Chemical Kinetics

1.1 Introduction to Chemical Kinetics

The rate at which a chemical reaction occurs is often very important to us. A common task of chemists is to find ways to change the rates of chemical reactions - we want our cars and buildings to rust more slowly and our food to spoil more slowly as well. But we need the reactions that produce economically important substances, such as ammonia and medical pharmaceuticals to occur quickly.

Key Questions

- How do you measure the speed, or rate, of a reaction?
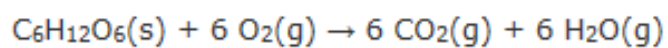- What factors influence how fast a reaction occurs?

1.2 Reaction Rates

Reaction rate

is a measure of how fast a reaction occurs, or how something changes during a given time period.

Consider the oxidation of glucose, $C_6H_{12}O_6$:

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g)$$

Things to consider...

‾does all the glucose get used up, and how quickly?

-how quickly does the carbon dioxide and water form?
-what happens to the **concentration** of any of the reaction participants?

Other reactions suggest other ways to measure their rates.

- change in conductivity
- change in pH
- colour change
- change in pressure as gases are formed or used up

A common measure of reaction rate is to express how the **concentration**

of a reaction participant changes over time.

It could be how the concentration of

a reactant decreases, or how the concentration of a product increases.

We often define the rate of a chemical reaction as:

$$\frac{\text{change in concentration}}{\text{change in time}}$$

Chemistry Notation for Concentration

represent concentration by using square brackets around the chemical formula of the substance

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

to indicate the concentration of $SO_2(g)$ in the following reaction we would write it as
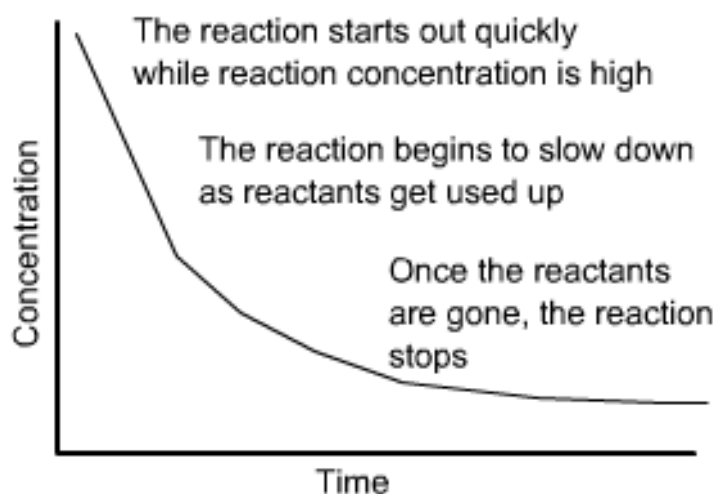
$$[SO_2].$$

we could either measure the change in concentration of a reactant or product and might use either of the following expressions to calculate our rate:

$$\text{rate} = \frac{\Delta[SO_2]}{\Delta \text{ min}} \qquad\qquad \text{rate} = \frac{\Delta[NO]}{\Delta \text{ sec}}$$

A graph illustrating reaction rate is often useful.

What would it look like and why?

The reaction starts out quickly while reaction concentration is high

The reaction begins to slow down as reactants get used up

Once the reactants are gone, the reaction stops

Concentration (y-axis), Time (x-axis)

Moral of the story - if we measured the rate at the start of the reaction, it would be different than if we measured the rate near the end of the reaction. Rate is not a constant - it changes during the course of the reaction.

For this reason, we will generally work with the **average rate of reaction**, and measure rate over a longer period of time.

(If you measured rate at a specific point in time, you would be measuring the **instantaneous rate**. Instantaneous rate will differ depending on when the rate is actually calculated.)

