Chapter 14: Chemical Kinetics

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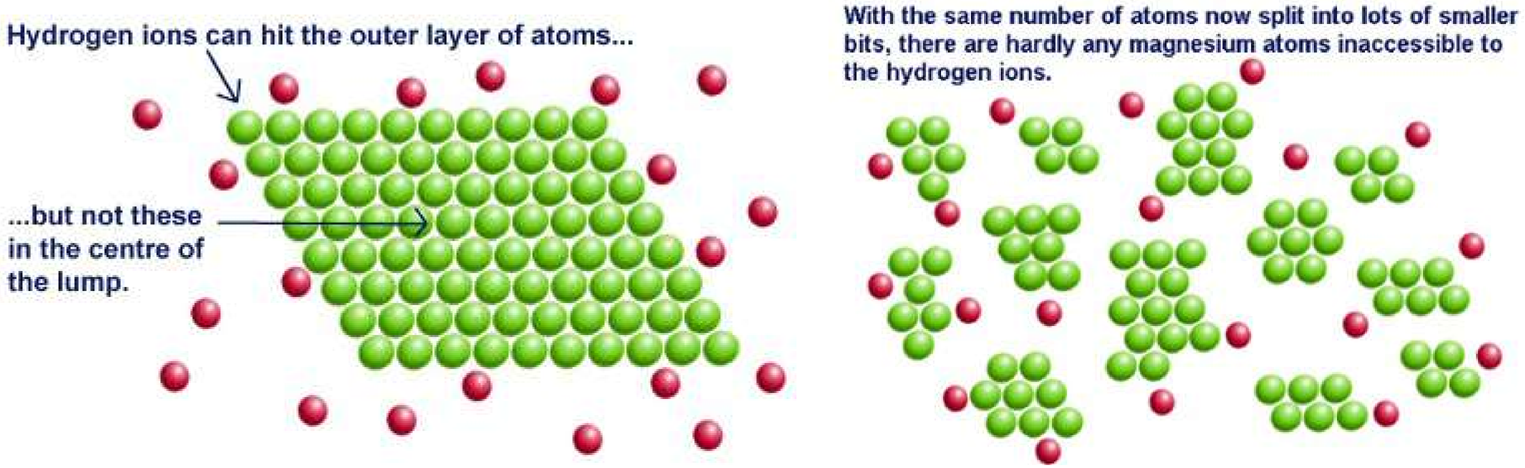
Section 14.1 – Factors that Affect Reaction Rates

- The area of chemistry that is concerned with the speeds, or rates, of reactions is called chemical kinetics.
- Reaction rates depend on the frequency of the collisions between the particles.
- The four factors that affect the rate of reaction are the physical states of the reactants, concentration of reactants, temperature, and presence of a catalyst.

Physical States

- Reactions occur the fastest when the molecules are colliding quickly.
- When the reactants are the same state of matter, reactions tend to occur faster.
- When a solid has a larger surface area (crushed), a reaction proceeds faster.



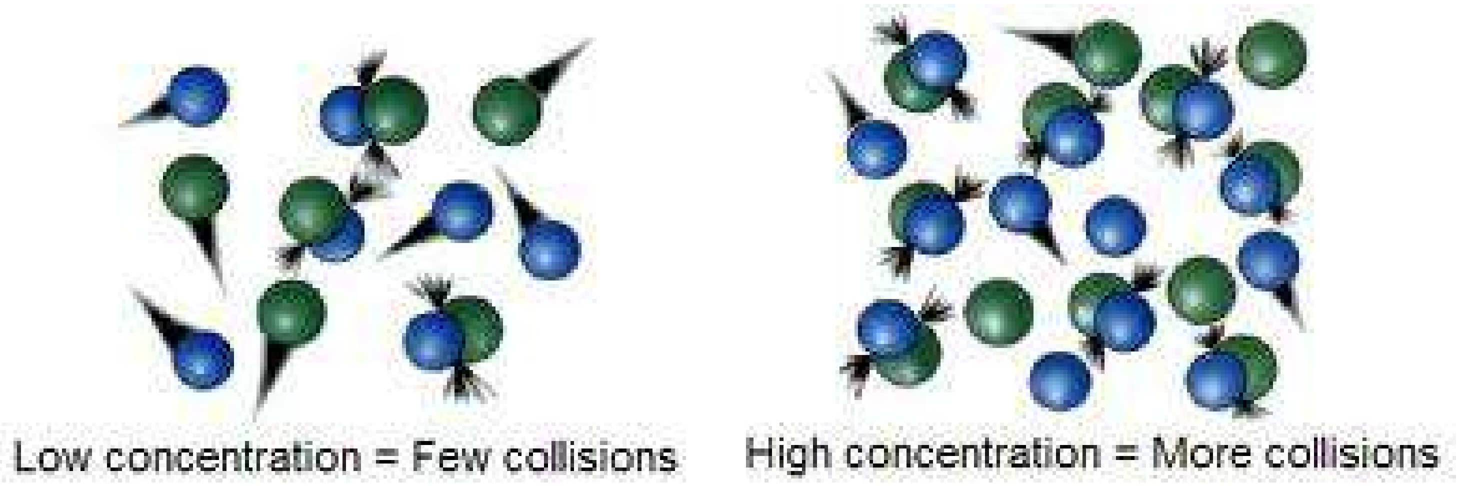
Hydrogen ions can hit the outer layer of atoms...

...but not these in the centre of the lump.

With the same number of atoms now split into lots of smaller bits, there are hardly any magnesium atoms inaccessible to the hydrogen ions.

Concentration

- Most chemical reactions proceeds faster if the concentration of one or more of the reactants is increased.
- The increase in reaction rate is due to an increase in collisions of particles.



Temperature

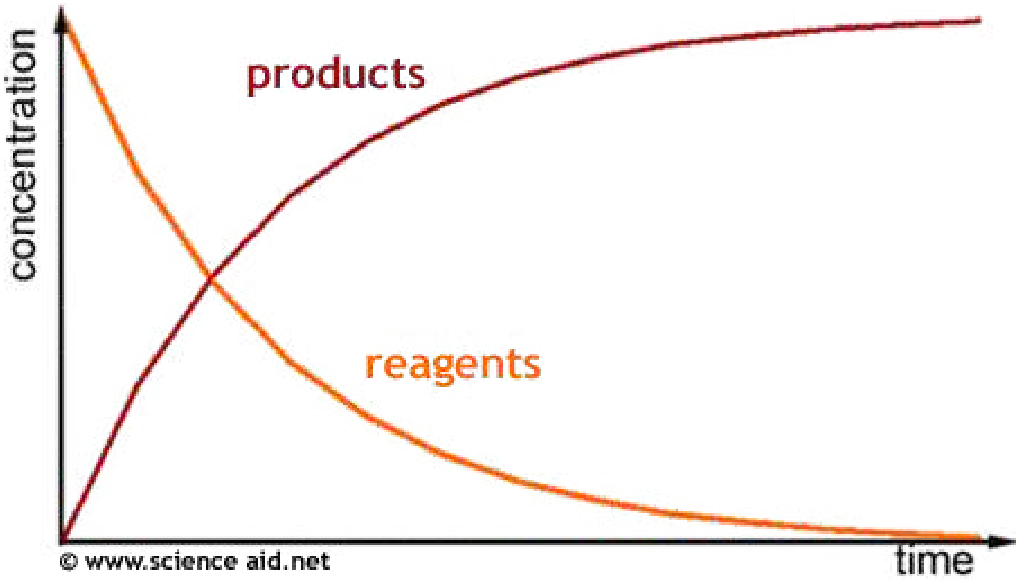
- The rate of a chemical reaction increases as temperature increases.
- As temperature increases, the particles collide more frequently and with greater energy.

Catalyst

- Catalysts speed up a reaction be changing the mechanism that leads to the products.
- Catalysts are not considered reactants or products and are listed about the yield sign.

Section 14.2 – Reaction Rates

- The speed of a chemical reaction – its reaction rate – is the change in the concentration of reactants or products per unit of time.
- The units are molarity per second (M/s).



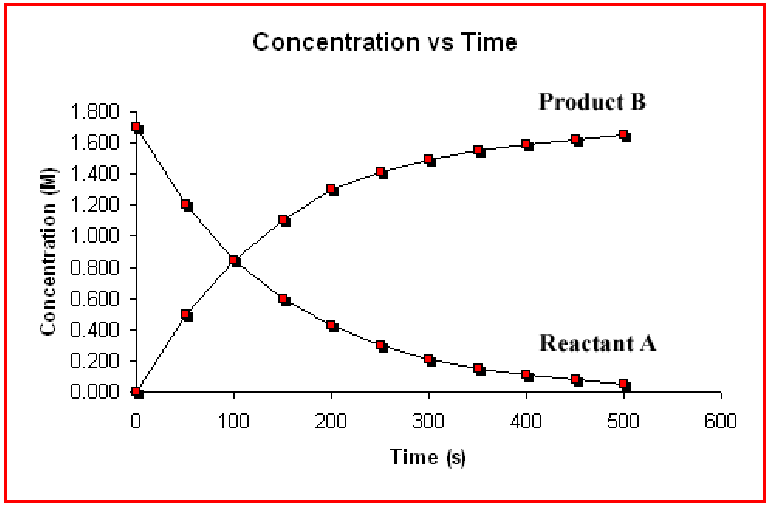
Reaction Rates

- The rate of a reaction can be expressed as either the disappearance of the reactant or the appearance of the product.

