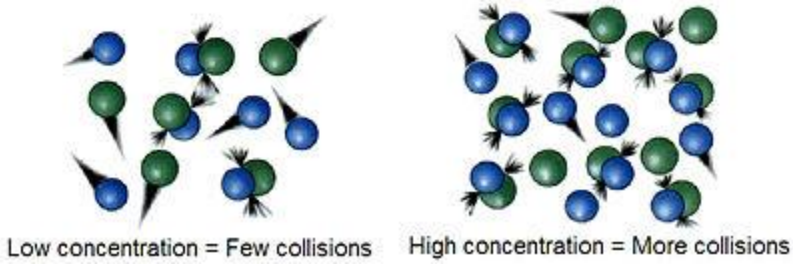
Kinetics Booklet



Chemistry focuses largely on chemical reactions. Some reactions, such as rusting, occur very slowly, while others, like explosions, occur quite fast. ______________________ ____.

Some reactions do not occur in one simple step. Some occur in several more complex steps. Part of Kinetics is studying ______________________________________, 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 chemical reactions in order to make them happen or not and to control the rate at which they happen.

Introduction to Reaction Rates

When we hear the word rate we often think of ___________________________, especially in terms of rate of motion. We will define rate and determine methods by which rate of a chemical reaction can be measured. We will use experimental data to graphically determine the average and instantaneous rates of a chemical reaction.

What is Rate?

Recall that a ____.
They are usually expressed in the shorthand form, known as a ____________________.
The chemical equation has _______________, usually written on the left side of an arrow, and the ________________ of the reaction, written on the right side of the arrow, as below:

REACTANTS → PRODUCTS

The **rate** of a reaction refers ____ _____________________. That is, how fast reactants are used up or products are formed.

Measuring Rate

How do we usually measure the how fast a reaction occurs?

Generally, we will measure the rate of a reaction by _____________________________ _________________________________ – slower reaction take a longer period of time. For example, an explosion is a very fast reaction because the explosive burns up in fractions of a second, while burning the wax in a candle could take hours. But the term fast or slow is relative. Chemists need a more consistent means of measuring the rate of a chemical reaction for comparisons and in order to manipulate the rates.

In grade 10 science, you learned that speed or velocity can also be called the rate of motion. When we measure rate of motion, ____________________________________ ____. We use these values to determine the speed or velocity by the equation below:

Reaction rate is measured by determining ______________________________________ ____.
The actual _______________ of these may not be able to be directly determined, so another observable property must be measured. The rate of a reaction is

$$\text{Rate of reaction} = \frac{\text{measured change in a property}}{\text{time for change to occur}}$$

Rate can be measured using several different methods.

The reaction below shows that A and B combine to form C and D and __________ is given off. Also, substance B has ____________________________ in solution and D has a _________________ in solution.

A(s) + **B**(aq) → C(g) + **D** (aq) + heat

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

i) ____ (°C/min)
As the reaction proceeds, _______________________________________. The faster heat is produced, the higher the rate.

As an aside: As temperature goes up _______ the reaction rate doubles. This relationship is not directly proportional.

ii) _____________________________________ (kPa/s or mmHg/s)
As the reaction proceeds, ___________________________. This increases the pressure of the system. The faster the pressure increases, the greater the rate.

iii) _____________________________ (g of C/min)
As the reaction proceeds, reactants are used up and converted to gas. This results______ ____, C.

iv) ______________________
Colour change is usually measured in terms of how much light of a specific wavelength can be absorbed. The amount of absorbance can be directly related to the concentration. The greater the concentration of D, the deeper the red colour and the more light that is absorbed.

v) Others
pH change, change in conductivity, etc. over a period of time.

Calculating Average Rate

The rate of a reaction is often described in terms of the ___________________________ of the reactants or the products.

The **average rate** of a reaction is the change ___________________________________ over a period of time. For the equation

$$A \rightarrow B$$

The average rate can be expressed mathematically as

or

Chemists often use the square brackets to mean "concentration of" the substance in the brackets.

The Δ or the Greek letter delta means "change in".

We can write this equation in another way, as well:

Calculating Average Rate

Let's look at the following example:

Example 1. According to the reaction A → B, the following data was collected:

Time (s)	Concentration of 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 20 s to 40 s?

Solution

a) recall, rate is a change over time

The units for rate can be written as mol/L/s, mol/Ls, or mol $L^{-1}s^{-1}$.

b)

Example 2. The decomposition of nitrogen dioxide produces nitrogen monoxide and oxygen according to the reaction:

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

the following data has been collected:

Time (s)	**[NO_2] (mol/L**	**[NO] (mol/L)**	**[O2] (mol/L)**
0.0	0.100	0.00	0.00
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 the average rate of decomposition of NO_2 over 400 s.

Solution:

Note that the calculated rate is a negative number. Rate is always expressed as a POSITIVE value. The actual value of the average rate is 1.75×10^{-4} mol/Ls.

We should rewrite the equation for the average rate of a reactant with a negative sign as shown below:

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

Average Rate Exercises

1. For the reaction A → products, the following data was collected:

Time (min)	Mass of A (g)
0.0	25.0
1.0	20.0
2.0	17.0
3.0	15.0
4.0	13.0
5.0	12.0

a) What is the average rate, in g A/min, over the entire 5 minutes?
b) What is the average rate for the interval between 2.0 and 4.0 minutes?

2. The decomposition of acetaldehyde to methane and carbon dioxide occurs according to the following equation:

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

The results of an experiment are given below:

Time (s)	$[CH_3CHO]$ (mol/L)
42	0.00667
73	0.00626
105	0.00586
190	0.00505
242	0.00464
310	0.00423
384	0.00383
480	0.00342
665	0.00282
840	0.00241

a) What is the rate of decomposition of acetaldegyde between 42 s and 105 s?
b) What is the rate of decomposition in the interval 190 s to 480 s?

3. Below is the data from an experiment that studied the following reaction:

$2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_{2(g)}$

HCl was placed in a beaker and massed immediately after adding $CaCO_3$ chips (time = 0). The mass of the beaker was recorded at 1.0 minute intervals for a total of 15 min. We will assume the loss of mass is the amount of carbon dioxide gas that escapes from the beaker.

Time (min)	**Mass of beaker and contents (g)**	**Mass loss (CO_2 produced) (g)**
0.0	200.00	
1.0	199.40	
2.0	199.00	
3.0	198.65	
4.0	198.35	
5.0	198.10	
6.0	197.90	
7.0	197.75	
8.0	197.65	
9.0	197.57	
10.0	197.52	

a) Complete the table.

b) Determine the average rate, in g of CO_2/min, over the entire 10 minutes.

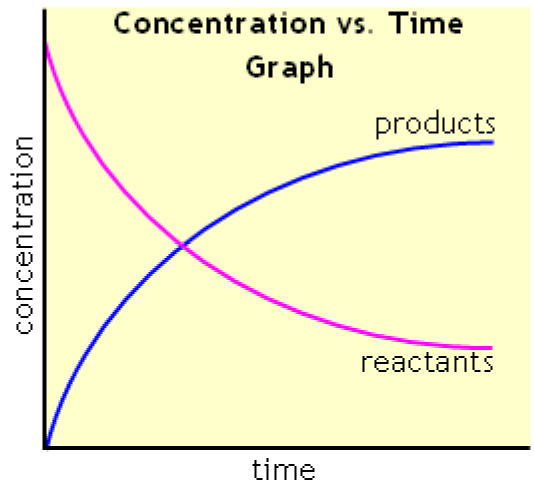
c) Determine the average rate for the intervals:

i) First 3 minutes.
ii) Last 3 minutes.

Instantaneous Rate

Reactions often start quickly, but slow down over time. You have noticed this if you light a match. The match starts quickly, but the flame slowly diminishes until it goes out. We will discuss why this occurs in lesson 3.

If we graph the ____
we find that the graphs ______________________.



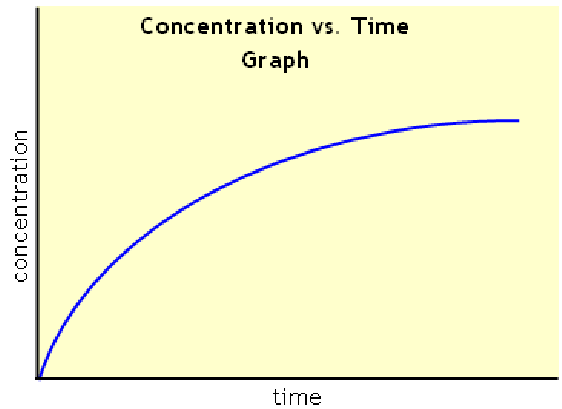
The shape of the curves suggests that _________________________________
throughout the reaction.

The ________________________ is the rate at an __________________, while the __________________ describes the rate _____________________.

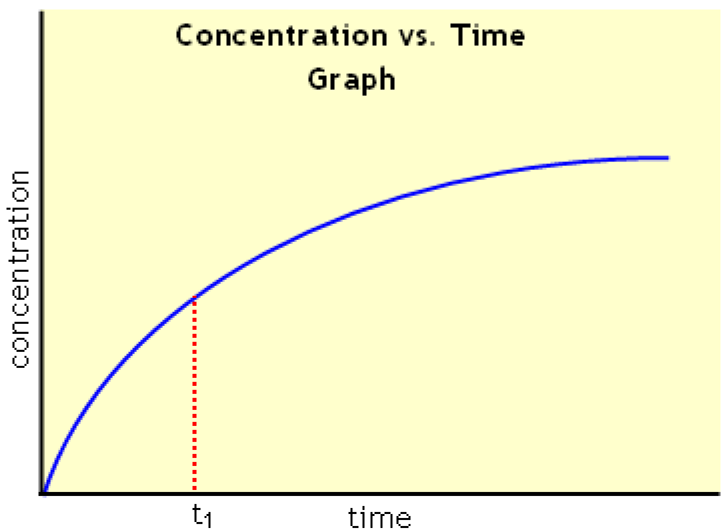
The difference between these can be explained in an analogy of driving from Winnipeg to Brandon (about 200 kilometers). If it takes you 2 hours to drive from Winnipeg to Brandon, what is your average speed?

