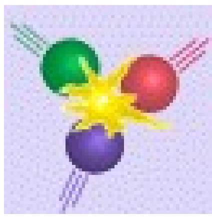


40S Chemistry

Kinetics

What is Kinetics?

- Chemistry focuses largely on chemical reactions. Some reactions, such as rusting, occur very slowly, while others, like explosions, occur quite fast.
- **Kinetics** is the branch of chemistry that studies the speed or rate with which chemical reactions occur.

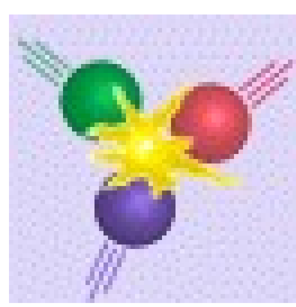
- Some reactions do not occur in one simple step. Some occur in several more complex steps.
- Part of Kinetics is studying the steps, or **mechanism**, of a chemical reaction.

- It is important for chemists to understand the mechanism of a reaction and the factors that affect its rate.
- With this knowledge, chemists can control a chemical reaction in order to make the manufacturing of commercial products efficient and practical.

Unit Topics:

- ❖Reaction Rates
- ❖Collision Theory
- ❖Factors Affecting Reaction Rates
- ❖Reaction Mechanisms
- ❖Quantitative Effects of Concentration Changes on Rate
- ❖Determining Rate Law Experimentally

Reaction Rates



Outcomes:

- Identify variables used to monitor reaction rate. Formulate operational definition for reaction rate in terms of rate units - change per unit time.
- Measure average rate of a chemical reaction.
- Relate rate of formation of product to the rate of disappearance of reactant given experimental data and reaction stoichiometry.

Lesson Overview:

- Defining rate
- Measuring rate
- Average and instantaneous rate
- Calculating average rate
- Average Rate Example 2
- Rate and Stoichiometry
- Rate and Stoichiometry Problems

A Chemical Reaction:

Results in a new substance being formed.

- Is usually expressed in the shorthand as a chemical equation.

REACTANTS $\longrightarrow$ PRODUCTS

- Reaction rate is the speed with which a chemical reaction takes place - how fast reactants are used up or products are formed.

Measuring Rate:

- This reaction shows that A and B combine to form C and heat is given off:

$$\mathbf{A(s) + B(l) \longrightarrow C(g) + heat}$$

- In this reaction, rate can be measured in terms of several different properties:

$$A(s) + B(l) \longrightarrow C(g) + \text{heat}$$

i) Temperature change over time (°C/min)

ii) Pressure change over time (kPa/s or mmHg/s)

- iii) Mass change over time (g of C/min)
- iv) Other possibilities:

- Rate is usually described in terms of change in concentration of reactant or product over time.

$$\text{Rate of Reaction} = \frac{\text{Measured change in a property}}{\text{Time for change to occur}}$$

- Or, in this example:

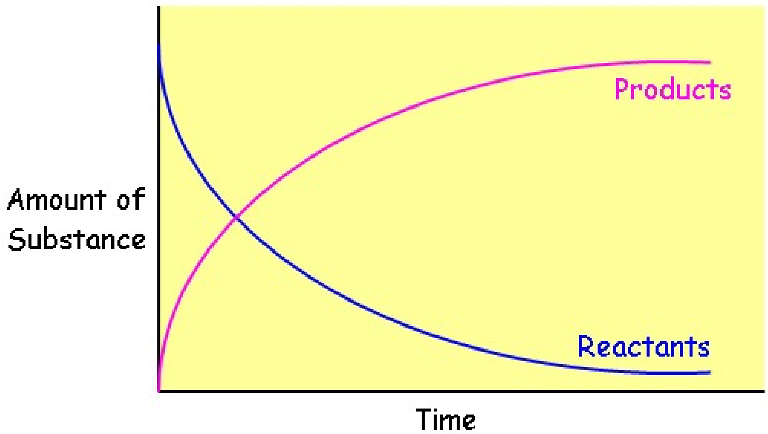
$$\text{Rate} = \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta[B]}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta[C]}{\Delta t}$$

Where:

- $\Delta[A]$ = change in concentration of A, etc.
- Δt = change in time

Average Rate:

- The numerical value for the rate of a reaction can be determined by examining the change in the amount of a substance at a particular time, or over a period of time.
- The graphical representation of this may look like . . .



- The average rate for a reaction is given by the following equation:

$$\text{Rate} = \frac{\text{(final concentration of A)} - \text{(initial concentration of A)}}{\text{final time} - \text{initial time}}$$

or

$$\text{Rate} = \frac{[A]_{final} - [A]_{initial}}{t_{final} - t_{initial}}$$

- The instantaneous rate of a reaction is the rate at a specific time.
- Determined this by calculating the slope of the line tangent to the point on the concentration vs time curve.

Calculating Average Rate:

Example 1:

- According to the reaction A B, the following data was collected:

Time(s)	[B] (mol/L)
0.0	0.0
10.0	0.30
20.0	0.50
30.0	0.60
40.0	0.65
50.0	0.67

a) What is the average rate over the entire 50 seconds?

b) What is the average rate for the interval 20s to 40 s?

Solution (1a):

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

$$\text{rate} = \frac{\text{final concentration of B - initial concentration of B}}{\text{final time - initial time}}$$

$$\text{rate} = \frac{0.67 \text{ mol/L} - 0.0 \text{ mol/L}}{50 \text{ s} - 0 \text{ s}}$$

$$\text{rate} = \frac{0.67 \text{ mol/L}}{50 \text{ s}}$$

rate = 0.0134 mol/Ls

Solution (1b):

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

$$\text{rate} = \frac{\text{final concentration of B - initial concentration of B}}{\text{final time - initial time}}$$

$$\text{rate} = \frac{0.65 \text{ mol/L} - 0.50 \text{ mol/L}}{40 \text{ s} - 20 \text{ s}}$$

$$\text{rate} = \frac{0.15 \text{ mol/L}}{20 \text{ s}}$$

rate = 0.0075 mol/Ls

Example 2

- The decomposition of nitrogen dioxide produces nitrogen monoxide and oxygen according to the reaction:

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

- The following data has been collected:

Time (s)	$[NO_2]$ (mol/L)	$[NO]$ (mol/L)	$[O_2]$ (mol/L)
0	0.100	0	0
100	0.066	0.034	0.017
200	0.048	0.052	0.026
300	0.038	0.062	0.031
400	0.030	0.070	0.035

Calculate:

a) The average rate of decomposition of NO_2 over 400 s.

b) The average rate of production of NO over 400 s.

c) The average rate of production of O_2 over 400 s.

