

Chapter 15: Phenomenon

Phenomenon: The reaction $A(aq) + B(aq) \rightarrow C(aq)$ was studied at two different temperatures (298K and 350K). For each temperature the reaction was started by putting different concentrations of the 3 species that take part in the reaction into an otherwise empty container. The reaction rate was then measured. What patterns do you notice about the reaction rates? Can reaction rates be predicted?

Data Taken at 298K				
Exp.	[A]	[B]	[C]	Rate
1	1 M	1 M	1 M	$10 \frac{\text{mol}}{\text{L sec}}$
2	1 M	0 M	1 M	$0 \frac{\text{mol}}{\text{L sec}}$
3	1 M	1 M	0 M	$10 \frac{\text{mol}}{\text{L sec}}$
4	0 M	1 M	1 M	$0 \frac{\text{mol}}{\text{L sec}}$
5	1 M	2 M	1 M	$10 \frac{\text{mol}}{\text{L sec}}$
6	1 M	3 M	0 M	$10 \frac{\text{mol}}{\text{L sec}}$
7	2 M	1 M	1 M	$40 \frac{\text{mol}}{\text{L sec}}$
8	4 M	1 M	1 M	$160 \frac{\text{mol}}{\text{L sec}}$
9	2 M	2 M	2 M	$40 \frac{\text{mol}}{\text{L sec}}$
10	0.5 M	6 M	3 M	

Data Taken at 350K				
Exp.	[A]	[B]	[C]	Rate
1	1 M	1 M	1 M	$200 \frac{\text{mol}}{\text{L sec}}$
2	1 M	0 M	1 M	$0 \frac{\text{mol}}{\text{L sec}}$
3	1 M	1 M	0 M	$200 \frac{\text{mol}}{\text{L sec}}$
4	0 M	1 M	1 M	$0 \frac{\text{mol}}{\text{L sec}}$
5	1 M	2 M	1 M	$200 \frac{\text{mol}}{\text{L sec}}$
6	1 M	3 M	0 M	$200 \frac{\text{mol}}{\text{L sec}}$
7	2 M	1 M	1 M	$800 \frac{\text{mol}}{\text{L sec}}$
8	4 M	1 M	1 M	$3,200 \frac{\text{mol}}{\text{L sec}}$
9	2 M	2 M	2 M	$800 \frac{\text{mol}}{\text{L sec}}$
10	0.50 M	6 M	3 M	

Chapter 15

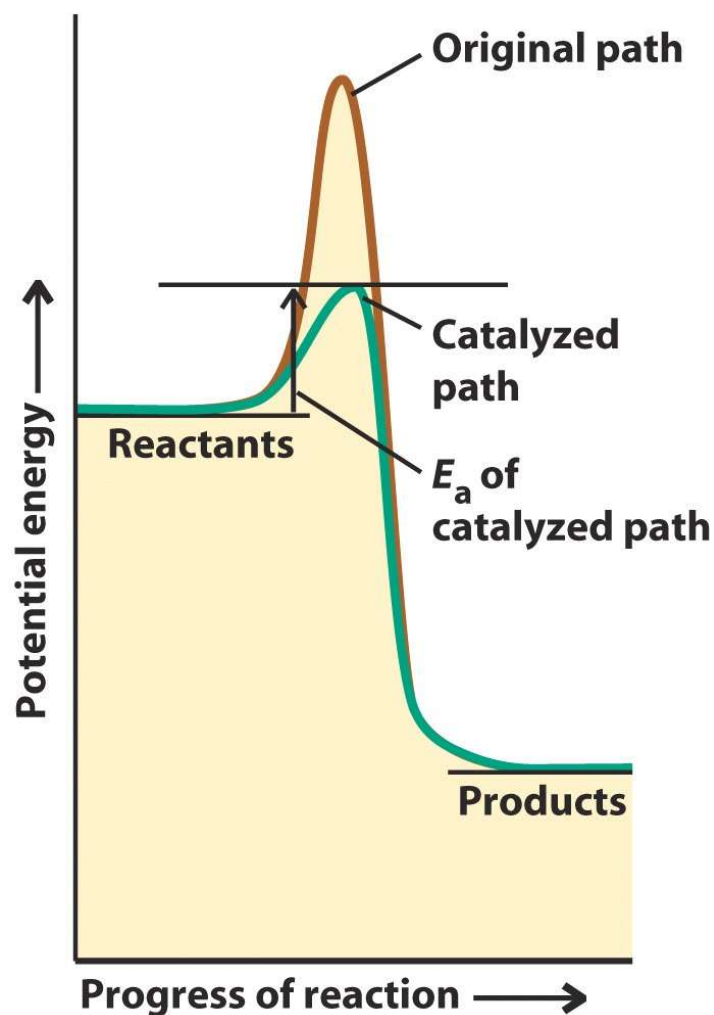
Chemical Kinetics

Big Idea: The rates of chemical reactions are described by simple expressions that allow us to predict the composition of a reaction mixture at anytime. These expressions also suggest the steps in which the reactions takes place.