$$A \rightarrow B$$

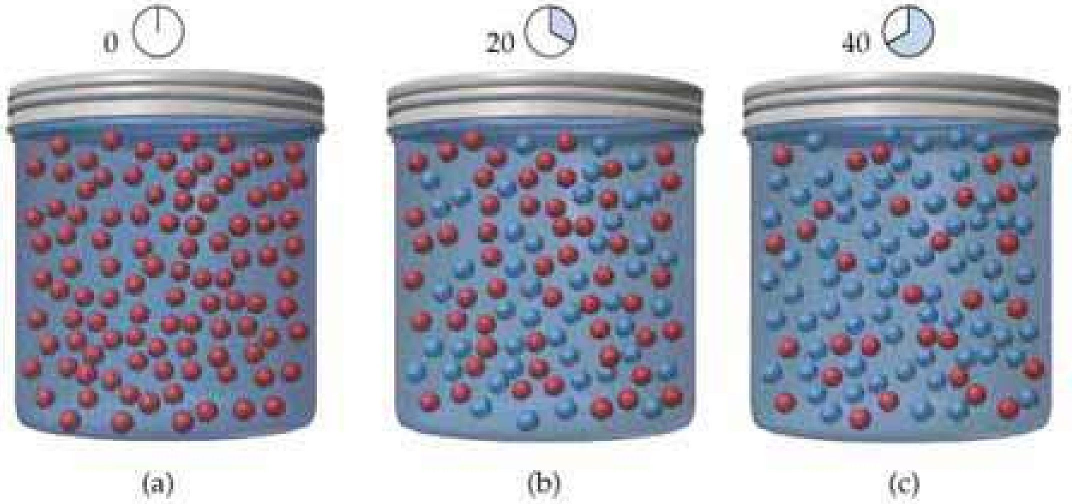
$$\text{Appearance of B} = \frac{\Delta[B]}{\Delta t}$$

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



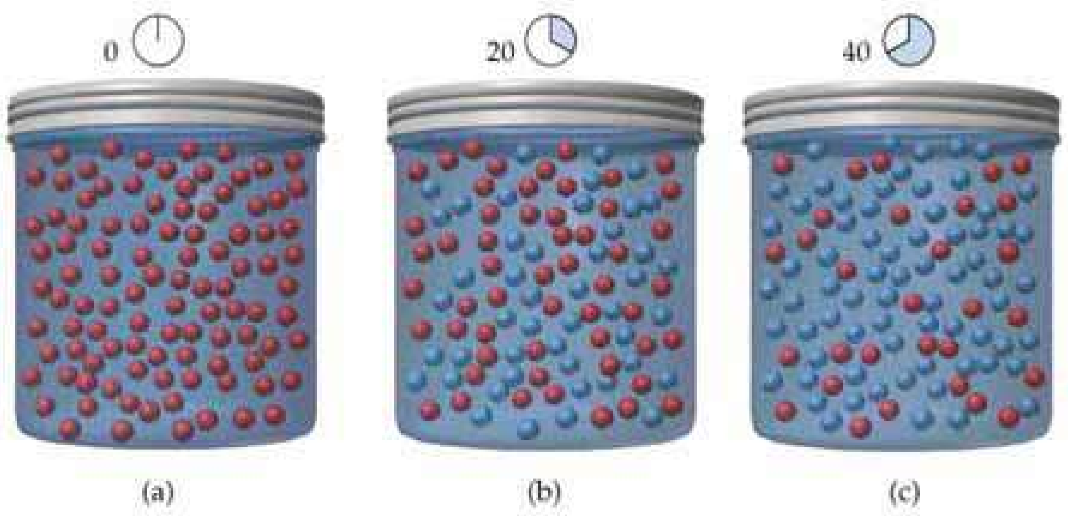
Sample Exercise 14.1

- From the data given below, calculate the average rate at which A disappears over the time interval from 20s to 40s.



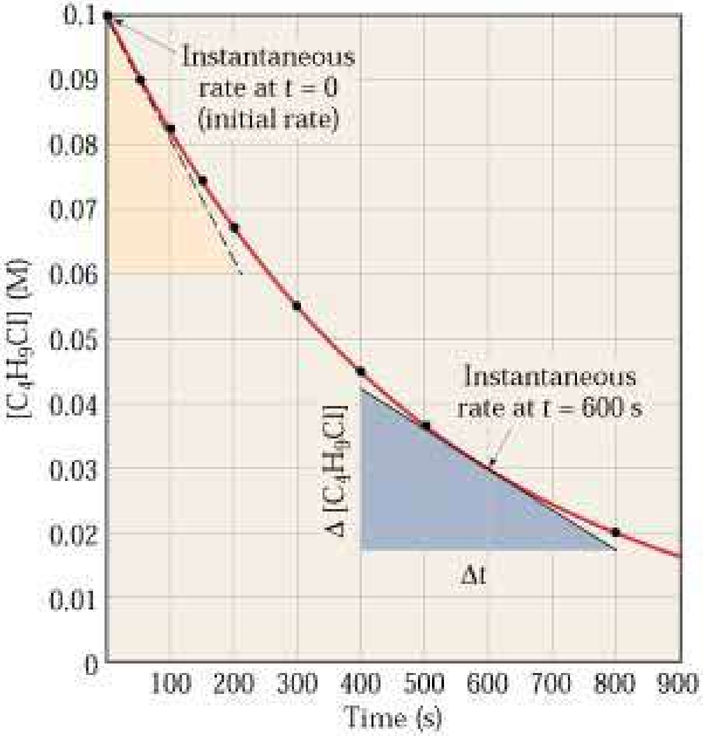
Practice Exercise

- For the reaction in the previous question, calculate the average rate of appearance of B over the time interval from 0s to 40s.



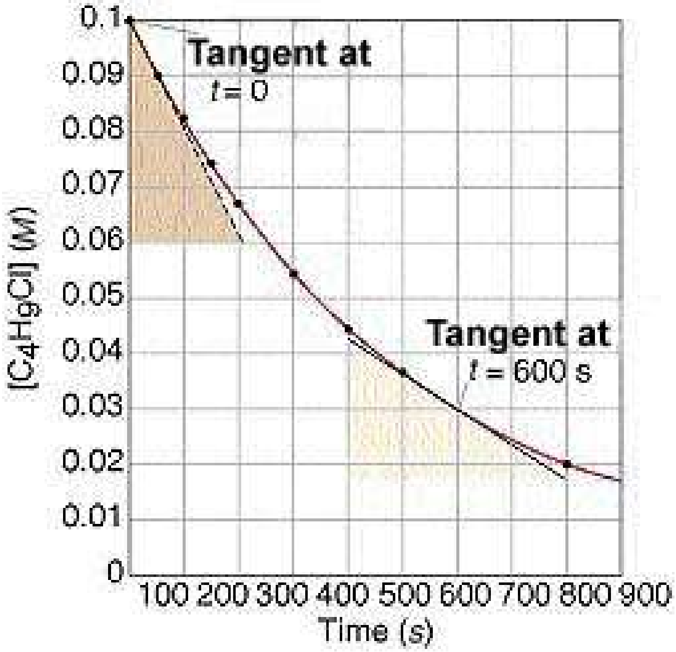
Reaction Rates with Time

- It is typical for rates to decrease as a reaction proceeds because the concentration of reactants decreases.



Instantaneous Rate

- Graphs showing us the change in concentration with time allow us to calculate the instantaneous rate, the rate at a particular moment.
- The instantaneous rate is the slope of a line drawn at a point on the graph. (tangent)



Initial Rate

- The initial rate is the instantaneous rate at t = 0s.

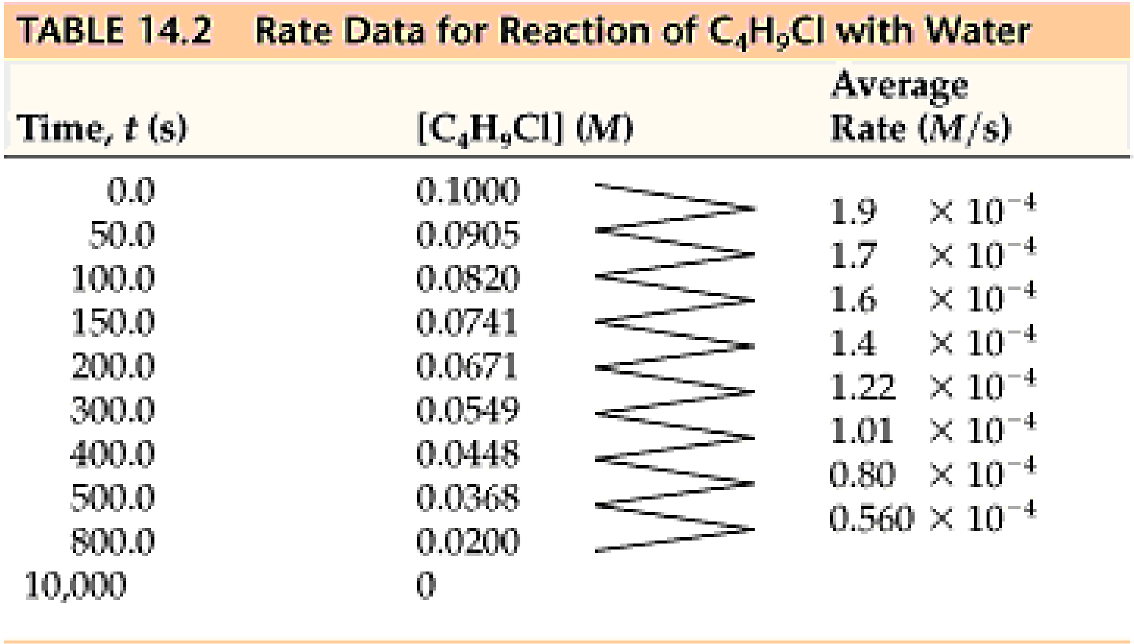
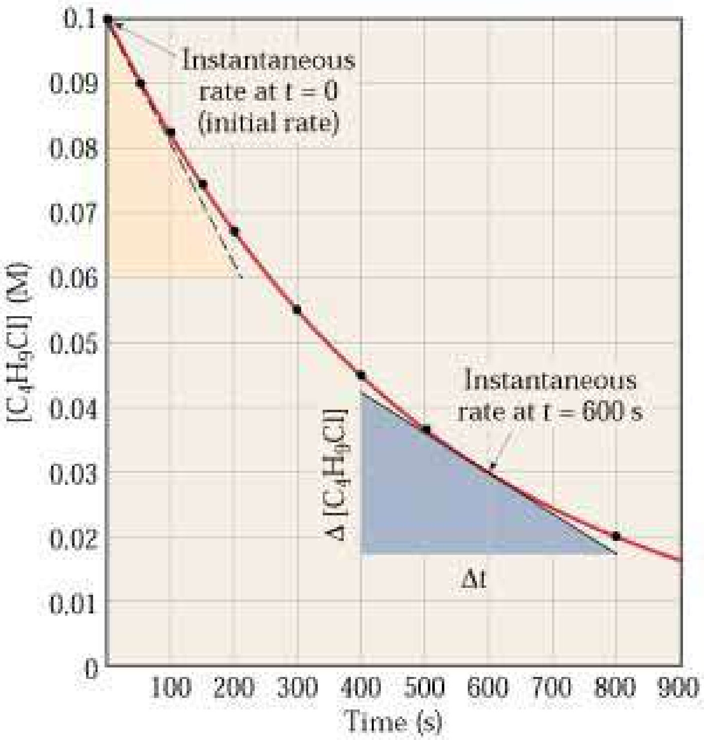


TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water

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	

Sample Exercise 14.2

- Using the following graph, calculate the instantaneous rate of disappearance of C_4H_9Cl at t = 0s.