Concentration of reactant vs time

Rate = −Slope = 1.06×10^{-2} M/sec
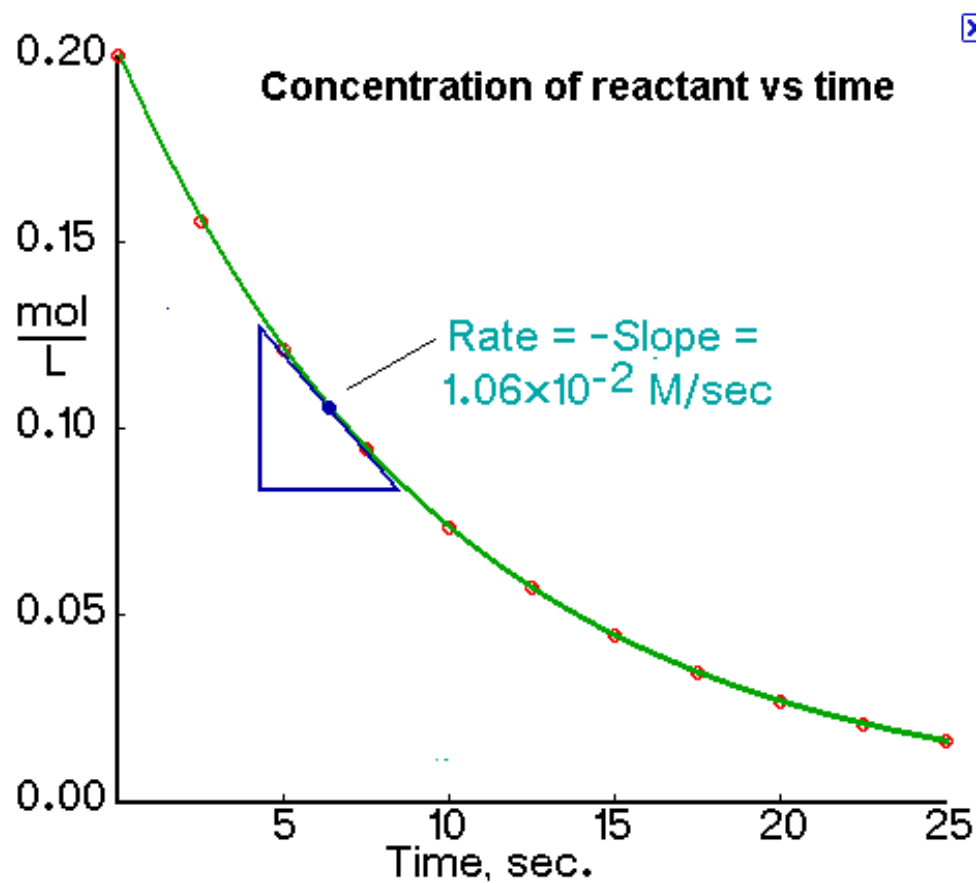
$$\text{Average rate of change} = \frac{f(a+h) - f(a)}{h}$$

$$\text{Instantaneous rate of change} = \lim_{h \to 0} \frac{f(a+h) - f(a)}{h}$$

1.3 Calculating Reaction Rates

Let's try an example of calculating a reaction rate. Consider the following reaction:

$$A \rightarrow B$$

The following data were obtained for how the concentration of these substances changed during the experiment (

Time (min)	[A] (mol $\cdot L^{-1}$)	[B] (mol $\cdot L^{-1}$)
0.0	1.000	0.000
3.0	0.400	0.600
6.0	0.250	0.750

We could measure the rate of the reaction

either by measuring how the concentration of reactant A changes
or how the concentration of product B changes

Pull

$$rate \quad = \quad \frac{\Delta [A]}{\Delta \ time}$$

rate   =   _____

   =

Pull

Compare this rate to the rate of just the first three minutes of the reaction:

rate   =   _____

   =

Pull

the rate did slow down as the overall rate is slower than the rate of the first three minutes of the reaction.

If we calculate the average rate based on the production of product B:

$$\text{rate} \quad = \quad \frac{\Delta [B]}{\Delta \text{ time}}$$

rate   =   _____

=

Notice that we must compare rates measured during the same time period.

We would not find the same rates if we did not have a 1:1 relationship between reaction participants.

$$A \rightarrow B$$

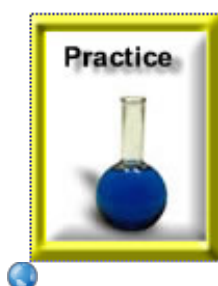examine the following reaction:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

only one mole of oxygen forms for every two moles of hydrogen peroxide that decomposes.

If 2 moles of H_2O_2 decompose   then   1 mole of O_2 is formed

if the rate of decomposition of H_2O_2 **then**   the rate of formation of O_2 is ½ × 4.00 or

is <u>4.00 mol $\cdot$ L$^{-1}\cdot$ min $^{-1}$</u>   <u>**2.00 mol $\cdot$ L$^{-1}\cdot$ min $^{-1}$**</u>

Practice

Assignment

$Zn_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + ZnCl_{2(aq)}$
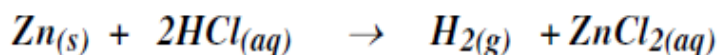
rate of decomposition of Zn is $1.83 \, mol \cdot L^{-1} \cdot sec^{-1}$

$Mg_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + MgCl_{2(aq)}$
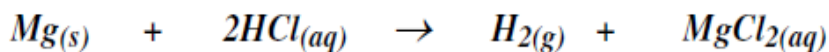
rate of decomposition of HCl is $0.56 \, mol \cdot L^{-1} \cdot hr^{-1}$

$2NaOCl_{(aq)} \rightarrow 2NaCl_{(aq)} + O_{2(g)}$
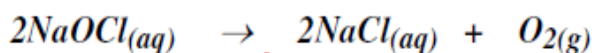
rate of formation of NaCl is $2.52 \, mol \cdot L^{-1} \cdot min^{-1}$

$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$
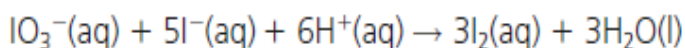
rate of formation of H_2O is $0.183 \, mol \cdot L^{-1} \cdot min^{-1}$

2.1 The Collision Theory

The Collision Theory

The collision theory states that for a chemical reaction to occur the reacting particles must collide with one another.

