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Chapter 11

Rate of Reaction

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Outline



1. Meaning of reaction rate
2. Reaction rate and concentration
3. Reactant concentration and time
4. Models for reaction rate
5. Reaction rate and temperature
6. Catalysis
7. Reaction mechanisms

Thermochemistry



- We have looked at the energy involved in a chemical reaction
 - Chapter 7
 - Some reactions evolve heat (exothermic)
 - Some reactions absorb heat (endothermic)
 - In order for a chemical reaction to be ***feasible***, it must occur at a ***reasonable rate***

Factors that Influence the Rate of Reaction



- Concentration of reactants
- Process by which the reaction takes place
- Temperature
- Presence of a catalyst
- Reaction mechanism

11.1 Meaning of Reaction Rate

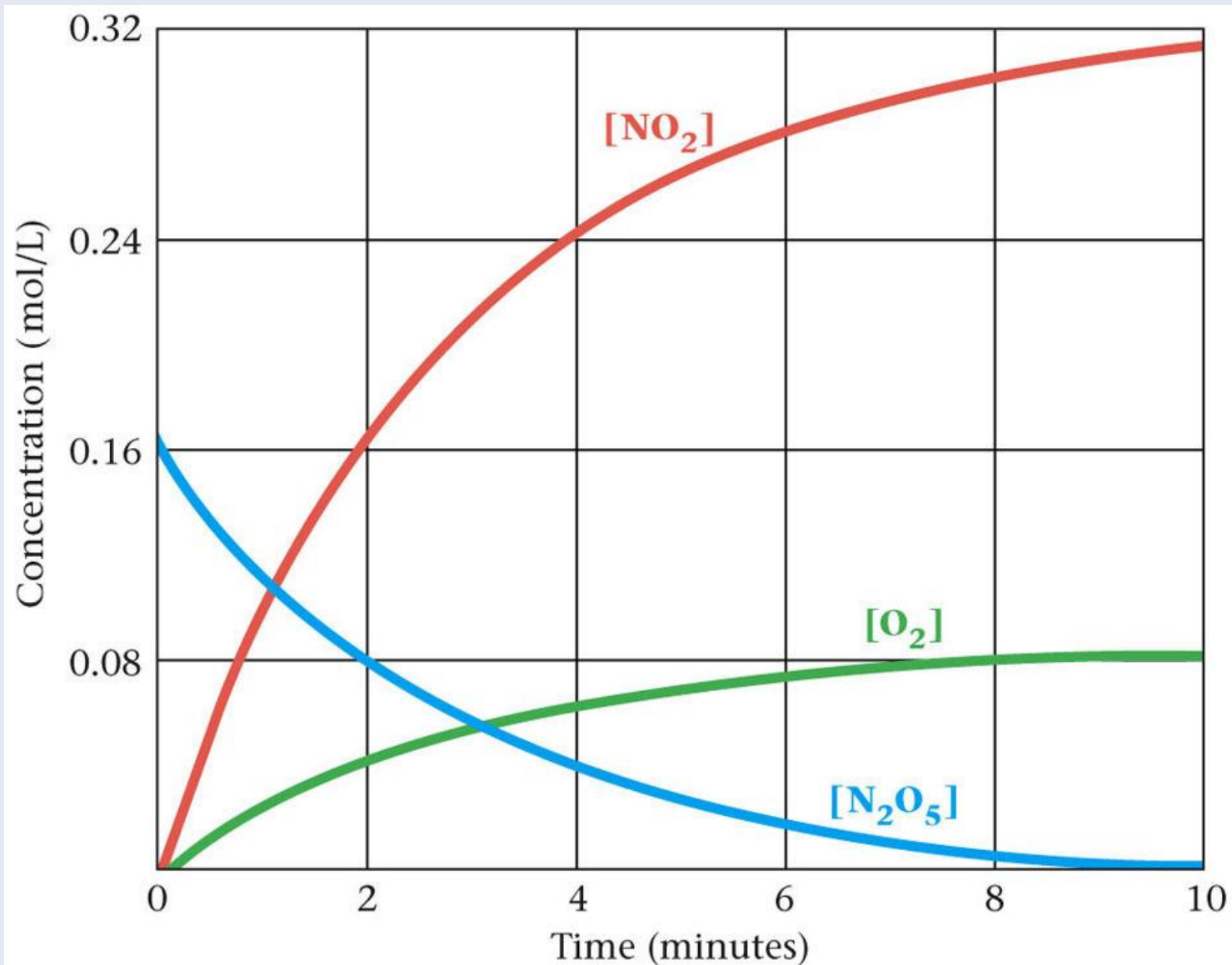


- $N_2O_5 (g) \rightarrow 2NO_2 (g) + \frac{1}{2}O_2 (g)$
 - What happens to the concentrations with time?
 - $[N_2O_5]$ decreases
 - $[NO_2]$ and $[O_2]$ increase
 - Mathematically, we can express the changes as

$$-\Delta[N_2O_5] = \frac{\Delta[NO_2]}{2} = \frac{\Delta[O_2]}{\frac{1}{2}}$$

$$rate = -\frac{\Delta[N_2O_5]}{\Delta t} = \frac{\Delta[NO_2]}{2\Delta t} = \frac{\Delta[O_2]}{\frac{1}{2}\Delta t}$$

Figure 11.1 Changes in reactant and product concentrations with time.



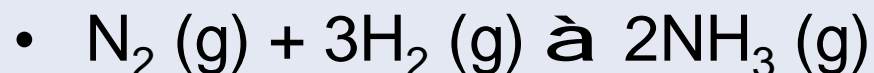
General Form of the Rate Relationship



- For a reaction where $aA + bB \rightarrow cC + dD$

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

Formation of Ammonia



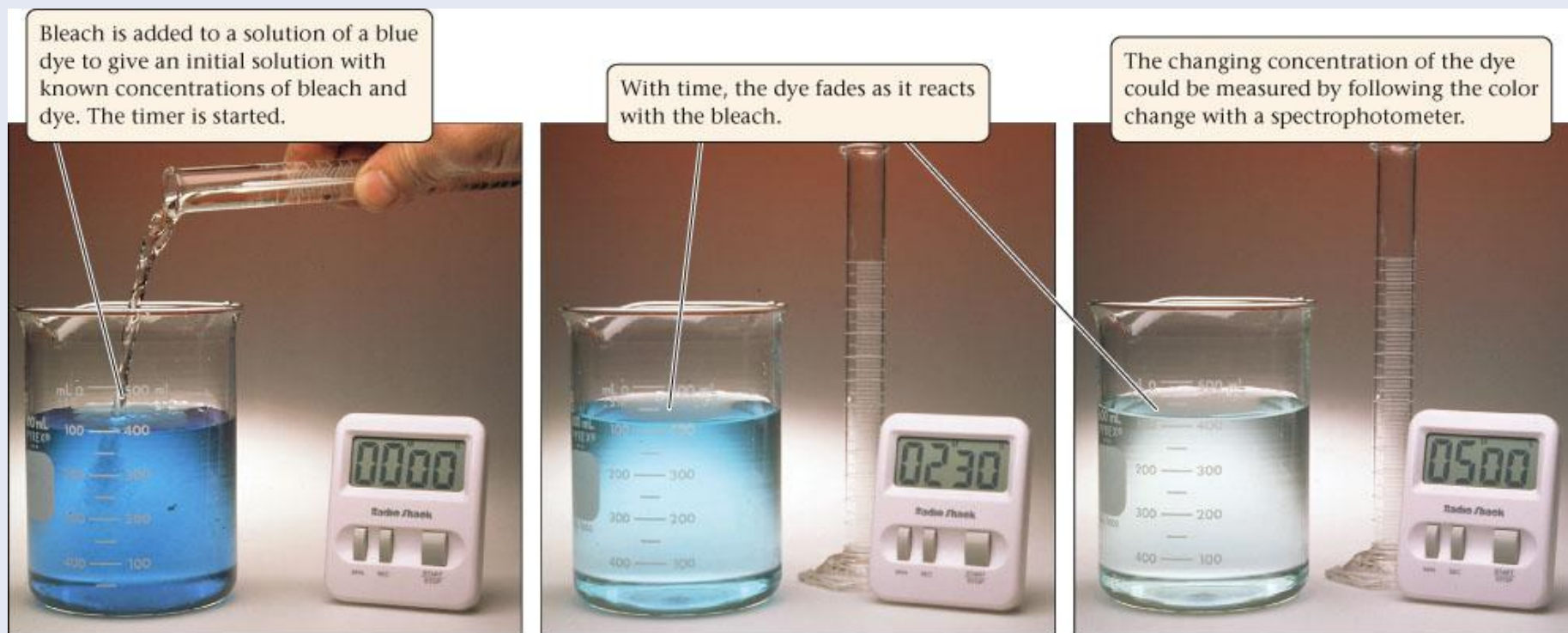
$$rate = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{-\Delta[NH_3]}{2\Delta t}$$

- If the N_2 is disappearing at 0.10 mol/L-min, the H_2 is disappearing at the rate of 0.30 mol/L-min and ammonia is appearing at a rate of 0.20 mol/L-min

Rate Measurements



- In order to measure a rate, something observable must change



(a)

(b)