Practice Exercise

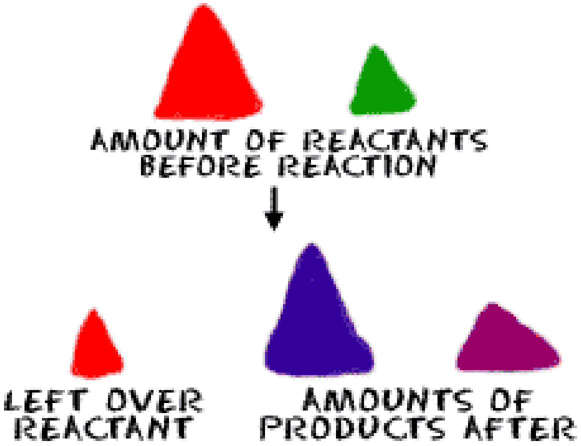
- Using the graph from the previous question, determine the instantaneous rate of disappearance of C_4H_9Cl at t = 300s.

Stoichiometry

- When determining the reaction rates for a chemical reaction, the coefficients must be used.

$$aA + bB \rightarrow cC + dD$$

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



Sample Exercise 14.3

a. How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2O_{3(g)} \rightarrow 3O_{2(g)}$?

b. If the rate at which O_2 appears 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this time?

Practice Exercise

- The decomposition of N_2O_5 proceeds according to the following reaction:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7} M/s, what is the rate of appearance of NO_2 and O_2?

Section 14.3 – The Rate Law: The Effect of Concentration on Rate

- The rate law shows how the rate of a reaction depends on the concentration of the reactants.
- The rate law of a reaction can only be determined experimentally, not by the coefficients of a reaction.

$$aA + bB \longrightarrow \text{products}$$

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

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

k is the **rate constant**

Rate Law

- The rate law is written as follows:

$$aA + bB \rightarrow cC + dD$$

Rate = $k[A]^m[B]^n$

k = rate constant which changes with temperature

m and n = typically small whole numbers

Determining Rate Law

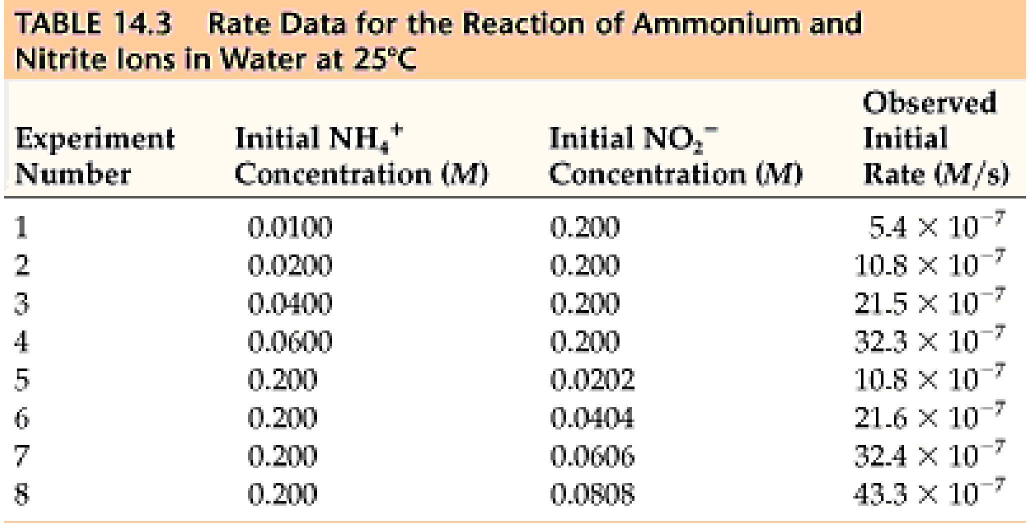


TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

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}

- Using the chart, we can see that the rate law would be

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

Since the rates change with a direct proportion to the concentrations of both reactants.

Reaction Orders

- The exponents m and n in a rate law are called the reaction orders.
- The overall reaction order is the sum of the reaction orders.

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

NH_4^+ = 1st order

NO_2^- = 1st order

Overall reaction order = 2nd order

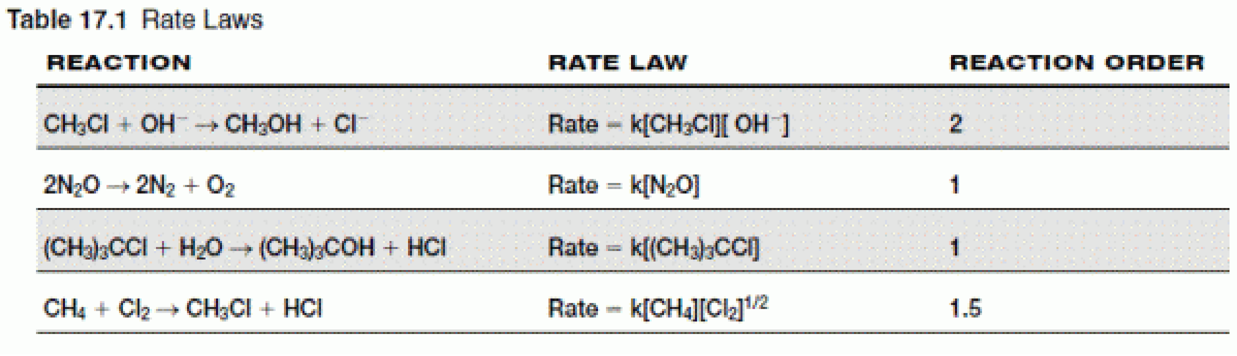
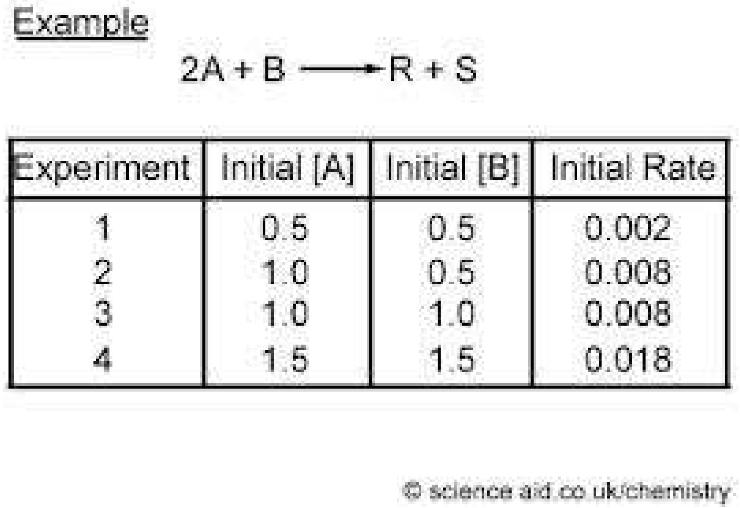


Table 17.1 Rate Laws

REACTION	RATE LAW	REACTION ORDER
$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	Rate = $k[CH_3Cl][OH^-]$	2
$2N_2O \rightarrow 2N_2 + O_2$	Rate = $k[N_2O]$	1
$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + HCl$	Rate = $k[(CH_3)_3CCl]$	1
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	Rate = $k[CH_4][Cl_2]^{1/2}$	1.5

Exponents

- The exponents/order are determined by how the rate changes with concentration.
- If the reaction is 1st order, then if the concentration doubles, the rate doubles.
- If the reaction is 2nd order, then if the concentration doubles, the rate quadruples.
- If the reaction is 3rd order, then if the concentration doubles, the rate increases by the power of 9.



Example

$$2A + B \longrightarrow R + S$$

Experiment	Initial [A]	Initial [B]	Initial Rate
1	0.5	0.5	0.002
2	1.0	0.5	0.008
3	1.0	1.0	0.008
4	1.5	1.5	0.018

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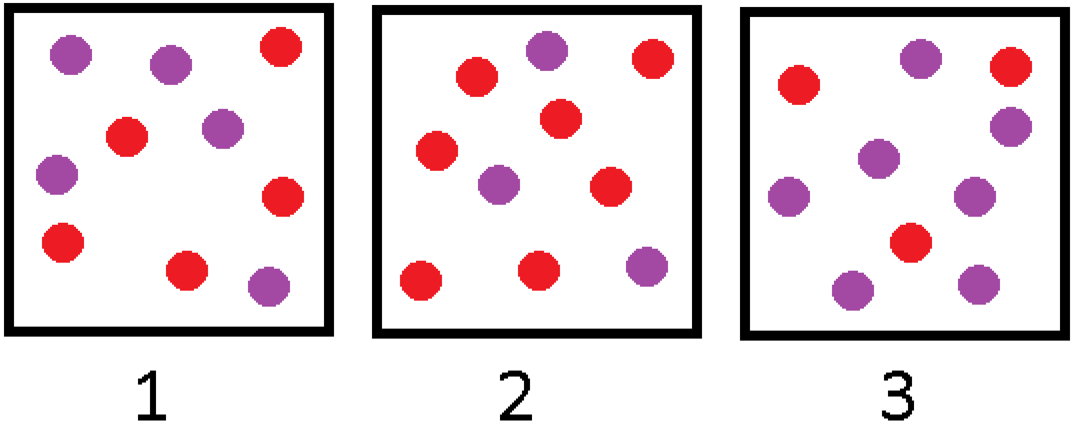
Sample Exercise 14.4

- Consider a reaction A + B → C for which rate = $k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank the mixtures in order of increasing rate of reaction.