But, you do not travel at 100 km/h at every moment. There are times where you must stop for a light or a train. There are places where the speed limit is below 100 km/h, so you slow down. There are also places where you may exceed the 100 km/h speed limit (I am not, however, condoning speeding). ____________________________________
____.

Unfortunately chemical reactions do not have speedometers for us to determine the instantaneous rate. In order to determine the instantaneous rate we must first draw a ______________________ (or other property like pressure or mass) vs. _______________.

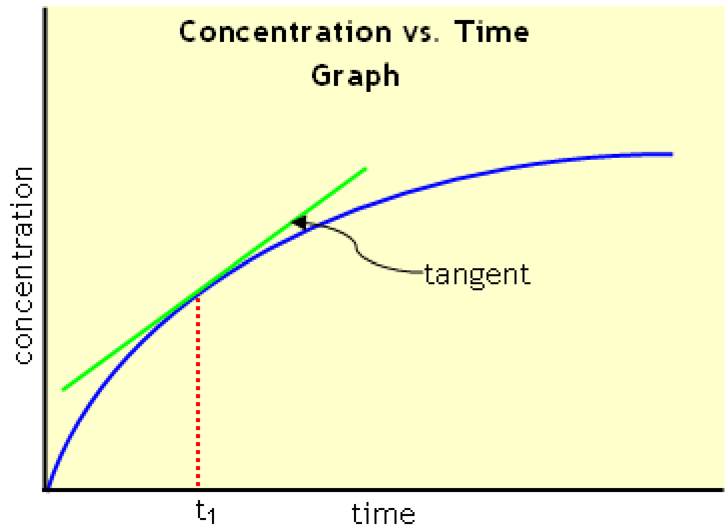


Then you determine at which time you wish to find the rate. Draw a line to the concentration vs. time curve.



Draw the tangent line to that point on the curve. A tangent is a line drawn to a curve that touches the curve at only one point. If we imagine the curve is part of a circle, the tangent is also perpendicular to the radius of the circle.

The instantaneous rate at time t_1 is the slope of the tangent drawn to that point.



So far you have learned:

- Rate is a measure of ____ ________________ in a chemical reaction.
- Rate is determined by ____ in an observable property over a period of time.
- The average rate is _____________________________ by finding the change in concentration of a reactant or product divided by the amount of time for that change to occur.
- Rate is always a ______________ value.
- Instantaneous is the rate at a specific instant in time and is found by ___________ _________________ of the tangent line drawn to a concentration vs. time graph.

Instantaneous and Average Rate Questions

The formation of nitrogen dioxide from nitrogen dioxide and oxygen gas was studied. The balanced equation for the reaction is:

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

The chemist measured the concentration of the three gases at various time intervals. Construct a well labeled graph (labeled axis with units, a title, etc.) to represent this data. Along the y-axis plot gas concentration and time on the x-axis.

Time (min)	Concentration (mol/L)		
	O_2	NO	NO_2
0.0	0.000343	0.000514	0.000000
2.0	0.000317	0.000461	0.000053
4.0	0.000289	0.000406	0.000108
6.0	0.000271	0.000368	0.000146
10.0	0.000242	0.000311	0.000204
16.0	0.000216	0.000259	0.000256
26.0	0.000189	0.000206	0.000308
41.0	0.000167	0.000162	0.000353
51.0	0.000158	0.000143	0.000372
61.0	0.000150	0.000127	0.000387
71.0	0.000144	0.000116	0.000399

Submit Kinetics Assignment #1

Rate & Stoichiometry Problems

Remember the graph assignment you did last class…

The equation for the reaction was $O_2(g) + 2\ NO(g) \rightarrow 2\ NO_2\ (g)$.

When you look at the graph, the concentration of the NO_2 increases about the same amount as the NO decreases and the concentrations of the NO and NO_2 change about twice the amount that the O_2 changes.

The average rates you calculated show that the rate of NO and NO_2 are approximately equivalent and that they are about twice the rate of O_2.

These ratios are the same ratios as those found in the reaction **stoichiometry**.

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

Or…

$$\text{rate} = -2\ \frac{\Delta[NO]}{\Delta t} = 2\ \frac{\Delta[NO2]}{\Delta t} = -\frac{\Delta[O2]}{\Delta t}$$

Why are some of the rate equations written with a negative symbol?

Rate and Stoichiometry Problems

Example 1. The decomposition of nitrogen dioxide occurs according to the equation below.

$$2\ NO_2 \rightarrow O_2 + 2\ NO$$

If the rate of decomposition of NO_2 is determined to be 0.50 mol/Ls at a certain temperature, predict the rate of creation of both products.

Solution:

Use the molar ratios to determine rates.

Example 2. For the reaction 2 A + B → 3 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?

Solution:

Use the molar ratios to determine rates.

by using the molar ratio of A to C we can make the equation:

by using the molar ratio of A to B we get:

Lesson Summary
In this lesson we have learned:

- The rate of the formation of products and consumption of reactants is related to their stoichiometry.

Practice Questions:

1. In the reaction $4NO + 6H_2O \rightarrow 5O_2 + 4NH_3$, if the rate of formation of NH_3 is 0.090 mol/Ls find the rate of decomposition of NO, H_2O and the rate of formation of O_2.

2. Write the balanced equation for the combination of NO_2 and O_2 to form N_2O_5. If the rate of formation of N_2O_5 is 0.20 mol/Ls, find the rate of decomposition of each reactant.

3. The rate of decomposition of H_2 is 0.8 mol/Ls what would be the average rates of I_2 and HI? Hint – write out the equation first.

Factors Affecting Reaction Rates

It is important for chemists to understand the factors which affect reaction rates. If we can understand those factors, we may be able to control the rates of some reactions. We will look at six factors.

A. The Nature of Reactants

Chemical reactions involve the ____ ________________________________ and ____________________________________ _______________. The breaking of bonds requires energy and the forming of bonds releases energy. It makes sense then that the ____________________________________ _____________________ will affect the rate of a reaction.

1. The _________ the bonds to be broken the __________ the reaction.

In general, covalent bonds are much stronger than ionic bonds. As a result, reactants that require the breaking of covalent bonds will be _________________ those involving ionic bonds. Ionic compounds in aqueous solutions are already separated into ions, so these are ____________________.

For example, between these reactions which would be the fastest?

$H_2(g) + I_2(g) \rightarrow 2HI(g)$

$Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2\ NaNO_3(aq)$

The first reaction requires the breaking of 2 covalent bonds (an H-H bond and an I-I bond). The second reaction is between ionic compounds in aqueous solutions. Ionic compounds in water dissociate into ions. ___________________________________ __________________________________.

2. When comparing reactions with similar bonds, the ______________________ that must be broken the _____________________.

Think about dismantling an object if you want to fix it. The more parts that you need to separate, generally the longer it will take.

For example, if we compare the following two reactions

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

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

Both reactions involve breaking covalent bonds. The first reaction is ________________ because it only involves the breaking of one O-O bond and 2 N-O bonds.

The second reaction is the burning of octane. This is a ___________________ because of the number of bonds that must be broken: 7 C-C bonds, 18 C-H bonds and 25 O-O bonds.

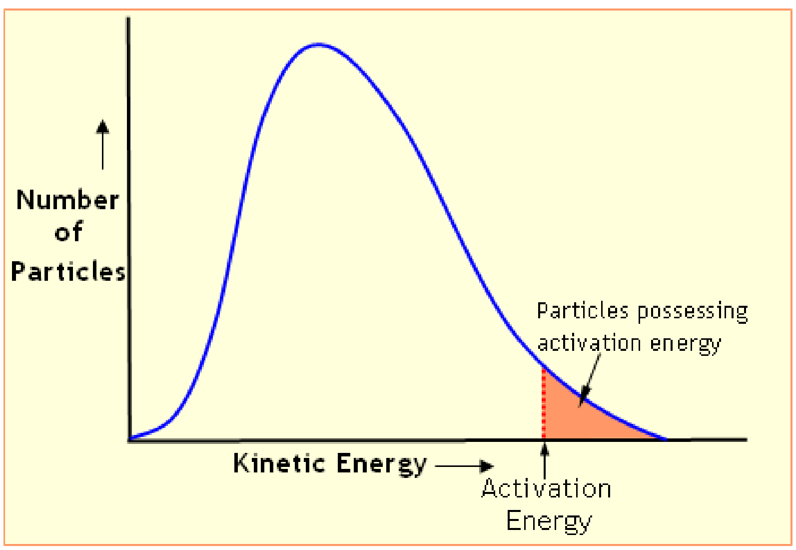
3. If the reactions have similar bonds and similar numbers of bonds, the _________ _______________________________.

Reactions with ____, followed by _____________, then _____________ and finally _________. Reactions between solids are usually slowest because the forces of attraction between the particles in a solid must be overcome before they can react. Reactions between aqueous reactants are often faster because there are fewer bonds to break. Reactions between gaseous reactants are also fairly quick because of the constant motion of the gas molecules and the greater likelihood of a collision occurring between the reactant particles.

B. Temperature Changes

According to the collision theory, the rate of a reaction is determined by the frequency or number of successful or effective collisions. ________________________________ ____ (more on this tomorrow). At any given temperature there are a fixed number of particles that ___________________________ to produce an effective collision, that is, ______________________. Typically, as temperature increases by 10°C the rate of the reaction doubles.

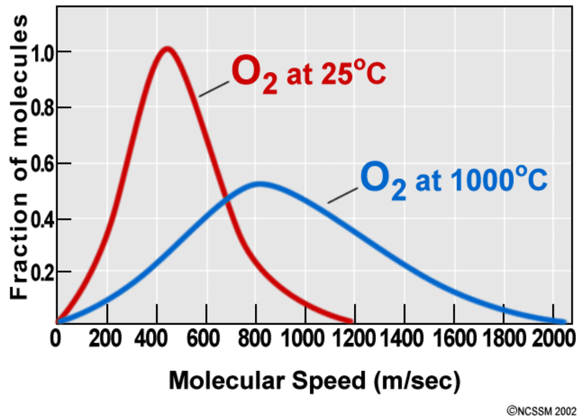
Kinetic Energy Distribution Curve.