- Thermo Review
- Reaction Rates
- Rate Laws
- Concentration and Time
- Reaction Mechanisms
- Explaining Reaction Rate Factors

Reaction Rates

- **Catalyst:** A substance that increases the reaction rate without being consumed in the reaction.
- **Homogeneous Catalyst:** A catalyst that is in the same phase as the reactants.
- **Heterogeneous Catalyst:** A catalyst that is in a different phase than the reactants.



Reaction Rates

- **Reaction Rates:** The change in concentration of one of the reactants or products divided by the time interval over which the change takes place.



Average Rate of Consumption of R:

$$\text{Rate} = -\frac{\Delta R}{\Delta t}$$

Average Rate of Production of P:

$$\text{Rate} = \frac{\Delta P}{\Delta t}$$

Note: Rates are always positive, therefore, since the reactants are consumed, a negative sign must be added to make the rate positive.

Unique Average Rate (UAR)

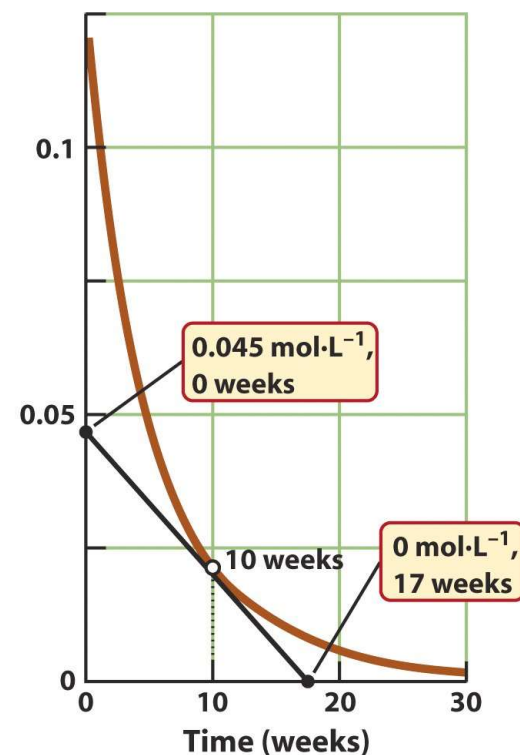
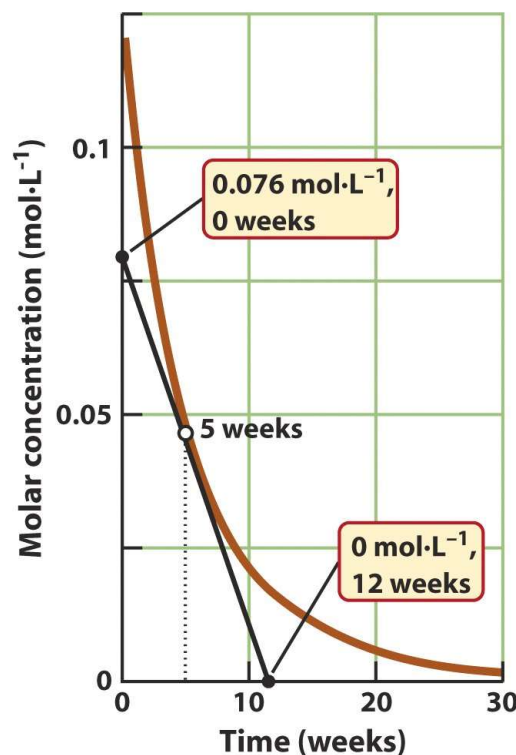


$$UAR = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t}$$

Reaction Rates

Instantaneous Rate of Reaction

- The best approximation to the rate at a single instant is obtained by drawing a line tangent to the plot of the concentration against time. The slope of the tangent line is called the instantaneous rate of the reaction.



Rate Laws

- **Rate Law:** An equation expressing the instantaneous reaction rate in terms of the concentrations, at any instant, of the substances taking part in the reaction.
- $Rate = k[A]^x[B]^y \dots$

Note: k is the rate constant and x, y, \dots are the orders of reaction.

Note: This form of the rate law is called the differential rate law.

Note: The units of rate are always $\frac{\text{particles}}{\text{volume} \times \text{time}}$, therefore, the units of k will differ depending on the overall reaction order.