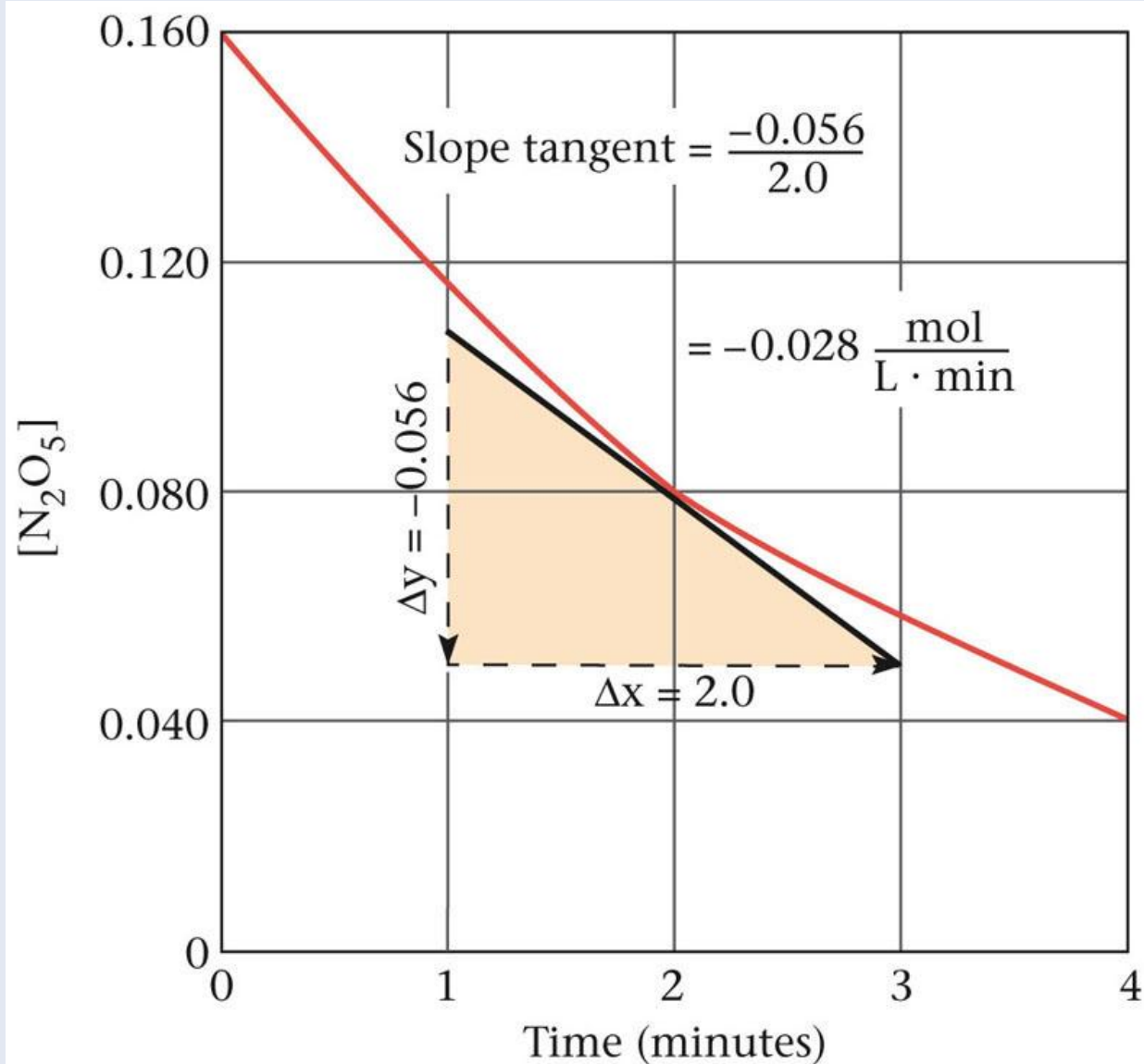
(c)

Rate Measurements, (Cont'd)



- The rate of a reaction can be determined by measuring
 - Absorption of visible light by the NO_2 that forms
 - NO_2 is reddish-brown
 - N_2O_5 is colorless
 - The change in pressure that results from the increase in the number of moles of gas
 - 1 mol reactant \rightarrow 2.5 mol product

Figure 11.2 – Instantaneous Rate



Instantaneous Rate



- The instantaneous rate of a reaction is determined by calculating the slope of the line tangent to the concentration-time curve at the desired time

11.2 Reaction Rate and Concentration

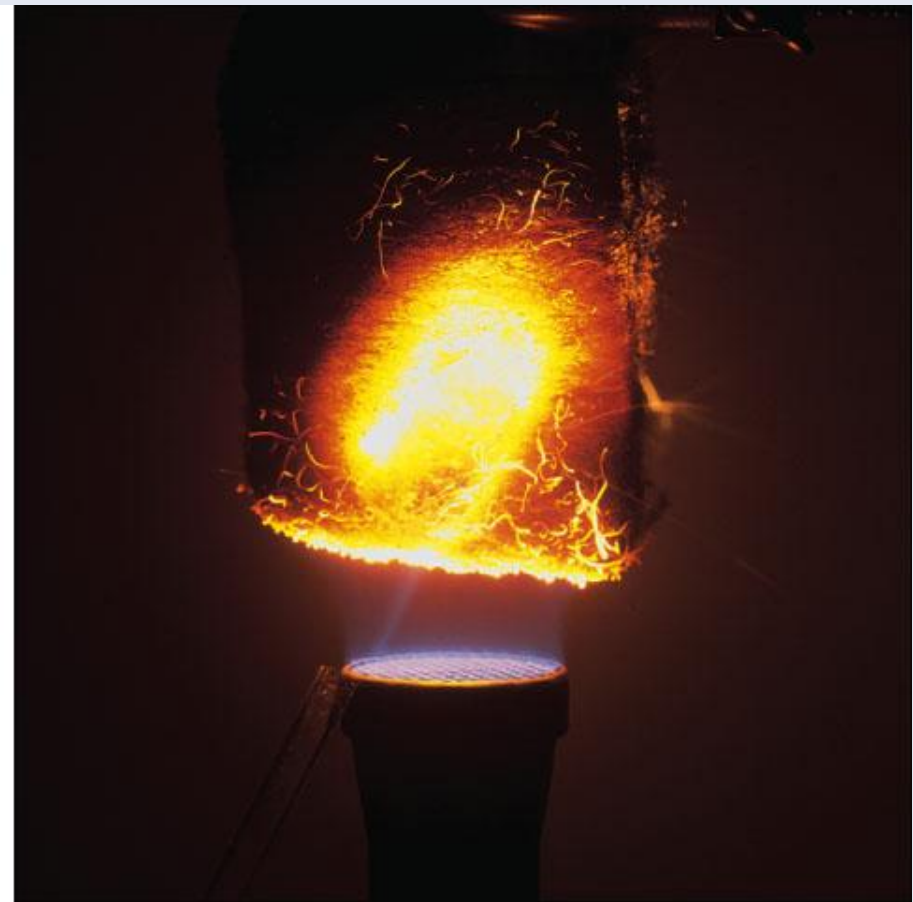


- Rate is directly related to reactant concentration
- Consider H_2O_2
 - $\text{H}_2\text{O}_2 (\text{l}) \rightarrow \text{H}_2\text{O} (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g})$
 - When pure, decomposition is fast and explosive
 - When dilute, such as drugstore peroxide, the reaction is much slower and the solution is stable for months

Oxygen Concentration and Rate of Combustion



(a)



(b)

Rate and Collision

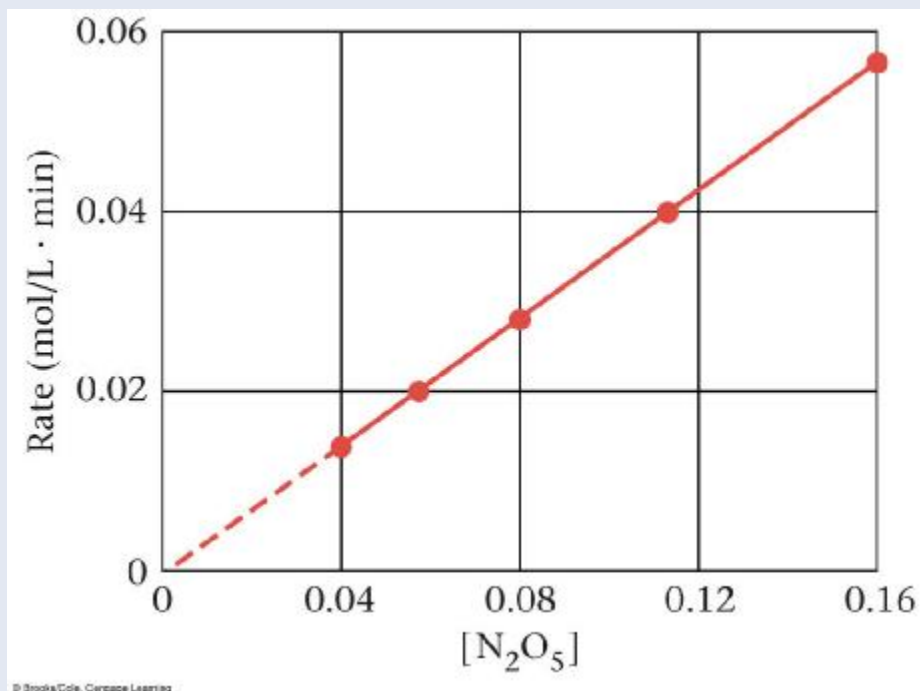


- Reactions occur when two particles of reactant collide with each other
 - The larger the concentration of reactant, the more likely molecules will collide
 - Rate depends on concentration

Rate Expression and Rate Constant



- Plotting the rate vs. the concentration for the decomposition of N_2O_5 gives a straight line



- The equation for the reaction is
 - Rate = $k[\text{N}_2\text{O}_5]$
 - k is the rate constant for the reaction

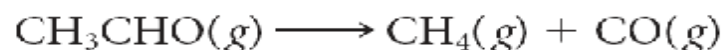
Order and Determination of Order of Reaction



- Experiment must be done to determine the dependence of the rate of a reaction on the concentration of reactant
- In general, for
 - $A \rightarrow \text{products}$
 - $\text{Rate} = k[A]^m$
 - m is the order of the reaction
 - m must be determined experimentally

Example 11.1

Acetaldehyde, CH_3CHO , occurs naturally in oak and tobacco leaves, and also is present in automobile and diesel exhaust. The initial rate of decomposition of acetaldehyde at 600°C



was measured at a series of concentrations with the following results:

$[\text{CH}_3\text{CHO}]$	0.20 M	0.30 M	0.40 M	0.50 M
Rate (mol/L·s)	0.34	0.76	1.4	2.1

Using these data, determine the reaction order; that is, determine the value of m in the equation

$$\text{rate} = k[\text{CH}_3\text{CHO}]^m.$$

Strategy Choose the first two concentrations, 0.20 M and 0.30 M . Calculate the ratio of the rates, the ratio of the concentrations, and finally the order of the reaction, using the general relation derived above.

SOLUTION

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.76}{0.34} = 2.2 \quad \frac{[\text{CH}_3\text{CHO}]_2}{[\text{CH}_3\text{CHO}]_1} = \frac{0.30}{0.20} = 1.5$$

Hence the general relation becomes

$$2.2 = (1.5)^m$$

Clearly, $m = 2$; the reaction is second order.

Reality Check You would get the same result ($m = 2$) if you used any two points. Try it!

Calculating k



- Once the order of the reaction is known, the rate constant is easy to calculate
 - Use the rate and concentration data to solve for the rate constant
 - Units
 - Rate is always in mol/L-time
 - If the reaction is first order, the rate constant will have units of 1/time
 - The units of the rate constant tell the order of the reaction if they are given

Order of Reaction with Multiple Reactants



- $aA + bB \rightarrow$ products
- Rate = $k[A]^m[B]^n$
- There are three orders:
 - The order with respect to A
 - The order with respect to B
 - The overall order ($m+n$)
- The orders can be determined the same way they are for single reactants



Example 11.2

Consider the reaction between t-butylbromide and a base at 55°C:



A series of experiments is carried out with the following results:

	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
$[(\text{CH}_3)_3\text{CBr}]$	0.50	1.0	1.5	1.0	1.0
$[\text{OH}^-]$	0.050	0.050	0.050	0.10	0.20
Rate (mol/L · s)	0.0050	0.010	0.015	0.010	0.010

Find:

- the order of the reaction with respect to both $(\text{CH}_3)_3\text{CBr}$ and OH^- .
- Write the rate expression for the reaction.
- Calculate the rate constant at 55°C.
- What effect does doubling the concentration of OH^- have on the reaction if $[(\text{CH}_3)_3\text{CBr}]$ is kept at 1.0 M?

