

## Part I. 1.1 Introduction to Chemical Kinetics

*How fast or slow will a reaction be? How can the reaction rate may be changed?*

\*In order to understand how these factors affect reaction rates, you will also learn about the collision theory, the theory that helps explain what happens at a molecular level during a chemical reaction.

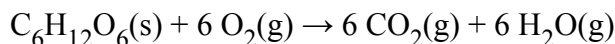
In a prior unit, one of the major areas of interest was in determining whether or not a reaction would occur spontaneously. **Thermodynamic factors** - enthalpy (heat content) and entropy (disorder or randomness) - were key determinants of whether a reaction would actually occur or not.

- 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,  $C_6H_{12}O_6$  :



One of the things that happens during this reaction is simply that glucose gets used up as it reacts with oxygen in the air, and carbon dioxide and water start to form.

How could we measure how fast this occurs? In this example, we might want to measure how quickly the mass of solid glucose decreases, or how quickly the gases (carbon dioxide and water) form. We might want to measure the volume of these gases.

Other reactions suggest other ways to measure their rates. Here are some other possible things that could be measured as they change: change in conductivity  
change in pH , color change or change in pressure as gases are formed or used up.

rate of a chemical reaction:

change in concentration
change in time

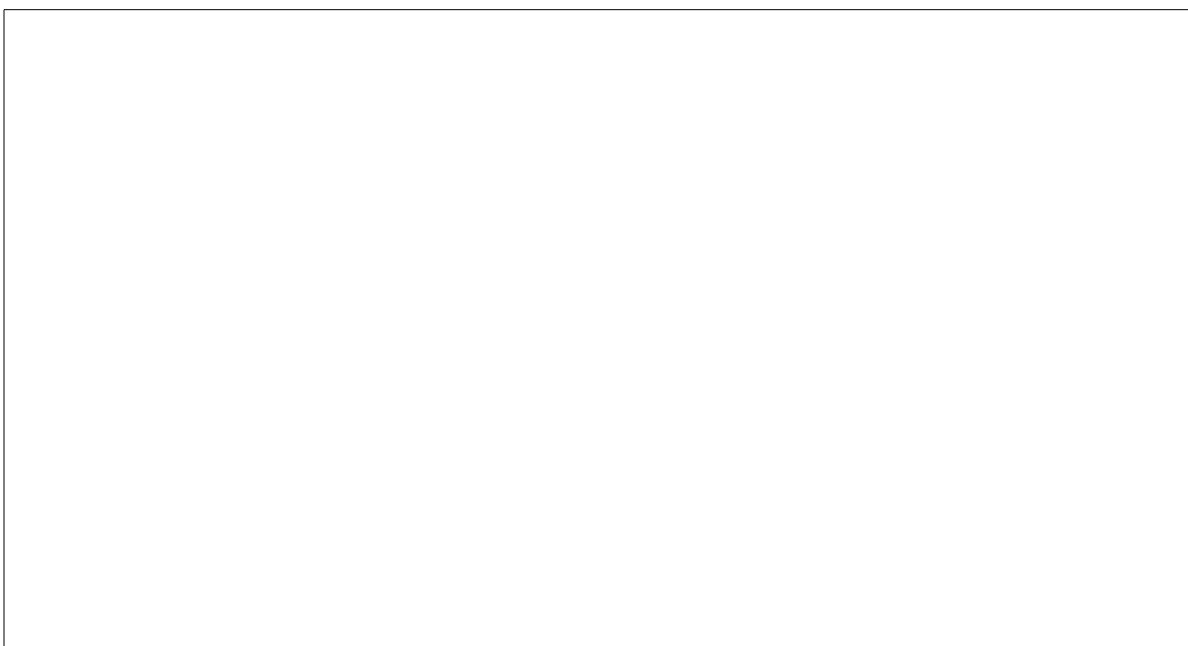
Units are: Concentration: Moles/L or M

Time: sec, min, hour

So, rate:  $\text{mol L}^{-1}\text{sec}^{-1}$  or M/sec

Therefore, if we wanted to express the rate of the following reaction:





time

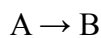
### To calculate rate from a graph

1. Rise/Run (if a straight line)
2. At any one point in time on the graph...instantaneous rate

**ALWAYS WRITE: rate = k[ ]<sup>n</sup>**

### 1.3 Calculating Reaction Rates

Consider the following reaction:



