Kinetics – Instantaneous rate calculations

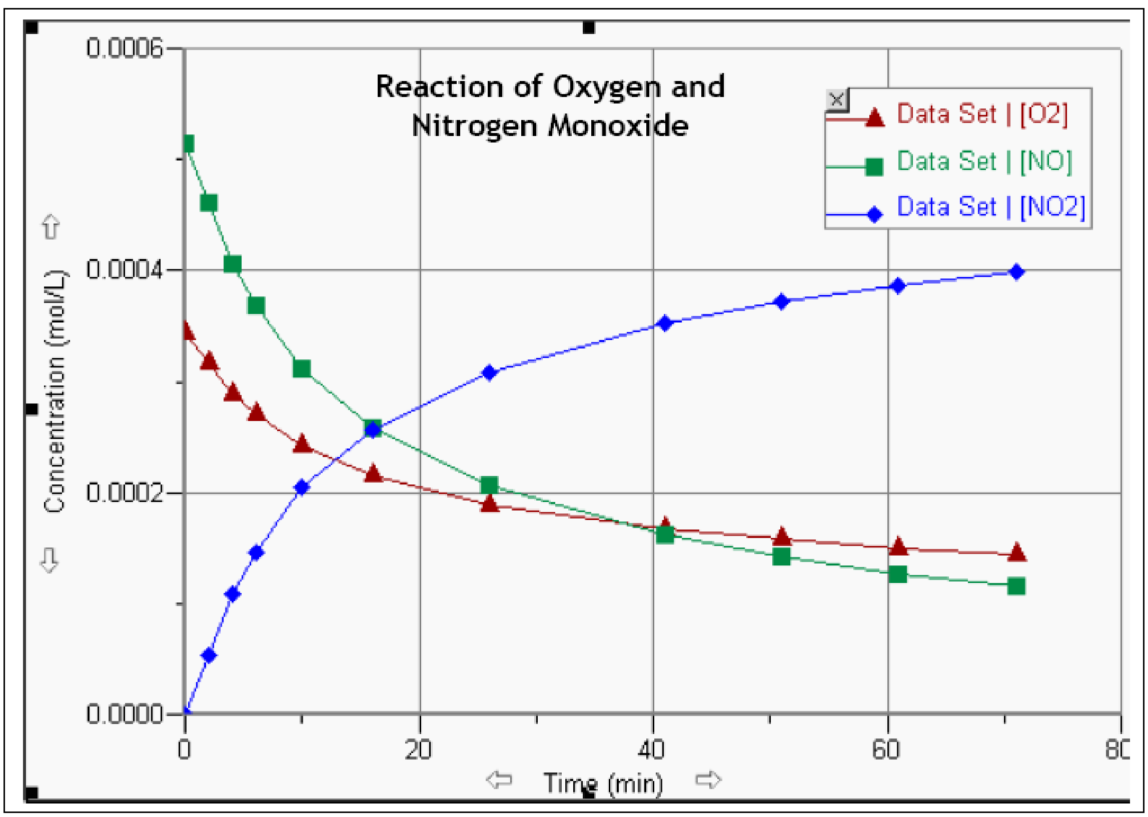
The formation of nitrogen dioxide from nitrogen dioxide and oxygen gas was studied. The balanced equation for the reaction is:

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

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

Answer the following questions.

1. Find the initial rates of consumption of O_2 and NO and the initial rate of formation of NO_2 as well as the rates at 4 minutes and 41 minutes into the experiment. Note: In order to draw a tangent at time = 0 you must have the "Interpolate" box checked in the "Graph Options" window.



Answer: Find the slope from each of time frame. SHOW ON GRAPH

They are a rough estimate – it is best to use a graphical analysis program to be precise.