Solution (2a):

$$\text{rate} = \frac{\Delta[NO_2]}{\Delta t}$$

$$\text{rate} = \frac{[NO_2]_{t=400} - [NO_2]_{t=0}}{400\text{s} - 0\text{ s}}$$

$$\text{rate} = \frac{0.030\text{ mol/L} - 0.100\text{ mol/L}}{400\text{ s}}$$

$$\text{rate} = -1.75 \times 10^{-4}\ \text{mol/L}\cdot\text{s}$$

Note:

⌘The rate "-" number.

⌘Rate is always expressed as a "+" value.

⌘The actual value of the average rate is

1.75 x 10-4 mol/Ls.

Solution (2b):

$$\text{rate} = \frac{\Delta[NO]}{\Delta t}$$

$$\text{rate} = \frac{[NO]_{t=400} - [NO]_{t=0}}{400s - 0\ s}$$

$$\text{rate} = \frac{0.070\ mol/L - 0\ mol/L}{400\ s}$$

$$\text{rate} = 1.75 \times 10^{-4}\ mol/L \cdot s$$

Solution (2c):

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t}$$

$$\text{rate} = \frac{[O_2]_{t=400} - [O_2]_{t=0}}{400s - 0\ s}$$

$$\text{rate} = \frac{0.035\ mol/L - 0\ mol/L}{400\ s}$$

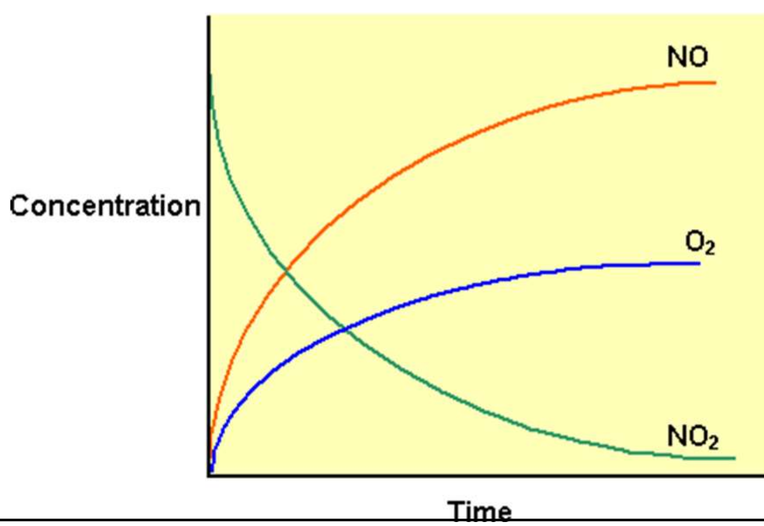
$$\text{rate} = 8.75 \times 10^{-5}\ mol/L \cdot s$$

Rate and Stoichiometry:

- Rate of creation of products or disappearance of reactants can be predicted from reaction stoichiometry.
- From example 2, for the reaction:

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

the graph appears as . . .



From the graph and the calculations:

- the rate of decomposition of NO_2 = to the production of NO. The ratio of the molar coefficients is 1:1.
- the rate of production of oxygen is half that of the NO. The ratio of the molar coefficients is 2:1.
- Therefore . . .

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Rate and Stoichiometry Problems:

Problem:

- For the decomposition of nitrogen dioxide, if the rate of decomposition is determined to be 0.50 mol/Ls at a certain temperature, predict the rate of creation of both products.

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

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

Solution:

- According to the molar ratio, NO_2:NO, the rate of decomposition should = the rate of production. The rate of production of NO should be 0.50 mol/Ls.
- The ratio of NO_2:O_2 is 2:1. The rate of production of oxygen should be one half the decomposition of NO_2, or

$$(0.5)(0.50\text{mol/Ls}) = 0.25\text{ mol/Ls}$$

Problem:

- For the reaction 2 A + B → 4 C, what is the rate of production of C and the rate of disappearance of B if A is used up at a rate of 0.60 mol/Ls?

2 A + B → 4 C

Solution:

- Use the molar ratio of A to C to make the equation:

$$(0.60\ \text{mol/L}\cdot\text{s A}) \times \left(\frac{4\ \text{moles C}}{2\ \text{moles A}}\right) = 1.2\ \text{mol/L}\cdot\text{s C}$$

- Using the molar ratio of A to B:

$$(0.60\ \text{mol/L}\cdot\text{s A}) \times \left(\frac{1\ \text{mole B}}{2\ \text{moles A}}\right) = 0.30\ \text{mol/L}\cdot\text{s B}$$

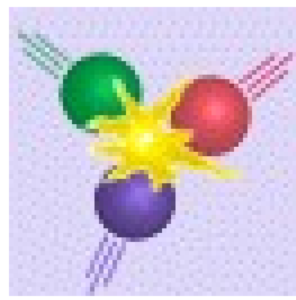
Lesson Summary:

- Rate is a change in the concentration of a reactant or product over a period of time.
- Rate can be determined by measuring many changes in properties.
- Rate is related to stoichiometry of the reaction's balanced equation.
- Average rate is determined over an interval: instantaneous rate is the rate at a certain moment.

Homework Assignment:

- Complete *Kinetics Assignment #1*.

Collision Theory



Introduction:

❖A theory is an explanation of why scientists believe a behavior exists.

❖This lesson examines theories scientists use to explain why and how chemical reactions occur . . .

Outcomes:

- ❖Define the Collision Theory for chemical reactions.
- ❖Draw a Kinetic Distribution curve
- ❖Describe the role of activation energy in chemical reactions.
- ❖Draw reaction coordinate diagrams for endothermic and exothermic reactions.

Lesson Overview:

- ❖Collision Theory
- ❖Activation Energy
- ❖Kinetic Energy Distribution
- ❖Enthalpy
- ❖Reaction Coordinate Diagrams

❖The collision theory states:

In order for a chemical reaction to occur, the reacting particles (molecules &/or atoms) must collide with each other. If the particles do not collide, no reaction occurs.

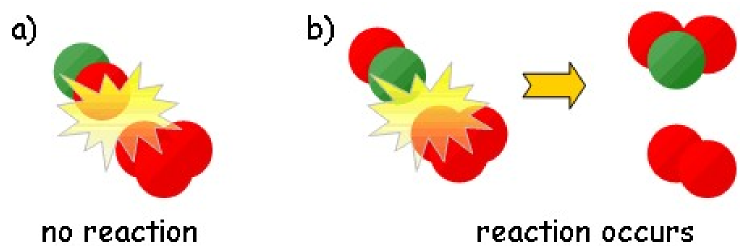
❖Not all collisions produce a reaction.

❖Particles must collide with the correct orientation. . .