Strategy To find the order of the reaction with respect to $(\text{CH}_3)_3\text{CBr}$, choose two experiments, perhaps 1 and 3, where $[\text{OH}^-]$ is constant. A similar approach can be used to find n ; compare experiments 2 and 5, where $[(\text{CH}_3)_3\text{CBr}]$ is constant. To write the rate expression, use the calculated reaction orders.

SOLUTION

- (a) For the order of the reaction with respect to $(\text{CH}_3)_3\text{CBr}$,

$$\frac{\text{rate}_3}{\text{rate}_1} = \left(\frac{[(\text{CH}_3)_3\text{CBr}]_3}{[(\text{CH}_3)_3\text{CBr}]_1} \right)^m \quad \frac{0.015}{0.0050} = \left(\frac{1.5}{0.50} \right)^m \quad 3 = 3^m$$

Example 11.2, (Cont'd)



Clearly, then, $m = 1$.

For the rate of the reaction with respect to OH^- ,

$$\frac{\text{rate}_5}{\text{rate}_2} = \left(\frac{[\text{OH}^-]_5}{[\text{OH}^-]_2} \right)^n \quad \frac{0.010}{0.010} = \left(\frac{0.20}{0.050} \right)^n \quad 1 = 4^n$$

In this case, $n = 0$.

(b) The rate expression is

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]^1[\text{OH}^-]^0 = k[(\text{CH}_3)_3\text{CBr}]$$

(c) You may choose any experiment to substitute a rate with its corresponding concentration. Choosing Experiment 3 gives

$$0.015 \frac{\text{mol}}{\text{L} \cdot \text{s}} = k(1.5) \frac{\text{mol}}{\text{L}}$$

$$k = 0.010 \text{ s}^{-1}$$

(d) Changing the concentration of OH^- has **no effect** on the rate of the reaction. The reaction is zero-order with respect to $[\text{OH}^-]$, which means that the rate is independent of concentration.

11.3 Reaction Concentration and Time



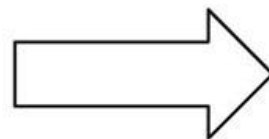
- The rate expression can be integrated (using calculus) to produce a concentration-time relationship
 - The relationship depends on the order of the reaction
 - A new term, the half-life, will also result

Rate and Concentration



0.1 M KMnO_4

(a)

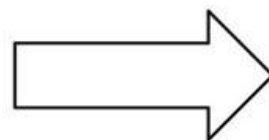


0.1 M KMnO_4 + 10 mL H_2O_2



5 M KMnO_4

(b)



5 M KMnO_4 + 10 mL H_2O_2

First-Order Reactions



- For $A \rightarrow$ products, the relationship is

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

- k is the rate constant
- t is time

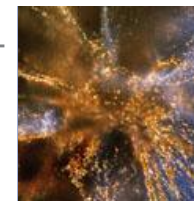
Graphical Interpretation of the First-Order Relationship



- We can put the first-order relationship into the form

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

- Where, using $y = mx + b$,
 - $\ln[A]$ is plotted on the y axis
 - t is plotted on the x axis
 - The slope of the line is $-k$
 - The y-intercept is $\ln[A]_0$



Example 11.3

For the first-order decomposition of N_2O_5 at 67°C , where $k = 0.35/\text{min}$, calculate

- the concentration after six minutes, starting at 0.200 M .
- the time required for the concentration to drop to 0.150 M .
- the time required for half a sample of N_2O_5 to decompose.

Strategy In each case, the equation

$$\ln [\text{N}_2\text{O}_5]_0/[\text{N}_2\text{O}_5] = (0.35/\text{min})t$$

is used. In (a) and (b), two of the three variables, $[\text{N}_2\text{O}_5]_0$, $[\text{N}_2\text{O}_5]$, and t , are known; the other is readily calculated. In (c), you should be able to find the ratio $[\text{N}_2\text{O}_5]_0/[\text{N}_2\text{O}_5]$; knowing that ratio, the time can be calculated.

SOLUTION

- (a) Substituting in the integrated first-order equation,

$$\ln \frac{0.200\text{ M}}{[\text{N}_2\text{O}_5]} = \frac{0.35}{\text{min}} (6.0\text{ min}) = 2.1$$

Taking inverse logarithms,

$$\frac{0.200\text{ M}}{[\text{N}_2\text{O}_5]} = e^{2.1} = 8.2; \quad [\text{N}_2\text{O}_5] = \frac{0.200\text{ M}}{8.2} = 0.024\text{ M}$$

Example 11.3, (Cont'd)



(b) Solving the concentration-time relation for t ,

$$t = \frac{1}{k} \ln \frac{[A]_o}{[A]} = \frac{1}{0.35/\text{min}} \ln \frac{0.200 M}{0.150 M} = 0.82 \text{ min}$$

(c) When half of the sample has decomposed,

$$[\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5]_o/2 \quad [\text{N}_2\text{O}_5]_o = 2[\text{N}_2\text{O}_5] \quad [\text{N}_2\text{O}_5]_o/[\text{N}_2\text{O}_5] = 2$$

Using the equation in (b),

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

With $k = 0.35/\text{min}$, we have

$$t = \frac{0.693}{0.35} = 2.0 \text{ min}$$

The Half Life

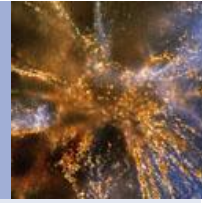


- The **half life** of a reaction is the time it takes for **half the initial concentration of reactant to react**
- For a first order reaction, at the half life, $[A] = 1/2[A]_0$ so

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

- Notice that for a first order reaction, the half life is independent of the starting concentration of reactant

Applications of First Order Kinetics



- Radioactive decay is a first-order process
- If X_0 is the initial amount of radioactive element,

$$\ln \frac{X_0}{X} = kt$$

Table 11.1



Table 11.1 Decomposition of N_2O_5 at 67°C ($t_{1/2} = 2.0$ min)

$t(\text{min})$	0.0	2.0	4.0	6.0	8.0
$[\text{N}_2\text{O}_5]$	0.160	0.080	0.040	0.020	0.010
Fraction of N_2O_5 decomposed	0	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{7}{8}$	$\frac{15}{16}$
Fraction of N_2O_5 left	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$
Number of half-lives	0	1	2	3	4

Example 11.4**Graded**

Plutonium-240 (Pu-240) is a byproduct of the nuclear reaction that takes place in a reactor. It takes one thousand years for 10.0% of a 4.60-g sample to decay.

- * (a) What is the half-life of Pu-240?
- ** (b) How long will it take to reduce a 2.00-g sample to 15% of its original amount?
- *** (c) What is the rate of decay of a 5.00-g sample in g/year?

Strategy Nuclear decays are first-order reactions. Use the first-order rate calculation to find k . Part (b) differs from part (c) in that (b) relates concentration and time, while (c) relates concentration and rate. For nuclear decay, “concentration” can be expressed in moles, grams, or number of atoms.

SOLUTION

(a) When the 4.60-g sample decays, the amount lost is

$$0.100 \times 4.60 \text{ g} = 0.460 \text{ g}$$

Thus, $X_0 = 4.60 \text{ g}$ and $X = 4.60 \text{ g} - 0.46 \text{ g} = 4.14 \text{ g}$. To find the rate constant, substitute into

$$\begin{aligned}\ln X_0 - \ln X &= kt \\ \ln 4.60 - \ln 4.14 &= k(1000 \text{ yr}) \\ k &= 1.05 \times 10^{-4} \text{ yr}^{-1}\end{aligned}$$

The half-life ($t_{1/2}$) is therefore

$$t_{1/2} = \frac{0.693}{k} \quad t_{1/2} = \frac{0.693}{1.05 \times 10^{-4} \text{ yr}^{-1}} = 6.60 \times 10^3 \text{ yr}$$

Example 11.4, (Cont'd)



(b) Reducing the sample to 15% of its original mass means that $X = 0.15(2.00)$ remains.

Thus

$$\ln 2.00 - \ln(0.15 \times 2.00) = 1.05 \times 10^{-4} \text{ yr}^{-1} \cdot t$$

$$t = 1.8 \times 10^4 \text{ yr}$$

(c) $\text{rate} = k (\text{mass of Pu-240})^1 = 1.05 \times 10^{-4} \text{ yr}^{-1} (5.00 \text{ g}) = 5.25 \times 10^{-4} \text{ g/yr}$

Reality Check In (b), reducing the amount present to 15% takes more time than two half-lives (i.e., more than the time to reduce to 25%). The answer is larger than $2(6.60 \times 10^3)$, as it should be. In (c), the rate is dependent on the initial concentration, unlike the half-life in (a)—which is independent of the initial amount.

Zero Order Reactions



- For a zero order reaction $A \rightarrow$ products

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

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

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

linear : $[A]$ vs. t

- Note that the ***half life of a zero order reaction does depend on the initial concentration*** of reactant

Decomposition of HI



- The decomposition of HI over a solid surface is one example of a zero order reaction

Au

- $\text{HI (g)} \xrightarrow{\text{Au}} \frac{1}{2} \text{H}_2 \text{(g)} + \frac{1}{2} \text{I}_2 \text{(g)}$

Table 11.2



Table 11.2

Characteristics of Zero-, First-, and Second-Order Reactions of the Form $A(g) \longrightarrow \text{products}$; $[A]$, $[A]_0 = \text{conc. A at } t \text{ and } t = 0, \text{ respectively}$

Order	Rate Expression	Conc.-Time Relation	Half-Life	Linear Plot
0	$\text{rate} = k$	$[A]_0 - [A] = kt$	$[A]_0/2k$	$[A]$ vs. t
1	$\text{rate} = k[A]$	$\ln \frac{[A]_0}{[A]} = kt$	$0.693/k$	$\ln [A]$ vs. t
2	$\text{rate} = k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$1/k[A]_0$	$\frac{1}{[A]}$ vs. t

Example 11.5



Example 11.5

The following data were obtained for the gas-phase decomposition of hydrogen iodide:

Time (h)	0	2	4	6
[HI]	1.00	0.50	0.33	0.25

Is this reaction zero-, first-, or second-order in HI?

Example 11.5, (Cont'd)



Strategy Note from the last column of Table 11.2 that—

- if the reaction is zero-order, a plot of $[A]$ versus t should be linear.
- if the reaction is first-order, a plot of $\ln [A]$ versus t should be linear.
- if the reaction is second-order, a plot of $1/[A]$ versus t should be linear.

Using these data, prepare these plots and determine which one is a straight line.