Rate Laws

Things to know about the rate law:

- Rate laws can contain products, reactants, catalysts but usually only starting material.
- Rate laws do not contain intermediates.
- Rate laws can ONLY be determined experimentally.
- Orders do NOT correlate with coefficients in balanced equation!
- Orders can be an integers, zeros, fractions, positives, OR negatives!
- Each species has its own individual reaction order.
- The overall reaction order is the sum of the individual orders found in the reaction.

Rate Laws

How to find the units of k

- Step 1: Determine the order of the reaction

Examples for rate=k[A][B]:
Overall order 2

- Step 2: Subtract 1 from the overall order

Examples for rate=k[A][B]:
1

- Step 3: Find $\frac{1}{\left(\frac{\text{mol}}{\text{L}}\right)^{\# \text{ step 2}} \cdot \text{s}}$

Examples for rate=k[A][B]:

$$\frac{1}{\left(\frac{\text{mol}}{\text{L}}\right)^1 \cdot \text{s}} = \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

Rate Laws

Order	0 th	1 st	2 nd
time			
Initial Concentration			
Rate Law	$Rate = k$	$Rate = k[A]$	$Rate = k[A]^2$

Rate Laws

Determine the rate law: $A + B + C \rightarrow 2D$

Experiment	$[A]_0$ (M)	$[B]_0$ (M)	$[C]_0$ (M)	Initial Rate $\left(\frac{\text{mol}}{\text{L}\cdot\text{s}}\right)$
1	1	6	4	20
2	2	6	2	80
3	2	3	2	40
4	1	6	2	20

- 1) General Rate Law:
- 2) Order with respect to A:
- 3) Order with respect to B:
- 4) Order with respect to C:

Rate Laws

- Determine the rate law and k for
 - $2A + B \rightarrow 2C$

Experiment	$[A]_0$ (M)	$[B]_0$ (M)	Initial Rate ($\frac{\text{mol}}{\text{L}\cdot\text{s}}$)
1	0.050	0.10	0.074
2	0.10	0.20	0.888
3	0.050	0.20	0.222

Rate Laws

Determining Order (long way)

- **Step 1:** Find two experiments in which the concentrations of everything, except one species, is held constant.
- **Step 2:** Divide the rate laws for these two experiments by each other.

Note: This will cancel out k and all other variables except for the order that you are trying to determine.

Math Note: $\frac{(x)^y}{(z)^y} = \left(\frac{x}{z}\right)^y$

- **Step 3:** Solve for order.

Math Note: It is sometimes useful to take the log of both sides of the equation. The $\log(x^y) = y\log(x)$.

Rate Laws

Student Question

The rate law for the following reaction



was experimentally found to be in the form

$$\text{rate} = k[\text{NO}]^x[\text{O}_2]^y$$

It was also found that when the NO concentration was doubled, the rate of the reaction increases by a factor of 4. In addition, when both the O₂ and the NO concentration were doubled, the rate increases by a factor of 8. What is the reaction order of O₂?