In the atmosphere, ozone is converted to oxygen gas and nitrogen dioxide by reacting with nitrogen monoxide, according to the following reaction.

$$\mathbf{NO(g) + O_3\,(g) \longrightarrow NO_2(g) + O_2\,(g)}$$

❖If the oxygen atoms collide no reaction occurs. But if the nitrogen atom collides with the oxygen atom a reaction occurs.



Activation Energy:

Particles must collide with enough energy.

❖Chemical reactions involve the making and breaking of bonds, which requires energy.

❖If colliding particles do not have sufficient velocity (Kinetic Energy) they will not produce a reaction.

- The minimum amount of energy required for colliding particles to produce a chemical reaction is called the Activation Energy (EA/E_A) of that reaction.
- The greater the activation energy, the slower the reaction rate, the longer the reaction takes.

Illustration:

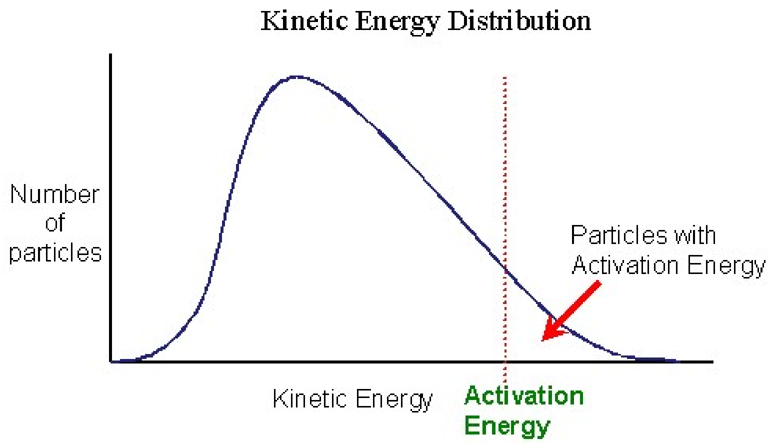
- H and O in the same container at room temperature - no reaction.
- Even though the molecules collide, they do not possess activation energy.
- Heat the mixture to 800°C, or introduce a flame or spark - explosive exothermic reaction!
- The heat, flame or spark provides enough energy for the particles to reach activation energy.

Kinetic Energy Distribution:

Maxwell and Boltzman experiments in 1866:

- demonstrated that not all particles at a specific temperature had exactly the same velocities.
- Some moved quite slowly, while others moved very quickly.
- Most fell somewhere in between . . .

- The velocities of these particles were directly related to the amount of Kinetic Energy (EK) they possessed.
- Plotted a curve to reflect the varying EKs. This curve is known as a Maxwell-Boltzman Curve or a Kinetic Energy Distribution Curve . . .



- Area under the curve represents the number of particles at a given kinetic energy.
- The area under the curve to the right of the activation energy represents the number of particles with sufficient energy to produce a collision capable of a reaction.
- Each reaction has its own specific activation energy . . .

Enthalpy:

- Rate of a reaction is determined by the height of the barrier that the particles must cross in order that they are converted into products.
- The **activation energy** is the barrier colliding particles must overcome.
- As the particles collide, they form an unstable intermediate particle called the **activated complex**.

- The energy required to produce the activated complex is the **activation energy**.

- **Enthalpy** (H) is the heat content or total energy possessed by the particles in a system.
- Energy released or absorbed by a reaction is called the **change in enthalpy**, ΔH, or **heat of reaction**.

$$\Delta H = H_{PRODUCTS} - H_{REACTANTS}$$

- ΔH is the change in enthalpy or energy that occurs during a reaction in Joules (J).

Exothermic Reactions:

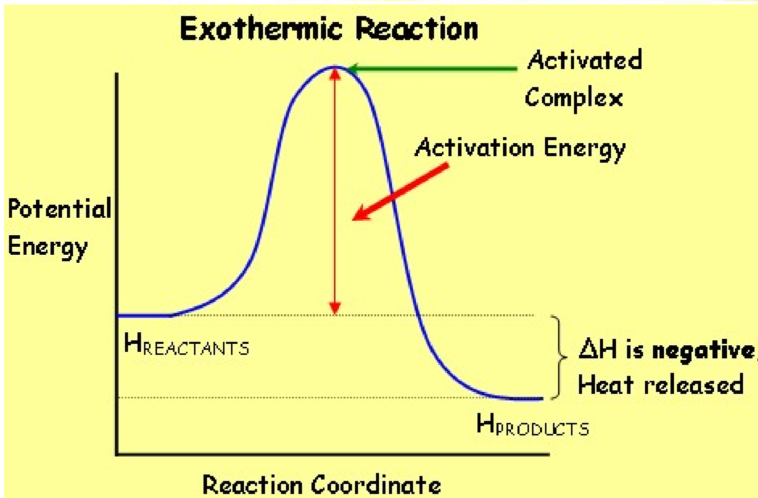
- If ΔH is negative, heat flows out of the system.
- This type of reaction gives off heat and the reaction vessel feels warmer.
- This is called an **exothermic reaction**.

Endothermic Reactions:

- If ΔH is positive , heat is absorbed or flows into the system.
- The reaction vessel feels cooler as energy is absorbed from the surroundings.
- This type of reaction is called an **endothermic reaction**.

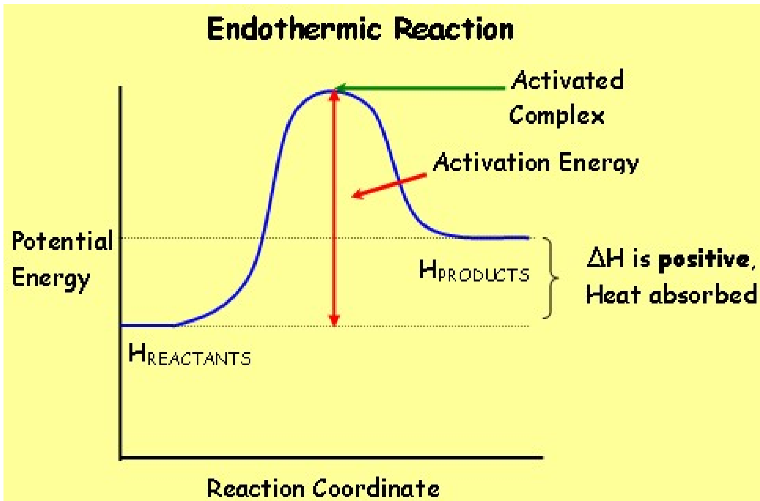
Reaction Coordinate Diagrams:

- A **reaction coordinate diagram**, or **potential energy (EP) diagram** represents the energy change that occurs during a chemical reaction.
- Reaction coordinate diagrams appear different for endo- and exothermic reactions . . .