The area under the curve represents the __________________ at a given kinetic energy.

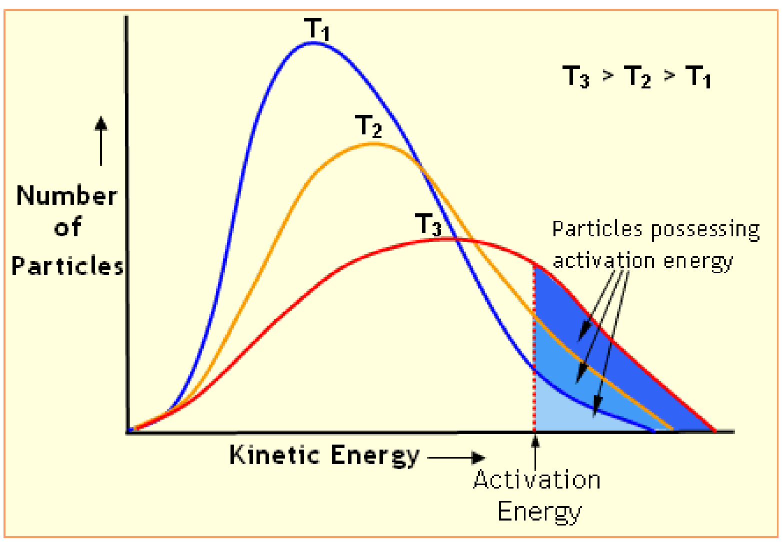
The area under the curve to the right of the activation energy (shaded in this diagram) represents the number of particles with sufficient energy to produce a reaction. ______ ____. The lower the activation energy is the more particles in the system that will possess enough energy to produce a reaction.

The diagram below shows the kinetic energy distribution curves of a substance at ___________________________________.



The area under the 2 curves remains constant, but the _____________________________ as the temperature changes.

We can look at the effect of changing temperature on the number of particles with _________________________, that is, particles able to make a ______________________.



At which temperature do the most particles posses more than the activation energy, and are therefore able to make successful collisions? ________

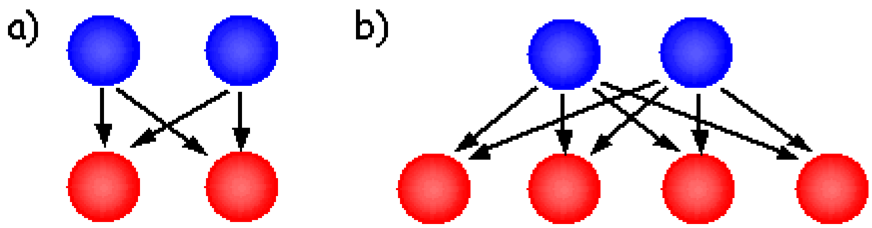
Notice how the number of particles possessing activation energy ___________________ __________________________________. You should also notice that changing the temperature ______________________________________. As temperature increases, the average kinetic energy of the particles increases and ______________________________ ______________________________. Since the number of particle with activation increases, the number of successful collisions will also increase.

Lowering the temperature reduces the average kinetic energy of the particles. This reduces the speed of the reactant particles and the number of reactant particles with activation energy. As a result, the frequency of effective collisions is decreased and the ___________________________________.

C. Concentration Changes

Recall that concentration refers to the amount of reactant per unit volume. The units for concentration are mol/L.

Increasing the concentration of reactants __________________ of particles in a container. If the number of particles in a container increases, so do the number of particles with activation energy. Increasing the number of particles in a container will also increase the chances of a collision. The diagram below illustrates the effect of doubling the concentration of just one of the reactants:



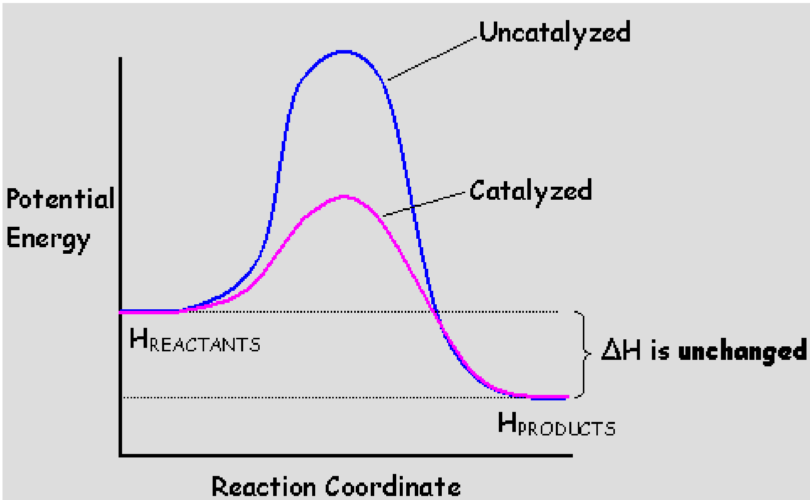
In (a), with two particles of each, there exists four possible collisions which could produce a reaction.

In (b), by doubling the number of red particles, the number of possible collisions increases to eight! This will increase collision frequency.

We can think of this in terms of collisions with cars as well. During rush hour, there are more accidents because there are more vehicles on the road at one time. The frequency of collisions increases because the "concentration" of vehicles is larger and the space between each vehicle is less, increasing chances of collision.

D. Catalysts

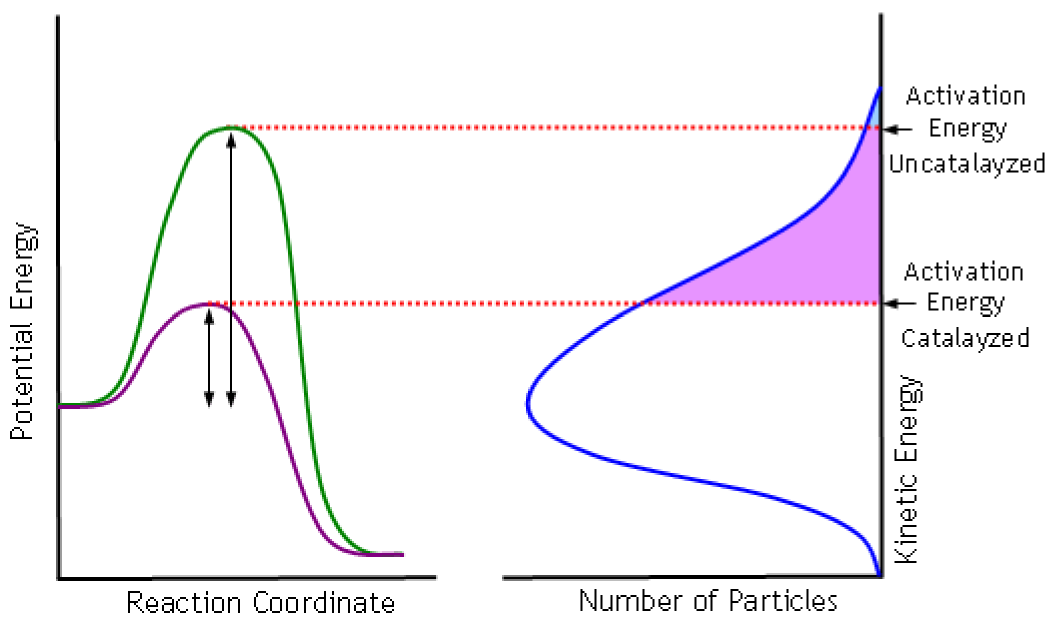
A **catalyst** is a substance that speeds up or initiates a reaction without itself being ____.



The reaction coordinate diagram, above, _______________________________________ ____, the reaction must overcome.

Catalysts will only provide an ______________________ for the reaction to proceed.

Lowering the activation energy of a reaction ______________________________________ ________________________________ to produce an effective collision. More particles with activation energy mean more frequent effective collisions and an increased reaction rate.



Examples of Catalysts

Enzymes are known as biological catalysts. Most biological reactions, including digestion of food and clotting of blood, are controlled by enzymes.
Enzymes are capable of increasing the rate of biological reactions by over one million times! Enzymes accomplish this by bringing the reactants, called substrates, together. The reactants bind to a certain part of the enzyme, called the active site. The reactants are then placed into a position which favours a reaction. The active sites can be very specific, binding to only one set of reactants, or they can catalyze several different types of reactions.

E. Pressure Changes

Changing the pressure on a system usually only affects the reaction rates of ______________ reactions.

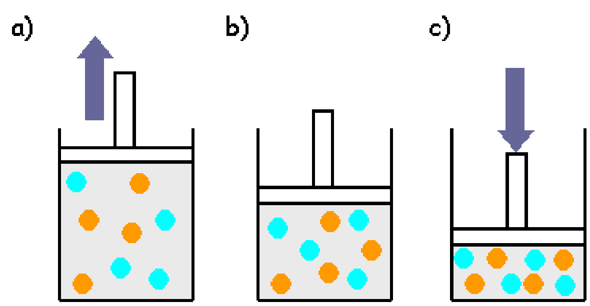
Pressure is the ________________ upon the walls of their container. If the number of particles in a container _____________ without changing volume, the ________________ ___________________.

There are 3 ways to change pressure:

- ______________ product and/or reactant particles to the container.
- Increase or decrease ______________ of the container
- __________ an inert or unreactive gas.