Initial Rate	4 mins	41 mins
O_2=1.30 × 10^{-5} mol/Lmin NO=2.65 × 10^{-5} mol/Lmin NO_2=2.65 × 10^{-5} mol/Lmin	O_2=9.00 × 10^{-6} mol/Lmin NO=1.90 × 10^{-5} mol/Lmin NO_2=1.90 × 10^{-5} mol/Lmin	O_2=9.00 × 10^{-7} mol/Lmin NO=1.90 × 10^{-6} mol/Lmin NO_2=1.90 × 10^{-6} mol/Lmin

Kinetics – Stoichiometric calculations

For the reaction from above:

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

If 2 mols of NO decomposes then 2 mols of NO_2 are formed
The ratio of NO to NO_2 is 1:1
NO decomposes at the same rate as NO_2 is formed

If 1 mol of O_2 decomposes then 2 mols of NO_2 are formed
The ratio of O_2 to NO_2 is 1:2
O_2 decomposes ½ of the rate as NO_2 is formed

If we look at the rate data, the initial rate of consumption of NO is about 2.65 × 10^{-5} mol/Ls and O_2 is 1.3 × 10^{-5} mol/Ls; the rate for NO is twice the O_2. The initial rate of formation of NO_2 is equal to the rate of consumption of NO and twice that of the O_2.

Therefore, the rate of NO and NO_2 are the same, and the rate for NO_2 is twice the rate of O_2.

Look at all the other rate calculations. You should see that this pattern is maintained. These ratios are the same ratios as those found in the reaction stoichiometry. We can write this in our rate equation as shown below:

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

or

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

The negative sign in front of the rates represents REACTANTS, to keep all rates positive!!

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.

We can solve this problem in a similar manner to how we solved stoichiometry problems in grade 11 chemistry.

Ratio of NO_2 to O_2 = 2:1
Therefore, the rate of O_2 will be half of the rate of NO_2
or 0.50/2 = 0.25 mol/Ls

Fill in the ratios

Another way of solving is canceling the NO_2 in the form

Rate of the compound you are solving for = given rate of the known X $\frac{\text{(what you are solving for)}}{\text{(what you know)}}$

$$\text{rate } O_2 = 0.50\ \text{mol/Ls}\ \cancel{NO_2}\left(\frac{1O_2}{2\cancel{NO_2}}\right) = 0.25\ \text{mol/Ls}\ O_2$$

$$\text{rate NO} = 0.50\ \text{mol/Ls}\ \cancel{NO_2}\left(\frac{1NO}{1\cancel{NO_2}}\right) = 0.50\ \text{mol/Ls NO}$$

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.

Rate of the compound you are solving for = given rate of the known X $\frac{\text{(what you are solving for)}}{\text{(what you know)}}$

$$\text{rate C} = 0.60\ \text{mol/Ls}\ \cancel{A}\left(\frac{3\ C}{2\ \cancel{A}}\right) = 0.90\ \text{mol/Ls C}$$

The "compound" cancels out with denominator

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

$$\text{rate B} = 0.60\ \text{mol/Ls}\ \cancel{A}\left(\frac{1\ B}{2\ \cancel{A}}\right) = 0.30\ \text{mol/Ls B}$$

Example 3.

If NOCl(g) is decomposing at a rate of 1.1×10^{-8} mol/L/min in the following reaction:

$$2\ NOCl(g) \rightarrow 2\ NO(g) + Cl_2(g)$$

a) What is the rate of formation of NO(g)?
b) What is the rate of formation of $Cl_2(g)$?

Explaining Why Reactions Occur

Why do different reactions occur at different rates?