- a) 0th
- b) 1st
- c) 2nd
- d) 3rd
- e) None of the above

Concentration and Time

Zero Order Integrated Rate Law

$$1) \text{ Rate} = k$$

$$\int dx = x + \text{const}$$

$$2) -\frac{dA}{dt} = k$$

$$5) [A] - [A]_0 = -kt$$

$$3) dA = -kdt$$

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

$$4) \int_{[A]_0}^{[A]} dA = -k \int_0^t dt$$

Concentration and Time

○ First Order Integrated Rate Law

$$1) \text{ Rate} = k[A]$$

$$\int \frac{1}{x} dx = \ln x + \text{const}$$

$$2) -\frac{dA}{dt} = k[A]$$

$$5) \ln[A] - \ln[A]_0 = -kt$$

$$3) \frac{1}{[A]} dA = -k dt$$

$$4) \int_{[A]_0}^{[A]} \frac{1}{[A]} dA = -k \int_0^t dt$$

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

Concentration and Time

Second Order Integrated Rate Law

$$1) \text{ Rate} = k[A]^2$$

$$\int \frac{1}{x^2} dx = -\frac{1}{x} + \text{const}$$

$$2) -\frac{dA}{dt} = k[A]^2$$

$$5) -\frac{1}{[A]} + \frac{1}{[A]_0} = -kt$$

$$3) \frac{1}{[A]^2} dA = -kdt$$

$$4) \int_{[A]_0}^{[A]} \frac{1}{[A]^2} dA = -k \int_0^t dt$$

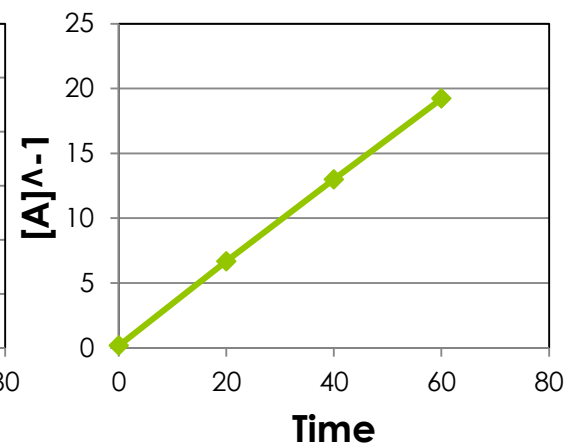
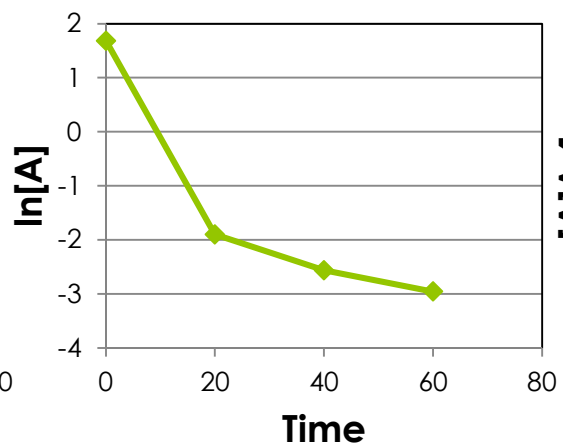
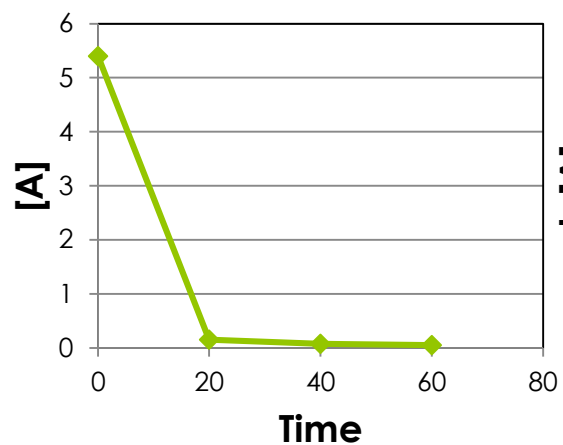
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Concentration and Time

- Find the rate law for $A+B \rightarrow C + D$.
- Initial Concentrations
 - $[A] = 5.4 \text{ M}$
 - $[B] = 1000. \text{ M}$
- General Rate Law
- **Pseudo Order Reaction:** A reaction in which the rate law can be simplified because all but one of the species have virtually constant concentrations.
- Pseudo Order Rate Law

Concentration and Time

Time (s)	[A] (M)	ln[A]	[A] ⁻¹ (M ⁻¹)
0	5.4	1.7	0.19
20.	0.15	-1.9	6.7
40.	0.077	-2.6	13
60.	0.052	-3.0	19



Concentration and Time

Calculate the concentration of N_2O after the first order decomposition:



The rate of decomposition of $\text{N}_2\text{O} = k[\text{N}_2\text{O}]$.

The reaction has continued at 780°C for 100. ms, and the initial concentration of N_2O was 0.20 M and $k = 3.4 \frac{1}{\text{s}}$.

Concentration and Time

- **Half Life:** Time it takes for the concentration to drop to half the initial amount

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

0th Order

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

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

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

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

1st Order

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

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

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

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

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

Concentration and Time

2nd Order

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

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

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

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

Concentration and Time

Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of the straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Reaction Mechanisms

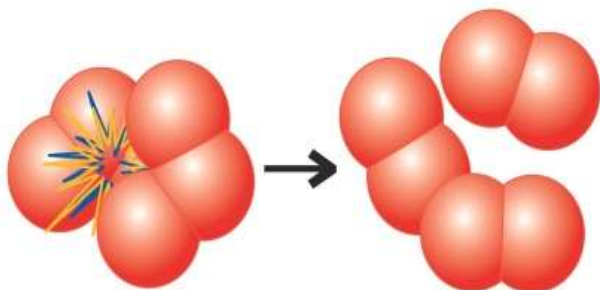
- **Reaction Mechanism:** The steps by which a reaction takes place.
- **Elementary Reaction:** One of the reaction steps in an overall reaction.

Note: RATE LAWS CAN BE DETERMINED FROM ELEMENTARY REACTIONS.

Note: In order to be a valid mechanism the sum of the elementary reactions must equal the overall reaction.