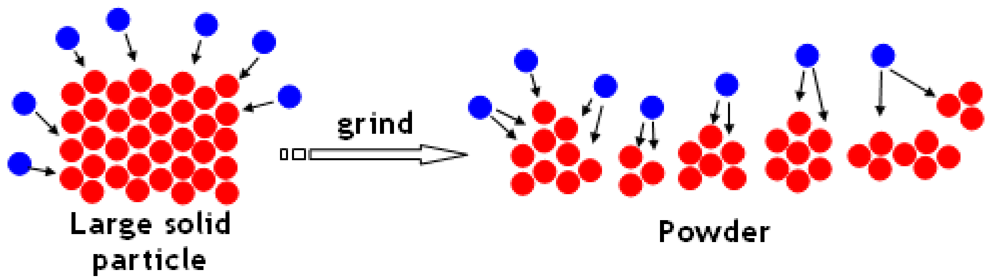
If pressure is increased by adding ________________ particles, the concentration increases causing an ______________ rate. If the pressure is reduced by ______________ _____________, the rate decreases due to ________________ concentration.

If you __________________ of a container without changing the number of particles in the container the concentration of the reactants increases. The spaces between the particles decreases, increasing the chances of a collision. If the concentration of the reactants increases, _________________________.



F. Surface Area

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 increases. Like a sugar cube in coffee compared to a spoonful of sugar in coffee.



Increasing ___________________________ the frequency of collisions, ____________ __________________.

Lesson Summary

In this lesson we have learned:

- The **number and strength of the bonds** which must be broken affect the rate of a reaction.
- **Increasing temperature** increases reaction rate by increasing the speed of reacting particles and the number of particles with activation energy.
- Increasing concentration of reactants increases reaction rates by increasing the number of particles with activation energy and increasing the frequency of collisions.
- Pressure changes only affect reactions containing gaseous reactants. Increasing pressure decreases the space between the particles, increasing the number of collisions.
- A catalyst is a substance which speeds up a reaction by reducing activation energy. A reduction in the activation energy increases the number of particles that can produce a successful collision.
- Grinding or powdering a solid reactant will increase reaction rates because of increased surface area in contact with other reactants.

Practice Questions on Factors

1. In general, what effect does an increase in the concentration of the reactants have on the rate of the reaction?

2. How do changes each of the following factors affect the rate of a chemical reaction? You may use diagrams to clarify your explanations.

a) temperature

b) particle size

c) pressure

3. Which equation of the following pairs of equations would occur the fastest at under the same conditions. Explain your answers.

a. i) $Zn^{2+}(aq) + S^{2-}(aq) \rightarrow ZnS(s)$
   ii) $Zn(s) + S(s) \rightarrow ZnS(s)$

b. i) $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(l)$
   ii) $Cu(s) + 2\ AgNO_3(aq) \rightarrow 2\ Ag^{+}(aq) + Cu(NO_3)_2(aq)$

c. i) $Pb(NO_3)_2(aq) + 2\ KI(aq) \rightarrow PbI_2(aq) + 2\ KNO_3(aq)$
   ii) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$

d. i) $2\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$
   ii) $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

Factors Influencing Reaction Rate - Nature of Reactants

1. Which one of the following reactions would you expect to be fastest at room temperature and why?

$Pb^{2+}_{(aq)} + 2\ Cl^{-}_{(aq)} \rightarrow PbCl_{2\ (s)}$

$Pb_{(s)} + Cl_{2\ (g)} \rightarrow PbCl_{2\ (s)}$

2. Consider the following reactions. Which do you predict will occur most rapidly at room conditions? Slowest?

$C_2H_{6\ (g)} + O_{2\ (g)} \rightarrow 2\ CO_{2\ (g)} + 3\ H_2O_{(g)}$

$Fe_{(s)} + O_{2\ (g)} \rightarrow Fe_2O_{3\ (s)}$

$H_2O_{(l)} + CO_{2\ (g)} \rightarrow H_2CO_{3\ (g)}$

$2\ Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2\ Fe^{2+}_{(aq)} + Sn^{4+}_{(aq)}$

Factors Influencing Reaction Rate – Concentration & Pressure

1. Consider the following reaction that occurs between hydrochloric acid, HCl, and zinc metal:

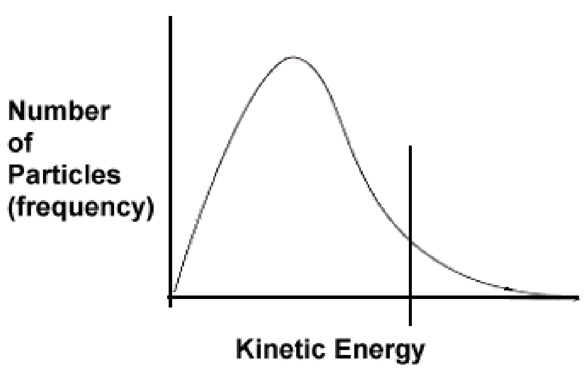
   $HCl_{(aq)} + Zn_{(s)} \rightarrow H_{2\,(g)} + ZnCl_{2\,(aq)}$

   Will this reaction occur fastest using a 6 M solution of HCl or a 0.5 M solution of HCl? Explain.

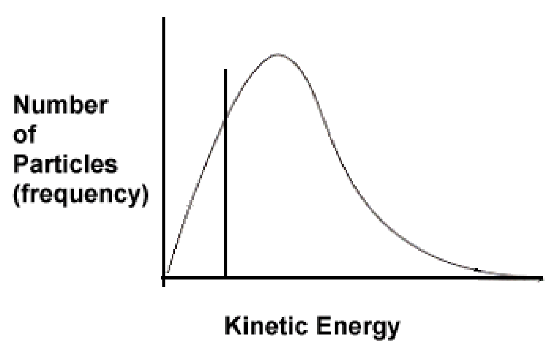
2. Again consider the reaction between hydrochloric acid and zinc. How will increasing the temperature affect the rate of the reaction? Explain.

3. Based on the following kinetic energy curves, which reaction will have a faster rate - A or B? Explain. Also, which reaction, A or B, would benefit most in terms of increased rate if the temperature of the system were increased?

A



B



The Collision Theory

The **collision theory** states:

____
____
____

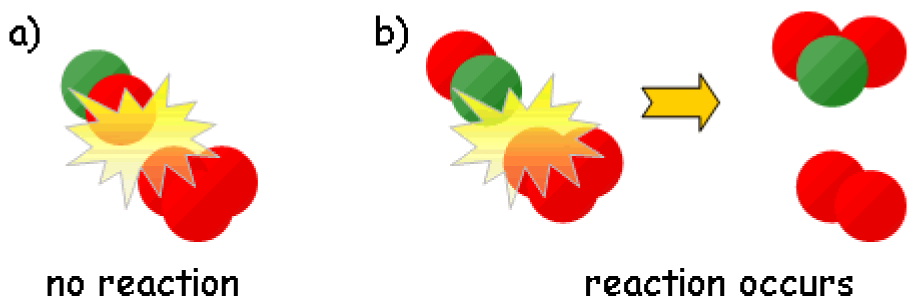
However, not all collisions produce a reaction.

The particles must collide with the ______________________. Consider the following example:

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

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

If the oxygen atoms collide in orientation (a), no reaction occurs. But if the nitrogen atom collides with the oxygen atom (b), a reaction occurs.



Activation Energy

Not only do particles need collide with the ______________________________, they must also collide with ______________________________.

Chemical reactions involve the making and breaking of bonds, which requires energy. If colliding particles ____ they will not produce a reaction.

The minimum amount of energy required for colliding particles to produce a chemical reaction is called the ____ of that reaction.

The ____, the longer the reaction takes.

Heat of Reaction

The rate of a reaction is determined ______________________________ that the particles must cross in order that they are converted into products. The ____________________________ is the barrier colliding particles must overcome.

As the particles collide, they form an _____________________________ particle called the ________________________________. The energy required to produce the activated complex is the _____________________. The activated complex has a maximum amount of potential energy but exists for a very small instant in time.

_____________________ is the heat content or total energy possessed by the particles in a system.

The energy ____________________________ by a reaction is called the ________________________ or **heat of reaction**.

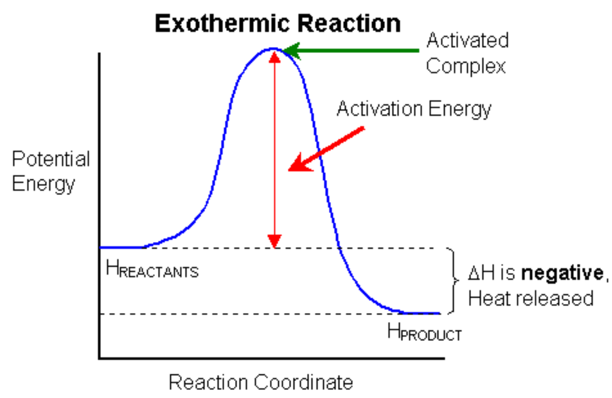
$\Delta H = H_{PRODUCTS} - H_{REACTANTS}$

If ΔH is _______________, the products have _________ enthalpy (energy) than the reactants. As a result _______________ of the system. This type of reaction gives off heat and the reaction vessel feels warmer. This is called an ______________________.

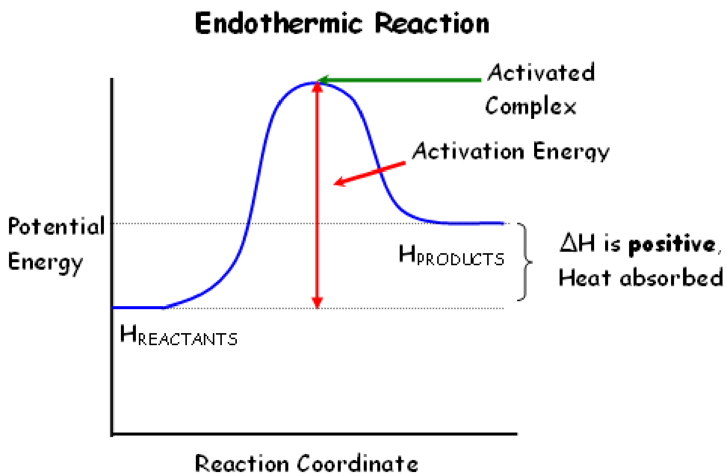
If ΔH ___________ , heat is absorbed or flows into the system because the products have _______ enthalpy than the reactants. The reaction _____________________ as energy is absorbed from the surroundings. This type of reaction is called an __________________.