Exothermic Diagrams:

- ❖In exothermic reactions, products possess less energy than the reactants.
- ❖During the reaction, heat is lost from the system and ΔH is a negative value.



Endothermic Reactions:

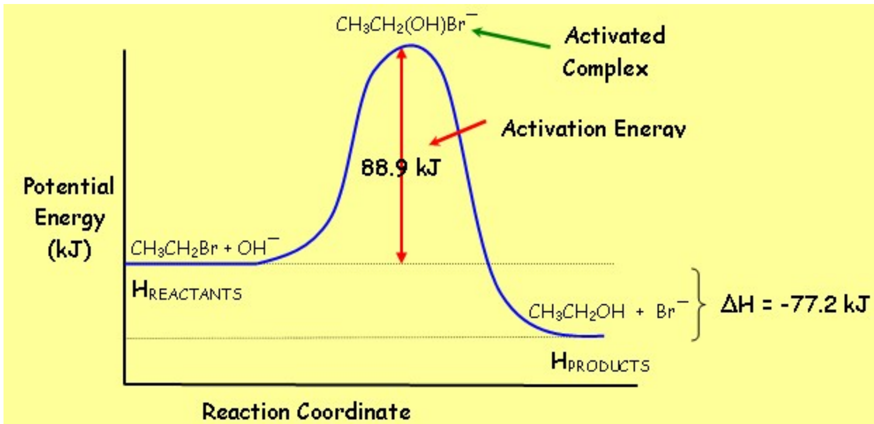
- In an endothermic reaction, the products possess more potential energy than the reactants.
- This energy is absorbed from the surroundings, increasing the systems energy content, giving a positive ΔH value.

- In a chemical reaction, energy is added to overcome the activation energy, and to form the activated complex.
- Once the activated complex is formed the reaction proceeds.
- No energy, no reaction.

Example 1

- Consider the reaction,

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$



❖ The activated complex in this reaction is $CH_3CH_2(OH)Br^-$.

❖ The activation energy is 88.9 kJ per mole of CH_3CH_2Br.

❖ The enthalpy change is -77.2 kJ, indicating an exothermic reaction. This reaction does not take place unless 88.9 kJ per mole of CH_3CH_2Br is added to the system.

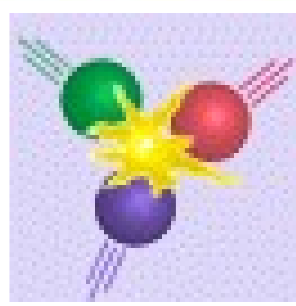
- The collision theory states that particles must collide in order for a reaction to happen.
- The activation energy is the minimum energy for a reaction to occur, or the energy to form the activated complex.
- Reaction coordinate diagrams provide a visual representation of the energy changes occurring as a reaction proceeds.

- All particles in a system have different amounts of kinetic energy. The distribution of kinetic energy can indicate how many particles possess activation energy.
- An exothermic reaction has a negative enthalpy change.
- An endothermic reaction has a positive enthalpy change.

Homework Assignment:

❖Complete *Kinetics Assignment #2*.

Factors Affecting Reaction Rate



Outcomes:

- Identify the factors that could affect the rate of a chemical reaction.
- Describe qualitatively the relationship between factors that affect the rate of chemical reactions and the relative rate of a reaction.
- Use the Collision Theory to explain the factors influencing the rate of a reaction.

- Explain the effect of temperature increases on kinetic energy distribution curve shape.
- Explain the effect of concentration changes on the rate of a chemical reaction using a KE distribution curve.
- Explain the effect of a catalyst on the rate of a chemical reaction using a reaction coordinate diagram as well as a kinetic energy distribution curve.

Lesson Overview:

- Effect of the nature of reactants on reaction rate.
- Effect of temperature on reaction rate.
- Effect of concentration on reaction rate.
- Effect of catalysts on reaction rate.
- Enzymes.
- Effect of pressure on reaction rate.
- Effect of reactant size on reaction rate.

Nature of Reactants:

- Some chemical reactions involve the rearrangement of atoms as a result of bond breaking and new bond formation.
- Other reactions are a result of electron transfer.
- The nature of the reactants involved in the reaction will affect reaction rate . . .

1) The fewer the number of bonds broken, the faster the rate.

- Consider these reactions:

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

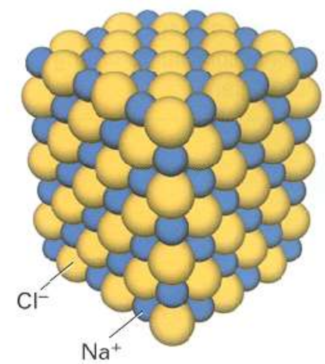
$$2\ C_8H_{18}\ (l) + 25\ O_2\ (g) \longrightarrow 16\ CO_2\ (g) + 18\ H_2O(g)$$

- Formation of NO_2 requires breaking one covalent bond.
- Combustion of gasoline requires breaking over fifty covalent bonds!

2) The rate of a chemical reaction depends on what kinds of bonds are being formed and broken.

- Bonds that are difficult to break slow down the reaction because the energy of activation is higher.
- In aqueous solution, reactions with molecular reactants (covalent bonds) are usually slower than ionic reactions (instantaneous)

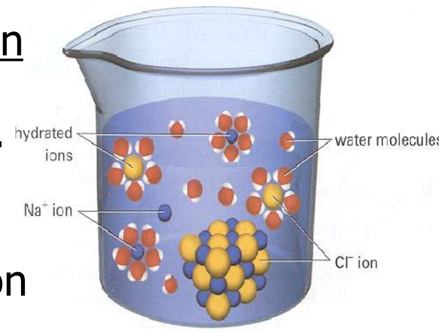
- This might lead one to believe that ionic compounds react more slowly than covalent compounds, because ionic bonds are generally stronger than covalent bonds.



- However, when in aqueous solution, ionic compounds often react more quickly than covalent compounds . . .

❖This is because <u>ionic bonds have already been dissociated</u> when they have dissolved in water.

❖Also, charged particles are attracted to each other in aqueous solution and this tends to speed things up.