Practice Exercise

- Assuming that rate = k[A][B], rank the previous mixtures in order of increasing rate.

Units for Rate Constants

- The units for the rate constant depend on the overall reaction order of the rate law.

$$k = \frac{\text{Rate}}{[\text{B}]^2}$$

in terms of units:

$$k = \frac{M/s}{(M)^2} = {}^{1}\!/_{M \cdot s} \, (= M^{-1} s^{-1})$$

Sample Exercise 14.5

a. What are the reaction orders for the following reactions?

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + +O_{2(g)}$$

$$Rate = k[N_2O_5]$$

$$CHCl_{3(g)} + Cl_{2(g)} \rightarrow CCl_{4(g)} + HCl_{(g)}$$

$$Rate = k[CHCl_3][Cl_2]^{1/2}$$

Sample Exercise 14.5 con’t

b. What are the units of the rate constant for the first reaction from the previous question?

Practice Exercise

a. What is the reaction order of the reactant H_2 in the following equation?

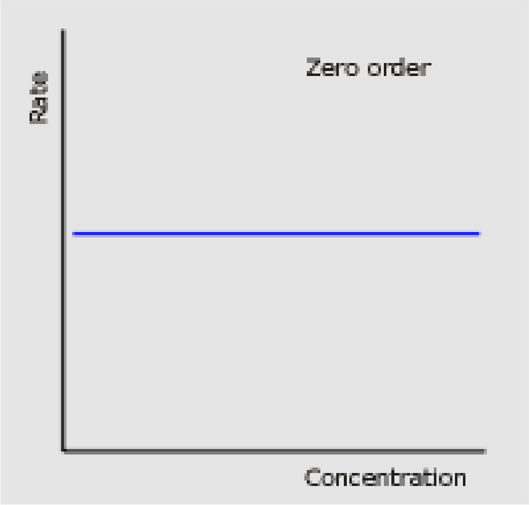
$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

$$\text{Rate} = k[H_2][I_2]$$

b. What are the units of the rate constant for the equation?

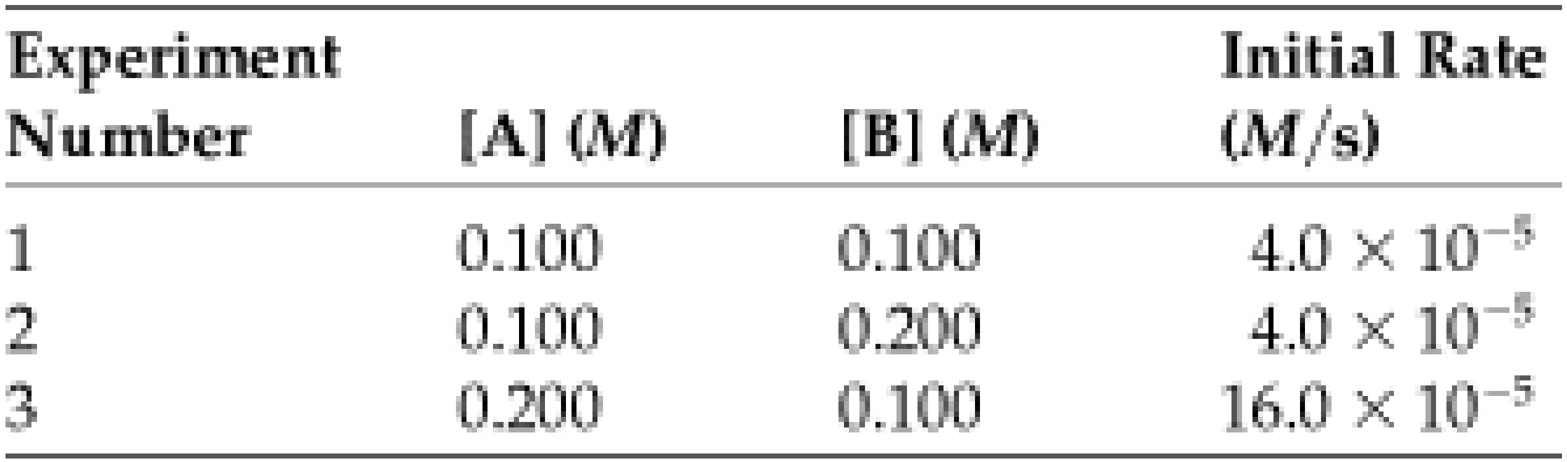
Determining Rate Laws

- If a reaction is zero order, then changing the concentration of the reactant will have no effect.
- The rate of a reaction depends on concentration, but the rate constant (k) does not.
- The rate constant is affected by temperature and the presence of a catalyst.



Sample Exercise 14.6

- The initial rate of a reaction A + B → C was measured for several different starting concentrations of A and B, and the results are as follows:



Experiment Number	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Sample Exercise 14.6 con't

a. Using the data, determine the rate law for the reaction.

b. Determine the rate constant.

c. Determine the rate of the reaction when [A] = 0.050M and [B] = 0.100M.

Practice Exercise

- The following data was measured for the reaction of nitric oxide with hydrogen:

$$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

Experiment Number	[NO] (M)	$[H_2]$ (M)	Initial Rate (M/s)
1	0.1	0.1	1.23×10^{-3}
2	0.1	0.2	2.46×10^{-3}
3	0.2	0.1	4.62×10^{-3}

Practice Exercise con’t

a. Determine the rate law for this reaction.

a. Calculate the rate constant.

a. Calculate the rate when [NO] = 0.050M and [H_2] = 0.150M.

Section 14.4 – The Change of Concentration with Time

- A first order reaction is one whose rate depends on the concentration of a single reactant to the first power.

  Differential Rate Law   Rate = k[A]

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

- You can use this equation to solve for concentration or time.

Practice Exercise 14.7

- The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12°C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3. Assume that the average temperature of the lake is 12°C.

a. What is the concentration of the insecticide on June 1 of the following year?

Sample Exercise 14.7 con’t

b. How long will it take fort he concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

Practice Exercise

- The decomposition of dimethyl ether, $(CH_3)_2O$, at 510°C is a first-order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$:

$$(CH_3)_2O_{(g)} \rightarrow CH_{4(g)} + H_{2(g)} + CO_{(g)}$$

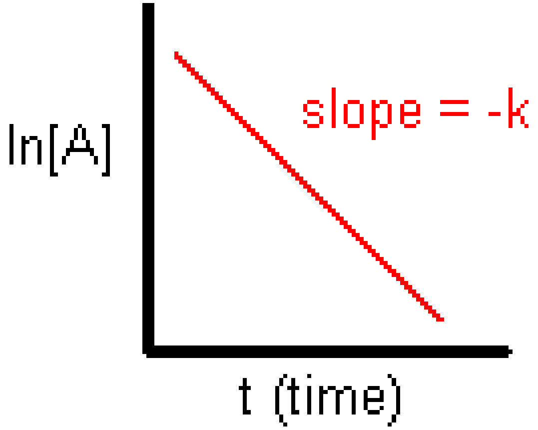
If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420s?

Reaction Rate Graphs

- For a 1st order reaction, a graph of $\ln[A]_t$ vs. time will give a straight line.

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

$$y \quad = mx + \quad b$$



$\ln[A] = -kt \qquad \frac{d[A]}{dt}$

Second Order Rates

- A second order reaction is one whose rate depends on the reactant concentration to the 2nd power or 2 reactants to the 1st power.

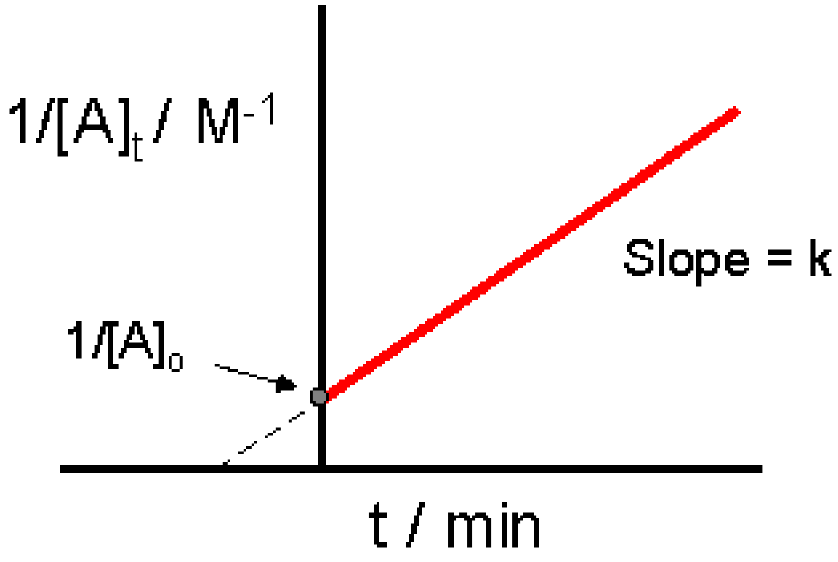
Differential Rate Law $\text{Rate} = k[A]^2$

Integrated Rate Law $1/[A]_t = kt + 1/[A]_0$

$y \quad = mx + \; b$

Reaction Rate Graphs

- For a second order reaction, a graph of $1/[A]_t$ vs. time gives a straight line.