Potential Energy Diagrams

A _____________________________ represents the energy change that occurs during a reaction.



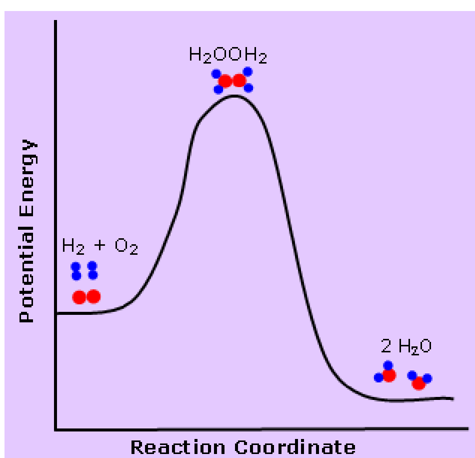
In the exothermic reaction, ____.
During the reaction, heat is lost from the system and ΔH is a ___________ value.



In an _______________________, the _______________________________________
_____________________. This energy is absorbed from the surroundings, increasing the systems energy content, giving a ________________ value.

Reaction coordinate or potential energy diagrams provide a picture of the energy changes which occur as a chemical reaction proceeds. The energy changes during a chemical reaction are much the same as those occurring during a roller coaster ride. The beginning of a roller coaster ride is a long, slow, uphill ride. Energy is expended by motors, in the effort to get the cars to the top of the first hump. Once the cars reach the top of the first hump, it's all down hill. The cars have enough energy for the entire ride, regardless of the number of ups, downs, twists and turns.

Let's look at the potential energy diagram for the formation of water from hydrogen and oxygen: $2 H_2 + O_2 \rightarrow 2 H_2O$



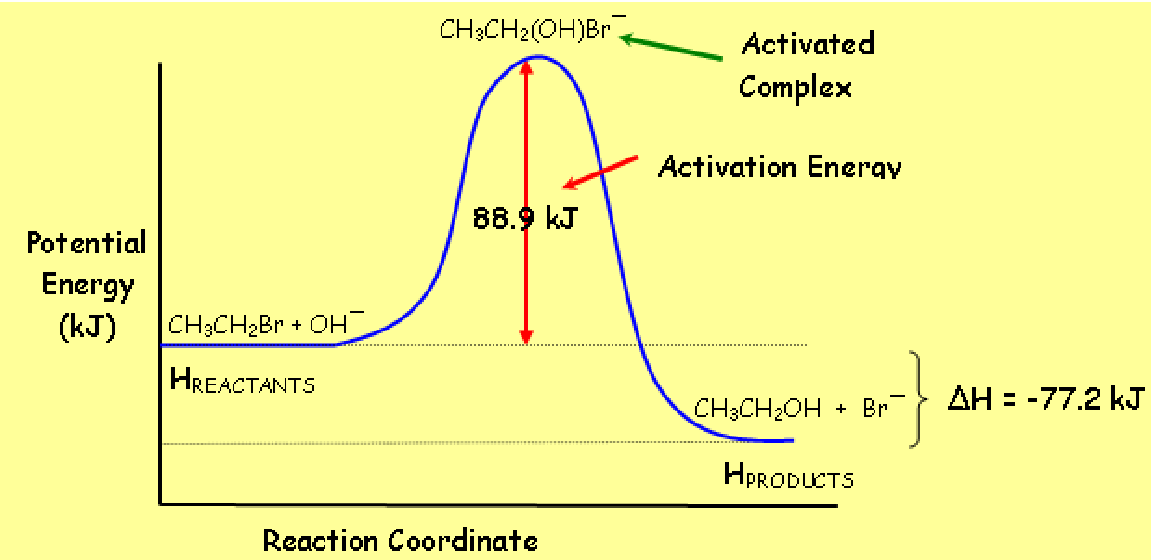
Hydrogen and oxygen can exist together without exploding or burning due to the need to overcome activation energy. ____ ______________________ hydrogen-hydrogen bonds in hydrogen molecules and oxygen-oxygen bonds in oxygen molecules. Notice that the transition state or activated complex is a single particle. This H_2OOH_2 particle ____________________, but must be formed in order for hydrogen to burn. The ____________ in the formation of water is released in the form of heat and light energy. All combustion reactions are __________.

Example 2

In the reaction,

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

the reaction coordinate diagram is shown below:



The activated complex in this reaction is $CH_3CH_2(OH)Br^-$. It is a single particle formed by the all the reactant particles.

The activation energy is ________ per mole of CH_3CH_2Br.

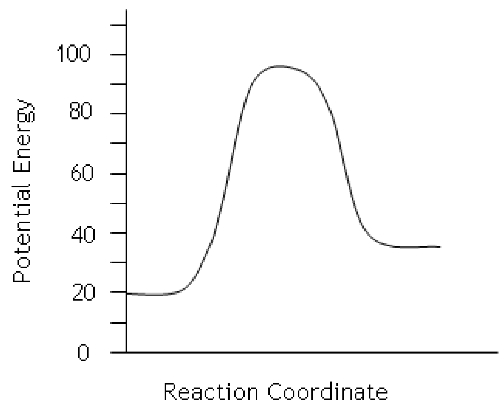
The enthalpy change is ________, indicating an _____________ reaction. Consequently, this reaction does not take place unless 88.9 kJ per mole of CH_3CH_2Br is added to the system.

Lesson Summary

- According to the collision theory, in order for a chemical reaction to occur reacting particles must collide with enough energy and the correct orientation.
- The rate of a reaction is determined by the number of successful collisions.
- The activation energy is the minimum amount of energy needed to produce a reaction, or the amount of energy needed to form the activated complex.
- The higher the activation energy, the lower the number of particles that can produce a successful collision.
- Heat of Reaction is the change in enthalpy when a reaction is complete or the difference between the enthalpy of the products (final) and the enthalpy of the reactants (initial).

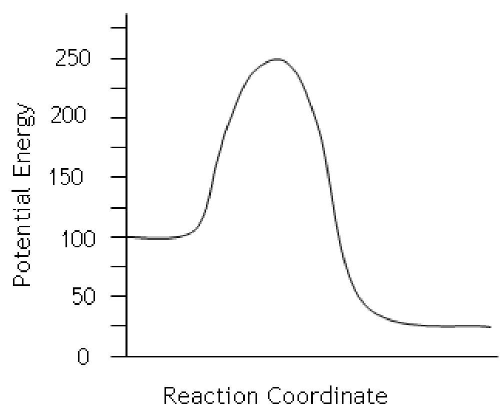
Exercises

1. Given the following reaction coordinate diagram



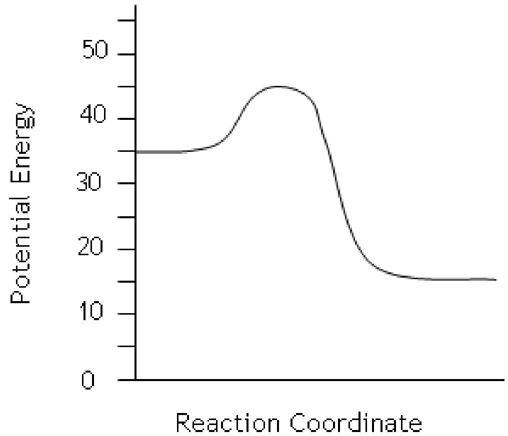
a) What is the activation energy of the reaction shown by the diagram?
b) What is the enthalpy change for this reaction?
c) Is this reaction endothermic or exothermic?

2. Given the following reaction coordinate diagram



a) What is the activation energy of the reaction in the diagram to the left?
b) What is the enthalpy change for this reaction?
c) Is this reaction endothermic or exothermic?
d) What would be the activation energy of the **reverse** reaction?

3. Given the following reaction coordinate diagram



a) What is the activation energy of the diagram to the left?
b) What is the enthalpy change for this reaction?
c) Is this reaction endothermic or exothermic?
d) What would be the activation energy of the reverse reaction?

4. What is the activated complex or transition state and how is it related to reaction rates? Label the position of the activated complex in each of the diagrams above.

5. Does every collision between reactant particles produce a reaction? Explain.

6. Explain why the enthalpy change for an exothermic reaction is negative, even though the container gets warmer.

Mid Unit Review

Calculating Reaction Rates

1. In the following decomposition reaction,

   $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$

   oxygen gas is produced at the average rate of 9.1×10^{-4} mol · $L^{-1} \cdot s^{-1}$. Over the same period, what is the average rate of the following:

   the production of nitrogen dioxide

   the loss of nitrogen pentoxide

2. Consider the following reaction:

   $N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

   If the rate of loss of hydrogen gas is 0.03 mol · $L^{-1} \cdot s^{-1}$, what is the rate of production of ammonia?

Factors Influencing Reaction Rate - Activation Energy

1. Answer the following questions based on the potential energy diagram shown here:

   a. Does the graph represent an endothermic or exothermic reaction?

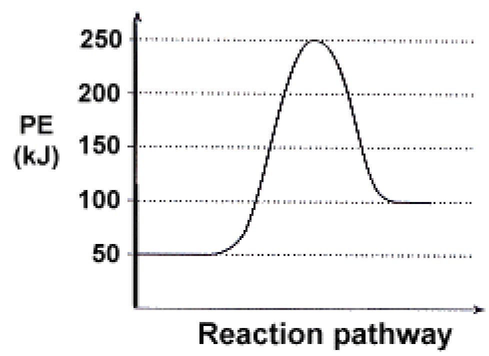
   b. Label the postion of the reactants, products, and activated complex.

   c. Determine the heat of reaction, ΔH, (enthalpy change) for this reaction.

   d. Determine the activation energy, Ea for this reaction.

   e. How much energy is released or absorbed during the reaction?

   f. How much energy is required for this reaction to occur?



2. Sketch a potential energy curve that is represented by the following values of ΔH and Ea. You may make up appropriate values for the y-axis (potential energy).

   $\Delta H = -100$ kJ and $E_a = 20$ kJ

   Is this an endothermic or exothermic reaction?