The rate of the reaction depends on the frequency of collisions

The theory also tells us that reacting particles often collide *without* reacting. Certain requirements must be met if the collisions are effective enough to cause a reaction:

In order for collisions to be successful, reacting particles must collide:

- with sufficient energy, and
- with the proper orientation

|		
START	STOP	HOME

animation by Gary Frederickson & Terry Biss
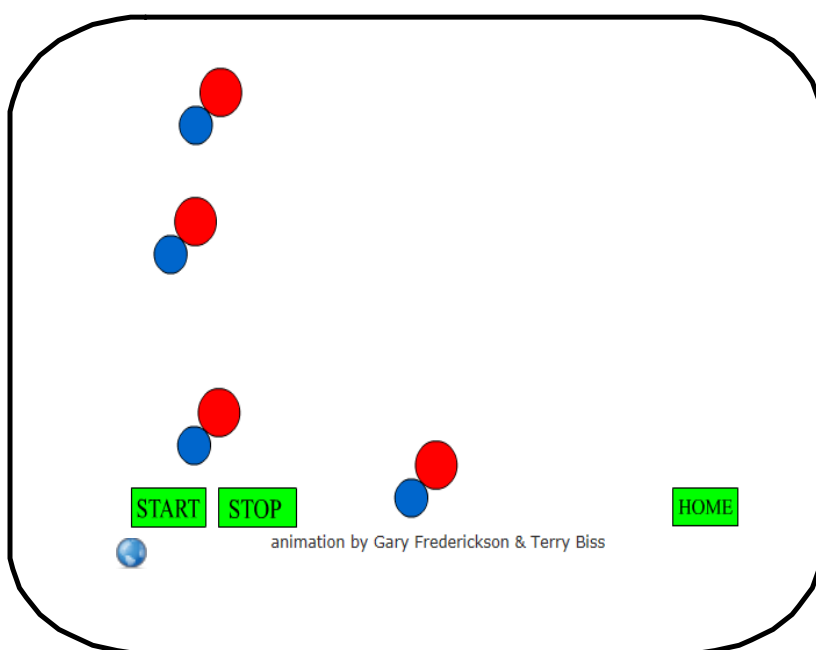
- how often collisions occur. More frequent collisions will mean a faster rate.
- more effective collisions in terms of collisions occurring with sufficient energy
- more effective collisions in terms of collisions occurring with the proper orientation.

2.2 Reaction Mechanism & the Rate-Determining Step

Chemical reactions follow the same principles.

When we write a chemical equation such as:

$$2\ C_2H_2 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$$
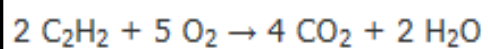
two molecules of acetylene (C_2H_2) react with 5 molecules of oxygen.

it is highly unlikely that 7 molecules would collide together all at once.
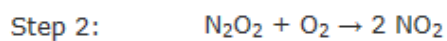
Instead, the reaction most likely occurs in a series of simple steps
which only required two or three molecules colliding at any one instant

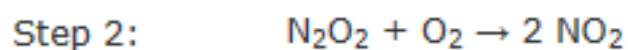nitrogen monoxide reacts with oxygen according to the equation

$$2\ NO(g) + O_2 \rightarrow 2\ NO_2$$
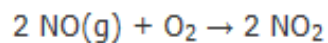
This reaction does not occur in a single step, however, but rather through these two steps:

Step 1: $2\ NO \rightarrow N_2O_2$

Step 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$

The series of steps a
reaction undergoes is called
the

reaction mechanism.

add these two reactions together,

Step 1: $2\ NO \rightarrow N_2O_2$

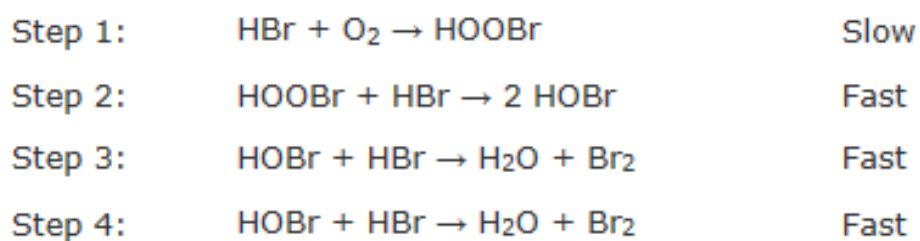Step 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$

Pull

Given an overall reaction, it will not be possible for you to predict what the reaction mechanism would be.

However, if you are given the steps of a reaction

mechanism you will need to be able to add together individual steps to end up with the overall reaction.

Rate Determining Step

Here is another reaction mechanism with some additional information

Step 1:	$HBr + O_2 \rightarrow HOOBr$	Slow
Step 2:	$HOOBr + HBr \rightarrow 2\ HOBr$	Fast
Step 3:	$HOBr + HBr \rightarrow H_2O + Br_2$	Fast
Step 4:	$HOBr + HBr \rightarrow H_2O + Br_2$	Fast

Overall:

would you consider the overall reaction to be fast or slow?