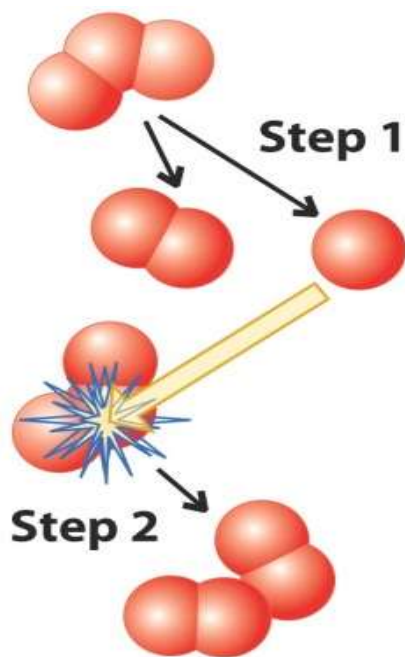
Reaction Mechanisms

o Mechanism 1:



Elementary Reaction(s):

o Mechanism 2:



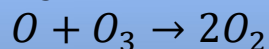
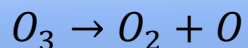
Elementary Reaction(s):

Note: In order to be a valid mechanism the rate law derived from the elementary reactions must match the experimentally determined rate law.

Reaction Mechanisms

- **Reaction Intermediate:** A species that plays a role in the reaction but does not appear in the reaction.
- **Molecularity:** The number of reactant molecules/atoms taking part in an elementary reaction.

Examples:



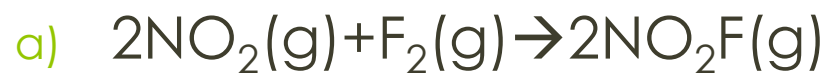
Molecularity of 1

Molecularity of 2

Reaction Mechanisms

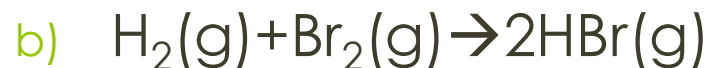
Student Question

Use the experimentally found rate laws given below to determine which reaction is most likely to occur in a single step.

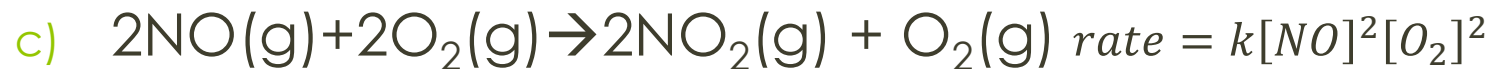


Experimentally
Found Rate Laws

$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$



$$\text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$$



$$\text{rate} = k[\text{NO}]^2[\text{O}_2]^2$$

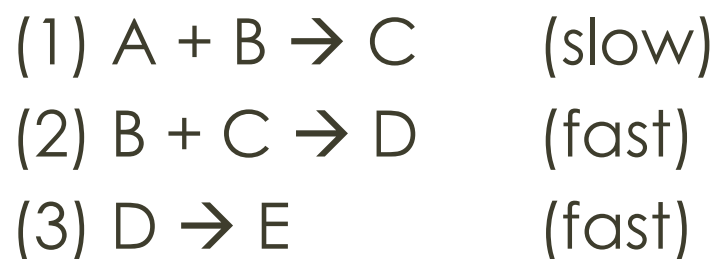


$$\text{rate} = k[\text{NO}_2]^2$$

Reaction Mechanisms

Student Question

Consider the following hypothetical reaction:
 $A + 2B \rightarrow E$. The mechanism for this reaction is:



The rate law consistent with this mechanism is:

- a) $\text{rate} = k[A][B]$
- b) $\text{rate} = k[A]^2[B]$
- c) $\text{rate} = k[A]^2$
- d) $\text{rate} = k[A][B]^2$
- e) None of the above

Reaction Mechanisms

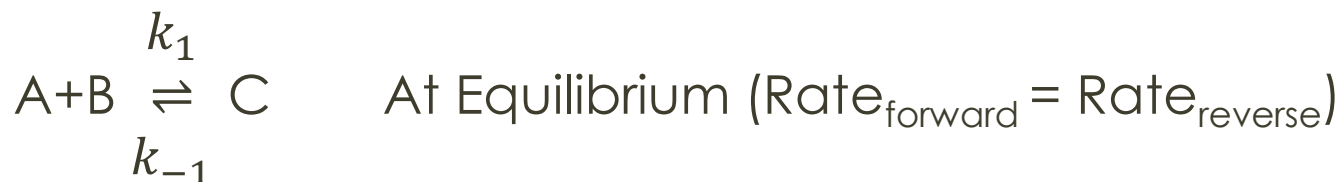
Student Question

The reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ was experimentally found to have the rate law: $\text{rate} = k[\text{Cl}_2][\text{NO}]^2$. Which mechanism could **not** be the correct mechanism?