Sample Exercise 14.8

- The following data was obtained fort he gas-phase decomposition of nitrogen dioxide at 300°C, $NO_{2(g)} \rightarrow NO_{(g)} + \frac{1}{2} O_{2(g)}$:

Time (s)	$[NO_2]$ (M)
0	0.01
50	0.00787
100	0.00649
200	0.00481
300	0.0038

Is the reaction first or second order in NO_2?

Practice Exercise

- Consider again the decomposition of NO_2. The reaction is second order in NO_2 with $k = 0.543\ M^{-1}s^{-1}$. The initial concentration of NO_2 in a closed vessel is 0.0500M, what is the remaining concentration after 0.500 hours?

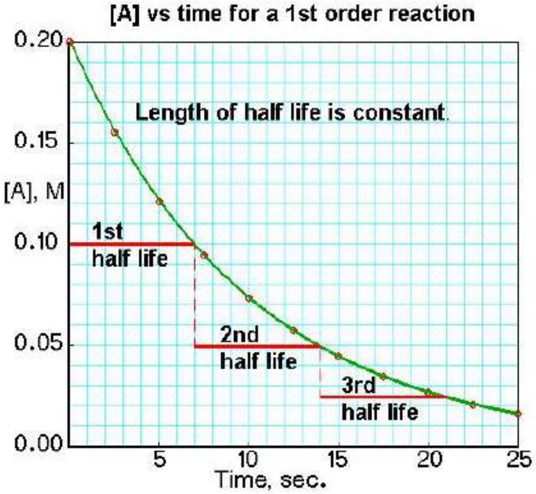
Half-Life

- The half-life of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach one-half of its initial value, $[A]_{t1/2} = ½ [A]_0$.
- A fast reaction will have a short half-life.
- Half-life for a 1st order reaction.

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

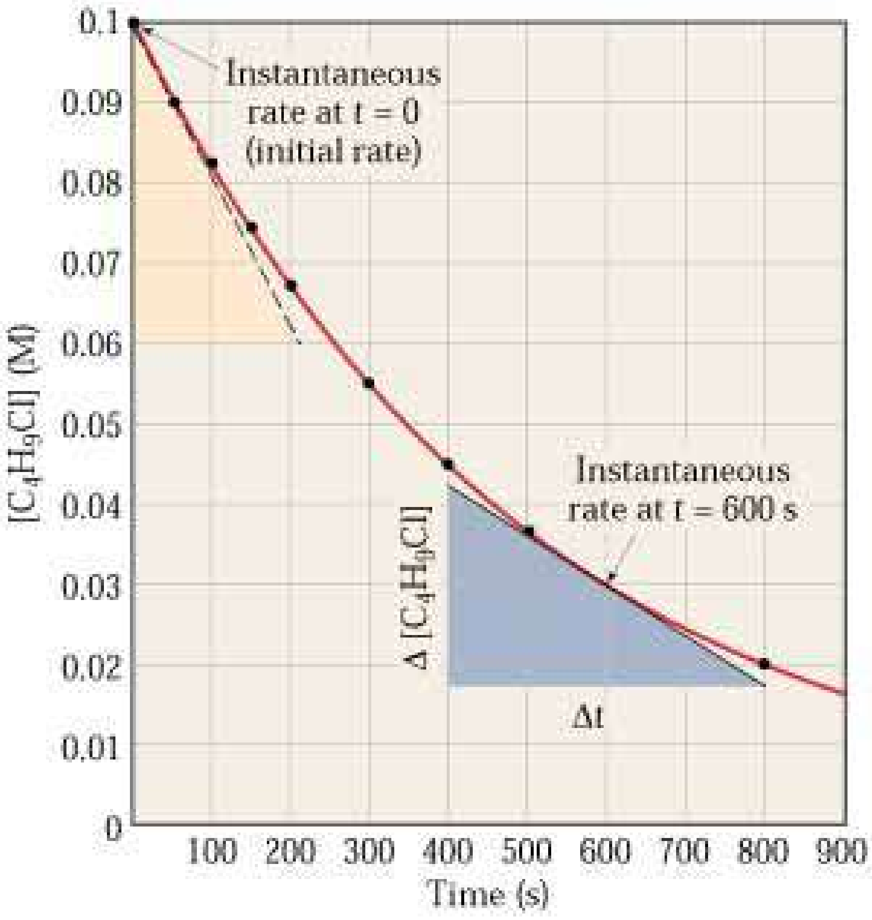
Half-Life

- Using the equation from the previous slide, you can see that the half-life of a first order reaction does not depend on initial concentration.
- In a 1st order reaction, the concentration of the reactant decreases by ½ in each of a series of regularly spaced time intervals, $t_{1/2}$.



Sample Exercise 14.9

- The reaction of C_4H_9Cl with water is a first-order reaction. The following graph shows how the concentration of C_4H_9Cl changes with time at a particular temperature.



Sample Problem 14.9

a. From that graph, estimate the half-life for this reaction.

b. Use the half-life from part a to calculate the rate constant.

Practice Exercise

a. Calculate the $t_{1/2}$ for the decomposition of the insecticide from Sample Exercise 14.7.

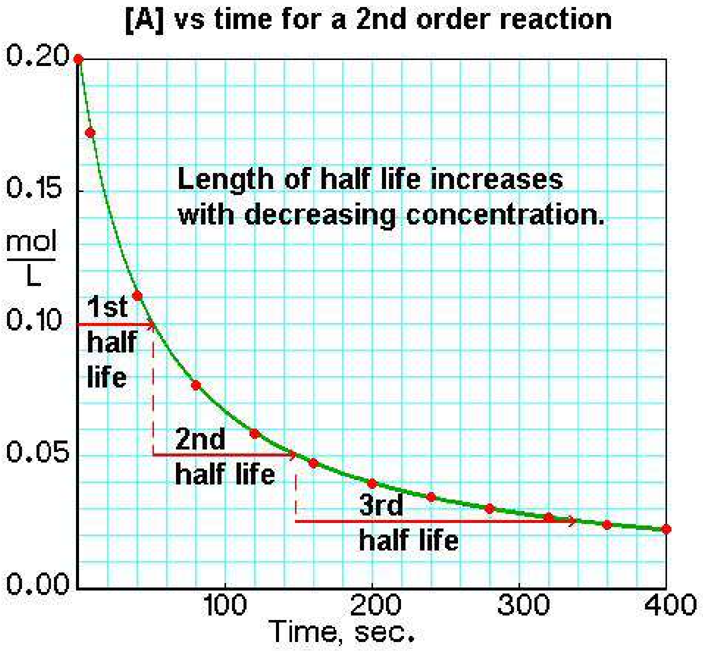
b. How long does it take for the concentration of the insecticide to reach ¼ of the initial value?

Half-life for 2nd Order

- The half-life of a 2nd order reaction does depend on initial concentration.

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

The lower the initial concentration, the larger the half-life.

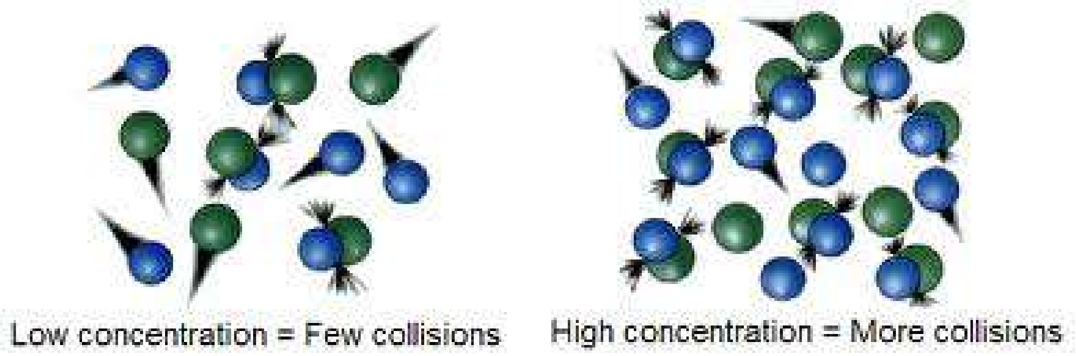


Section 14.5 – Temperature and Rate

- The rates of most chemical reactions increase as the temperature increases.
- The rate constant for a reaction increases as temperature increases.

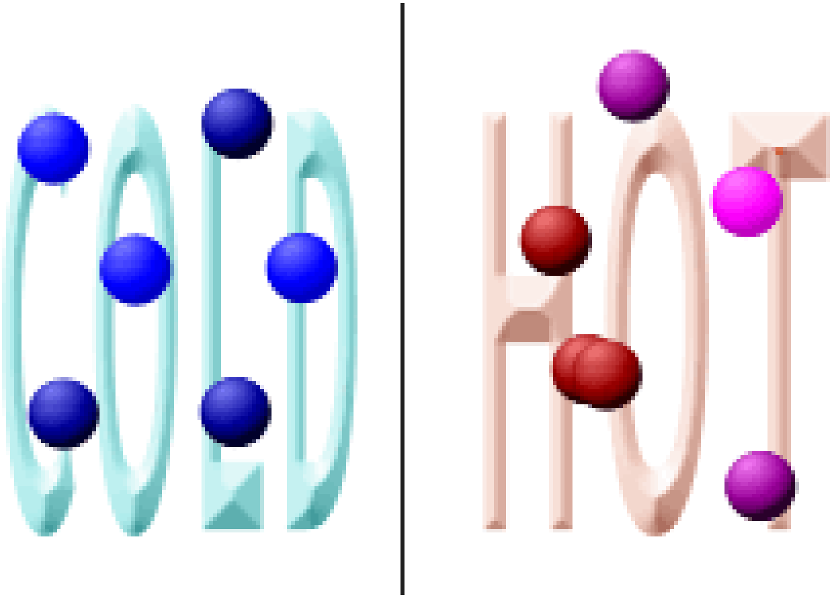
Collision Model

- The collision model is based on the idea that particles must collide in order to react.
- The greater the number of collision, the greater the reaction rate.
- As the concentration of reactants decreases, the number of collisions decreases.