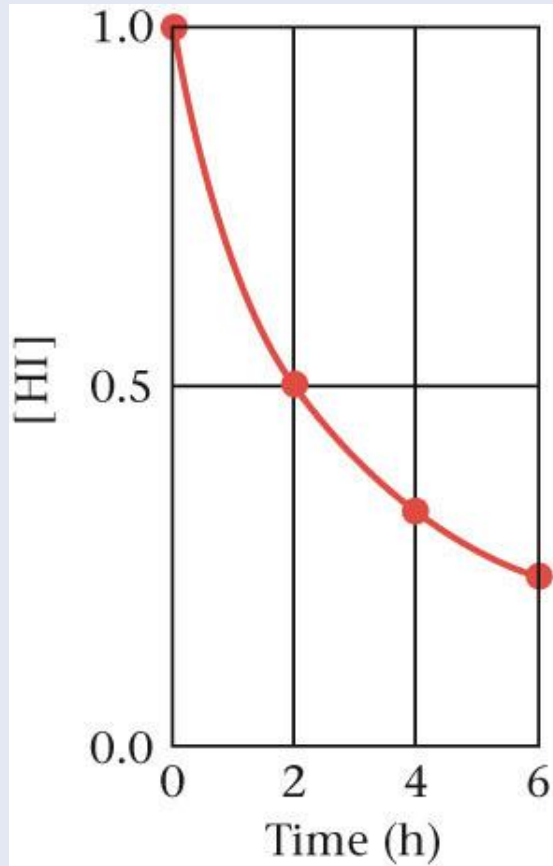
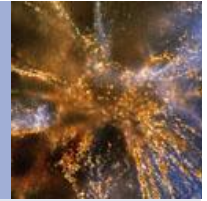
SOLUTION It is useful to prepare a table listing $[HI]$, $\ln [HI]$, and $1/[HI]$ as a function of time.

$t(\text{h})$	$[HI]$	$\ln [HI]$	$1/[HI]$
0	1.00	0	1.0
2	0.50	-0.69	2.0
4	0.33	-1.10	3.0
6	0.25	-1.39	4.0

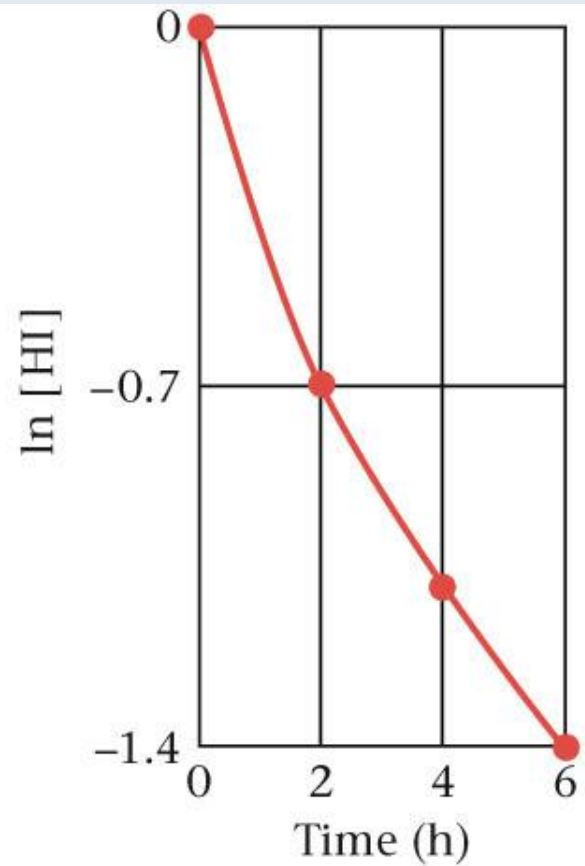
If it is not obvious from this table that the only linear plot is that of $1/[HI]$ versus time, that point should be clear from Figure 11.5. **This is a second-order reaction.**

Reality Check Notice that the concentration drops from 1.00 M to 0.50 M in 2 h. If the reaction were zero-order, it would be all over after four hours. If it were first-order, the concentration would be 0.25 M after four hours.

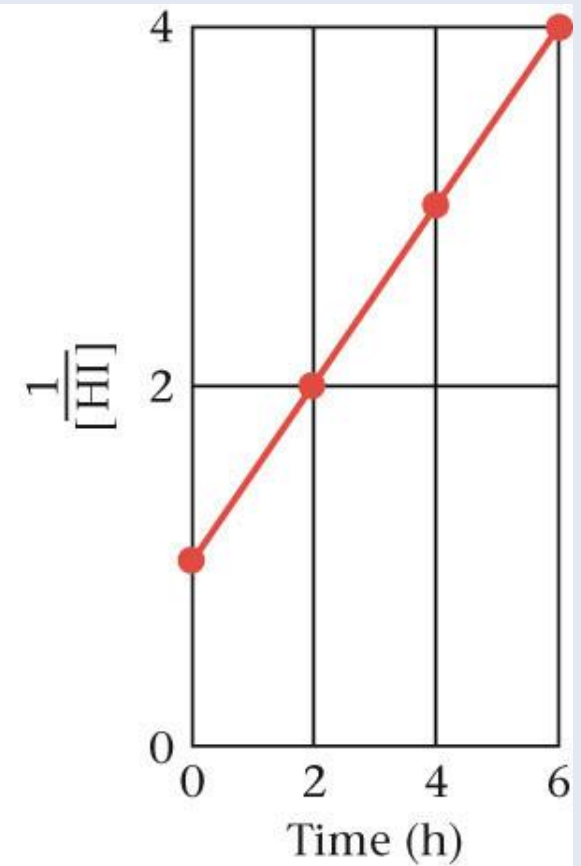
Figure 11.5



(a)



(b)

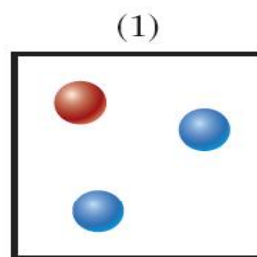


(c)

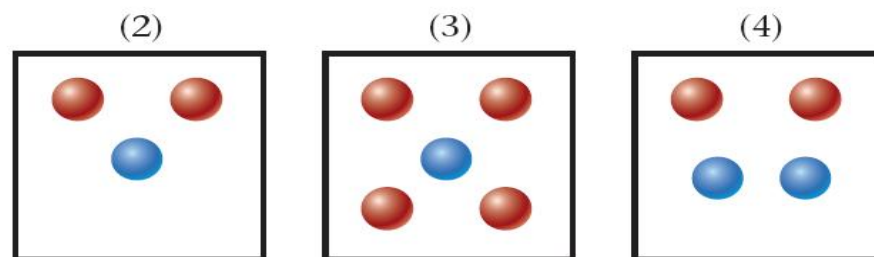
Example 11.6

Conceptual

A certain reaction is first-order in A and second-order in B. In the box shown below, which is assumed to have a volume of one liter, a mole of A is represented by ●, a mole of B by ●.



In which of the three boxes shown below is the rate of reaction the same as that in the box shown above?



SOLUTION Write down the rate expressions for each box and compare.

$$(1) \text{ rate} = k(1)(2)^2 = 4k \quad (3) \text{ rate} = k(4)(1)^2 = 4k$$

$$(2) \text{ rate} = k(2)(1)^2 = 2k \quad (4) \text{ rate} = k(2)(2)^2 = 8k$$

Clearly, the rate in **box (3)** is the same as that in box (1).

Second-Order Reactions



- For $A \rightarrow$ products, $\text{Rate} = k[A]^2$

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

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

$$\text{linear} : \frac{1}{[A]} \text{ vs. } t$$

11.4 Modeling Reaction Rates



- Two basic models of reaction rates
 1. Collision Model
 2. Transition State Model

Collision Model: Activation Energies



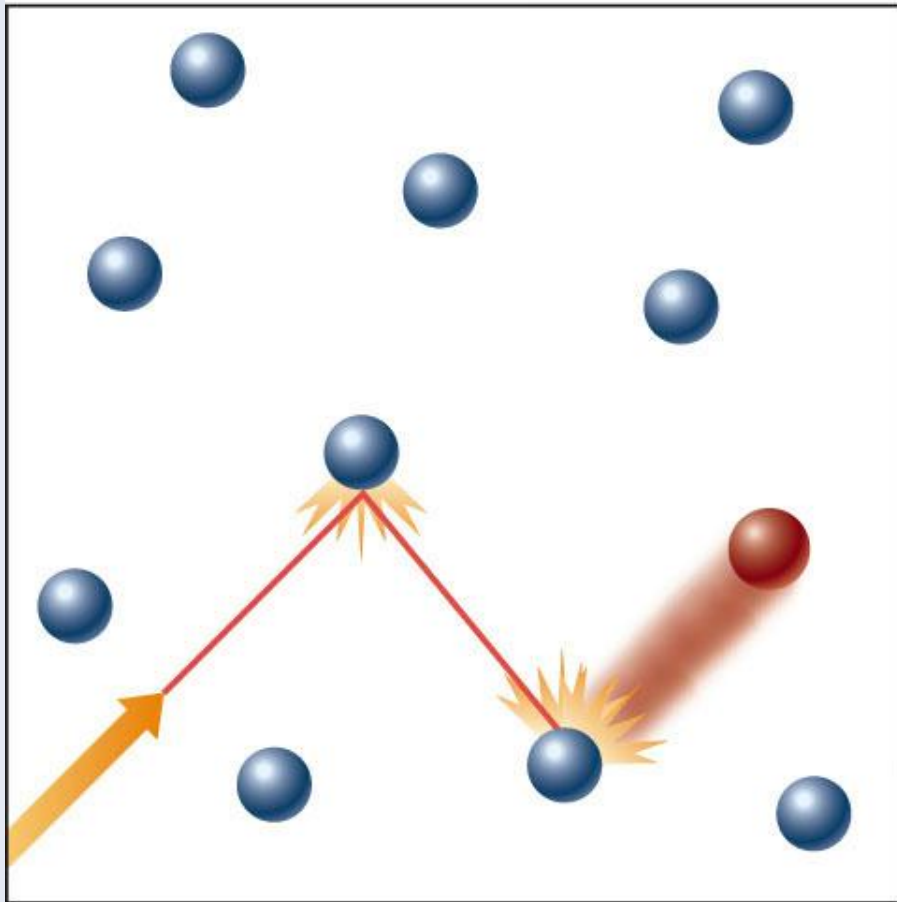
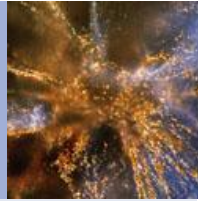
- $\text{CO (g)} + \text{NO}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)} + \text{NO (g)}$
- Reaction takes place directly between CO and NO_2
 - Doubling $[\text{CO}]$ doubles the rate
 - Doubling $[\text{NO}_2]$ doubles the rate
- Experimentally, the rate expression is
 - $\text{Rate} = k[\text{CO}][\text{NO}_2]$
- From kinetic theory, every CO molecule should collide with 10^9 molecules of NO_2 in one second
 - Reaction should be over in a fraction of a second
 - In reality the half life is about 10 sec, so not every collision leads to a reaction