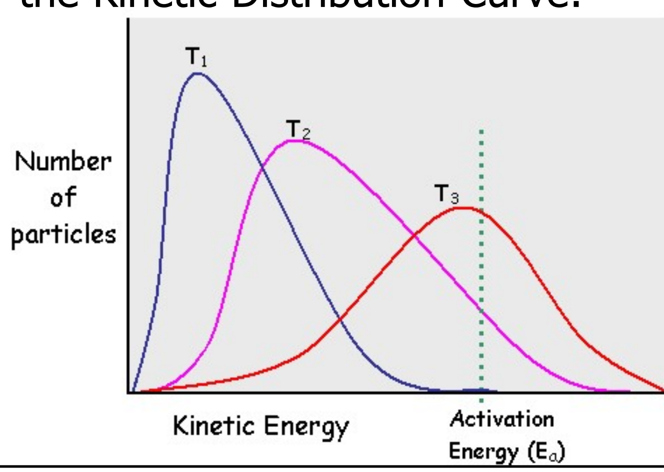
3)State of reactants affects reaction rate.

❖Gaseous reactants > liquid reactants > solid reactants.

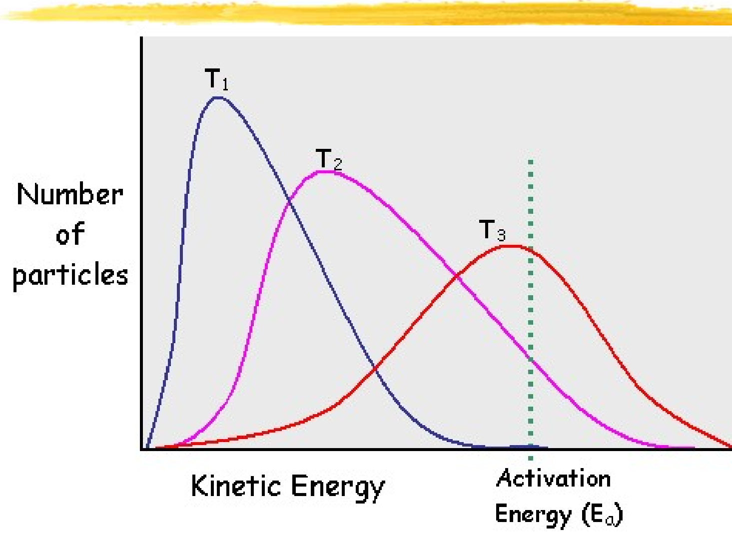
Temperature Change:

- Collision theory states that reaction rate is determined by frequency of collisions between molecules . . .
- High energy = frequent collisions.
- The Kinetic Molecular Theory states that the speed (Kinetic Energy) of particles increases as temperature increases.

- Changes in temperature affect the shape of the Kinetic Distribution Curve:



- If activation energy and number of particles remain constant, increasing temperature from T2 to T3, shifts the curve to the right.
- Since the activation energy does not change, there are more particles with enough energy, activation energy, to produce an effective collision.



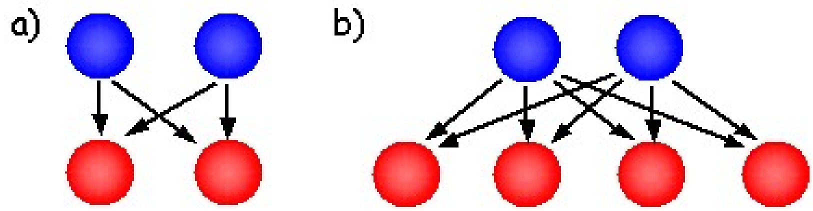
- A decrease in temperature to T1, shifts the curve to the left, decreasing the number of particles with activation energy.
- This decreases the reaction rate. There are little or no particles with activation energy.
- For many reactions, a 10°C increase in temperature will double reaction rate . . .

- The number of particles with activation energy increases exponentially with an increase in temperature.
- Food spoil quickly on the counter, at room temperature. In the refrigerator food spoils at a much slower rate, while food can last much longer in the freezer.
- Cooler temperatures slow reaction rate.

Effect of Concentration:

- Concentration refers to the amount of reactant per unit volume.
- The units for concentration are mol/L.
- Increasing concentration of reactants increases the total number of particles in a container.
- This increases the number of particles with activation energy which increases the frequency of effective collisions.

- Increasing the number of particles in a container will also increase the chances of a collision.
- The effect of doubling the concentration of just one of the reactants . . .



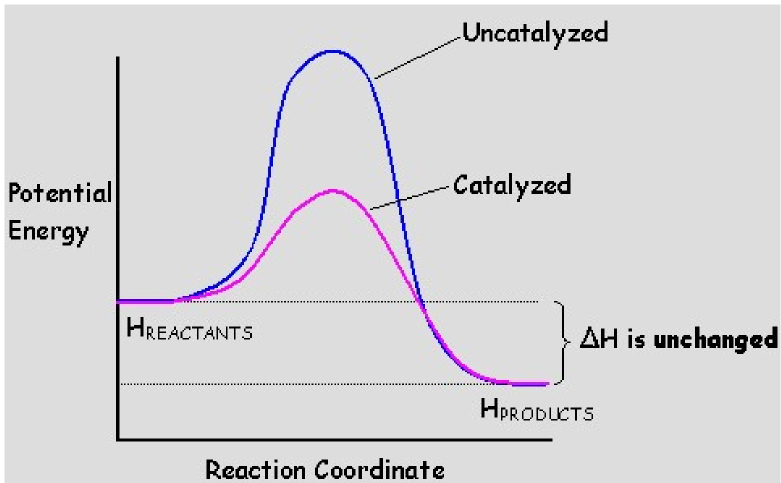
❖2 red particles, 4 possible collisions.

❖4 red particles, 8 possible collisions!

Effect of Catalysts:

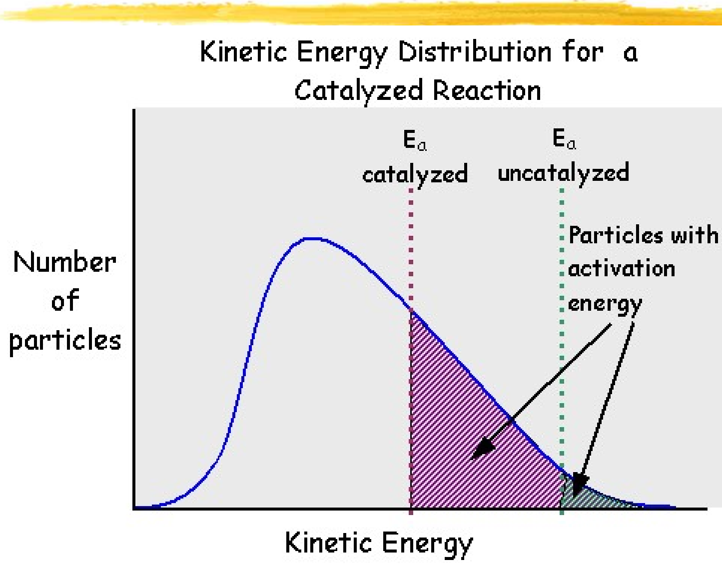
❖A **catalyst** is a substance that speeds up or initiates a reaction without itself being permanently changed.