3. In the next unit we will be discussing reactions that are reversible, and can go in either the forward or reverse directions. For example, hydrogen gas and oxygen gas react to form water, but water can also be broken down into hydrogen and oxygen gas.

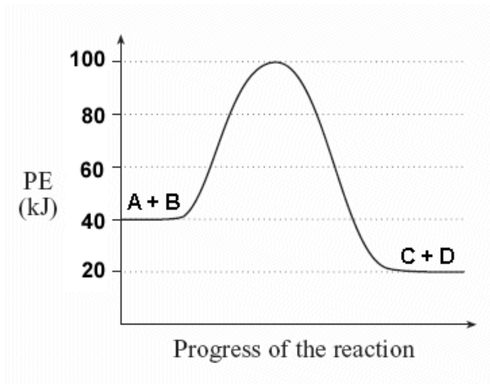
   $2\ H_2 + O_2 \leftrightarrow 2\ H_2O$

   This reaction is exothermic in the forward direction:

   $2\ H_2 + O_2 \rightarrow 2\ H_2O + 285$ kJ

   but endothermic in the reverse direction:

   $2\ H_2O + 285\ \text{kJ} \rightarrow 2\ H_2 + O_2$



   Given this potential energy diagram for this reaction, determine ΔH and Ea for both the forward and reverse directions. Is the forward reaction endothermic or exothermic?

4. Sketch a potential energy diagram for a general reaction A + B ≡ C + D

   Given that $\Delta H_{reverse} = -10$ kJ and E_a forward = +40 kJ

Reaction Kinetics Sample Multiple Choice

1. The rate of a reaction may be affected by each of the following EXCEPT
    a. nature of reactants involved
    b. amount of energy liberated
    c. temperature of the reaction
    d. concentration of the reactants
    e. surface area of the reactants

2. The collision theory is based on each of the following assumptions EXCEPT
    a. temperature of the reactants
    b. surface of the reactants
    c. nature of the reactants
    d. nature of the catalyst
    e. concentration of the reactants

3. Sawdust is blown into some types of furnaces to increase the rate at which wood burns because
    a. surface area of reacting particles is increased
    b. reacting particles become ionic
    c. reacting particles become molecules
    d. reaction requires a catalyst
    e. reaction requires a very high temperature.

4. It is incorrect to say that a catalyst changes the rate of a reaction
    a. by means of physical absorption
    b. by means of chemical absorption
    c. but is recovered in its original state
    d. without taking part in it
    e. by lowering its activation energy

5. Three different substances A, B, and oxygen are mixed. A two-step reaction occurs.

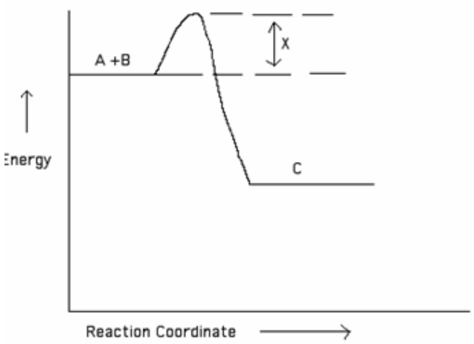
    1. $A + O_2 \rightarrow AO_2$
    2. $B + AO_2 \rightarrow A + BO_2$

    Which substance is the catalyst?
    a. O_2
    b. BO_2
    c. AO_2
    d. B
    e. A

6. Raising the temperature of a reaction mixture increases the rate of the reaction but does NOT significantly increase the

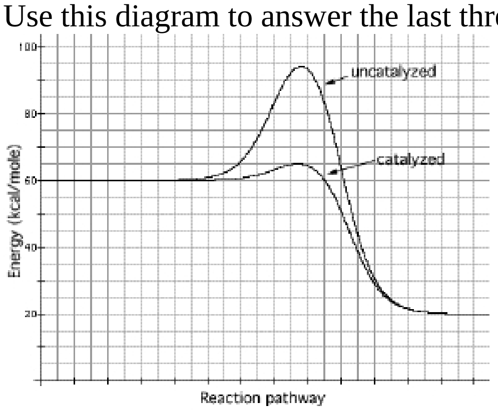
    a) activation energy
    b) average velocity of the reacting molecules
    c) number of collisions
    d) number of successful collisions
    e) fraction of the reacting molecules that possess energies greater than activation energy

7. In the following figure, how can the interval "x" be changed in the potential energy diagram for the reaction A + B => C



a) introduce a catalyst b) change the volume c) increase the pressure
d) add more of substance A e) remove substance C as fast as it is formed

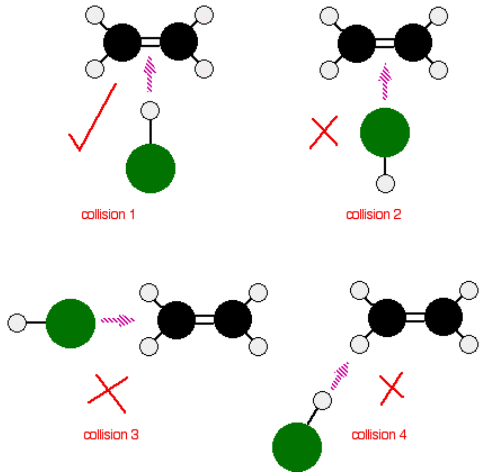
Use this diagram to answer the last three questions.



8. The activation energy for the forward reaction in the presence of the catalyst, in kcal/mol is about ____________________.

9. For the uncatalyzed reaction, the overall heat of reaction in kcal/mol is about ____________________.

10. The activation energy for the reverse reaction without catalyst, in kcal/mol, is about ___________________.



Collision Theory and Mechanisms

Consider the reaction:

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

According to the collision theory, for this reaction to occur in one step, 3 particles must collide: 2 NO molecules and 1 O_2. ____
____
____.

Successful three particle collisions, all at the same time, in the right direction, with enough energy are quite rare. In order for chemical reactions to occur more quickly, reactions tend to ____________________________________, with each step involving a ____, or **bimolecular**. The chance of a two particle collision being successful is much greater than a collision between three or more particles.

Reaction Intermediates

Reactions which take place in _______ step are called ____________________________.

Reactions which take place in ____ are called ______________________________.

The complex reaction: $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

Does not take place in one step, but actually takes place in two steps:

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

Compounds such as N_2O_2, ____ ____,
are called **reaction intermediates**. All complex reactions contain at least one __________________________. Reaction intermediates should not be confused with the activated complex. The activated complex is a _________________________________ ____________________, while the reaction intermediate is a _______________________ or reaction in a mechanism.

Net Reactions

The steps in which a reaction occurs is called that reaction's mechanism. The _________ ________________ of a mechanism must equal the total or ____________________.

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:	$NO_2 + CO \rightarrow NO + CO_2$

The ________ is the reaction intermediate, so it _____________ appear in the net reaction. Since NO_2 is found twice on the left and once on the right, we can ___________ one of the NO_2's just as we would adding equations in math.

__________________, as well as intermediates, do not appear in the overall reaction.

The decomposition of ozone using chlorine as a catalyst is illustrated in this mechanism:

Step One	$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)}$
Step Two	$O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$
Step Three	$ClO_{(g)} + O_{(g)} \rightarrow Cl + O_{2(g)}$
Overall	$2\ O_{3(g)} \rightarrow 3\ O_{2(g)}$

In the above example, the __________ is a catalyst and the _________is an intermediate. The catalyst can be identified in the mechanism by appearing as a __________________, __________________________________ in a following step.

Hints: Intermediates are produced and then used.

Catalysts are used and then produced.

Rate Determining Step

Not all steps in a mechanism have the same rate. The step with the __________________ is called the ____, since that step affects the rate of the reaction more than the others.

Imagine a sports team must take a trip to another city for a game. If half the team flies (fast step) and half the team take a bus (slow step), it does not matter how fast the flight is because the team cannot play until the bus arrives. The only way to get the whole team to the game faster is to speed up the bus trip. The bus trip is similar to the rate determining step because it has _____________________________________ the team reaches the city.

According to our last 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 because it is the _______________________.

Examples

Example 1. Given the following mechanism:

P + Q	→	X + T	(slow)
X + P	→	Y + R	(fast)
Y + S	→	T	(moderate)

a) What is the net reaction?

b) What are the reaction intermediates?

c) Which is the rate determining step?

d) What would be the effect of increasing the concentration of P?

e) What would be the effect of decreasing the concentration of Q?

f) What would be the effect of increasing the concentration of S?

Solution:

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

P + Q	→	X + T	(slow)
X + P	→	Y + R	(fast)
Y + S	→	T	(moderate)
2 P + Q + S	→	R + 2 T	

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

c) P + Q 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

In this lesson you have learned:

- 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.

Collision Theory & Reaction Mechanism Practice

1. Nitrogen monoxide reacts with hydrogen gas to produce nitrogen gas and water vapour. The mechanism is believed to be:

   Step 1: $2\ NO \rightarrow N_2O_2$

   Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

   Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

   For this reaction find the overall balanced equation and list any reaction intermediates.

Practice Problems

1. Given the following reaction mechanism:

$$H_2O_2 + I^- \rightarrow H_2O + IO^-$$
$$H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

a)Write the balanced net reaction.

b) Identify the reaction intermediate(s) and catalyst(s).

2. Examine the following reaction mechanism:

$$P + Q \rightarrow I_1 + R \quad \text{slow}$$
$$I_1 + P \rightarrow I_2 + W \quad \text{moderate}$$
$$I_2 + S \rightarrow T \quad \text{fast}$$

a) Write out the net reaction.
b) Identify the overall rate of the net reaction.
c) Increasing [P] , increases the rate of the net reaction.
Increasing [Q] , increases the rate of the net reaction.
Increasing [S] , has no effect of the rate.
Explain why this is possible.