Collisions, Effective and Ineffective

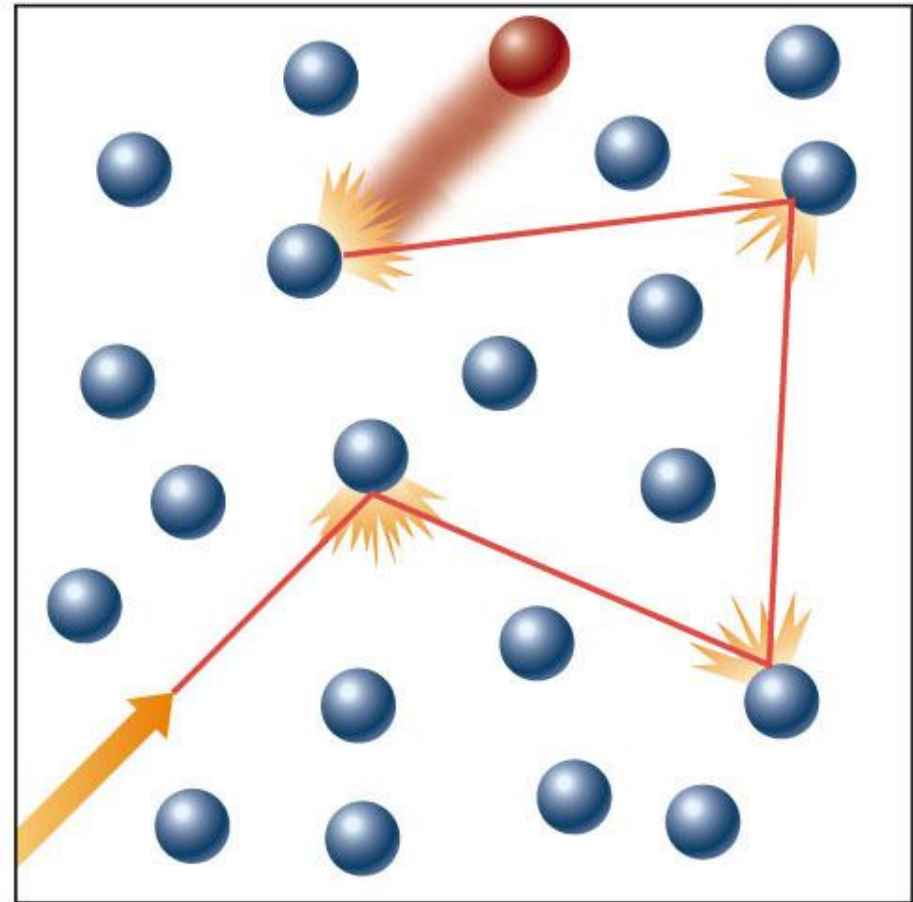


- Why does every collision not lead to a reaction?
 - Molecules have to be oriented properly (sterics)
 - Kinetic energy of collision may not be high enough to overcome repulsions of electrons in molecules
 - For every reaction, there is a minimum energy which the molecules must possess to react
 - This energy is the ***activation energy***

Figure 11.6

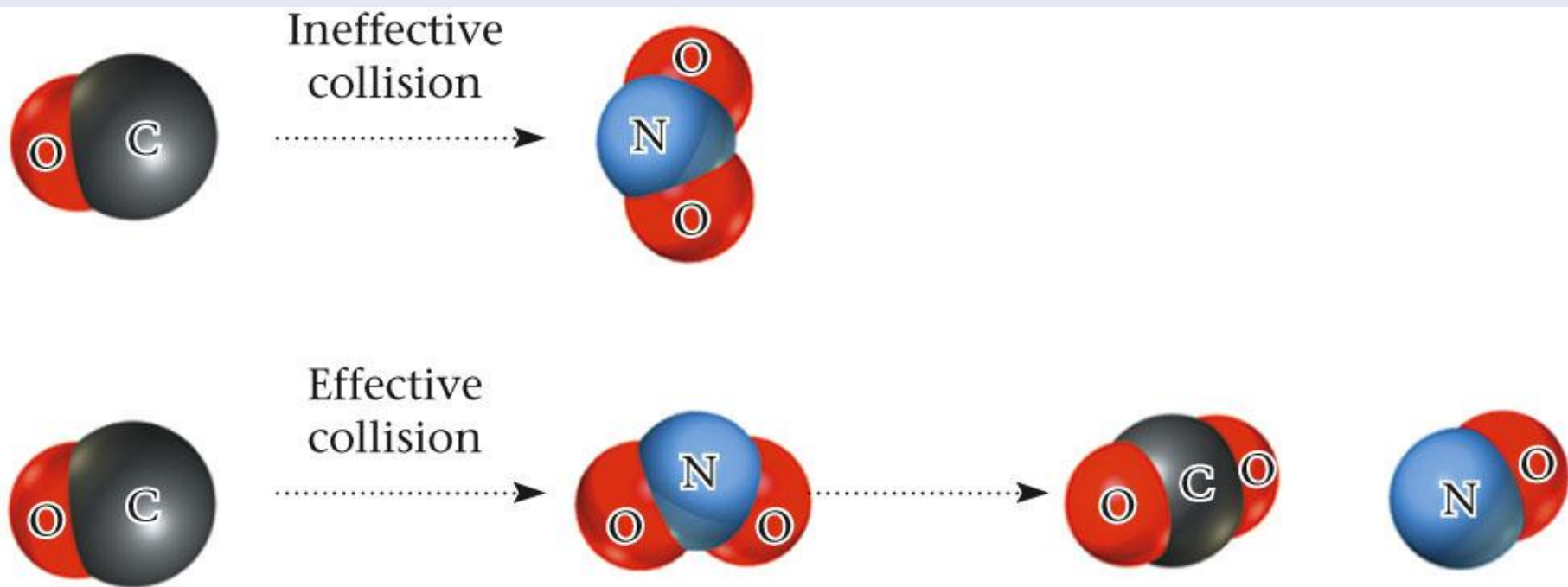


(a)



(b)

Figure 11.7



Quantitative Aspects of Collision Theory



- $k = pZf$
 - p is the steric factor, accounting for the fact that only certain orientations of molecules will lead to effective collision
 - Z is the collision frequency, the number of collisions per unit time at unit concentrations of reactants
 - f is the fraction of collision in which the energy of collision is equal to or greater than the activation energy

Collision Frequency Relationship



$$f = e^{\frac{-E_a}{RT}}$$

- E_a is the activation energy
- R is the gas constant in J/mol-K
- T is the Kelvin temperature

$$k = pZe^{\frac{-E_a}{RT}}$$

- This combined equation tells us that the larger the activation energy, the smaller the rate constant

Table 11.3



Table 11.3

Observed and Calculated Rate Constants for Second-Order Gas-Phase Reactions

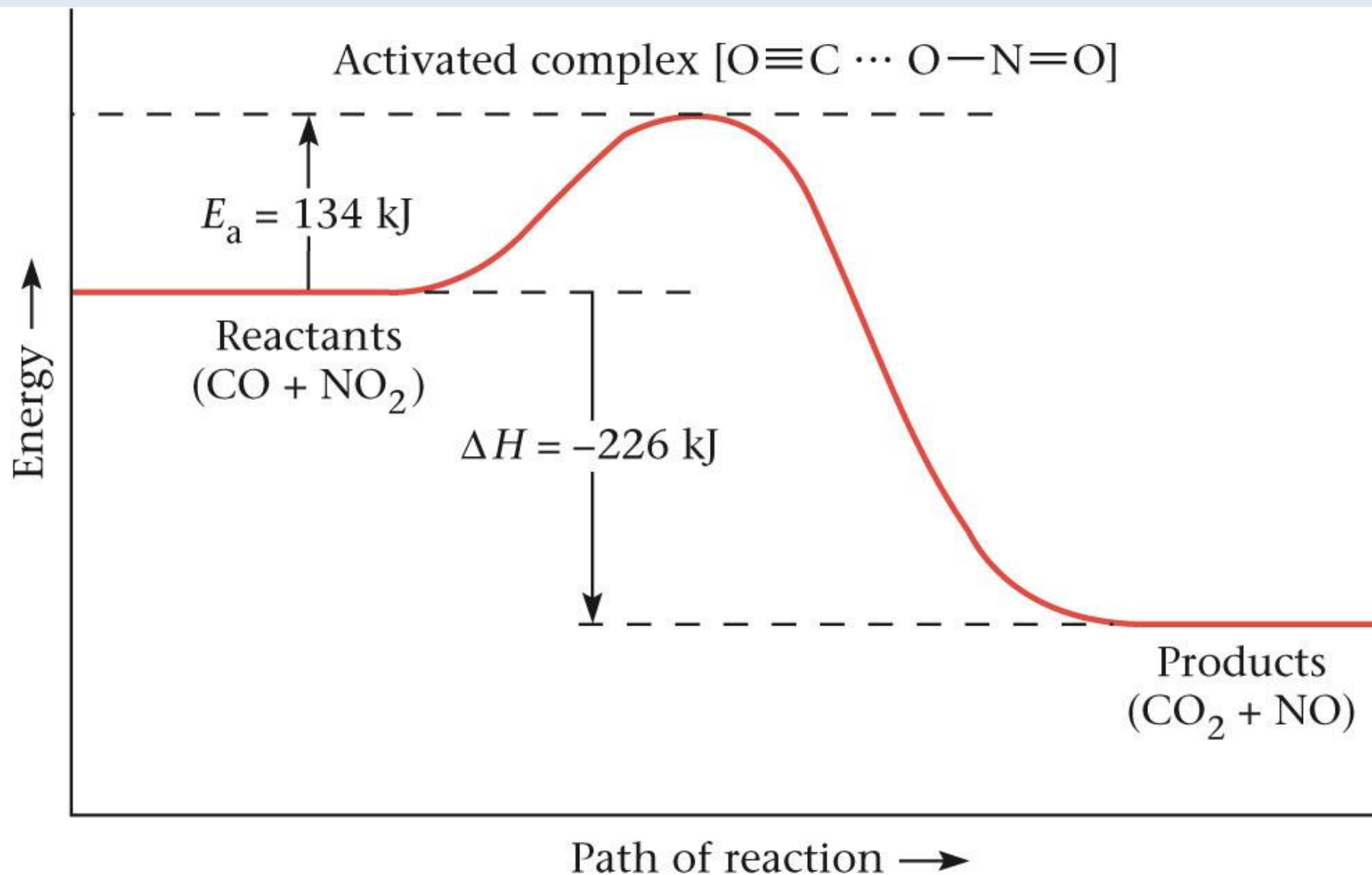
Reaction	k Observed	Collision Model	Transition-State Model
$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$	6.3×10^7	4.0×10^9	3.2×10^7
$\text{NO} + \text{Cl}_2 \longrightarrow \text{NOCl} + \text{Cl}$	5.2	130	1.6
$\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$	1.2×10^{-4}	6.4×10^{-4}	1.0×10^{-4}
$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$	5.0×10^{-3}	1.0×10^{-1}	1.2×10^{-2}