- a) $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ (fast equilibrium)
 $2\text{Cl} + 2\text{NO} \rightarrow 2\text{NOCl}$ (slow)
- b) $2\text{NO} + 2\text{Cl}_2 \rightarrow 2\text{NOCl}_2$ (slow)
 $2\text{NOCl}_2 \rightleftharpoons \text{NOCl}_3 + \text{NOCl}$ (fast equilibrium)
 $\text{NOCl}_3 \rightleftharpoons \text{NOCl} + \text{Cl}_2$ (fast equilibrium)
- c) $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$
- d) $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (fast equilibrium)
 $\text{N}_2\text{O}_2 + \text{Cl}_2 \rightarrow 2\text{NOCl}$ (slow)
- e) All of the above are possible mechanisms

Reaction Mechanisms

o Relating the Rate and Equilibrium Constants



Equilibrium Constant

$$K = \frac{[C]}{[A][B]}$$

Rate Constant

$$k_1[A][B] = k_{-1}[C]$$
$$\frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}}$$

$$K = \frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}}$$

$$K = \frac{k_1}{k_{-1}}$$

Multi Step Reactions With Unknown Speeds

- **Step 1:** Write an expression for the rate of formation of one of the final products (sometimes the product of interest is specified). If possible select a product that is only in 1 step.
- **Step 2:** Use the steady state approximation to solve for the concentration of intermediates.
- **Step 3:** Plug back into overall rate equation.

Explaining Reaction Rate Factors

Student Question

The rate constant for the second-order gas-phase reaction $\text{HO(g)} + \text{H}_2\text{(g)} \rightarrow \text{H}_2\text{O(g)} + \text{H(g)}$ varies with the temperature as shown here:

Temperature (K)	Rate Constant ($\frac{\text{mol}}{\text{L}\cdot\text{s}}$)
373	1.1×10^{-9}
473	1.8×10^{-8}
573	1.2×10^{-7}
673	4.4×10^{-7}

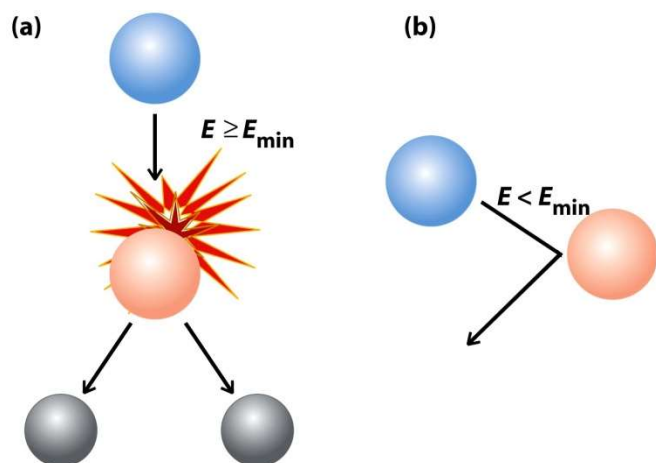
Determine the activation energy.

- a) $2.4 \times 10^{-5} \frac{\text{J}}{\text{mol}}$ b) $4.0 \times 10^3 \frac{\text{J}}{\text{mol}}$
c) $4.2 \times 10^4 \frac{\text{J}}{\text{mol}}$ d) None of the above

Explaining Reaction Rate Factors

Collision Theory (Gases Only)

- Rate = Collision Frequency × Fraction with Sufficient Energy



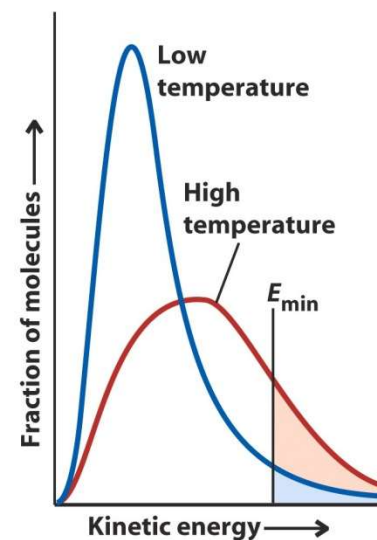
How would we get collision frequency

- Size of the molecules/atoms
- Average velocity of the molecules/atoms
- Concentration of molecules/atoms

How would we get fraction with sufficient energy?