But let's make up some extreme numbers and ask the question again:

Step 1:	$HBr + O_2 \rightarrow HOOBr$	1 year
Step 2:	$HOOBr + HBr \rightarrow 2\ HOBr$	0.1 s
Step 3:	$HOBr + HBr \rightarrow H_2O + Br_2$	0.1 min
Step 4:	$HOBr + HBr \rightarrow H_2O + Br_2$	0.1 min

Overall: $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

would you consider the overall reaction to be fast or slow?

The slowest step of a reaction mechanism is the

rate determining step

Practice

2.3 Threshold Energy

Let's return to one of the key points of the collision theory   –

reacting particles must collide with sufficient force or energy.

Consider two cars about to become involved in an accident.

If both cars are moving very slowly, say 2 km/hr when they collide,
not much is going to happen. Perhaps the drivers don't even realize they've hit one another.

But if the cars are both travelling at 40 km/hr

(the greater speed indicates the cars have more energy),

then the collision is going

to be effective and damage will be done.

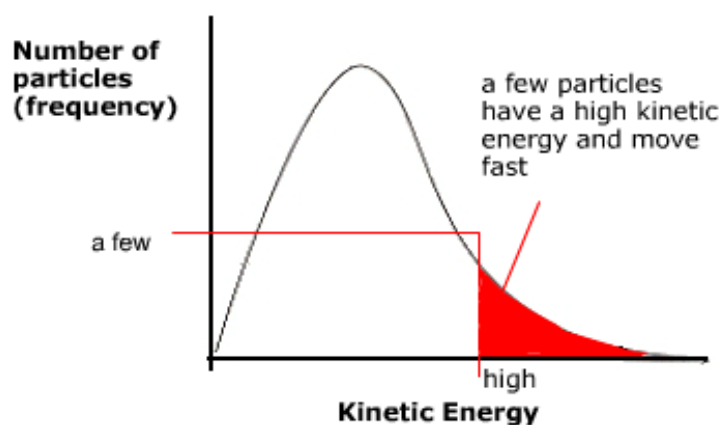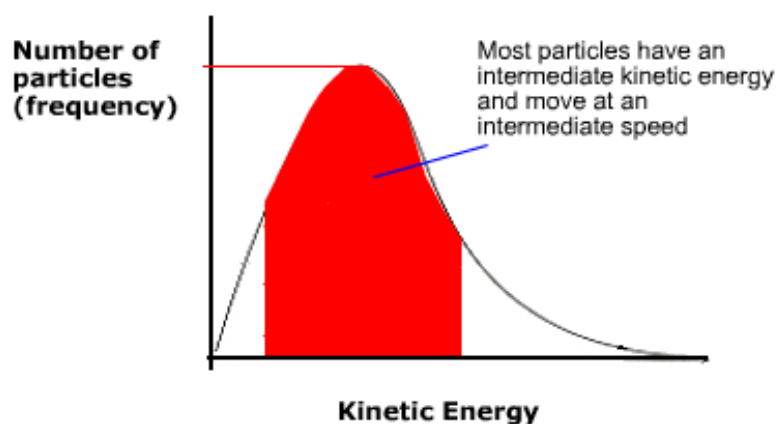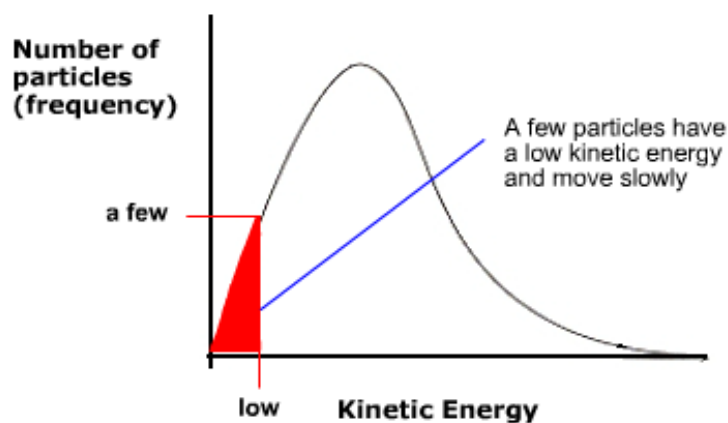In our scenario there is a certain speed at which damage will be done to the cars.

Activation energy
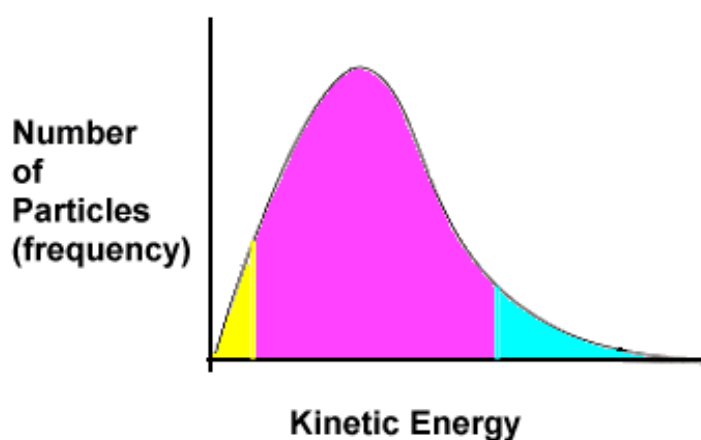is the minimum amount of
energy
required for a successful
collision.