Transition-State Model



- Consider the activation energy diagram for the CO-NO₂ reaction
 - In it, energy is plotted on the y-axis
 - Reaction path is plotted on the x-axis
- The reactants form an intermediate called an ***activated complex***
 - The state of the system at the activated complex is called a ***transition state***

Figure 11.8

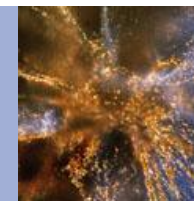


Understanding Activation Energy Diagrams



- Note the similarity of the diagram to the energy diagrams introduced in Chapter 8
 - An additional feature is the high-energy **activated complex** that forms upon collision
 - The activated complex is at low concentration, in equilibrium with reactant and product
 - The activated complex may proceed to form product, or fall back to reactant(s)
 - The activation energy is the difference in energy between reactant and activated complex
 - ΔH is the difference in energy between reactant and product, just as it was in Chapter 8

Transition States and Activated Complexes



- In this model, the rate of reaction is controlled by the rate at which the activated complex forms
- The transition state model is somewhat more accurate than the collision model, at least when $p=1$
- Transition state model explains why the activation energy is ordinarily much smaller than the bond enthalpies in the reactant molecules

11.5 Reaction Rate and Temperature



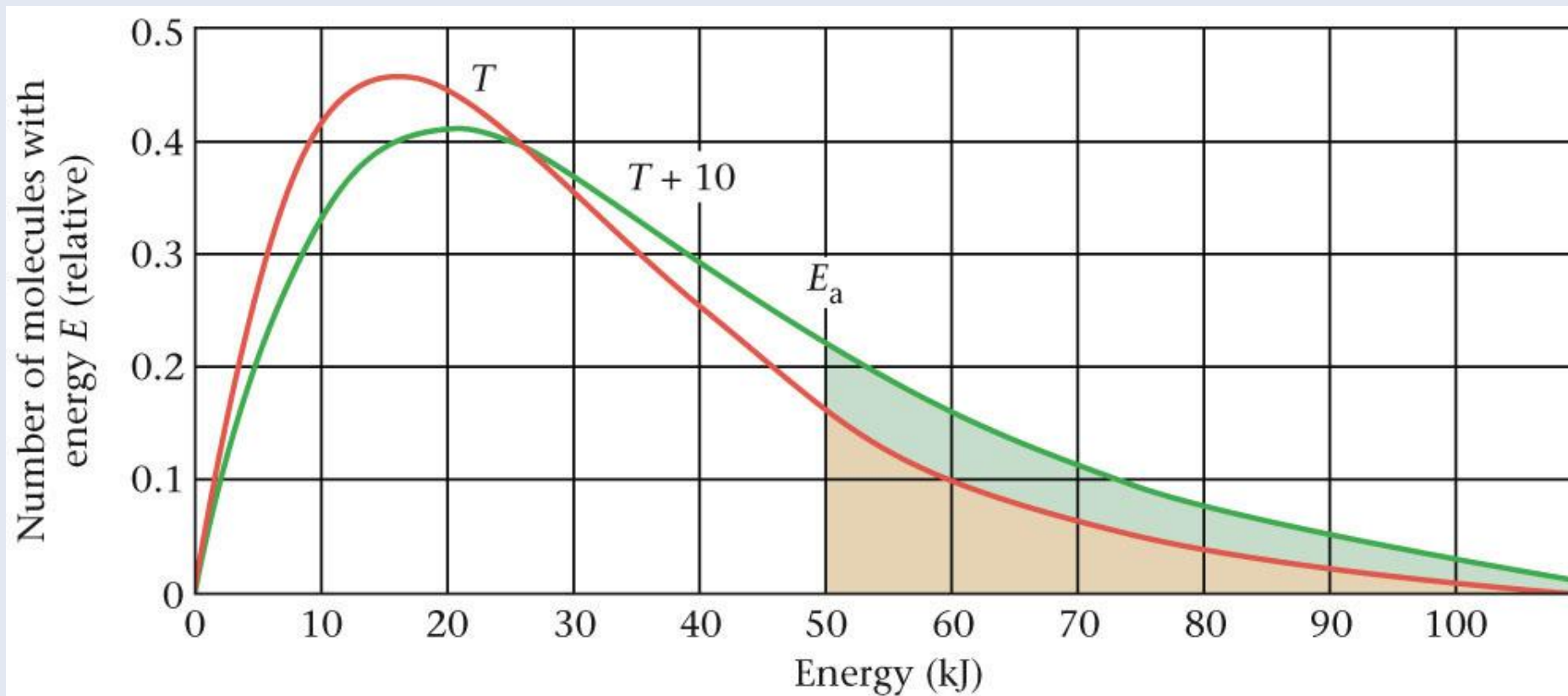
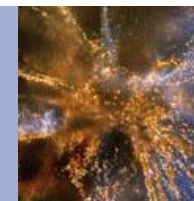
- Reaction rate ordinarily increases with temperature
 - To cook food more quickly, raise the oven temperature
 - To slow the reactions that lead to food spoilage, lower the temperature in the refrigerator or freezer
- Every 10°C increase in temperature doubles the reaction rate

Kinetic Theory Revisited



- Recall from kinetic theory of gases that the temperature is a measure of the average kinetic energy of molecules
 - Higher temperatures mean higher kinetic energies
 - The higher the temperature, the larger the fraction of molecules that possess the activation energy (or greater)
 - With a larger fraction of molecules possessing E_a , a larger fraction of effective collisions results

Figure 11.9



Temperature and Reaction Rate



The sticks outside the beaker at room temperature are brighter than the two sticks cooled to 0.2 °C because the reaction rate is larger at the higher temperature.



(a)

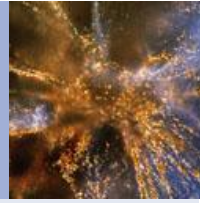
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With the sticks in the beaker heated well above room temperature, to 59 °C, these sticks are now much brighter than those at room temperature.



(b)

Arrhenius Theory



- Recall from the collision model

$$k = pZ e^{\frac{-E_a}{RT}}$$

- Combining p and z into a single term called the Arrhenius pre-exponential, A , results in

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

Graphical Interpretation of the Arrhenius Equation



- The Arrhenius equation can be put into $y=mx+b$ form

$$\ln k = \ln A - \frac{E_a}{RT}$$

- A plot of $\ln(k)$ on the y-axis vs. $1/T$ on the x-axis yields
 - A slope equal to $-E_a/R$
 - A y-intercept equal to $\ln(A)$
- ***By obtaining experimental data that allows the calculation of k at various temperatures, the activation energy can be determined***

Recall the Two-Point Vapor Pressure Equation



- Clausius-Clapeyron
 - Taking two temperatures and two vapor pressures, the ΔH_{vap} can be determined
 - The ***Arrhenius equation*** is similar in nature and can be used for two k values and two temperatures
 - E_a may then be calculated

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Example 11.7



Example 11.7 Graded

Consider the first-order decomposition of A. The following is known about it—

- the rate constant doubles when the temperature increases from 15°C to 25°C.
- the rate constant for the decomposition at 40°C is 0.0125 s^{-1} .
- * (a) What is the activation energy for the decomposition?
- ** (b) What is the half-life of A at 78°C?
- *** (c) What is the rate of the decomposition of a 0.200 M solution of A at 78°C?
- *** (d) At what temperature will the rate of the decomposition of 0.165 M be $0.124 \text{ mol/L} \cdot \text{s}$?

Example 11.7, (Cont'd)



SOLUTION

(a) $k_2/k_1 = 2.00$ $\ln k_2/k_1 = \ln 2.00 = 0.693$ $T_2 = 298 \text{ K}$ $T_1 = 288 \text{ K}$

Substituting into the two-point form of the Arrhenius equation,

$$0.693 = \frac{E_a}{8.31 \text{ J/mol} \cdot \text{K}} \left[\frac{1}{288 \text{ K}} - \frac{1}{298 \text{ K}} \right]$$

Solving

$$E_a = 4.9 \times 10^4 \text{ J/mol} = 49 \text{ kJ/mol}$$

(b) In order to calculate the half-life at 78°C, you must first find k at 78°C. Substituting into the Arrhenius equation, we get

$$\ln \frac{k_2}{k_1} = \frac{49,000 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{313 \text{ K}} - \frac{1}{351 \text{ K}} \right) = 2.04 \quad \frac{k_2}{k_1} = 7.69$$

Taking $k_1 = 0.0125 \text{ s}^{-1}$,

$$\frac{k_2}{k_1} = \frac{k_2}{0.0125} = 7.69$$

$$k_2 = 0.0961 \text{ s}^{-1}$$

Then the half-life is

$$t_{1/2} = \frac{0.693}{0.0961 \text{ s}^{-1}} = 7.21 \text{ s.}$$

Example 11.7, (Cont'd)



(c) The rate expression for this first-order reaction is

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

Substituting the value of the rate constant at 78°C, we get

$$\text{rate} = 0.0961 \text{ s}^{-1} (0.200 \text{ mol/L}) = 0.0192 \text{ mol/L} \cdot \text{s}$$

(d) First, we find the rate constant for the decomposition at the unknown temperature.

$$0.165(\text{mol/L})(k) = 0.124 \text{ mol/L} \cdot \text{s} \quad k = 0.752 \text{ s}^{-1}$$

Again we use the Arrhenius equation, where

$$T_1 = 313 \text{ K}, \quad k_1 = 0.0125 \text{ s}^{-1} \quad \text{and} \quad k_2 = 0.752 \text{ s}^{-1}$$

$$\ln \left(\frac{0.752}{0.0125} \right) = \frac{49,000 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{313 \text{ K}} - \frac{1}{T_2} \right)$$