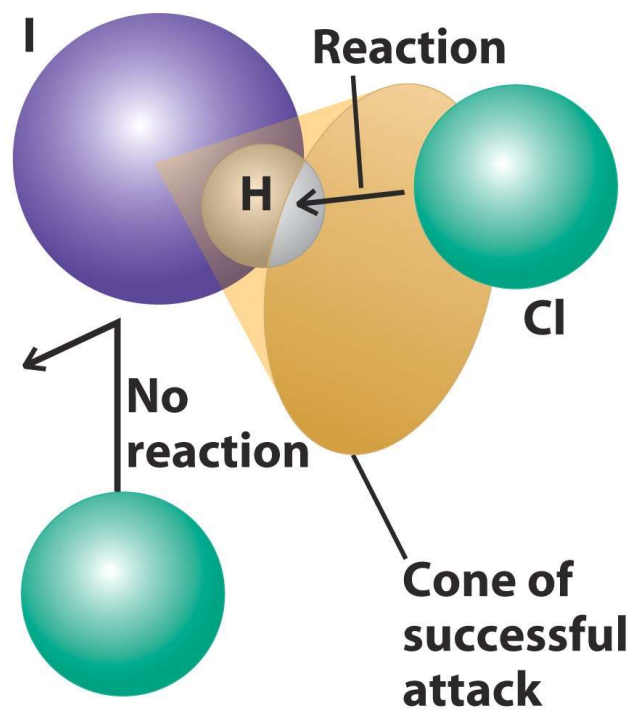
- Boltzmann distribution

- $$f(u) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-\frac{mu^2}{2k_B T}}$$



Explaining Reaction Rate Factors

- **Problem:** Although the rate has the right form (Arrhenius) it predicts a larger reaction rate than is found.
- **Solution:** Sterics need to be taken into account.



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

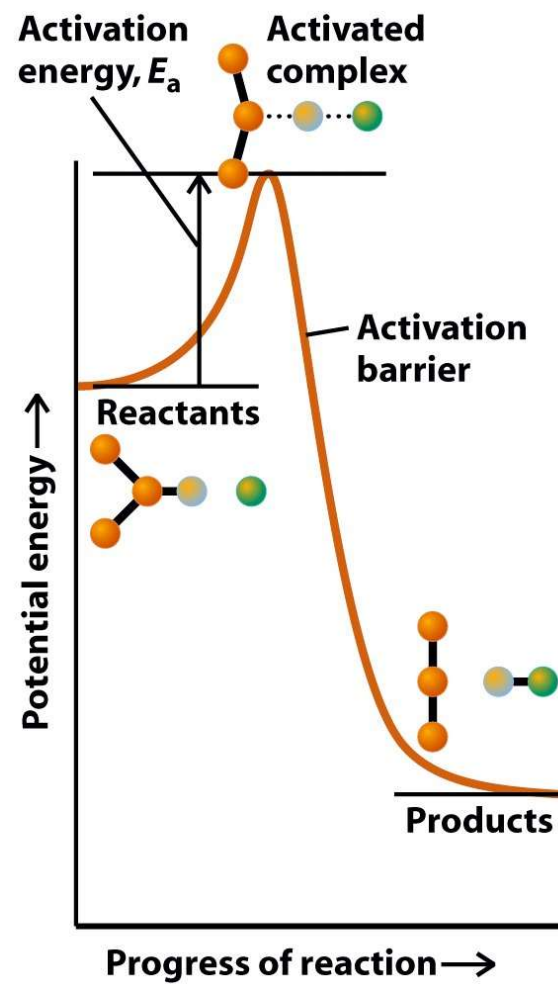
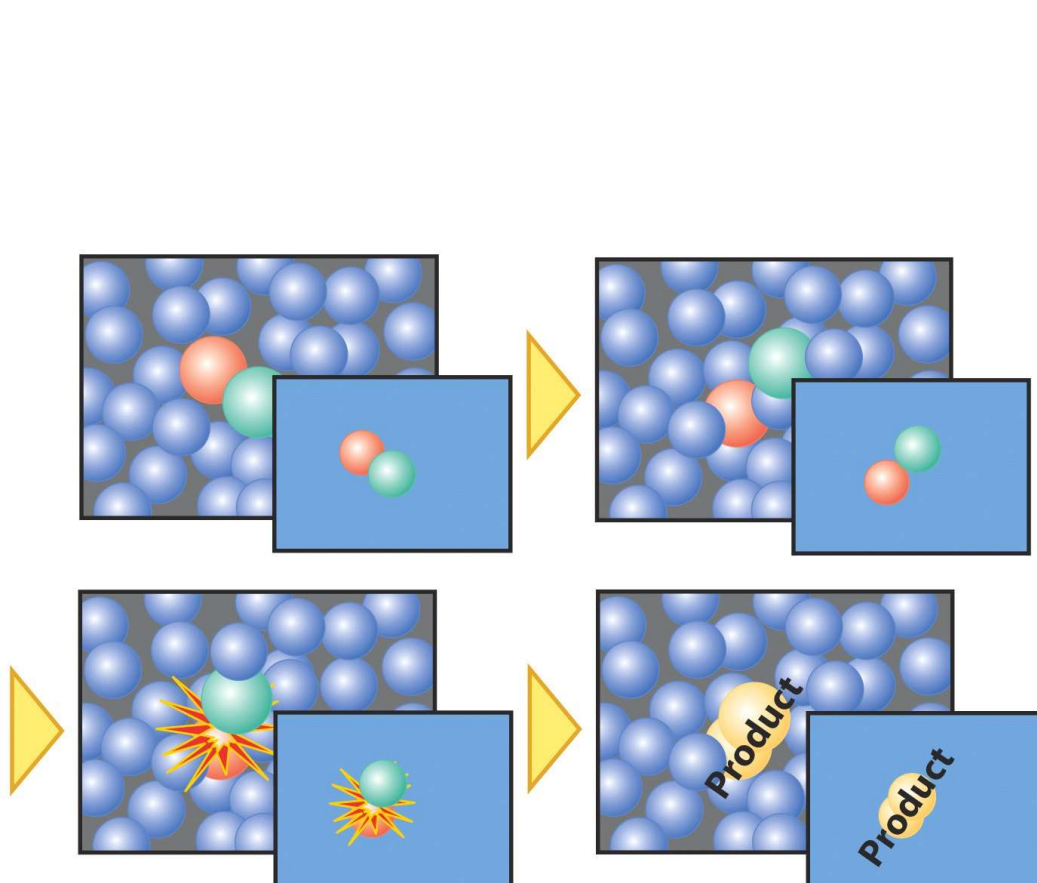
$$k = Ae^{-\frac{E_a}{RT}}$$