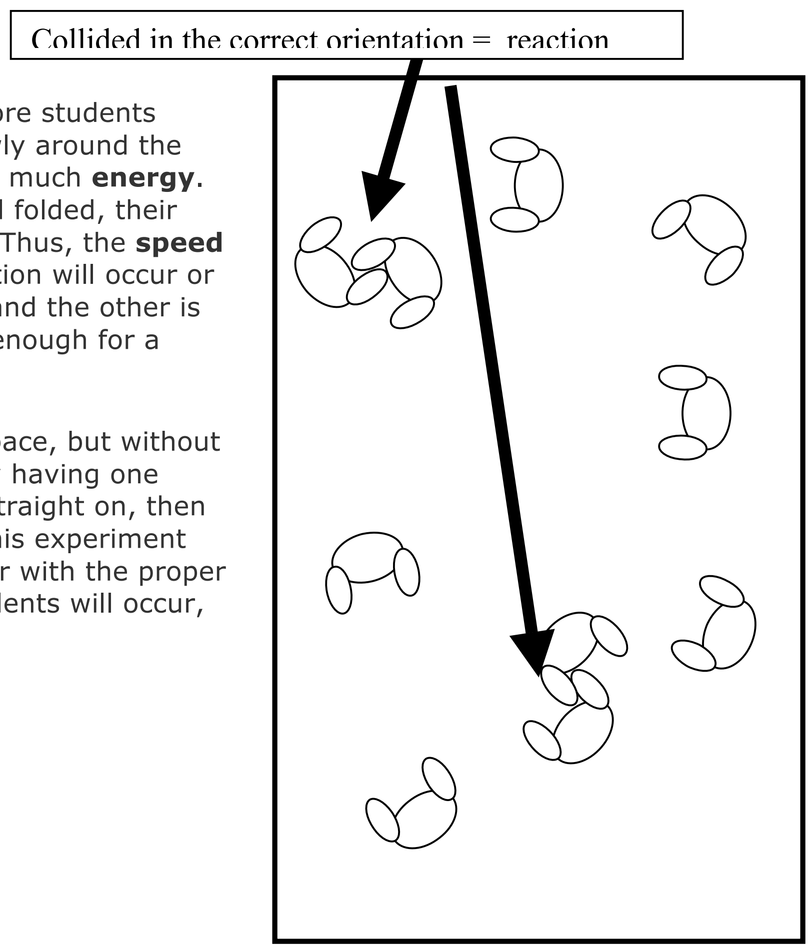
The Collision Theory

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

But not all collisions produce a reaction.

They must collide with the proper orientation and energy to produce a reaction.

Analogy:



Picture an empty classroom with 10 or more students blinded folded. If they were to move slowly around the classroom, their collisions will not have as much **energy**. But if they were asked to run around blind folded, their collision will cause more hurt a lot more. Thus, the **speed** or the **energy** will dictate whether a reaction will occur or not. Even if one student is running fast, and the other is just briskly walking, the energy could be enough for a reaction to occur but just not as much.

Next, have the students move at a brisk pace, but without running. If the students hit each other by having one shoulder hit the other person's shoulder straight on, then they would have a successful collision. This experiment helps us realized that collisions must occur with the proper orientation. Again, collisions between students will occur, but only some will be successful.

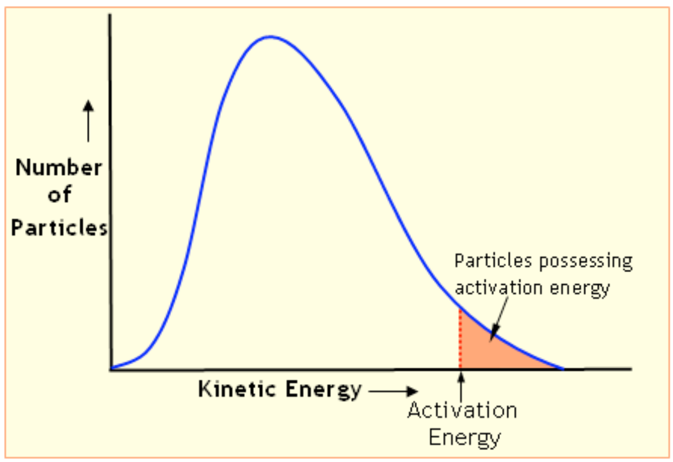
Activation energy

- The minimum amount of energy required for colliding particles to produce a chemical reaction

The greater the activation energy, the slower the reaction rate, the longer the reaction takes.

> For example, hydrogen and oxygen can be kept in the same container at room temperature without a reaction occurring. Even though the molecules collide, they do not possess activation energy. If the mixture is heated to 800°C, or a flame or spark is introduced, an explosive exothermic reaction occurs. The heat, flame or spark provides enough energy for the particles to reach activation energy. They are able to strike each other with enough energy to break the hydrogen-hydrogen and oxygen-oxygen bonds.