Symbol: E_a

Sometimes referred to as
threshold energy.

We can graphically represent threshold energy on a <u>kinetic energy diagram</u>

Number of particles (frequency)

a few

A few particles have a low kinetic energy and move slowly

low   **Kinetic Energy**

Number of particles (frequency)

Most particles have an intermediate kinetic energy and move at an intermediate speed

Kinetic Energy

Number of particles (frequency)

a few

a few particles have a high kinetic energy and move fast

high
Kinetic Energy

This graph illustrates that some particle have a low amount of kinetic energy (yellow region), some are very energetic and fast moving and have a lot of kinetic energy (blue), while most particles have some intermediate amount of kinetic energy (purple).

Number of Particles (frequency)

Kinetic Energy

E_a

Threshold energy is the minimum amount of energy needed for particles to react. For a particular reaction, the threshold energy might be as shown here:

Only particles that have at least as much energy as the required threshold energy will have enough energy to have a *successful* collision. Thus only particles in the green area of the graph will actually react because only they have more than the minimum amount of energy needed.
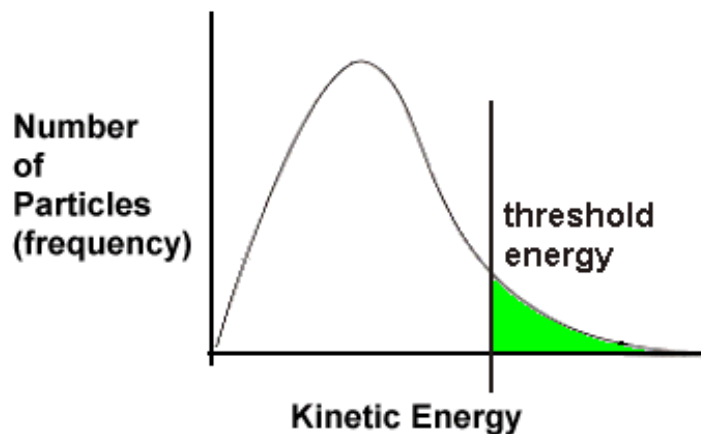
In the next graph representing a different reaction, the threshold energy is lower; more particles meet this minimum requirement, so more particles will successfully collide. This, in turn, means that this reaction will have a faster rate.
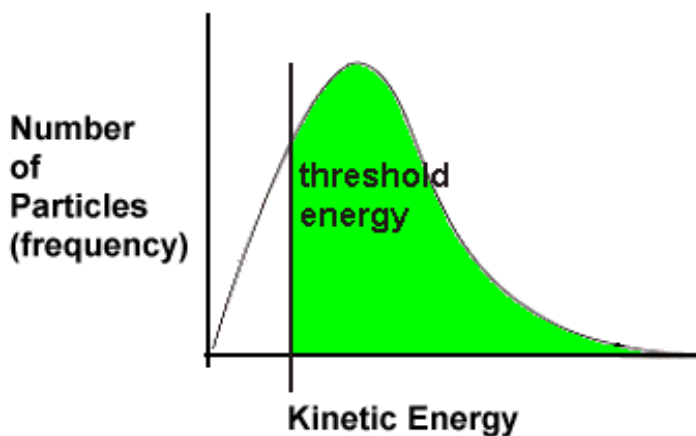
3.1 Activation Energy

The amount of energy required to reach the activated complex is called the **activation energy, E_a**.

Activation energy is essentially what we called **threshold**

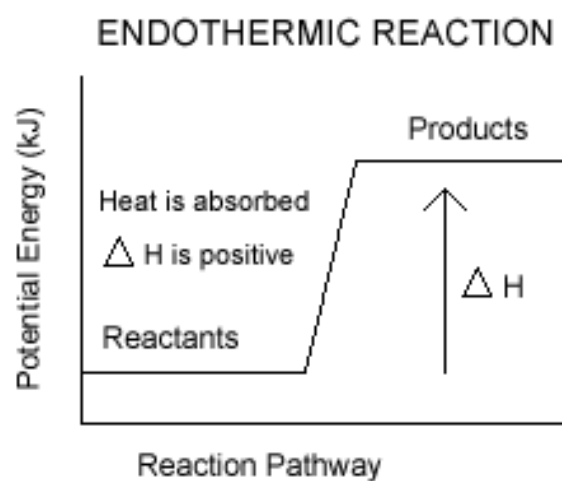**energy** when we discussed kinetic energy diagrams.

3.2 Potential Energy Diagrams Revisited

Endothermic reactions
require a net input of energy.