E_a = Minimum energy needed for reaction to occur.

A = Takes into account number of collisions and sterics.

Explaining Reaction Rate Factors

● Activated Complex Theory (Solutions)



Take Away From Chapter 15

- **Big Idea:** The rates of chemical reactions are described by simple expressions that allow us to predict the composition of a reaction mixture at anytime. These expressions also suggest the steps in which the reactions takes place.
- **Thermo Review**
 - Know the difference between thermo and kinetics
 - Thermodynamics allows us to predict if a reaction will occur.
 - Kinetics allows us to predict how fast a reaction will occur.
 - Be able to draw reaction coordinates along with labeling reactants, products, intermediates, transition states, and activation energy. (86,87,88)
- **Reaction Rates**
 - Be able to explain how a catalyst can increase reaction rate. (90)

Numbers correspond to end of chapter questions.

Take Away From Chapter 15

○ **Reaction Rates** (Continued)

- Be able to calculate the average rate of reaction of 1 species given the average rate of reaction of another species.
- Be able to calculate the unique average rate of a reaction.

○ **Rate Law**

- Know that rate laws must be determined experimentally.
- Be able to determine the order of a reaction and each individual species.
- Be able to calculate rate law from experimental data. (18,19, 20,21,22,23)
 - Double concentration and rate stays the same: 0th order
 - Double concentration and rate doubles: 1st order
 - Double concentration and rate quadruples: 2nd order
 - If none of these use the math trick $\log(a^x) = x\log(a)$
- Be able to determine the units of the rate constant (14,15)
 - The units of concentration are constant (M)
 - The units of rate are constants $\left(\frac{\text{particles}}{\text{volume}\cdot\text{time}}\right)$

Numbers correspond to end of chapter questions.

Take Away From Chapter 15

○ Concentration and Time

- Be able to use the integrated rate law to perform calculations. (43,47,48,52)
 - 0th order: $[A] = -kt + [A]_0$
 - 1st order: $\ln[A] = -kt + \ln[A]_0$
 - 2nd order: $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
- Know that rate problems can be simplified when the concentration of 1 species is high and essentially unchanging (pseudo order reactions). (36,39,54)
- Be able to identify the order of the reaction by plotting data. (30,31,32,33,35,38)
 - $[A]$ vs. t linear 0th order, slope = $-k$
 - $\ln[A]$ vs. t linear 1st order, slope = $-k$
 - $[A]^{-1}$ vs. t linear 2nd order, slope = k
- Be able to calculate half-life/ 2^{nd} half-life/etc..

Numbers correspond to end of chapter questions.

Take Away From Chapter 15

- **Reaction Mechanisms (56)**
 - Be able to write a rate law of an elementary reaction. (59)
 - Be able to determine the rate law of multi step reactions. (60,61)
 - Be able to eliminate intermediates from multi step reactions.
 - Equilibrium (63,65,68)
 - Steady state approximation (69,70)
- **Explaining Reaction Rate Factors**
 - Concentration
 - Catalyst (94)
 - Be able to draw potential energy diagram of reactions
 - Temperature
 - Know that most reactions follow Arrhenius behavior. (8,72,79,80,81,84)
 - $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
 - $\ln(k) = -\frac{E_a}{RT} + \ln(A)$

Numbers correspond to end of chapter questions.

Take Away From Chapter 15

- **Explaining Reaction Rate Factors (continued)**
 - Surface Area
 - Know the ideas behind collision theory (gases).
 - Know the ideas behind activated complex theory (solutions).

Numbers correspond to end of chapter questions.