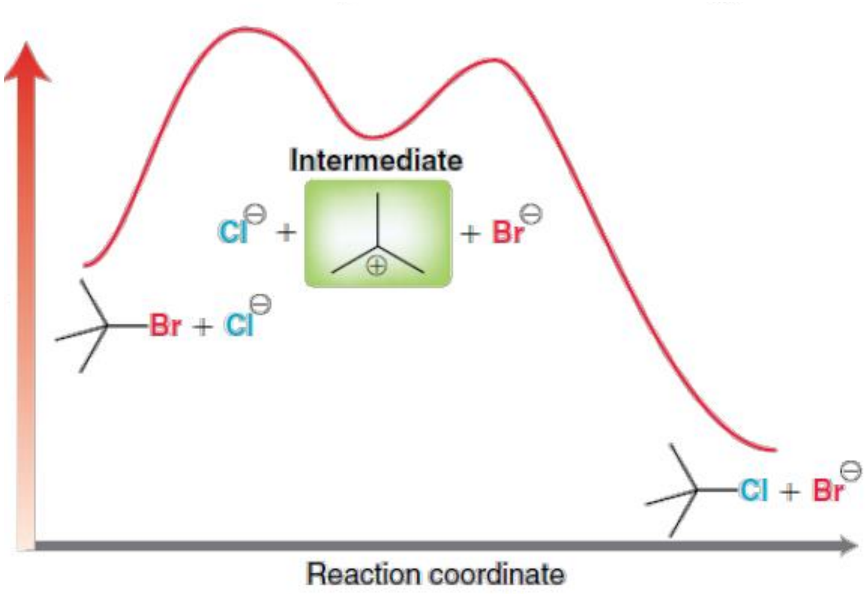


Sample problem

A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22 ˚C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

Reaction mechanisms

- Mechanism = how the reaction happens on a particle level
  - May have many **elementary steps**
  - Transition states
  - Intermediates
  - Relative energies of all species can be seen on the reaction coordinate



Overall reaction: $(CH_3)_3CBr + Cl^- \rightarrow (CH_3)_3CCl + Br^-$
Step 1: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$
Step 2: $(CH_3)_3C^+ + Cl^- \rightarrow (CH_3)_3CCl$

$(CH_3)_3C^+$ = intermediate

Molecularity of elementary steps

- Unimolecular = only one molecule involved in a step
- Bimolecular = two molecules involved
- Termolecular = three molecules involved
- Higher molecularities have not been observed in nature
  - The odds of >3 molecules colliding in a single step are low
- Rate laws of elementary steps can be seen from the stoichiometry
  - $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ rate = $k[(CH_3)_3CBr]$
  - $(CH_3)_3C^+ + Cl^- \rightarrow (CH_3)_3CCl$ rate = $k'[(CH_3)_3C^+][Cl^-]$

Determining the rate law of a multistep reaction from elementary steps

- The slowest step of the reaction will determine the overall reaction rate
    - Step with the highest E_a
    - Rate-determining step
- Intermediates should not be present in overall reaction rate laws
- Initial fast equilibrium step: $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$

Sample problem

One of the earliest kinetic studies involved the gas phase reaction of hydrogen gas with iodine gas to make hydrogen iodide:

H_2 (g) + I_2 (g) → 2 HI (g). A proposed mechanism for this process is

- Step 1: $I_2 \Leftrightarrow 2\ I$ (fast, equilibrium)
- Step 2: $I + H_2 \Leftrightarrow H_2I$ (fast, equilibrium)
- Step 3: $H_2I + I \rightarrow 2\ HI$ (slow)

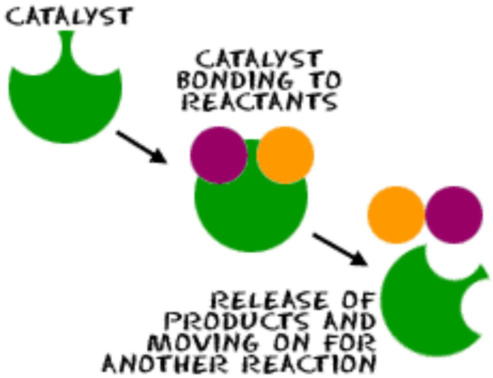
Write the rate law expected for this mechanism.

Determining mechanisms

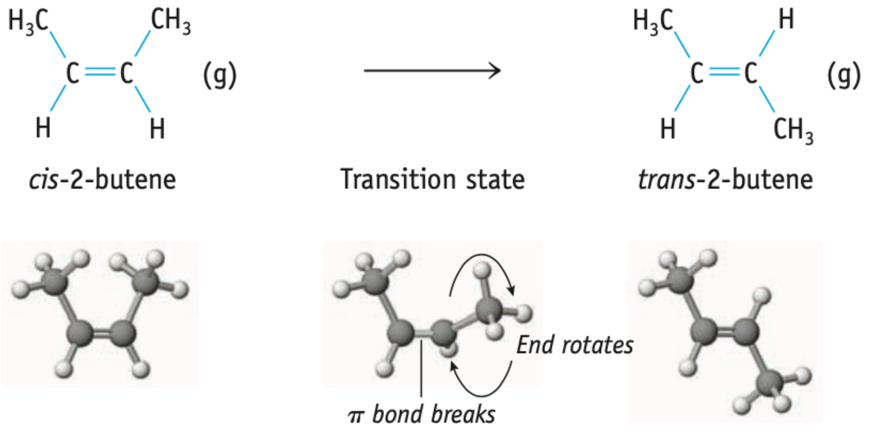
- Mechanisms cannot be “proven”
- We can gather experimental evidence that supports a mechanism
  - Figuring out on what species the rate depends (the rate law)
  - Isolating intermediates (if possible)
  - Eliminating alternative mechanisms (not consistent with experimental rate law)

Catalysts

- Not consumed during a reaction
- Accelerate reactions by providing an alternative mechanism with lower E_a
- Homogeneous and heterogeneous catalysis



Example: isomerization of *cis*-2-butene to *trans*-2-butene



E_a = 264 kJ/mol

Example: isomerization of *cis*-2-butene to *trans*-2-butene

I_2 catalyzes the reaction, providing an alternative mechanism
E_a ~ 150 kJ/mol