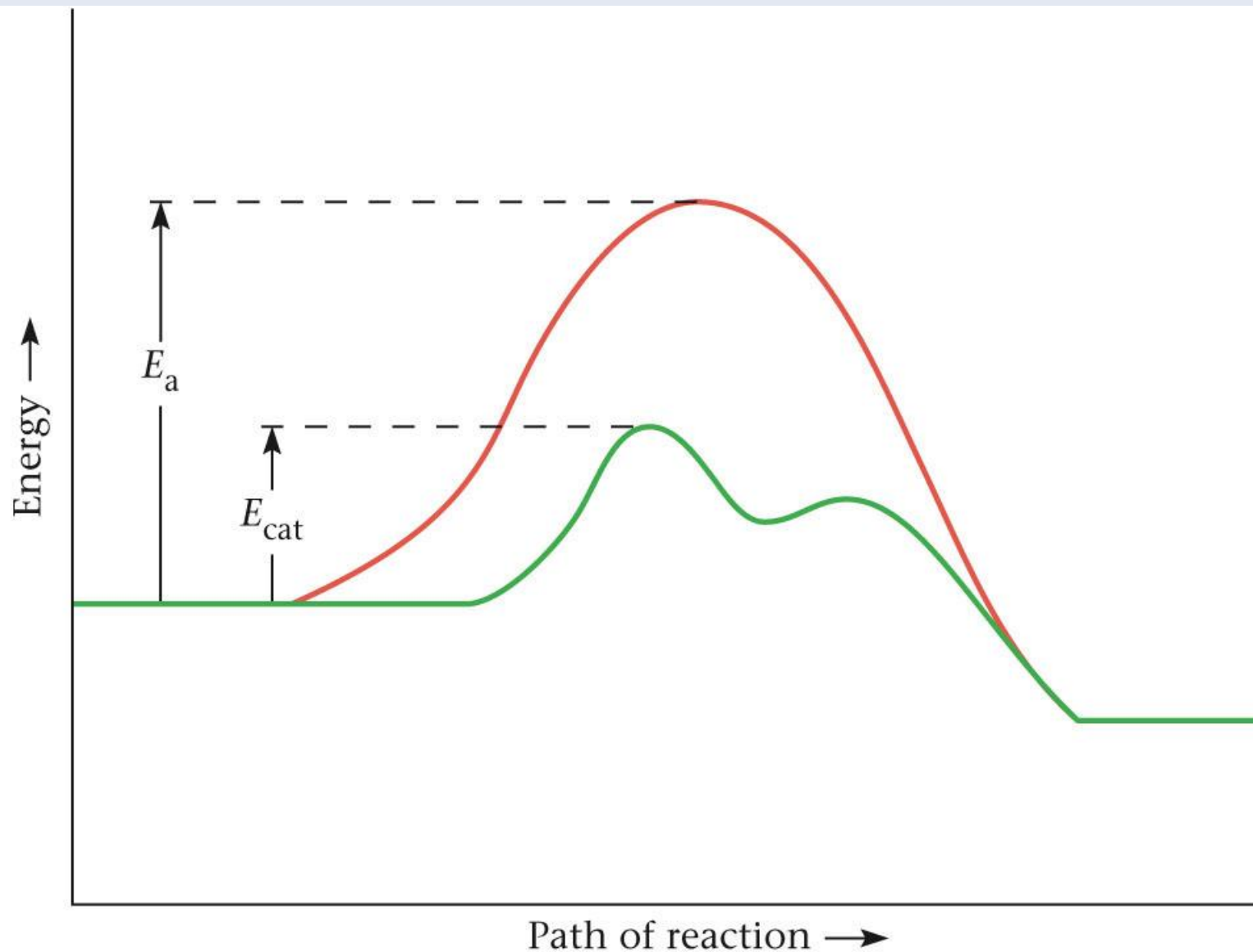
$$T_2 = 4.00 \times 10^2 \text{ K} = 1.3 \times 10^2 \text{ }^\circ\text{C}$$

11.6 Catalysis



- A ***catalyst*** is a ***substance that increases the rate*** of a reaction ***without being consumed*** by it
 - Catalysts act by introducing a lower-energy path by which the reaction can take place
 - An activated complex forms at lower energy than without the presence of the catalyst

Figure 11.11 – Reaction Diagram

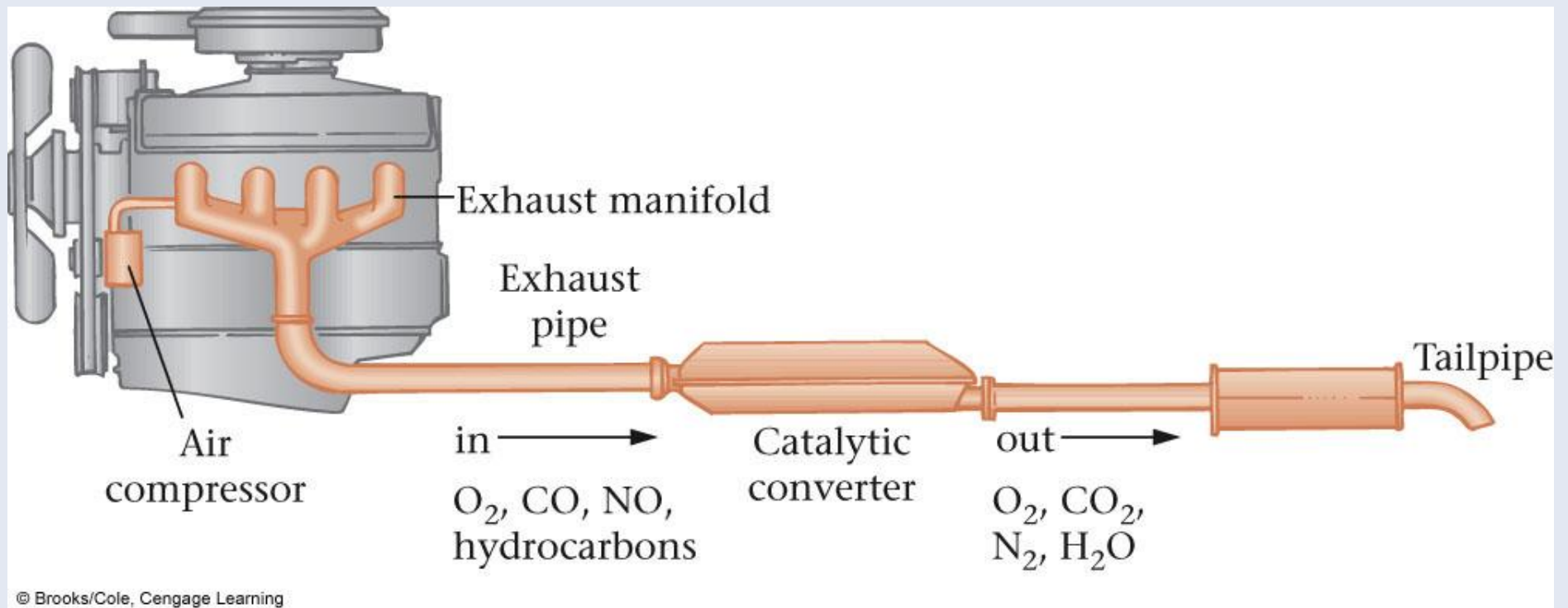


Heterogeneous Catalysis



- A **heterogeneous catalyst is in a phase different from that of the reaction mixture**
 - Commonly a solid that is used for a gas or liquid phase reaction
 - Decomposition of N_2O on a gold surface
- Common heterogeneous catalyst: the **catalytic converter**, which contains a metal such as Pt
 - Catalyzes the oxidation of CO to CO_2
 - Catalyzes the oxidation of unburned hydrocarbons to CO_2 and water

Figure 11.12

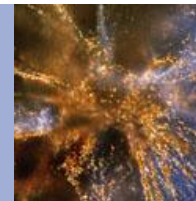


The Catalytic Converter



- The other component of a catalytic converter is a metal such as rhodium
 - Rh catalyzes the ***reduction*** of NO to nitrogen and oxygen
- The “magic” of the catalytic converter
 - By combining different metals, it is possible to carry out oxidation and reduction simultaneously, on different molecules, within the same catalytic converter

Homogeneous Catalysis



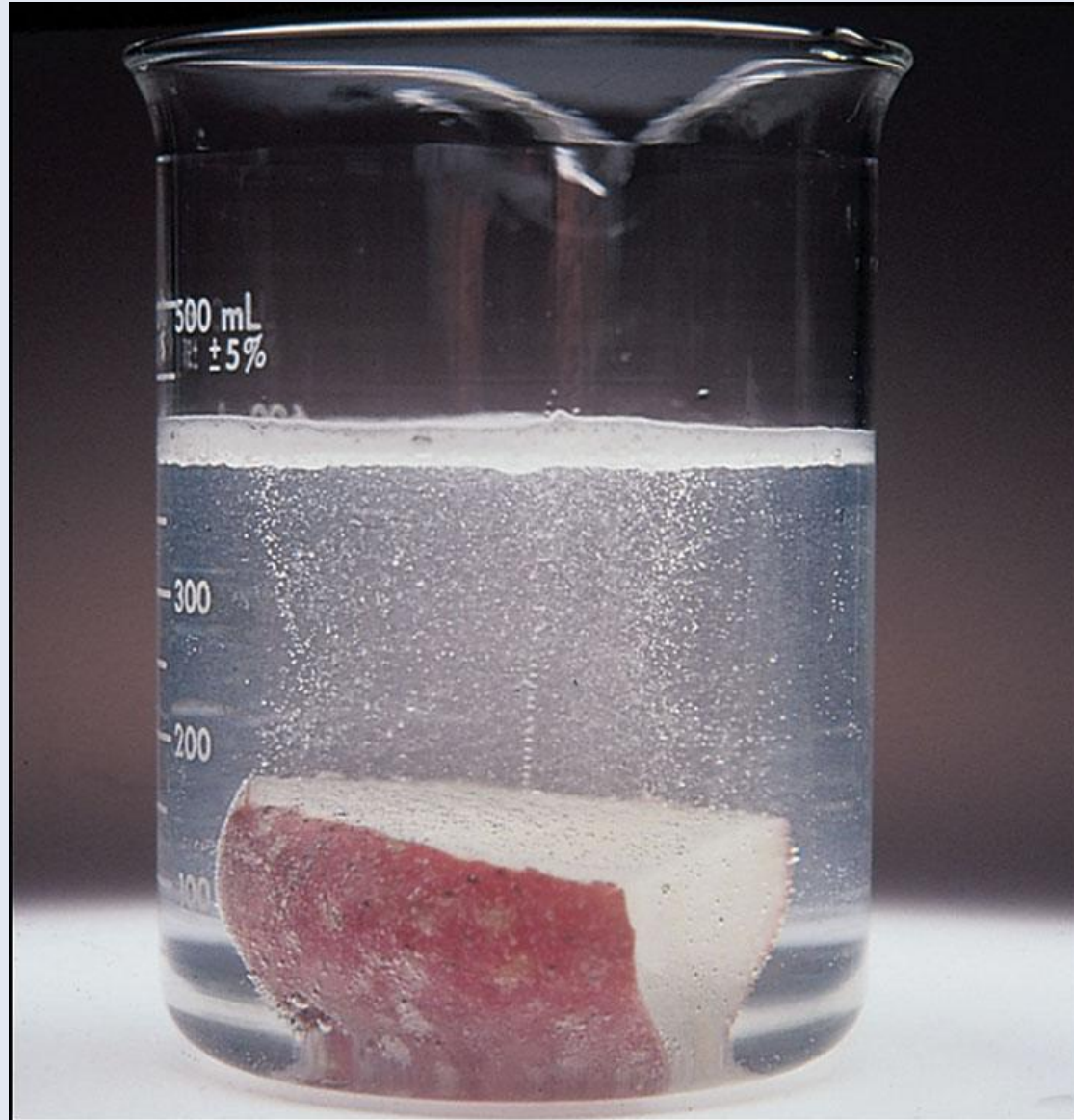
- Homogeneous catalysts are present in the same phase as the reactants
 - Example: decomposition of H_2O_2
 - $\text{H}_2\text{O}_2 (\text{aq}) \rightarrow 2\text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})$
 - Reaction is slow without a catalyst
 - Reaction becomes rapid if $\text{NaI} (\text{aq})$ is added