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

Time (min)	[A] (mol · L <sup>-1</sup> )	[B] (mol · L <sup>-1</sup> )
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. Let's measure A's average rate of change first:

$$\text{rate} = \frac{\Delta [A]}{\Delta \text{time}} = \frac{(0.250 - 1.00)}{(6.00 - 0.00)} = -0.125 \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$$

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

$$\text{rate} = \frac{\Delta [A]}{\Delta \text{time}} = \frac{(0.400 - 1.00)}{(3.000 - 0.000)} = -0.200 \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$$

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

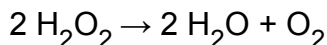
If we calculate the average rate based on the production of product B:

$$\text{rate} = \frac{\Delta [B]}{\Delta \text{time}} = \frac{(0.750 - 0.00)}{(6.00 - 0.00)} = 0.125 \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$$

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

You will see that we got the same rate, except for the sign, when we calculated the overall average rate for the disappearance of A as for the formation of B. This is only true, however, because our balanced equation shows us that one mole of A produces one mole of B.

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



we find that only one mole of oxygen forms for every two moles of hydrogen peroxide that decomposed

## 2.1 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

## 2.2 Factors Influencing Reaction Rate: Nature of Reactants

How can the rate of a chemical reaction be changed?

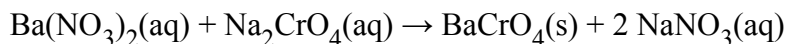
1. Nature of the reactants
2. Temperature
3. Concentration and Pressure
4. Catalysts

### A. Nature of Reactants

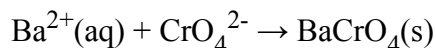
There are several points to consider when we examine how the properties of the reactants affects reaction rate.

- During chemical reactions, chemical bonds are broken and new bonds are formed. The nature (or type) of these chemical bonds - and how readily they are broken and formed - plays a critical role in the rate of a reaction. When the reaction involves primarily the exchange of electrons (as occurs in Redox reactions, reactions tend to be very rapid.)

For example, consider this very fast double displacement reaction that involves the formation of a yellow precipitate, barium chromate:



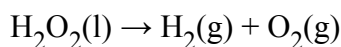
We can write the net ionic equation for this reaction:



Reactions such as this that involve **ions in solution** tend to be very rapid.

- As you might expect, however, if we had combined solid barium nitrate with solid sodium chromate, the reaction would be so slow that we would not be able to detect it. The **phase** of the reacting particles is important. **Reactants in solution, liquids, and gases will react much faster than solids.**

- Closely related to phase is the amount of **exposed surface area** of the reacting particles. If you put a lit match to a large log you wouldn't get much of a fire started. However, if you took the same log and increased its surface area by chopping it into kindling, you'd have much more success in starting your fire.
- Reactions involving **covalently-bonded molecules** tend to be **slow** unless highly exothermic. The decomposition of hydrogen peroxide into hydrogen gas and oxygen gas is a spontaneous reaction, but not a particularly fast one.