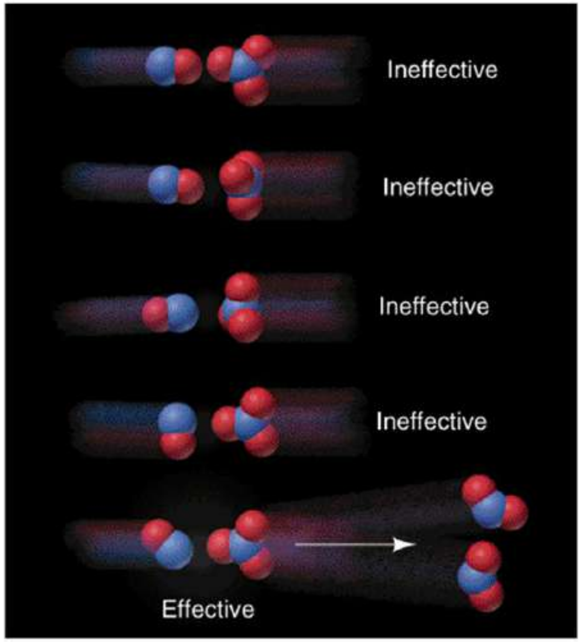
Collision Model

- As the temperature increases, the number of collisions increases. The energy of the collisions also increases.



Orientation Factor

- In most reaction, molecules must be oriented in a certain way during collisions.



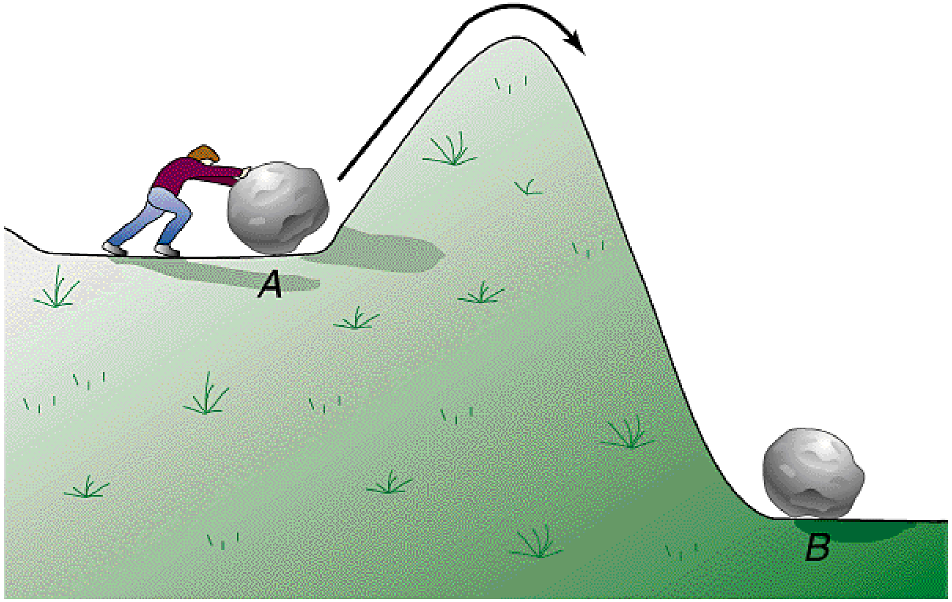
Collide and transfer kinetic energy but not enough to break bonds so they just bounce off

Pardon me – never mind

Collide with enough KE break bonds so that new ones form

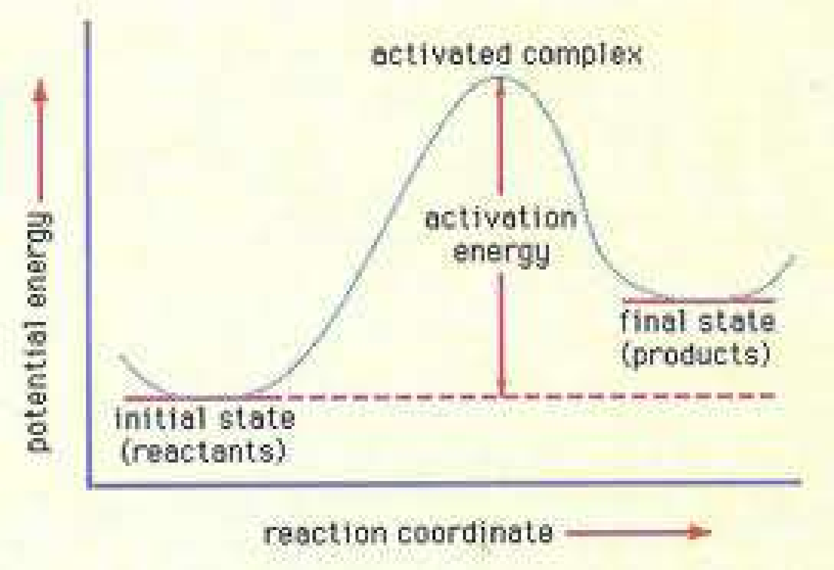
Activation Energy

- To react, colliding molecules must have a total kinetic energy equal to or greater than a minimum value called the activation energy, E_a.



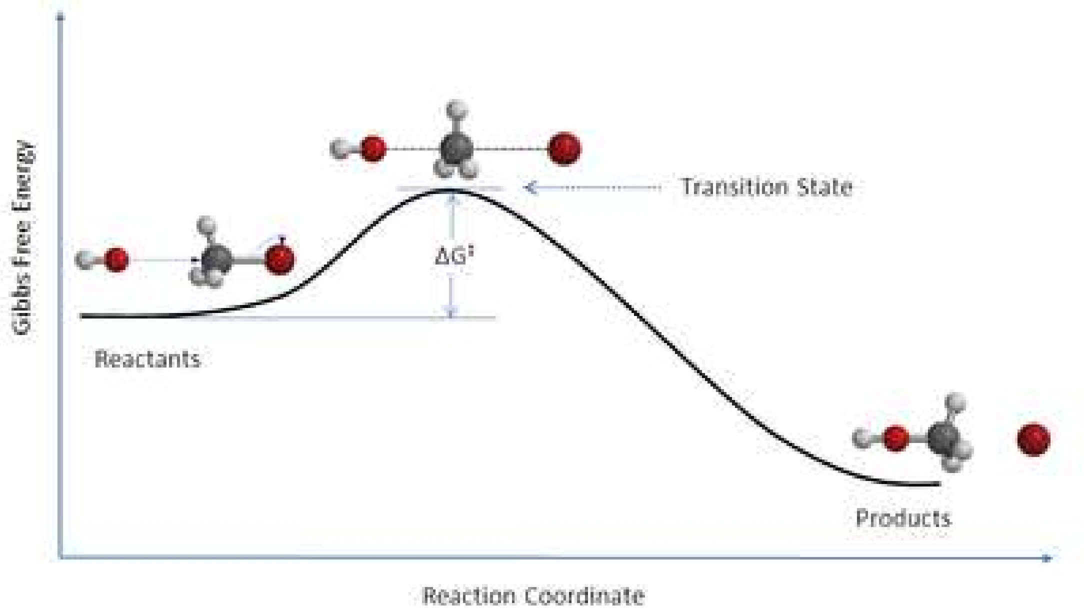
Activation Energy

- The activation energy is energy difference between the energy of the reactants and the highest point on the energy pathway.
- The highest point on the energy pathway is called the activated complex or transition state.

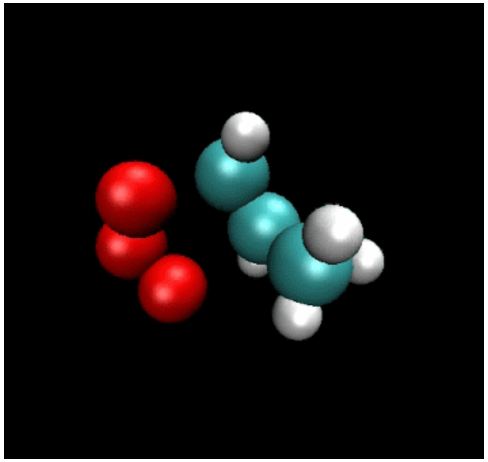


Transition State

- The transition state is very unstable.

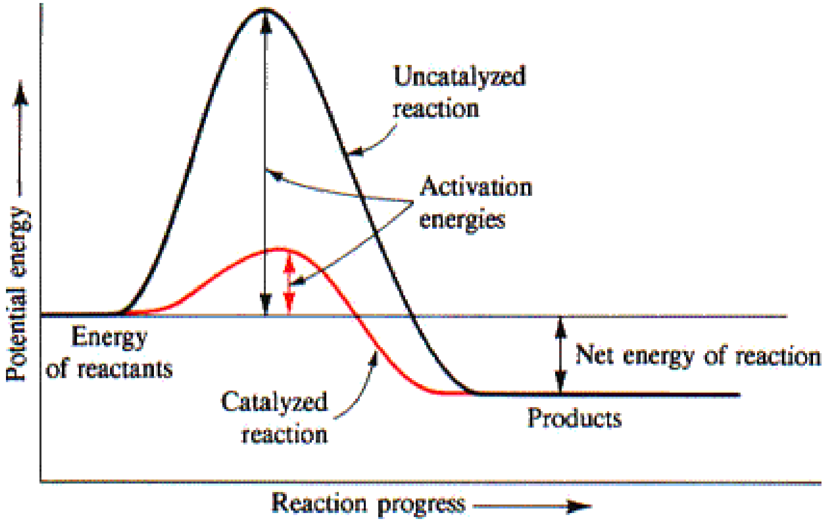


Reaction: $HO^- + CH_3Br \rightarrow [HO{-}{-}{-}CH_3{-}{-}{-}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$