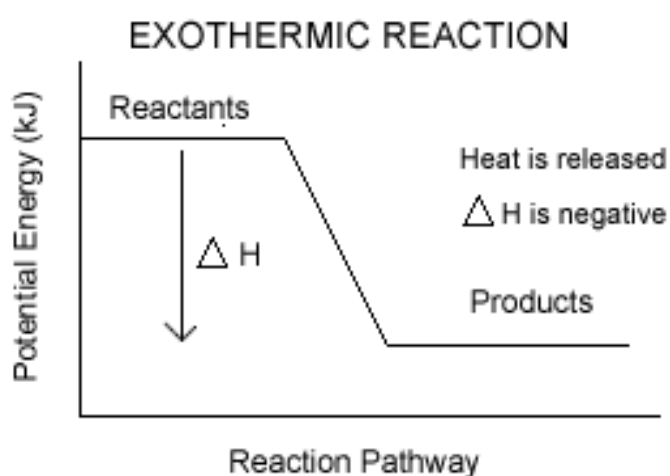**Exothermic reactions**
release energy to the surroundings.

Potential Energy Diagrams

Endothermic Reactions

ENDOTHERMIC REACTION

- the reactants have less potential energy than do the products. Energy must be input in order to raise the particles up to the higher energy level.

Exothermic Reactions

EXOTHERMIC REACTION

Reactants

Heat is released

$\triangle$ H is negative

$\triangle$ H

Products

Potential Energy (kJ)

Reaction Pathway

the reactants have more potential energy than the products have. The extra energy is released to the surroundings.

All reactions, even exothermic reactions, require some initial addition of energy. This energy is required to reach the unstable, high energy state known as the activated complex. Our potential energy graphs become:
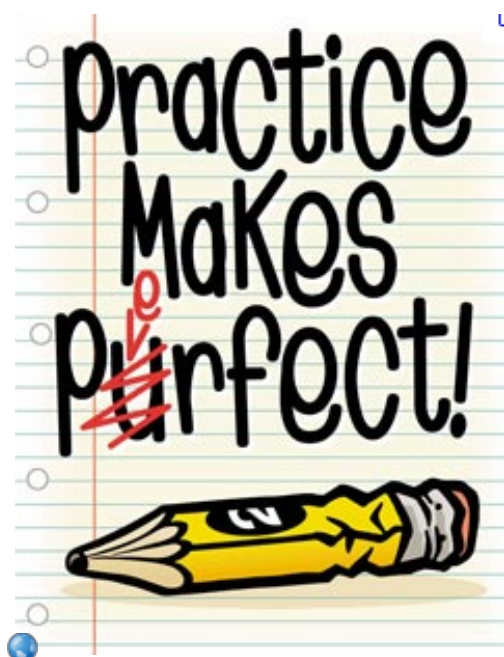
We now need to modify these diagrams to better fit with our collision model, specifically with what we have learned about activation energy and the activated complex.
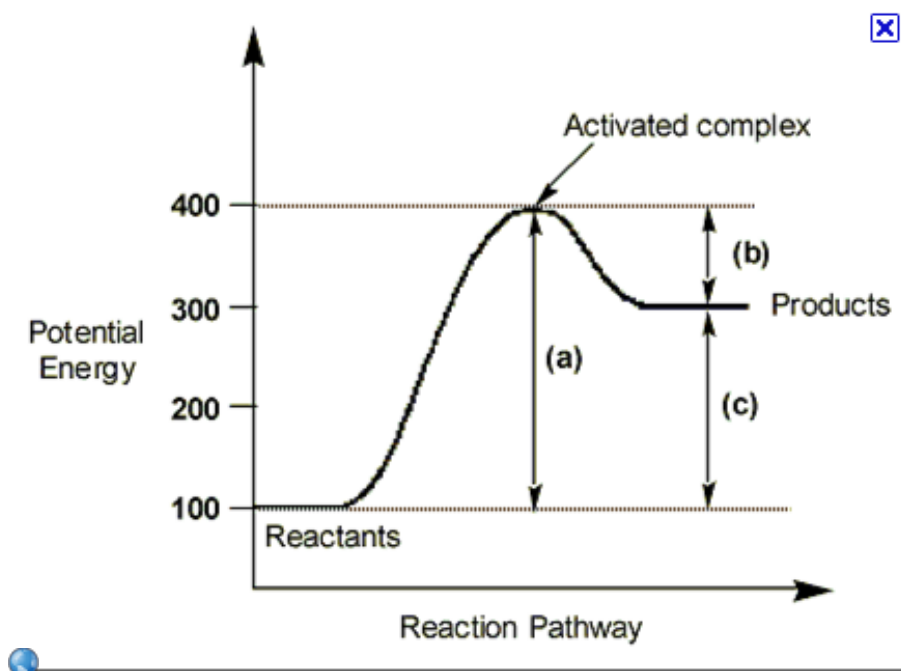
ENDOTHERMIC
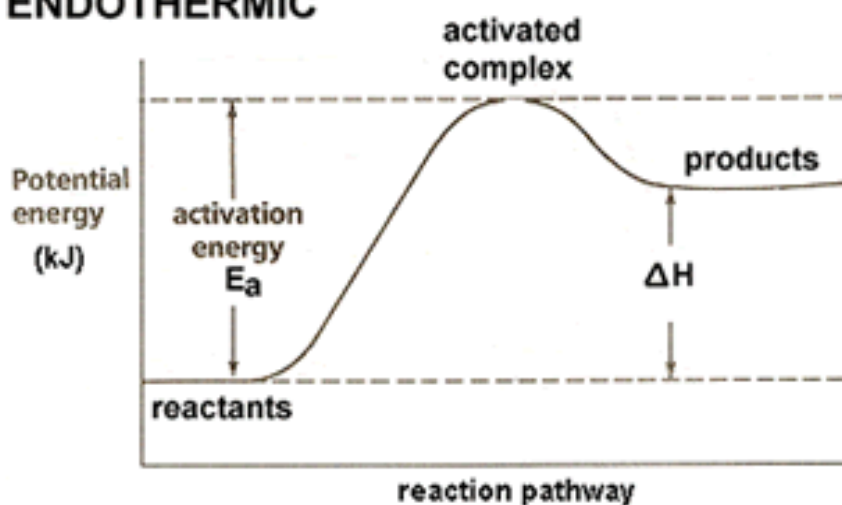
EXOTHERMIC
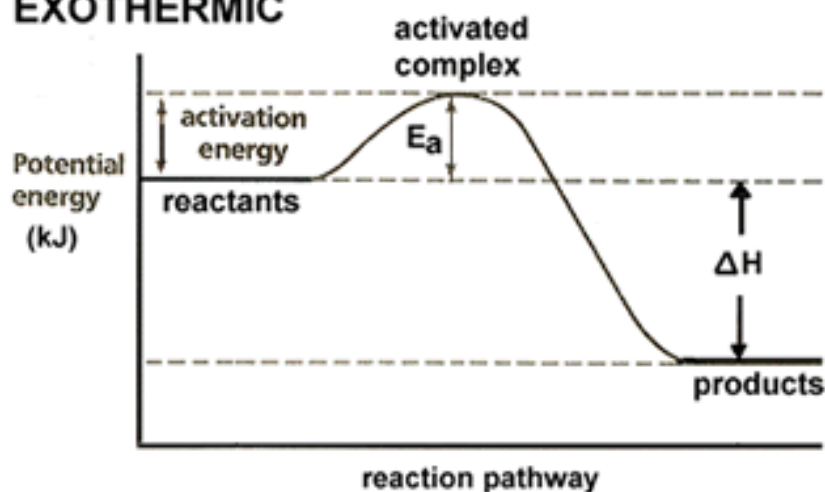
## 4.1 Factors Influencing Reaction Rate: Nature of Reactants