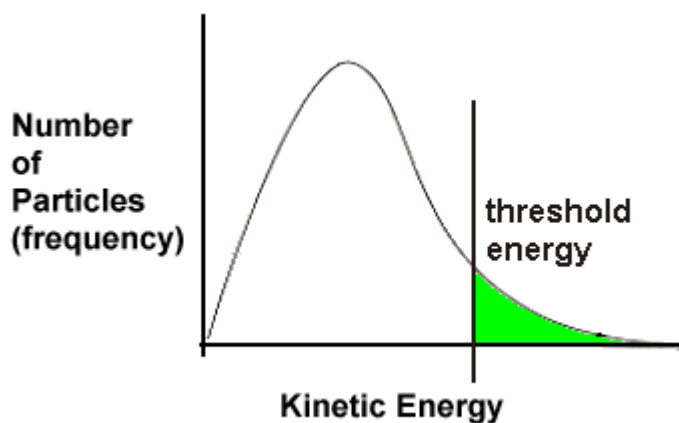
- Finally, we will include **stirring** as another factor that increases the rate of a reaction. Stirring causes the particles to collide more frequently since they will come into contact with one another more frequently.

One other thing - notice we are discussing the nature of the **reactants** here. Characteristics of the **products** - whether they are solids or gases, ionic or covalently-bonded, etc., are important in determining reaction rate.

## B. 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 (but "rules of thumb" are not iron-clad rule; exceptions exist).

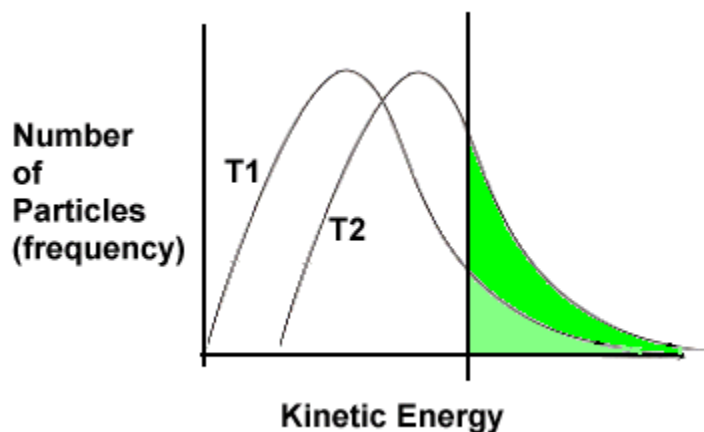
The collision theory helps us understand why this occurs.



It is important to remember what this curve represents - all particles in a sample of matter are in constant motion because they possess kinetic energy, but not all particles have the same amount of KE - some have only a little energy and are slow moving, some have a lot of energy and move fast, but most are somewhere in the middle.

In this unit we have added the idea of threshold energy - only particles having at least as much energy as the threshold energy have sufficient energy for a successful collision leading to a reaction.

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.



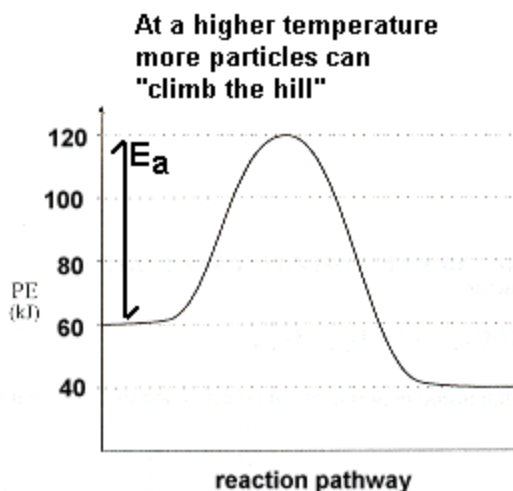
T1 represents the energy distribution at the lower temperature; T2 is the distribution at the higher temperature. The threshold energy is unchanged, but for the new curve (T2) more particles will be above the threshold energy, and thus will have successful reactions.

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. The graph below illustrates this:

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":



### C. 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? Concentration is a measure of how many particles are in a given volume. By packing more particles in the same space, collisions will occur more often, thus increasing the rate of the reaction.

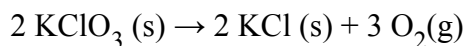
The concentration of gases is typically increased by decreasing the volume (making the container smaller). This forces the particles closer together, thus increasing their concentration.