ΔE

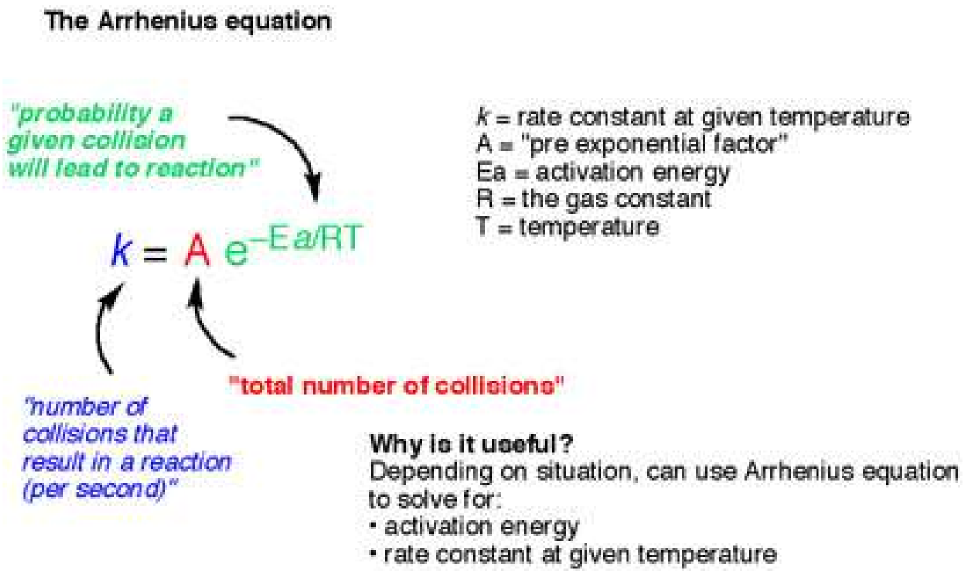
- The overall change in energy ΔE is the difference in energy between the products and the reactants.
  - ΔE has no effect on the rate of the reaction.
- The rate of a reaction depends on E_a.



Arrhenius Equation

- Arrhenius discovered that most reaction rate data obeyed 3 factors:

1. fraction of molecules possessing E_a.
2. number of collisions per second.
3. fraction of collisions with proper orientation.



The Arrhenius equation

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

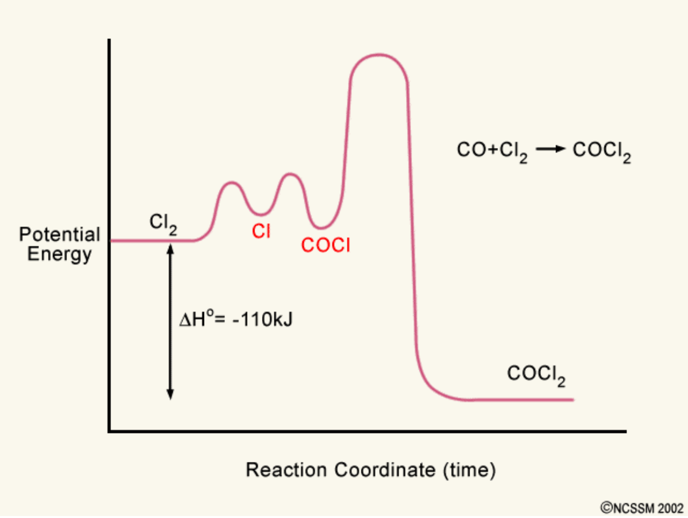
k = rate constant at given temperature
A = "pre exponential factor"
Ea = activation energy
R = the gas constant
T = temperature

Why is it useful?
Depending on situation, can use Arrhenius equation to solve for:

- activation energy
- rate constant at given temperature

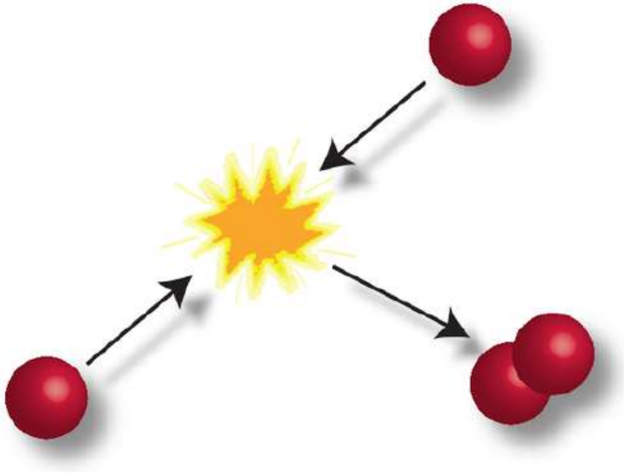
Section 14.6 – Reaction Mechanisms

- A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those produced as the reaction proceeds.
- The process by which a reaction occurs is called the reaction mechanism.



Elementary Reactions

- Reactions that occur in a single step are called elementary reactions.
- The number of molecules that participate are reactants in an elementary reactions defines the molecularity.



Molecularity

- Unimolecular = a single molecule is rearranged.
- Bimolecular = 2 molecules collide.
- Termolecular = 3 molecules collide.
- Elementary reactions that involve 3 or more molecules colliding are rarely encountered.

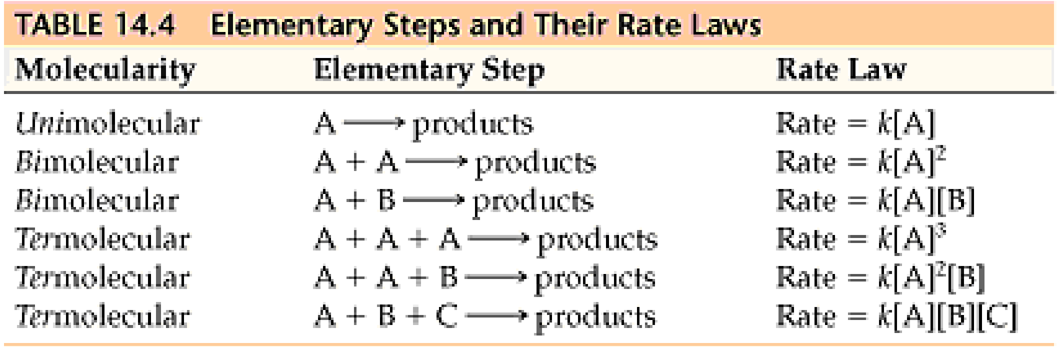
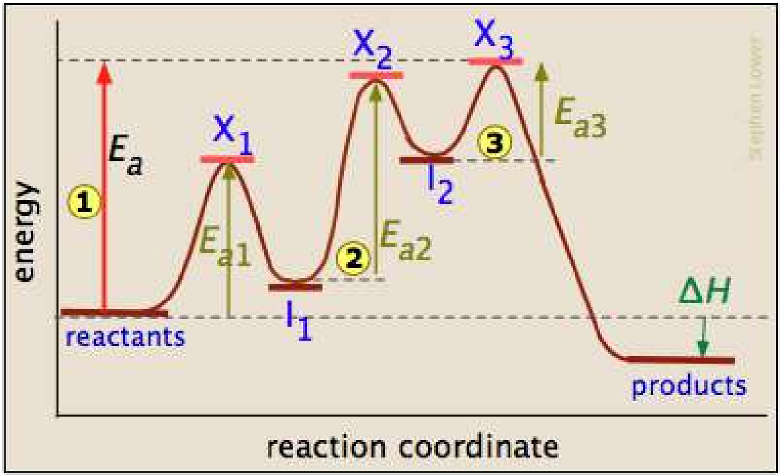


TABLE 14.4 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

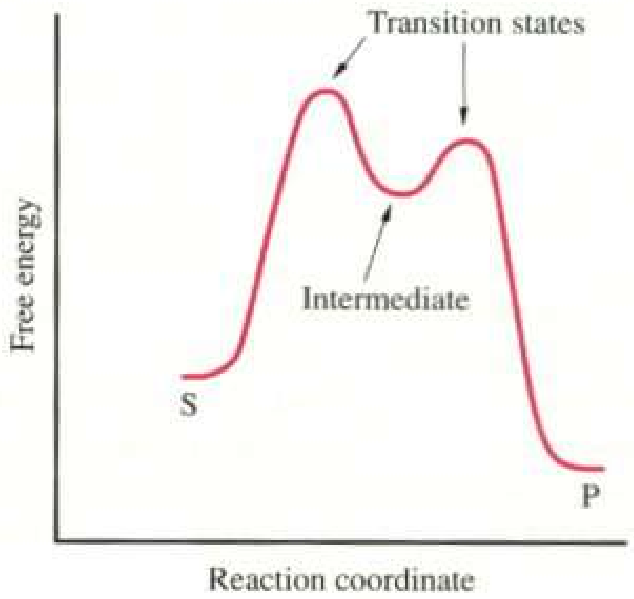
Multistep Mechanism

- Multistep mechanisms consist of multiple elementary reactions.
- The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.



Intermediate

- An intermediate is a substance formed and then consumed during the reaction mechanism.



Sample Exercise 14.12

- It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$$

$$O_{3(g)} + O_{(g)} \rightarrow 2O_{2(g)}$$

a. Describe the molecularity of each elementary reaction in this mechanism.

Sample Exercise 14.12 con’t

b. Write the equation for the overall reaction.

c. Identify the intermediates.

Practice Exercise

- For the reaction

$$Mo(CO)_6 + P(CH_3)_3 \rightarrow Mo(CO)_5P(CH_3)_3 + CO$$

the proposed mechanism is

$$Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$$

$$Mo(CO)_5 + P(CH_3)_3 \rightarrow Mo(CO)_5P(CH_3)_3$$

a. Is the proposed mechanism consistent with the equation for the overall reaction?

Practice Exercise

b. What is the molecularity of each of the mechanism?

c. Identify the intermediate.