3. Write the net reaction for the mechanism.

$$A + B \rightarrow I_1 + C \quad \text{very slow}$$
$$I_1 + A \rightarrow C + D \quad \text{fast}$$

4. A proposed mechanism for the preparation of the poisonous liquid nitrobenzene ($C_6H_6NO_2$) is

$$C_6H_6 + NO_2^+ \rightarrow C_6H_6NO_2^+ \quad \text{slow}$$
$$H_2SO_4 \rightarrow H^+ + HSO_4^- \quad \text{v. fast}$$
$$C_6H_6NO_2^+ + HSO_4^- \rightarrow C_6H_5NO_2 + H_2SO_4 \quad \text{fast}$$

a) What is the RDS? Why?
b) What is the net reaction?
c) Without H_2SO_4 this is a very slow reaction. Explain.

Factors Influencing Reaction Rate – Catalysts

1. Phosgene, $COCl_2$, one of the poison gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

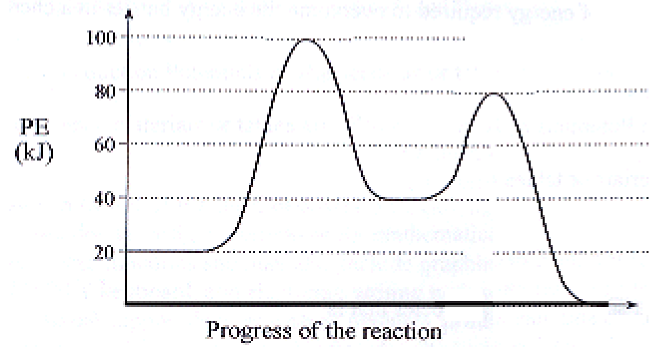
    step 1: $Cl + CO \rightarrow COCl$

    step 2: $COCl + Cl_2 \rightarrow COCl_2 + Cl$

    a. Write the overall reaction equation.
    b. Identify any reaction intermediates.
    c. Identify any catalysts.

2. We have typically been simplifying our potential energy curves somewhat; for multistep reactions, potential energy curves are more accurately shown with multiple peaks. Each peak represents the activated complex for an individual step.

    Consider the PE curve for a two-step reaction:



Answers

a. What is ΔH for the overall reaction? __________

b. What is ΔH for the first step of the reaction mechanism? __________

c. What is ΔH for the second step of the reaction mechanism? __________

d. What is ΔH for the overall reverse reaction? __________

e. What is E_a for the first step? __________

f. What is E_a for the second step? __________

g. Which is the rate-determining step - step 1 or step 2? How do you know? __________

h. What is E_a for the reverse of step 1? __________

i. Is the overall reaction endothermic or exothermic? __________

Introduction to Rate Law

We saw earlier, that the rate of a reaction is affected by the ______________________ ______________________. Using the rate law as a tool, scientists can determine the rate of a reaction with varying concentrations of reactants.

Rate Law is an expression which relates the _______________________________ to the ______________________________________. Rate law is a tool which helps us to calculate the rate of a reaction with given concentrations of reactants.

Remember that for the reaction: A → products

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

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

The rate law is only _____________________________________ not products. This is represented by the equation:

Rate = k[A]^x,

- k is the ____
- [A] is the concentration of A
- x is the power, called the ________________________________

The constant k, is known as the _________________________ for the reaction. _______ ____.

The rate constant is ______________________________ for each reaction at a specific _____________________, since its value depends upon the size, speed and types of molecules in the reaction.

Changing temperature would change the speed of the reactant particles and hence change the rate constant. ____ ____________________________________.

Order of Reaction

The **order** of a reaction indicates how ____________________________________ affects the ______________________________________.

For example, in our reaction where A → products,

If the order of the reaction was a ____________________________, ____________, this would mean the reaction rate was __________________________________ to changes in reactant concentration.
In a first order reaction, if the concentration of A were doubled, the rate would double. If the concentration were tripled, the rate would triple, etc.

If the reaction were a ____________________________, ___________, doubling the concentration would increase the rate by a ______________________ = $2^2 = 4$. That is, 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 ______________________ on the concentration of A, it would be a __________________________, _________. This means a change in the concentration of A does NOT change the rate of the reaction.

For a reaction with more than one reactant, such as A + B → products

The rate law would be: **Rate = $k[A]^x[B]^y$**

The rate depends on both A and B concentrations. Each reactant can affect the rate differently.

The ___________________________________ is the sum of the order with respect to A and the order with respect to B, that is, _________.

Example 1: Rate = $k[CO]^2[O_2]^1$

a) What is the total reaction order?
b) What happens to the rate if CO is doubled?
c) What happens to the rate if O_2 is tripled?

Example 2: Rate = $k[NO_2][NO_3]^0[O_2]^2$

a) What is the total reaction order?
b) What happens to the rate if NO_2 is doubled?
c) What happens to the rate if NO_3 is tripled?
d) What happens to the rate if is O_2 halved?

Example 3: If the rate of the above reaction is 2 moles/Ls; what is the new rate when O_2 is tripled, and when NO_2 is halved?

Rate Law and Stoichiometry

We have learned, for most reactions, the rate law, the specific rate constant, *k*, and the mechanism of a reaction can only be determined ______________________________, not from the reaction stoichiometry.

However, for reactions that occur in a single step __________________________________ ____ in the reaction's balanced equation.

For the elementary reaction:

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

the rate law is

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

Example 5. 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 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.

The rate law should be: **rate = k[O_3][NO]**

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.

Determining the Rate Law of a Reaction

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

We will be using the initial rates method of calculating rate laws in this course. The initial rates method uses the _______________________________________ of one reactant on the initial reaction rate, while _________________________________ ______________________________.

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	$[H_2O_2]$ (mol/L)	[HI] (mol/L)	Initial 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.

By comparing trials 1 and 2 it can be seen that keeping $[H_2O_2]$ constant while doubling [HI] doubles the rate. Using ratios makes the relationships easier to see:

This indicates that the reaction is _______________ in HI.

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 ____________________ in $[H_2O_2]$.

The rate law for this reaction is rate = $k[H_2O_2][HI]$

The total order of this reaction is the sum of the orders or exponents. Total order = ____________________

Example 2. For the reaction A + B → products, the following data was collected

Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0

Determine the rate law. Try and do the work on your own before looking at the answers.

Solution:

The rate law will have the form: Rate = $k[A]^x[B]^y$

Look for trial where one reactant remains constant and the other changes.

Using Trials 1 & 2, [B] remains constant.

Reactant A is second order.

There is no trial where [A] remains constant, so we must use both Δ[A] and Δ[B] to determine the order for [B].

If we use Trials 1&3, from the rate law, $(\Delta[A])^2 \times \Delta[B]^{order} = \Delta rate$)

The order is first for [B]

Therefore, the rate law is ______________________________________

Determining the Specific Rate Constant

Example 3. Determine the value of the specific rate constant, k, for the reaction in example 2. (The data for example 2 is shown below.)

Solution.

Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0

The rate law was determined to be rate = $k[A]^2[B]$

In order to determine the value of the rate constant we use the rate law and experimental data. We can use the data from any trial, substitute into the rate law and solve for k.

Let's use the data from trial 1:

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

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

$$k = \frac{2.0}{(0.10)^2(0.20)}$$

$$k = 1000$$

For our purposes, the value of k has no units.

Example 4. For the reaction

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

The following data was obtained:

Trial	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Initial 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. Write the rate law for this reaction.
b. Calculate the value of the rate constant.
c. Calculate the rate for Trial #5.
d. Calculate the concentration of A in Trial #6.

Try this question on your own and then check your work on the next page.

Solution to example 4

a. Comparing trials 1 and 2, [B] and [C] remain constant and doubling [A] increases rate 2x.

$$\frac{Rate_2}{Rate_1} = \frac{[A]_2}{[A]_1}$$

$$\frac{0.40}{0.20} = \left(\frac{0.20}{0.10}\right)^{order}$$

$$2 = 2^{order}$$

$$1 = order$$

Therefore the reaction is first order in A.

Comparing Trials 2 and 3, [A] and [C] remain constant and doubling [B] increases rate 4x.

$$\frac{Rate_3}{Rate_2} = \frac{[B]_3}{[B]_2}$$

$$\frac{1.60}{0.20} = \left(\frac{0.20}{0.10}\right)^{order}$$

$$4 = 2^{order}$$

$$2 = order$$

Therefore the reaction is second order in B.

Comparing Trials 2 and 4, [A] and [B] remain constant and doubling [C] results in no change in the rate.

$$\frac{Rate_4}{Rate_2} = \frac{[C]_4}{[C]_2}$$

$$\frac{0.40}{0.40} = \left(\frac{0.20}{0.10}\right)^{order}$$

$$1 = 2^{order}$$

$$0 = order$$

Therefore the reaction is zero order in C.

The rate law for the reaction is:

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, by rearranging the rate law, then substituting the values for [A] and [B] in Trial 1, we can solve for k.

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

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

$$= \frac{0.20}{(0.10)(0.10)^2}$$

$$k = 200$$

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 = $(200)(0.50 \text{ mol/L})(0.40 \text{ mol/L})^2$
rate = 16.0 mol/Ls

d. In order to determine the concentration of A, we can substitute known values into the rate law, then solve for [A].

Rearrange the rate law equation substitute values answer contains correct units

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

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

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

$$[A] = 0.083 \text{ mol/L}$$

Rate Law Practice Problems

1. A first-order reaction initially proceeds at a rate of 0.500 mol/Ls. What will be the rate when half the starting material remains? When one-fourth of the starting material remains?

2. Assume the $N_2O(g)$ and $O_2(g)$ react according to the rate law

   Rate = $k[N_2O]\,[O_2]$

   How does the rate change if:
   a) the concentration of O_2 is doubled?

   b) the volume of the enclosing vessel is reduced by half?

3. Assume that NO(g) and $H_2(g)$ react according to the rate law

   Rate = $k[NO]^2\,[H_2]$

   How does the rate change if:
   a) the concentration of H_2 is tripled?

   b) the concentration of NO is doubled?

   c) the volume of the enclosing vessel is reduced by half?

4. For the reaction: A + 2 B → 2 C

[A] mol/L	[B] mol/L	Rate (mol/Lmin)
1.0	1.0	0.50
3.0	1.0	1.5
3.0	2.0	3.0

   Find the rate law and calculate the value of the specific rate constant.