Changing the concentration, or increasing the pressure, does not affect the amount of energy particles collide with. It simply increases the rate by increasing the frequency of collisions.

Changes in concentration also explain why the rate of a reaction slows down as a reaction proceeds. As the reactant particles collide with one another to form products, there are fewer and fewer reactant particles as the reaction continues. This lowers their concentration (fewer particles in a given volume), thus the rate declines.

### D. Factors Influencing Reaction Rate: Catalysts

When solid potassium chlorate is heated, potassium chloride and oxygen are produced. The reaction is not particularly fast.



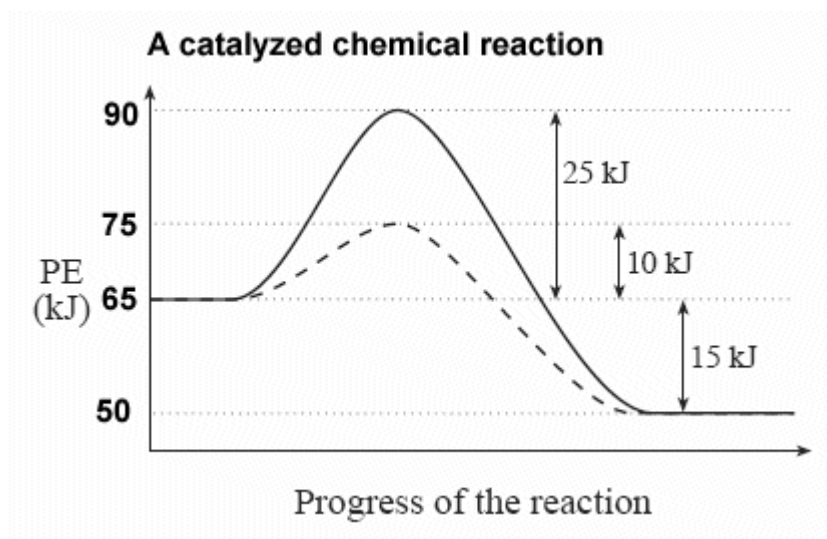
This reaction can take place much more rapidly, and at lower temperatures, if solid manganese dioxide ( $\text{MnO}_2$ ) is added. After the reaction is complete, no more potassium chlorate remains, but

all of the manganese dioxide remains.

Catalysts are very specific regarding which reactions they work with - the same catalyst will not necessarily work with many other (or any other) reactions. Finding a catalyst for a specific equation is one of the important jobs of an industrial chemist.

Catalysts most likely work by helping to promote a proper orientation between reacting particles. In doing so, it provides an **alternate** reaction pathway with a lower activation energy.

In the potential energy diagram shown here, the regular, uncatalyzed pathway is shown as a solid line, and the catalyzed pathway is shown as the dotted line:



$\Delta H$  for the both the catalyzed and uncatalyzed reaction is -15 kJ.

Since  $\Delta H$  is independent of the pathway, it is not changed by the presence of a catalyst.

Activation energy,  $E_a$ , does have different values for the catalyzed and uncatalyzed reactions.

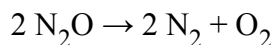
$$E_a \text{ for the uncatalyzed reaction} = +25 \text{ kJ}$$

$$E_a \text{ for the catalyzed reaction} = +10 \text{ kJ}$$

Because more particles will possess the new 10 kJ energy minimum for a successful collision, the rate of the reaction will increase.

It is important to note that the original pathway is still present, and reacting particles will still follow that route.

Here's another example:





$E_a$  for the uncatalyzed reaction is 250 kJ, but when a gold metal catalyst is used,  $E_a$  is lowered to 120 kJ.