❖A catalyst speeds up a reaction by lowering the barrier, or activation energy, the reaction must overcome . . .



- The catalyst does NOT affect the reaction products or the enthalpy change for the reaction.
- Both remain the same.
- Catalysts provide an easier path for the reaction to proceed.

- Lowering activation energy of a reaction, increases the number of particles with enough energy to produce an effective collision.
- More particles with activation energy means more frequent effective collisions and an increased reaction rate.



- An **inhibitor** is the opposite of a catalyst.
- It affects reaction rates by stopping or slowing down reactions.

Enzymes:

- **Enzymes** are biological catalysts.
- Most biological reactions, including digestion of food and clotting of blood, are controlled by enzymes.
- They are capable of increasing the rate of biological reactions by over one million times!
- In your body, simple sugars in food can be digested in a matter of minutes.

- The reaction is a two-step mechanism:

Enzyme + Substrate → Enzyme-substrate complex

Enzyme-substrate complex → Enzyme + Product

- Enzymes remain unchanged after a reaction and are able to catalyze another reaction.
- Enzymes can remain active for an indefinite number of reactions.

Lesson Overview:

- Effect of the nature of reactants on reaction rate.
- Effect of temperature on reaction rate.
- Effect of concentration on reaction rate.
- Effect of catalysts on reaction rate.
- Enzymes.
- Effect of pressure on reaction rate.
- Effect of reactant size on reaction rate.

Pressure Changes:

- Changing the pressure on a system usually only affects the reaction rates of gaseous reactions.
- Pressure is the force of particles upon the walls of their container.
- If the number of particles in a container increases without changing volume, the pressure increases.

There are 3 ways to change pressure:

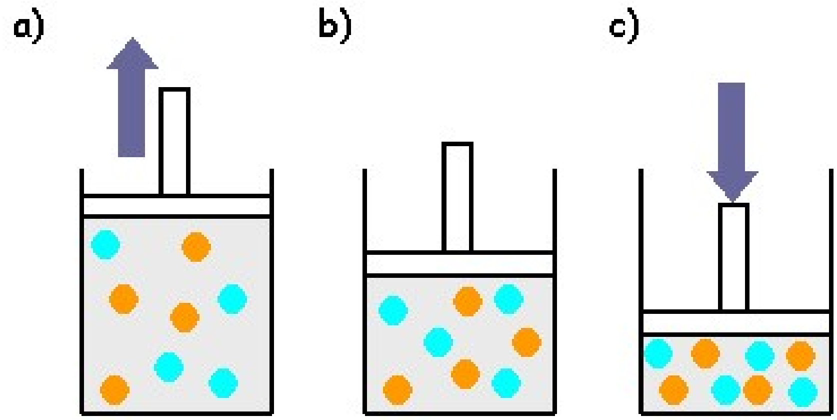
- Add more product and/or reactant particles to the container.
- Increase or decrease the volume of the container.
- Add an inert or unreactive gas.

Pressure Changes:

- If pressure is increased by adding more reactant particles, the concentration increases causing an increased rate.
- If the pressure is reduced by removing reactant, the rate decreases due to decreased concentration.

Volume Changes:

- Decrease the volume of a container without changing the number of particles in the container increases the concentration of the reactants.
- The spaces between the particles decreases, increasing the chances of a collision.
- If concentration of the reactants increases, the reaction rate increases.

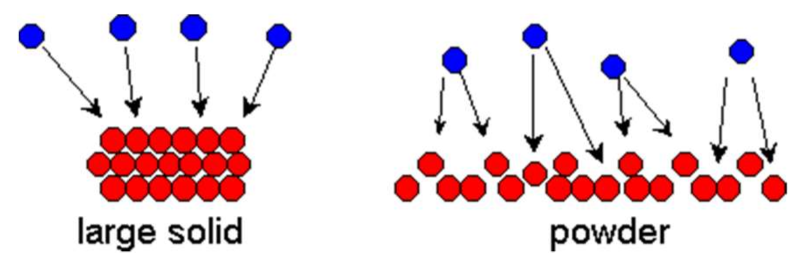


- If you increase the volume of a container without changing the number of particles, the concentration of the reactants decreases.
- The spaces between the particles increases, decreasing the chances of a collision.
- Decreasing the concentration of reactants decreases the reaction rate.

Effect of Particle Size:

- The size of the reactants, or surface area in contact, is usually only a factor in heterogeneous reactions.
- Increasing the surface area of the reactants by crushing, grinding or other means, increases the number of particles of reactants in contact.
- The rate of reactions increases when surface area in contact also increases.

- Increasing surface area increases the frequency of collisions, increasing reaction rate.

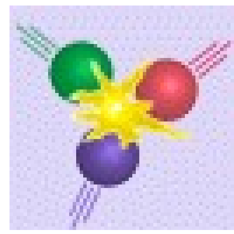


- When starting a campfire, it is easier to start with small kindling.
- This increases the wood's surface area and burning is much easier and faster.
- Logs are chopped to increase surface area of the wood, rather than adding whole logs to a fire.

Homework Assignment:

- Complete *Kinetics Assignment #3*.

Reaction Mechanisms



Introduction

- The rate of a reaction cannot always be determined from the reactants and products.
- This is because many reactions occur in several steps rather than in one simple step.

Outcomes

- Explain the concept of a reaction mechanism.
- Propose an analogy for a reaction mechanism
- Draw reaction coordinate diagrams for reaction mechanisms.
- Predict the relative rate of a chemical reaction or step of a mechanism based on reaction coordinate diagrams.

Lesson Overview

- Collision Theory and Reaction Mechanisms
- Reaction Intermediates
- Net Equations
- Rate Determining Step
- Energy Changes
- Mechanism Problems

Collision Theory and Reaction Mechanisms

- Reaction rate cannot always be determined from the chemical equation.

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

- According to the collision theory, for this reaction to occur in one step, 3 particles must collide: two NO molecules and one O_2 . . . Highly unlikely!

- These particles must collide at the same time with the correct orientation and enough energy.
- Chemical reactions tend to take place in steps, with each step involving a collision between two particles, or **bimolecular**.

Reaction Intermediates

- Reactions which take place in one elementary step are **simple reactions**.
- Reactions which take place in more than one step are **complex reactions**.

- The complex reaction:

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

- does not take place in one elementary step, but takes place in two steps:

Step 1	$2\,NO$	$\rightarrow N_2O_2$
Step 2	$N_2O_2 + O_2$	$\rightarrow 2\,NO_2$

- Products of one reaction that immediately become reactants in another reaction, are called **reaction intermediates**.
- All complex reactions contain at least one reaction intermediate.