Rate Laws

- Every reaction is made up of a series of one or more elementary steps, and the rate laws and relative speeds of these steps will dictate the overall rate law.
- If a reaction is an elementary reaction, then its rate law is based directly on its molecularity.

$$A \rightarrow \text{products}$$

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

Sample Exercise 14.13

- If the following reaction occurs in a single elementary reaction, predict its rate law:

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$$

Practice Exercise

- Consider the following reaction:

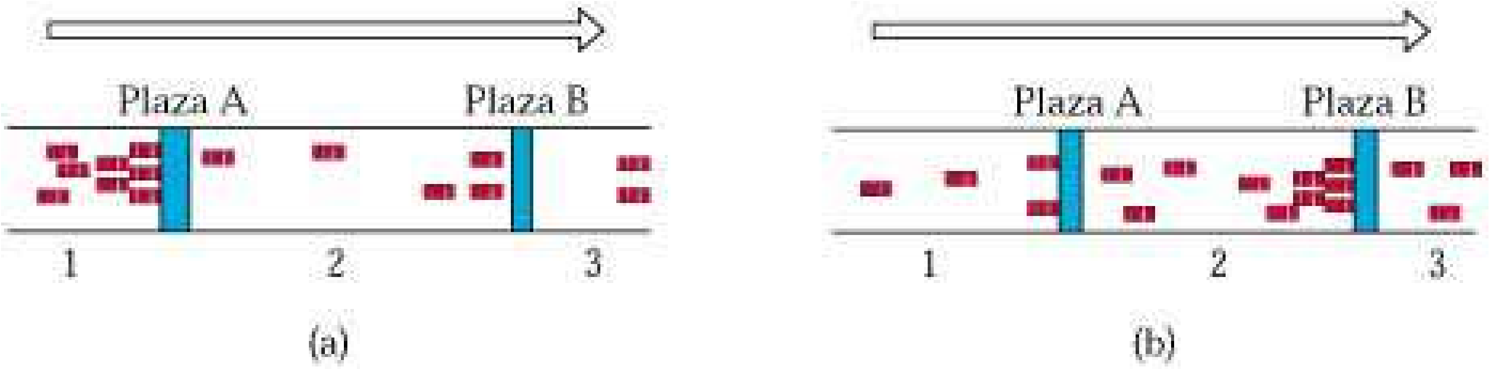
$$2NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{2(g)}$$

a. Write the rate law for the reaction, assuming it involves a single elementary reaction.

b. Is a single-step mechanism likely for this reaction?

Multistep Mechanism

- Each step of a mechanism has its own rate constant and activation energy.
- Often one step is slower than the others.
- The overall rate of a reaction cannot exceed the rate of the slowest elementary step, rate-determining step.



Multistep Reactions

- If the first step of the mechanism is slow, then the rate is based on the reactants of step 1.

$$\text{Step \#1:}\quad NO_2(g) + NO_2(g) \xrightarrow{k1} NO_3(g) + NO(g) \quad (\text{note: very } slow)$$

$$\underline{\text{Step \#2:}\quad NO_3(g) + CO(g) \xrightarrow{k2} NO_2(g) + CO_2(g)} \quad (\text{note: very } fast)$$

$$\text{Overall:}\quad NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Rate = $k[NO_2]^2$

Sample Exercise 14.14

- The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$N_2O_{(g)} + N_{2(g)} + O_{(g)} \quad \text{(slow)}$$

$$N_2O_{(g)} + O_{(g)} \rightarrow N_{2(g)} + O_{2(g)} \quad \text{(fast)}$$

a. Write the equation for the overall reaction.

Sample Exercise 14.14 con’t

b. Write the rate law for the overall reaction.

Practice Exercise

- Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

$$O_{3(g)} + 2NO_{2(g)} \rightarrow N_2O_{5(g)} + O_{2(g)}$$

This reaction is believed to occur in two steps:

$$O_{3(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + O_{2(g)}$$

$$NO_{3(g)} + NO_{2(g)} \rightarrow N_2O_{5(g)}$$

The experimental rate law is rate = $k[O_3][NO_2]$. What can you say about the relative rates of the two steps of the mechanism?

Fast Secondary Step

In general, when a fast step preceded a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the first step.

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

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

Rate = $k[NOBr_2][NO]$ (cannot contain intermediate

$[NOBr_2] = [NO][Br_2]$

Rate = $k[NO]^2[Br_2]$

Sample Exercise 14.15

- Show that the following mechanism for following reaction:

$2NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$

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

Step 1: $NO_{(g)} + NO_{(g)} \rightarrow N_2O_{2(g)}$ (fast)

Step 2: $N_2O_{2(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$ (slow)

Practice Exercise

- The first step of a mechanism involving the reaction of bromine is

$$Br_{2(g)} \rightarrow 2Br_{(g)} \quad \text{(fast, equilibrium)}$$

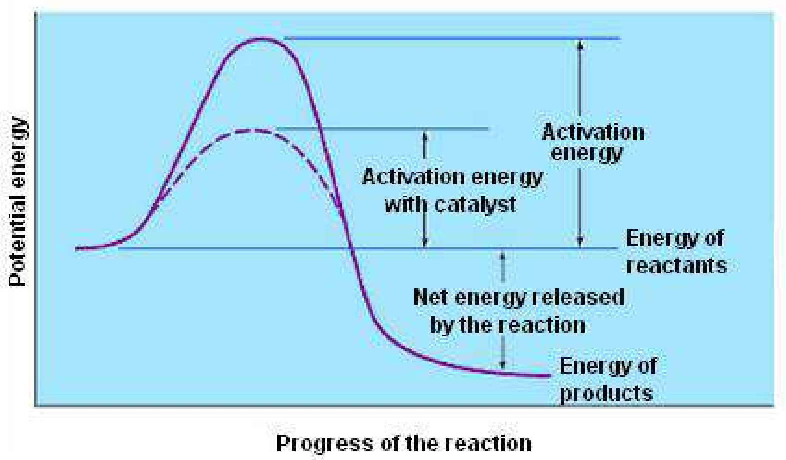
What is the expression relating the concentration of $Br_{(g)}$ to that of $Br_{2(g)}$?

Section 14.7 - Catalysis

- A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process.
- A catalyst that is present in the same phase as the reacting molecules is called a homogenous catalyst.

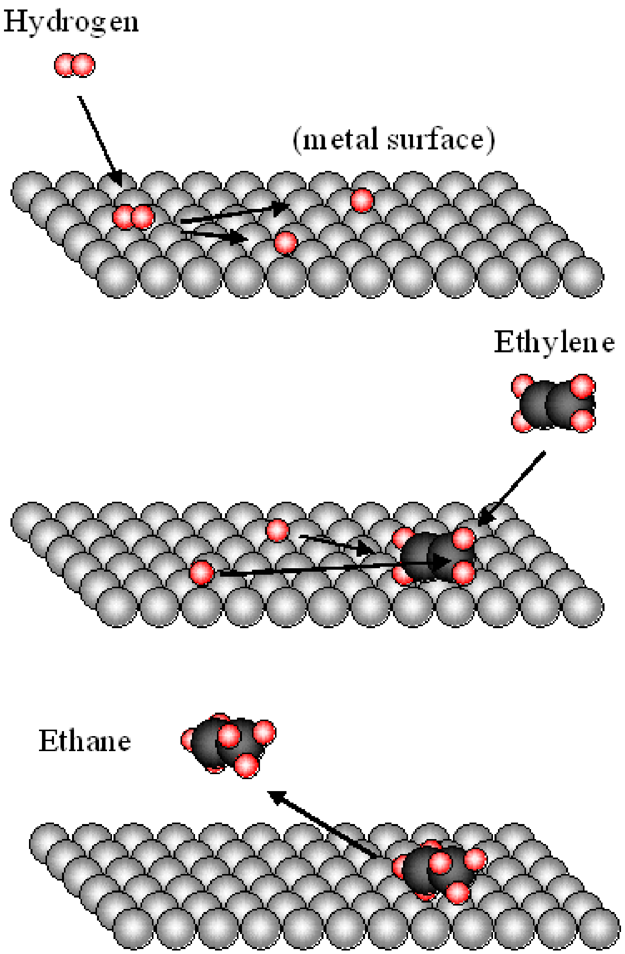
Catalyst

- Neither a catalyst nor an intermediate is listed in the overall reaction.
- The catalyst is there at the start of the reaction, whereas the intermediate is formed during the course of the reaction.
- A catalyst lowers the overall activation energy for the chemical reaction.



Catalyst

- A heterogeneous catalyst exists in a different phase from the reactant molecules, usually as a solid in contact with either gaseous reactants or with reactants in a liquid solution.
- The initial step in heterogeneous catalysis is usually adsorption of reactants.



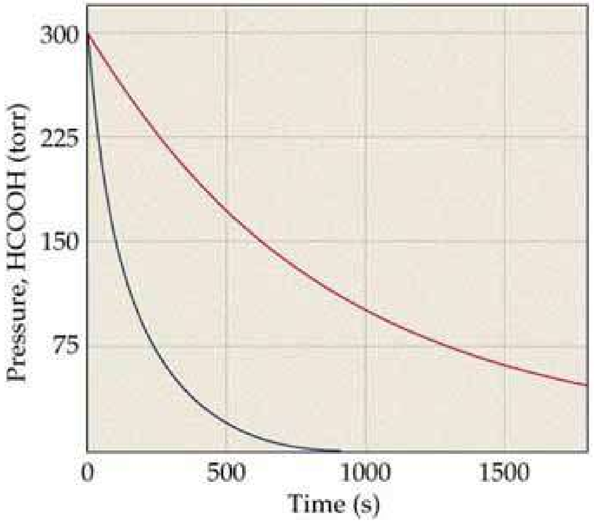
Sample Integrative Exercise

- Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:

$$HCOOH_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$$

The uncatalyzed decomposition reaction is determined to be first orde

A graph of the partial pressure of HCOOH versus time for decomposition at 838K is shown as the red curve.



Sample Integrative Exercise

- When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve.

a. Estimate the half-life and first-order constant for formic acid decomposition.

Sample Integrative Exercise

b. What can you conclude from the effect of added ZnO on the decomposition of formic acid?

c. The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of k?

Sample Integrative Exercise

d. The pressure of formic acid vapor at the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3, how many moles of gas occupy the reaction chamber at the end of the reaction?

Sample Integrative Exercise

- e. The standard heat of formation of formic acid vapor is ΔH°_{f} = -378.6 kJ/mol. Calculate ΔH° for the overall reaction. If the activation energy (E_a) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the

  reaction, and label

  E_a, ΔH°, and the

  transition state.