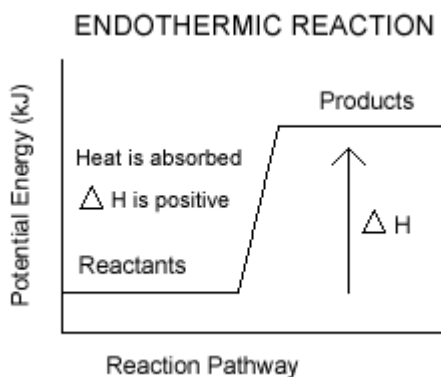
The  $N_2O$  is chemically adsorbed on the metal surface. A bond is formed between the O of the  $N_2O$  and an Au atom. This weakens the bond joining the O to the N, thus making it easier for the molecule to break apart.

## Inhibitors

Some substances, known as **inhibitors**, slow down chemical reactions. These work by tying the reactants up in "side reactions".

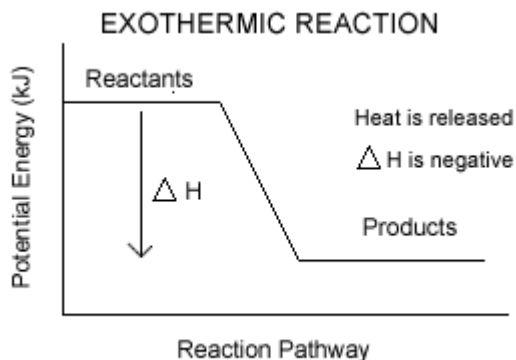
## 2.3 Potential Energy Diagrams Revisited

Potential energy diagrams were used to illustrate the input (endothermic) or release of energy (exothermic):



### Endothermic Reactions

- 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.

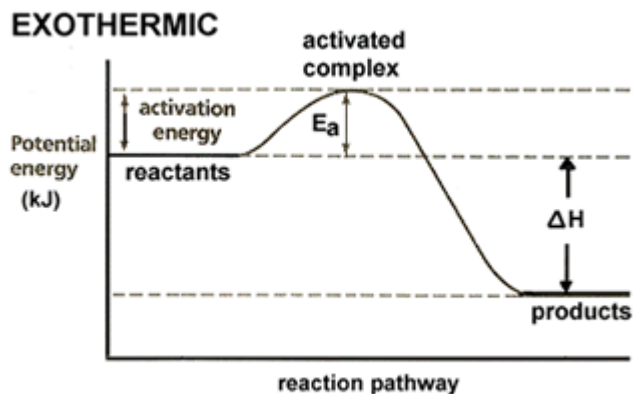
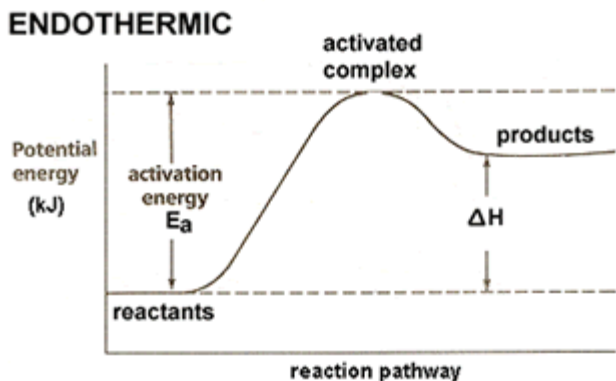


### Exothermic Reactions

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

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.

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:



Values for potential energy are often included along the y-axis, allowing us to determine values for activation energy and the heat of the reaction.

## Part II. Kinetics Math Notes: Rate Law, Order, & Half Life

(<https://sites.google.com/site/molelady/ap-chemistry/kineticmathnotes.pdf> )

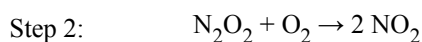
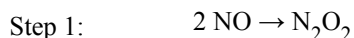
## Part III. Reaction Mechanism & the Rate-Determining Step

Chemical reactions like this one:  $2 \text{C}_2\text{H}_2 + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 2 \text{H}_2\text{O}$

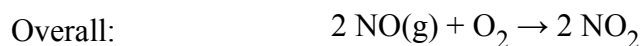
we see that two molecules of acetylene ( $\text{C}_2\text{H}_2$ ) react with 5 molecules of oxygen. According to the collision theory, molecules must collide in order to react. But it is highly unlikely that 7 molecules would collide together all at once. Instead, the reaction most likely occurs in a **series of simple steps** which only required two or three molecules colliding at any one instant. Although these steps cannot always actually be observed, chemists can often make predictions about the sequence of events.