We can now turn our attention to a question we asked earlier - how can the rate of a chemical reaction be changed? There are four main of factors to consider:

1. <u>Nature of the reactants</u>
2. Temperature
3. Concentration and Pressure
4. Catalysts

Nature of Reactants

There are several points to consider when we examine how the properties of the reactants affects reaction rate.

1.

ionic equation

$$Ba^{2+}(aq) + CrO_4^{2-} \rightarrow BaCrO_4(s)$$
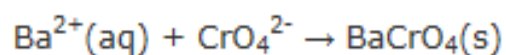
Reactions such as this that involve <u>**ions in solution**</u> tend to be very rapid.

2.

The **phase** of the reacting particles is important.

Reactants in solution, liquids, and gases will react much faster than solids.

3.

exposed surface area

What lights quicker? A large log or chopped up kindling?

Increasing SA increases reaction time.

4.

$$H_2O_2(l) \rightarrow H_2(g) + O_2(g)$$

Reactions involving **covalently-bonded molecules** tend to be **slow** unless highly exothermic.

5.

stirring

Stirring increases the rate of reaction.

Practice

4.2 Factors Influencing Reaction Rate: Temperature

The rate of almost all chemical reactions increases if the temperature of the system is increased.

A general rule of thumb is that the rate will double with an

increase of 10°C

Why does increasing temperature increase reaction rate?

When temperature is increased, all of the particles in the sample of matter now have more kinetic energy, and hence are moving faster. There are still some that are slower than the rest, others that are really fast, but most still in the middle. But the *average* kinetic energy of the entire sample increases.

Kinetic Energy
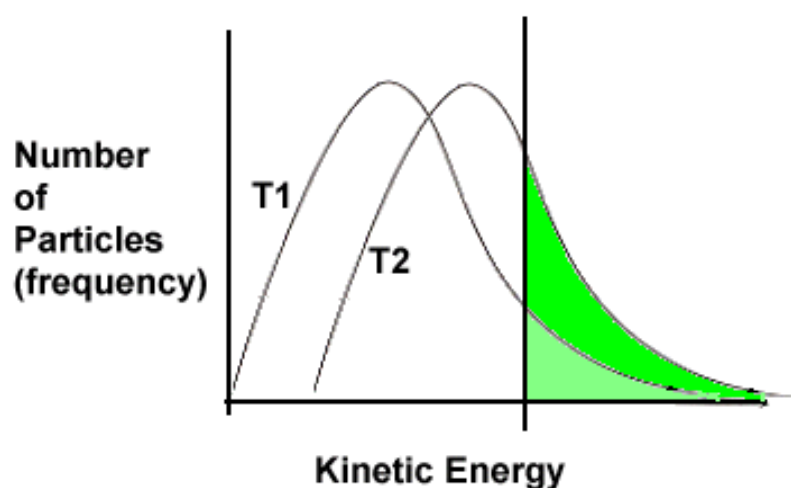
T1 represents the energy distribution at the lower temperature; T2 is the distribution at the higher temperature. The threshold energy is unchanged, but for the new curve (T2) more particles will be above the threshold energy, and thus will have successful reactions.