Enzymes



- Enzymes are biocatalysts
 - The same decomposition of hydrogen peroxide can be catalyzed by the enzyme called catalase
 - Enzymes can be very specific
 - One enzyme can be targeted to perform a very specific reaction
 - Maltose can be converted to glucose by maltase
 - Enzymes can speed up biological reactions by a factor of 10^{12} or greater

Figure 11.13



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11.7 Reaction Mechanisms



- A reaction mechanism is a description of a path, usually a series of steps, by which a reaction takes place
- Earlier, we saw the reaction
 - $\text{CO (g)} + \text{NO}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)} + \text{NO (g)}$
 - Takes place directly at high temperatures
 - Occurs as a series of steps at lower temperatures

The CO-NO₂ Reaction at Low Temperature



- At low temperature
 - $\text{NO}_2 (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{CO}_2 (\text{g})$
 - $\text{CO} (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NO} (\text{g})$
- Overall, the sum of the steps is the same:
 - $\text{CO} (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NO} (\text{g})$
- The ***nature of the rate expression*** and hence the ***reaction order depends on the mechanism by which the reaction takes place***

Elementary Steps



- The individual steps in a mechanism are called elementary steps
 - Almost always unimolecular, bimolecular or termolecular:
 - $A \rightarrow B + C$ rate = $k[A]$
 - $A + B \rightarrow C + D$ rate = $k[A][B]$
 - $A + B + C \rightarrow D + E$ rate = $k[A][B][C]$

Notes on Rate Expressions for Elementary Reactions



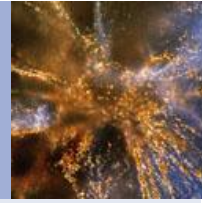
- Note that an elementary step implies that a reaction takes place exactly as written
 - This is different from an overall reaction, where the actual mechanism is unknown
- Therefore, ***the rate expression can be written directly from the elementary step equation***
 - This is ***only true for elementary steps***
 - ***For overall reactions, experiments must still be done to determine the rate expression***

Slow Steps



- In a mechanism, one step is often slower than the other (or others if more than two steps)
 - The ***slow step is rate-determining***
 - The rate of the slow step is the rate of the reaction

A Real-World Example



- Consider three people grading an examination
 - A spends 10 s grading question 1
 - B spends 15 s grading question 2
 - C takes 5 min to grade question 3
- The rate at which the exam is graded is

$$\frac{1 \text{ exam}}{10\text{s} + 15\text{s} + 300\text{s}} = 0.00308 \frac{\text{exam}}{\text{s}}$$

- The rate at which grader C graded is

$$\frac{1 \text{ exam}}{300\text{s}} = 0.00333 \frac{\text{exam}}{\text{s}}$$

- These numbers are approximately equal

Another Real-World Example



- On a two-lane highway, the slowest driver is the limiting factor in determining how fast cars following can proceed

Slow Steps



- Conclusions
 1. The overall rate of a reaction cannot exceed the rate of the slowest step
 2. If that step is by far the slowest, its rate will be approximately equal to that of the overall reaction
 3. The slowest step in a reaction will ordinarily be the one with the highest activation energy

Deducing a Rate Expression from a Proposed Mechanism

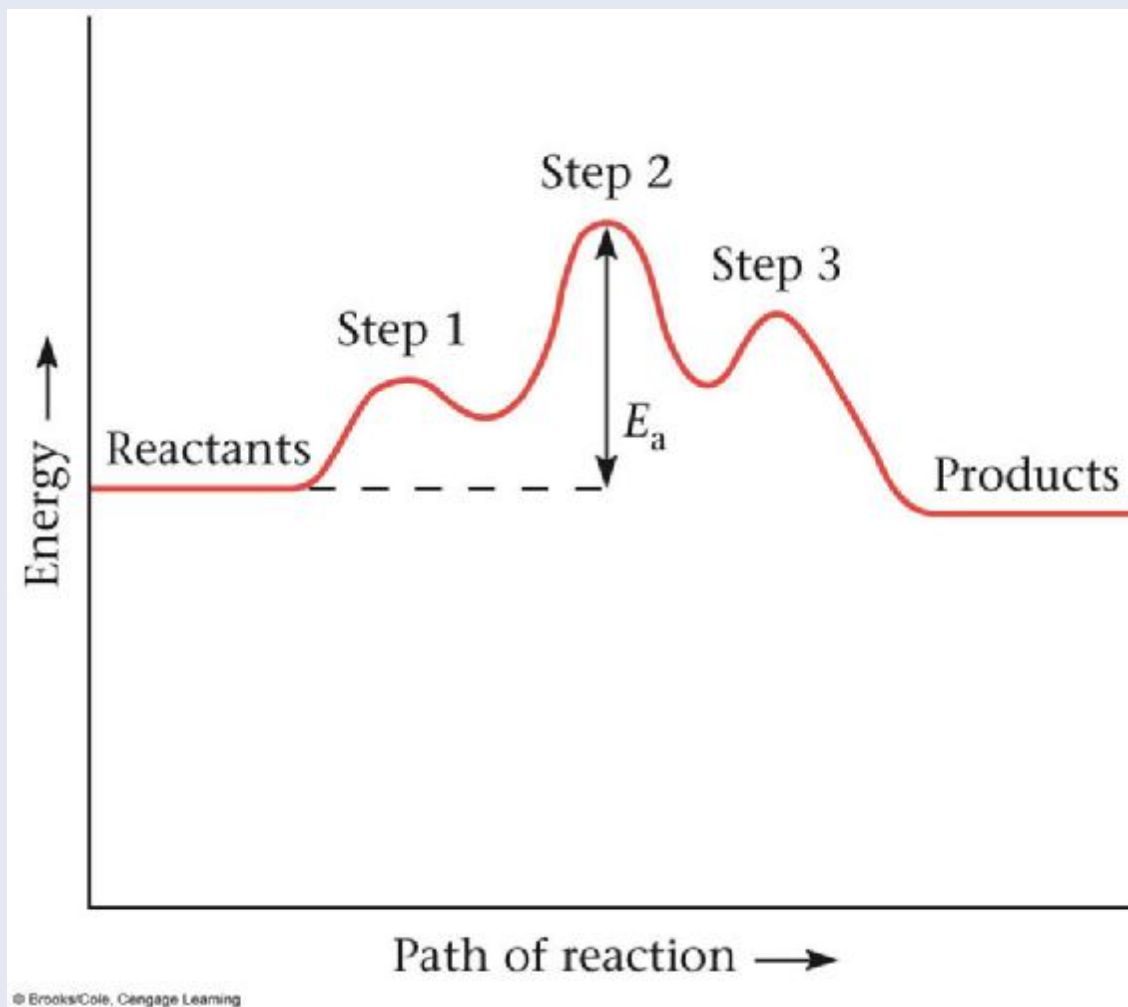


1. Find the slowest step and equate the rate of the overall reaction to the rate of that step
2. Find the rate expression for that slowest step

Figure 11.14



- In figure 11.14, clearly step 2 has the largest activation energy, so it is the slowest step



Deducing the Slower Step



- $\text{NO}_2 (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{CO}_2 (\text{g})$ (slow)
- $\text{CO} (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NO}_2 (\text{g})$ (fast)
- Overall, the sum of the steps is the same:
 - $\text{CO} (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NO} (\text{g})$
- Rate = $k[\text{NO}_2]^2$
- Note that ***this rate expression is different*** that the one we saw at high temperature; in other words, ***the rate expression depends on the mechanism***

Reactive Intermediates



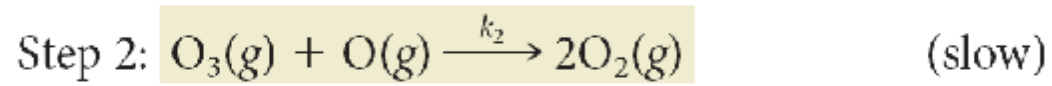
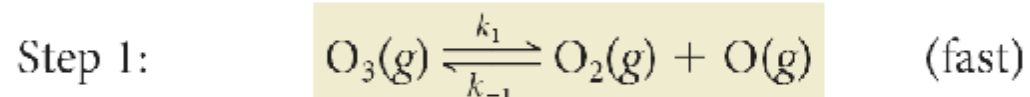
- Mechanisms often involve reactive intermediates
 - These are produced in one step and consumed in a subsequent step
 - These do not appear in overall reactions
 - Concentrations are too small to observe experimentally
 - The terms for such species are eliminated in the process of determining the rate expression

Example 11.8



Example 11.8

The decomposition of ozone, O_3 , to diatomic oxygen, O_2 , is believed to occur by a two-step mechanism:



Obtain the rate expression corresponding to this mechanism.

Example 11.8, (Cont'd)



Strategy Write the rate expression for the rate-determining second step. This will involve the unstable intermediate, O. To get rid of [O], use the fact that reactants and products are in equilibrium in step 1, so forward and reverse reactions occur at the same rate.

SOLUTION

$$(1) \text{ Overall rate} = \text{rate step 2} = k_2[\text{O}_3] \times [\text{O}]$$

$$(2) k_1[\text{O}_3] = k_{-1}[\text{O}_2] \times [\text{O}]$$

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

$$(3) \text{ Overall rate} = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]} = \frac{k [\text{O}_3]^2}{[\text{O}_2]}$$

Reality Check Notice that the concentration of O_2 , a product in the reaction, appears in the denominator. The rate is inversely proportional to the concentration of molecular oxygen, a feature that you would never have predicted from the balanced equation for the reaction. As the concentration of O_2 builds up, the rate slows down.

Limitations on Mechanism Studies



- More than one mechanism is usually compatible with the data obtained from experiment
- It can be difficult to ascertain which mechanism is the true mechanism for a reaction

Key Concepts



1. Determine the reaction order from
 - Initial rate data
 - Concentration-time data
 - The reaction mechanism
2. Relate concentration and time for various orders of reaction
3. Use the Arrhenius equation to relate the activation energy to temperature