Net Equations

- The steps in which a reaction occurs is called that reaction's **mechanism**.
- The sum of the steps of a mechanism must equal the total or **net equation**.
- For the reaction,

$$NO_2 + CO \rightarrow NO + CO_2$$

the mechanism is as follows. . .

Step 1	$NO_2 + \cancel{NO_2} \rightarrow \cancel{NO_3} + NO$
Step 2	$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$
Net reaction:	$NO_2 + CO \rightarrow NO + CO_2$

- ❖This mechanism agrees with the initial equation for this reaction, as the sum of the steps equals the original reaction.
- ❖The NO_3 is the reaction intermediate, so it does not appear in the net reaction.

Rate Determining Step

- ❖Not all steps in a mechanism have the same rate.
- ❖The step with the slowest rate is called the **rate determining step** (**RDS**).
- ❖That step affects the rate of the reaction more than the others.

- According to this mechanism:

Step 1 $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

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

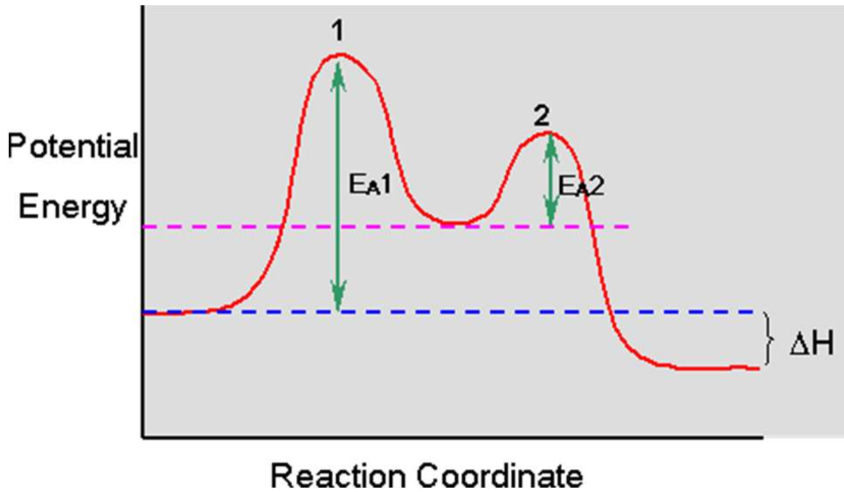
- step 1 is the RDS since it is the slowest step.

Step 1 $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

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

Predict the shape of the curve:

- The larger the E_A, the slower the reaction. Step 1 is the RDS, so it should have the largest E_A.
- Step 2 is fast. It should have the lowest activation energy. The E_A for Step 2 begins where Step 1 ends.
- The $\mathbf{H}_{reactants}$ should be higher than the $\mathbf{H}_{products}$.



Mechanism Problems

- Since the RDS affects the rate of the entire reaction the most, changes to the reactants in the other steps will have very little effect on the rate of the reaction.

Example 1

❖Given the following mechanism:

$$P + Q \longrightarrow X + T \quad \text{(slow)}$$
$$X + P \longrightarrow Y + R \quad \text{(fast)}$$
$$Y + S \longrightarrow T \quad \text{(moderate)}$$

Use this information to answer the questions on the *Reaction Mechanism Examples* worksheet.

Solution:

a)by adding the three steps, eliminating the compounds common to both sides:

$$P + Q \longrightarrow \cancel{X} + T \quad \text{(slow)}$$
$$\cancel{X} + P \longrightarrow \cancel{Y} + R \quad \text{(fast)}$$
$$\cancel{Y} + S \longrightarrow T \quad \text{(moderate)}$$
$$\overline{2P + Q + S \longrightarrow R + 2T}$$

b)The reaction intermediates are X and Y, since they are products in one step and become reactants in the next. They do not appear in the net equation.

c) $P + Q \longrightarrow X + T$ (the slowest step)

d)If the concentration of P were increased, the rate of the reaction would increase, since P is present in the RDS.

e)If the concentration of Q were decreased, the rate of the reaction would decrease, since Q is present in the RDS.

f) If the concentration of S were increased, there would be NO change in the rate of the reaction, since S is NOT present in the RDS.

Lesson Summary

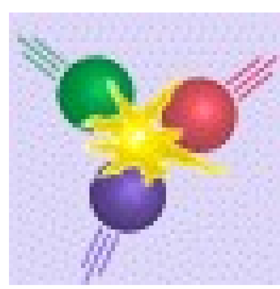
- Most reactions occur in several steps, each of which is usually bimolecular.
- The sum of these steps must equal the net equation.
- The mechanism for a reaction can only be determined experimentally.

- The rate determining step is the slowest step and affects the rate of the reaction the most.
- The rate determining step has the largest activation energy.

Homework Assignment

- Complete *Kinetics Assignment #4*.

Quantitative Effects



Introduction

- The rate of a reaction is affected by the concentration of its reactants
- Scientists find it useful to be able to control the rate of a reaction.
- Using the rate law as a tool, scientists can determine the rate of a reaction with varying concentrations of reactants.

Outcomes

- Determine the rate law of a chemical reaction from experimental data.
- Explain the effect of concentration on reaction rates in terms experimental data and rate law.
- Derive rate law form a reaction mechanism.
- Predict a reaction mechanism from rate law.

Lesson Overview

- ❖Rate Laws
- ❖Reaction Order
- ❖Calculating Rate Law
- ❖Calculating Rate Constant
- ❖Rate Law and Stoichiometry
- ❖Rate Law and Reaction Mechanism

Rate Law

- ❖an expression which relates the rate of a reaction to the concentration of the reactants.
- ❖a tool which helps us calculate the rate of a reaction with given concentrations of reactants.
- ❖shows the quantitative effect of concentration on reaction rate.

For the reaction:

A → products

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

- The rate of consumption of A is directly proportional to its concentration.
- The faster A is consumed, the lower its concentration.

This is represented by the equation:

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

- where: k is the constant of proportionality
- [A] is the concentration of A
- x is the power, called the **order** of the reaction.

- The constant *k*, is known as the specific rate constant for the reaction.
- The rate constant and the order can **only be determined experimentally**.
- The rate constant is specific for each reaction at a specific temperature, since it's value depends upon the size, speed and types of molecules in the reaction.

- **Temperature is the only factor which affects the rate constant.**
- Changing temperature would change the speed of the reactant particles and change the rate constant.

Reaction Order

- The order of a reaction indicates how concentration of reactants affects the rate of a reaction. In the reaction:

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

- If the order of the reaction was a **first order reaction**, x = 1, this would mean the reaction rate was directly proportional to changes in reactant concentration.