5. The reaction

   $I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$

   Was studied and the following data were obtained:

Trial	$[I^-]$ mol/L	$[OCl^-]$ mol/L	Initial Rate (mol/L•s)
1.0	0.12	0.18	7.91×10^{-2}
2.0	0.060	0.18	3.95×10^{-2}
3.0	0.24	0.090	7.91×10^{-2}
4.0	0.060	0.090	1.98×10^{-2}

   a) What is the rate law?

   b) What is the value of the rate constant?

6. For the reaction: $A + B + C \rightarrow D$

Trial	[A] mol/L	[B] mol/L	[C] mol/L	Initial Rate (mol/L•min)
1.0	1.0	2.0	0.50	0.35
2.0	2.0	2.0	0.50	1.40
3.0	2.0	1.0	0.50	1.40
4.0	1.0	2.0	1.0	0.70

   Find the rate law and calculate the value of the specific rate constant.

7. For the reaction: $X + Y + Z \rightarrow S$

Trial	[X] mol/L	[Y] mol/L	[Z] mol/L	Initial Rate (mol/Lmin)
1.0	0.45	0.20	0.55	0.66
2.0	1.35	0.20	0.55	5.94
3.0	0.45	0.60	0.55	1.98
4.0	0.45	0.60	1.10	1.98

   Find the rate law and calculate the value of the specific rate constant.

8. The reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_3 + HI$ is run in the presence of an excess of acid. The following data were obtained:

Trial	Initial $[I_2]$ (mol/L)	Initial $[CH_3COCH_3]$ (mol/L)	Initial Rate (mol/Ls)
1.0	0.100	0.100	1.16×10^{-7}
2.0	0.100	0.0500	5.79×10^{-8}
3.0	0.500	0.0500	5.77×10^{-8}

a. What is the rate law?
b. What is the value of the rate constant?
c. What is the rate if the concentration of CH_3COCH_3 is 0.0700 mol/L and the concentration of I_2 is 0.0850 mol/L
d. What is the concentration of I_2 if the concentration of CH_3COCH_3 is 0.0250 mol/L and the rate is 3.10×10^{-8} mol/Ls?

9. For the reaction $A + 2\,B \rightarrow C + D$, the following data was collected

Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate ($molL^{-1}s^{-1}$)
1.0	0.0100	0.0240	1.45×10^{-4}
2.0	0.0100	0.0120	7.25×10^{-5}
3.0	0.0200	0.0480	5.80×10^{-4}

What is the rate law?

10. For the reaction $3\,A + B \rightarrow 2\,C + D$, the following data was collected

Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate ($molL^{-1}h^{-1}$)
1.0	0.0012	0.042	3.6×10^{-2}
2.0	0.00060	0.084	3.6×10^{-2}
3.0	0.00060	0.021	9.0×10^{-3}

What is the rate law?

11. For the elementary reaction $H_2 + I_2 \rightarrow 2\ HI$
    a. Write the rate law.

    b. Find k if HI is produced at a rate of 1.0×10^{-4} mol/Lmin when $[H_2]$ = 0.025 mol/L and $[I_2]$ = 0.050 mol/L.

    c. What is the rate of production of HI if the concentration of both reactants is 0.10 mol/L and the temperature is the same as in (b)?

    d. How would the rate be affected if $[H_2]$ is doubled AND the $[I_2]$ is halved?

12. For the one step reaction A(g) + 2 B(g) ? C(g)
    a. What is the rate law?

    b. How does the rate change if
        i. [A] is doubled?

        ii. [B] is tripled?

        iii. The volume of the container is doubled?

Long Answer Kinetics Question….

Given experimental data from the complex reaction $H_2 + S + 2O_2 \rightarrow H_2SO_4$ answer the following questions.

Trail	$[H_2]$	[S]	$[O_2]$	rate
1	0.1	0.4	0.3	2.0
2	0.2	0.4	0.3	4.0
3	0.2	0.8	0.3	4.0
4	0.2	0.4	0.6	16.0
5	0.15	0.65	0.25	???
6	??	0.25	0.25	0.75

a) Calculate the rate law

b) What is the total order of the reaction?

c) Calculate the specific rate constant

d) What is the rate in trial 5?

e) What is the $[H_2]$ in trial 6?

f) What will be the effect on the rate if the concentrations of all three reactants double?

g) If the initial rate was 2.0 mol/Ls and the concentration of O_2 is halved, what will the new rate be?

More Practice

Answer the following questions. Show your work for full credit.

1. For the reaction 2 A + B → C + 2 D, the following data was collected. What is the rate law? (2 marks)

Trial	$[A]_i$ mol/L	$[B]_i$ mol/L	Initial Rate ($molL^{-1}s^{-1}$)
1	0.25	0.060	0.041
2	0.75	0.060	0.12
3	0.50	0.12	0.33

2. For the reaction below,

$CH_3COCH_3 + Br_2 + H^+ \rightarrow CH_3COCH_3Br + Br^- + H^+$

The following experimental data was recorded:

Experiment	Initial $[CH_3COCH_3]$ (mol/L)	Initial $[Br_2]$ (mol/L)	Initial $[H^+]$ (mol/L)	Initial Rate (mol/L·s)
1	0.30	0.050	0.050	5.7×10^{-5}
2	0.30	0.10	0.050	5.7×10^{-5}
3	0.30	0.050	0.10	1.2×10^{-4}
4	0.40	0.050	0.20	3.1×10^{-4}
5	0.60	0.050	0.050	2.3×10^{-4}
6	**?**	0.50	0.25	6.2×10^{-5}
7	0.50	0.10	0.020	**?**

a. What is the order of the reaction with respect to CH_3COCH_3?
b. What is the order of the reaction with respect to Br_2?
c. What is the order of the reaction with respect to H^+?
d. Write the rate law for the reaction.
e. What is the value of the specific rate constant for the reaction? (include units)
f. What is the rate of experiment 7?
g. What is the $[CH_3COCH_3]$ in experiment 6?

Rate Law WS

1. The following data relate initial rate of reaction with initial concentration of reactants in the reaction:

   2A + 2B → C + D

Expt.	Initial conc. of A	Initial conc. of B	Initial rate of production of C (M/sec)
1	2.0	2.0	10.0
2	2.0	4.0	20.0
3	2.0	6.0	30.0
4	2.0	2.0	10.0
5	4.0	2.0	40.0
6	6.0	2.0	90.0

   a) Deduce the rate law for this reaction.

   b) Calculate the value of the specific rate constant k

2. The rate-determining-step of a gaseous reaction is:

   $2A_{(g)} + B_{(g)} \rightarrow$ products

   a) Write the rate law.

   b) By what factor does the rate change if the system is compressed to one-half the volume?

   c) By what factor does the rate change if the [A] is tripled?

3. a) Write the rate law for the reaction whose rate-determining-step is

   $A_{(g)} + B_{(g)} \rightarrow 2C_{(g)}$

   b) How is the specific rate constant (k) for this reaction affected by:

   i) a change in temperature?

   ii) A change in the [A] ?

4. a) Use the collision theory to explain why the rate of a chemical reaction depends on the concentration of the reactants.

   b) Use the collision theory to explain why the rate of a chemical reaction depends on the temperature.

5. Write the rate law for the reaction $A + 3B + C \rightarrow D$ and find k from these data:

Expt.	[A]	[B]	[C]	Rate of production of D (M/min)
1	1.0	2.0	0.10	0.0040
2	1.0	4.0	0.10	0.0040
3	1.0	4.0	0.050	0.0010
4	2.0	4.0	0.050	0.0020

6. a) Write the rate law for $2A + 3B + C \rightarrow D + 2E$ if the rate determining step is $2B \rightarrow D + F$

   b) If the rate of production of E is 1.2×10^{-2} M/min when all the concentrations ([A], [B], [C]) are 1.0 M, find k.

   c) What would the rate be if all the concentrations were 0.50M?

Rates as Functions of Reactant Concentrations

a* A + *b* B + *c* C = *products

If concentrations of B and C are kept constant, you can measure the reaction *rate* of A at various concentrations. You can then plot the rate as a function of [A]. For a zeroth order reaction, you will get a horizontal line, because

rate = *k* (a horizontal line)

```
rate
   |      /
   |     /rate = k [A]
   |    /
   |- -/- - - - - rate = k
   |  /
   | /
   |/_________________
   0   1   2   3   4  [A]
```

For a first order reaction, the plot is a straight line (linear), as shown above, because

rate = *k* [A] (a straight line)

For a second order reaction, the plot is a branch of a parabola, because

$rate = k\,[A]^2$

```
rate
   |      .
   |       rate = k [A]²
   |     .   (a branch of
   |          a parabola)
   |    .
   | - . - - - - - -
   |  .
   |._________________
   0   1   2   3   4  [A]
```

The variation of reaction *rate*s as functions of order and concentrations are summarized in the form of a Table below.

	Plot of *rate* vs [A]
0th order	horizontal line
first order	straight line with slope = *k*
second order	a branch of parabola

Kinetics Review Sheet

You should be able to write sentences or definitions for all of the following terms.

Average rate
Instantaneous rate
Nature of Reactants
Catalyst
Intermediate
Activated Complex
Potential Energy Graph
Kinetic Energy Graph
Activation Energy
Order
Rate Law
Collision theory
Orientation
Enthalpy
Endothermic
Exothermic
Reaction Mechanism
Net equations
Bimolecular
Rate Determining Step
Specific Rate Constant
Complex Reaction
Simple Reaction

Explain why and how the following affect reaction rates:

Nature of Reactants
Pressure
Concentration
Catalyst
Temperature
Surface Area

Calculate the following:

Average Rate
Instantaneous Rate
Rate Stoichiometry
Order
Rate Law
Concentration changes

Be able to interpret and draw single step and multi step reaction co-ordinate diagrams (potential energy diagrams).

Finally:

- Practice your handouts.
- Check your answers.
- Go over questions that stumped you the first time.
- Ask questions.