This will increase the rate for two reasons:

1. Because all particles are moving faster, there will be more frequent collisions, and thus an increase in rate.

2. Since all of the particles have more energy, more particles will meet the minimum energy threshold (or activation energy) required for a successful collision.

Potential Energy Curve

The potential energy curve will be unchanged when we illustrate a reaction occurring at a higher temperature.

But at a higher temperature more particles will have enough energy to get over the activation energy "hump":

At a higher temperature more particles can "climb the hill"

reaction pathway
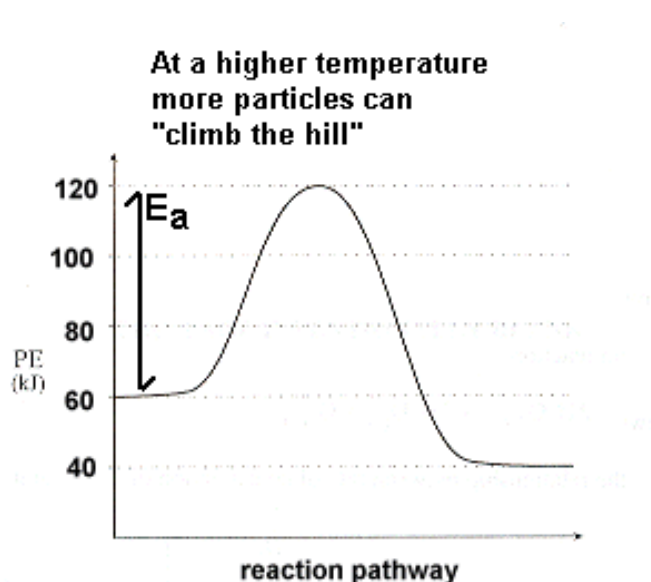
4.3 Factors Influencing Reaction Rate: Concentration & Pressure

Increasing the concentration of any one or more of the reactants will *usually* (but not always)

increase the rate of a reaction if the reactants are all in the

same phase (solid, liquid, gas, or aqueous).

Why?

By packing more particles in the same space, collisions will

occur more often, thus increasing the rate of the reaction.

The concentration of gases is typically increased by decreasing the volume

(making the container smaller).
Pressure

This forces the particles closer together,

increasing their concentration.

Practice

Assignment

4.4 Factors Influencing Reaction Rate: Catalysts

Catalysts most likely work by helping to promote a proper orientation between reacting particles.

it provides an *alternate* reaction pathway

with a lower activation energy.

A catalyzed chemical reaction

Progress of the reaction
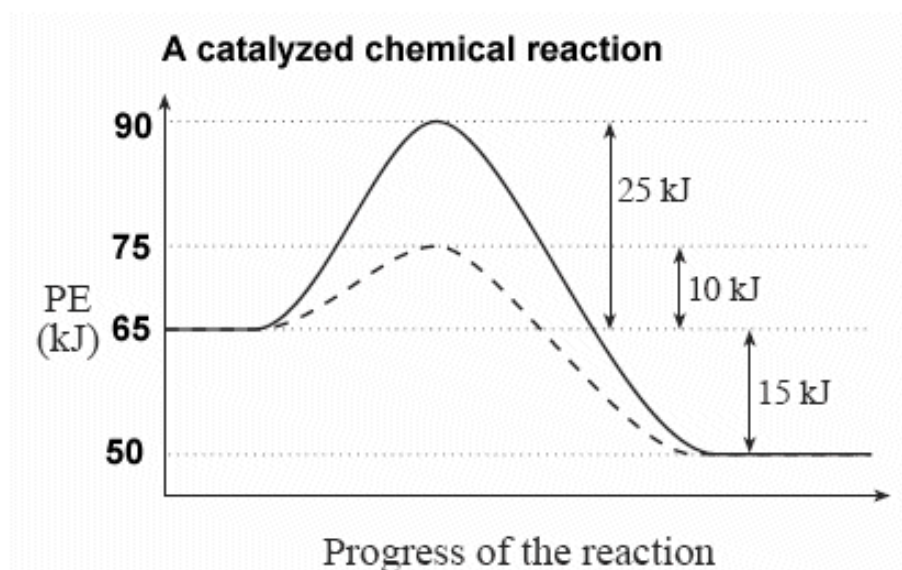
E_a for the uncatalyzed reaction = +25 kJ

E_a for the catalyzed reaction = +10 kJ

Because more particles will possess the new 10 kJ energy minimum

for a successful collision, the rate of the reaction will increase.

> Since ΔH is independent of the pathway, it is not changed by the presence of a catalyst.

Inhibitors

Some substances, known as **inhibitors**, slow down chemical reactions.

Practice