- If the reaction were a **second order reaction**, x = 2, doubling the concentration would increase the rate by a factor of $2^x = 2^2 = 4$.
- The rate would increase four times.
- Tripling the concentration of A would cause the rate to increase nine times ($3^x = 3^2 = 9$).

- If the rate of the reaction did not depend on the concentration of A, it would be a **zero order reaction**, x = 0.
- This means a change in the concentration of A does NOT change the rate of the reaction.

Calculating Rate Law

- **The rate law can only be determined experimentally.**
- **The rate law cannot usually be determined from the molar coefficients.**

- One method of determining rate law is by measuring the effect of changes in concentration of one reactant on the initial reaction rate, while keeping the other reactant concentrations constant.

Example 1:

- What is the rate law for the following reaction, given the experimental data below?

$$H_2O_2 + 2\ HI \rightarrow 2\ H_2O + I_2$$

Trial Number	$[H_2O_2]$ (mol/L)	[HI] (mol/L)	Rate (mol/Ls)
1	0.10	0.10	0.0076
2	0.10	0.20	0.0152
3	0.20	0.10	0.0152

Solution:

- According to reaction stoichiometry, we expect the rate law to be:

$$\text{rate} = k[H_2O_2][HI]^2$$

- By comparing trials 1 and 2 we see that keeping $[H_2O_2]$ constant while doubling $[HI]$ doubles the rate.
- This indicates that the reaction is **first order in HI**, NOT second order as the stoichiometry suggests.

- Next we choose two trials where $[H_2O_2]$ is changed but $[HI]$ does not change.
- We can use trials 1 and 3: doubling $[H_2O_2]$ doubles the rate as well. The reaction is then **first order in $[H_2O_2]$**.
- The rate law for this reaction is

$$\mathbf{rate} = k[H_2O_2][HI]$$

Calculating Rate Constant

Example 2: For the reaction

3 A(g) + B(g) + 2 C(g) $\longrightarrow$ 2 D(g) + 3 E(g)

The following data was obtained:

Trial	**[A] (mol/L)**	**[B] (mol/L)**	**[C] (mol/L)**	**Rate (mol/Ls)**
1	0.10	0.10	0.10	0.20
2	0.20	0.10	0.10	0.40
3	0.20	0.20	0.10	1.60
4	0.20	0.10	0.20	0.40
5	0.50	0.40	0.25	**?**
6	**?**	0.60	0.50	6.00

a) The rate law for the reaction is:

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

b) To find the value of k, we use that data from any one trial. We can use data from trial #1:

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

by rearranging the rate law, we can solve for k.

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

substitute the values for [A] and [B]

$$= \frac{0.20 \text{ mol/L}}{(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2}$$

$$= 200 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

value of k includes appropriate units

c) If we know the value of the rate constant, we can just substitute values into our rate law:

rate = $k[A][B]^2$

rate = $(200.\,L^2/mol^2s)(0.50\ mol/L)(0.40\ mol/L)^2$

rate = 16 mol/Ls

d) We can substitute known values into the rate law, then solve for [A].

rate = $k[A][B]^2$

rearrange the rate law equation

$$[A] = \frac{rate}{k[B]^2}$$

$$= \frac{6.00\ mol/Ls}{(200L^2/mol^2s)(0.60mol/L)^2}$$

substitute values

$[A] = 0.083\ mol/L$

answer contains correct units

Rate Law and Stoichiometry

- For elementary reactions the order of each reactant in the rate law is equal to the coefficient in the reaction's balanced equation.
- For the elementary reaction:

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

the rate law is

$$\text{rate} = k[A]^a[B]^b,$$

where *a* and *b* are the molar coefficients for the elementary reaction.

Example 1:

One of the reactions that results in smog is the reaction of ozone, $O_3(g)$ and nitrogen monoxide, NO(g). This reaction is thought to occur in a single elementary step according to the equation:

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$

Determine the rate law for this reaction.

Solution:

- Since this is an elementary reaction, the molar coefficients become the order for each reactant. Therefore, the reaction is first order in ozone and first order in nitrogen monoxide.
- The rate law should be:

$$\text{rate} = k[O_3][NO]$$

Example

The mechanism for the reaction

$$3\,M + N \rightarrow P + 2\,Q$$

is below:

$$2\,M \rightarrow P + X \text{(slow)}$$
$$X + M \rightarrow Q + Y \text{(moderate)}$$
$$N + Y \rightarrow Q \text{(fast)}$$

a)What is the rate law for this reaction?
b)What would be the effect of tripling the [M]?
c)What would be the effect of doubling the [N]?

Solution:

a) Since the only reactant present in the RDS is M, and its coefficient is 2, the order of the reaction will be 2.

The rate law is: Rate = $k[M]^2$

b) 3 x [M] causes the rate to increase by

$3^{order} = 3^2 = 9$. The rate increases by 9 times.

c) N is not present in the RDS. The reaction is then zero order in N. There is, therefore, no effect on the rate by changing the concentration of N.

Rate Law and Reaction Mechanism

- Chemists deduce the mechanism of a reaction by first determining the rate law experimentally, then proposing a mechanism.
- For the reaction

  $$2\ NO_2(g) + Cl_2(g) \rightarrow 2\ NO_2Cl(g),$$

  the rate law was determined to be

  Rate = $k[NO_2][Cl_2]$

- A suggested mechanism would have the molar coefficients of NO_2 and Cl_2, in the RDS, equal to one.
- The product of this step would have to reflect this, likely resulting in a reaction intermediate.
- The remaining steps would be acceptable if the sum of all steps resulted in the net equation

A possible RDS could be

$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$$

Cl would be a reaction intermediate.

A step to follow might be

$$NO_2 + Cl \rightarrow NO_2Cl$$

- To check if the mechanism is acceptable, are the sum of the steps equal to the net equation?

$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl \text{ (slow)}$$
$$NO_2 + Cl \rightarrow NO_2Cl \text{ (fast)}$$
$$2\,NO_2 + Cl_2 \rightarrow 2\,NO_2Cl$$

- Remember, chemists cannot determine a mechanism definitively, just suggest a possible mechanism which reflects experimental data.

Lesson Summary

- Rate Law describes the relationship between rate and concentration of reactants.
- Rate law can only be determined experimentally.
- Rate law does not usually correspond with reaction stoichiometry.
- Rate law can be predicted using the coefficients of balanced elementary reactions and rate determining steps of reaction mechanisms.

Homework Assignment

- Complete *Kinetics Assignment #5*.
- Complete *Kinetics Assignment #6*.
- Complete *Kinetics Assignment #7*.