For ex.,  $2 \text{NO}(\text{g}) + \text{O}_2 \rightarrow 2 \text{NO}_2$

This reaction does not occur in a single step, however, but rather through these two steps:



Notice that if you add these two reactions together, you end up with the overall reaction:

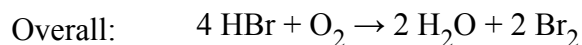
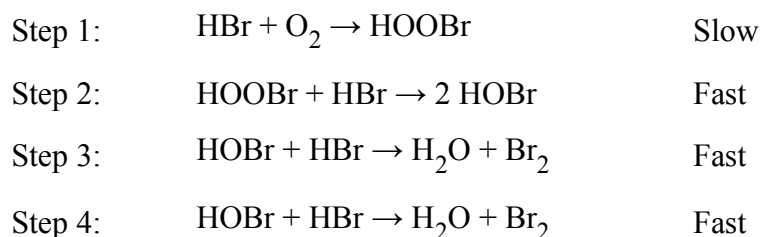


The series of steps a reaction undergoes is called the **reaction mechanism**.

Notice that in our example dinitrogen dioxide ( $\text{N}_2\text{O}_2$ ) cancels out and does not appear in our overall equation. Substances such as this are called **reaction intermediates** and are typically short-lived.

### Rate Determining Step

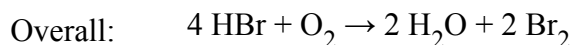
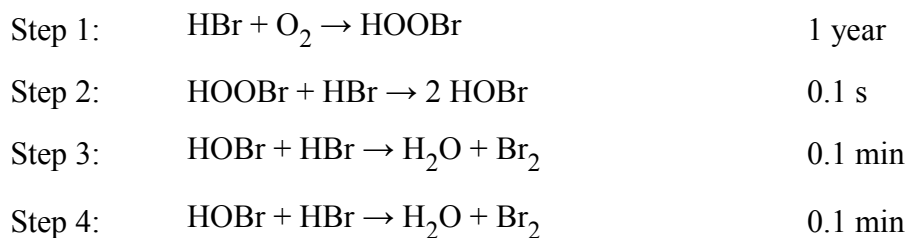
Here is another reaction mechanism with some additional information concerning the relative rates of each of the individual steps:



We don't have values for the actual rates of these individual steps, but here's a question for you to consider - would you consider the overall reaction to be fast or slow?

With two fast steps and only one slow step, many of you will predict that the reaction will be fast.

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



Now would you consider the overall reaction to be fast or slow? Clearly it is a slow reaction, taking over a year to complete despite some fast steps.

The overall rate of any reaction depends on the rate of the slowest step. This slowest step is called the **rate determining step**. If you want to speed up a reaction, this is where you should focus your attention.

The slowest step of a reaction mechanism is the

**rate determining step**

**Threshold Energy: reacting particles must collide with sufficient force or energy**

**Activation energy**

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

Symbol:  $E_a$

Sometimes referred to as threshold energy

**Activation Energy**

Another aspect of the collision theory describes what happens to reacting particles as they change from the reactant state to the product stage. When the particles collide, the theory (transition state theory) tells us that a temporary, unstable grouping of particles forms - bonds are in the process of both being broken and being formed. This unstable association of particles is called the **activated complex** or transition state. This unstable complex is at a high energy level.

The activated complex is similar to the reaction intermediates, but it is an even more unstable state.

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.