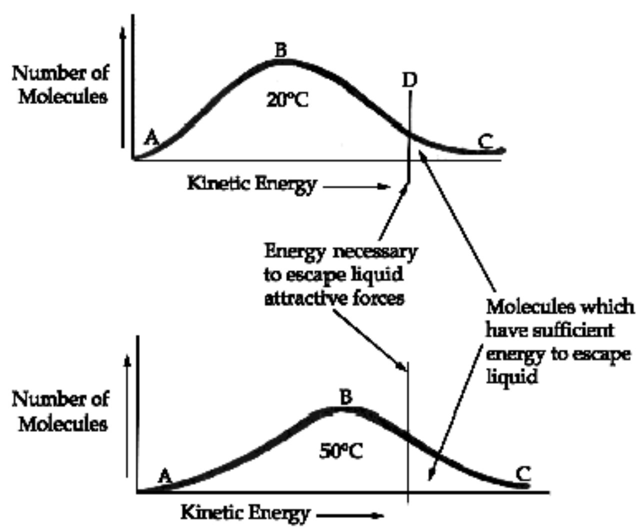
Kinetic Energy Distribution Curve



The area under the curve represents the number of particles at a given kinetic energy.

The area under the curve to the right of the activation energy represents the number of particles with sufficient energy to produce a reaction capable of a reaction. Each reaction has its own specific activation energy. The lower the activation energy, the more particles in the system that possess enough energy to produce a reaction.

Increasing the temperature will "squish" the curve down. Or more particles will be distributed past the activation energy line.



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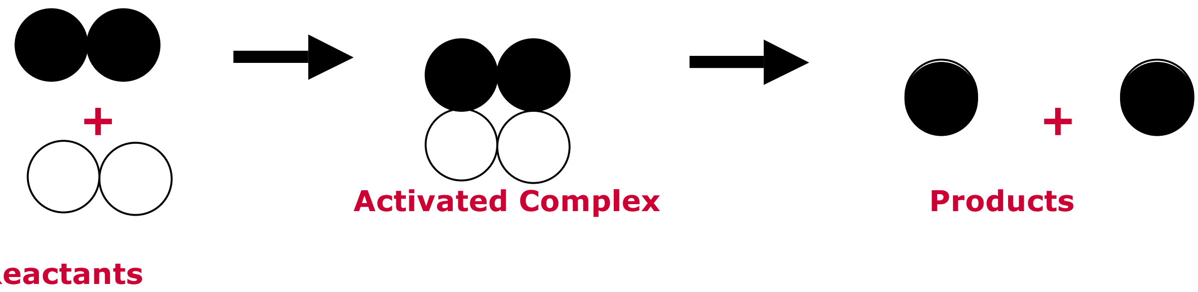
Heat of Reaction

As the particles collide, they form an unstable intermediate particle called the **activated complex** or **transition state**. The energy required to produce the activated complex is the **activation energy**. The activated complex has a maximum amount of potential energy but exists for a very small instant in time.

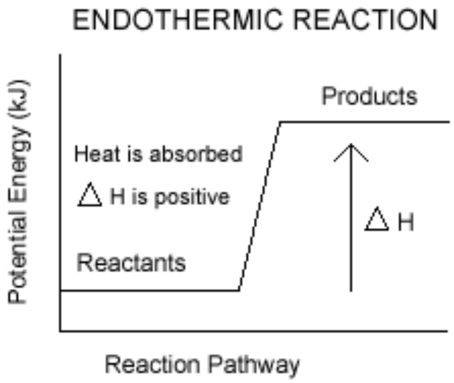


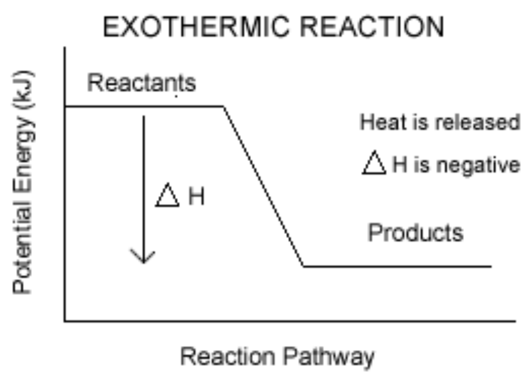
Enthalpy (**H**) is the heat content or total energy possessed by the particles in a system. The energy released or absorbed by a reaction is called the **change in enthalpy**, **ΔH**, or **heat of reaction**.

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

where ΔH is the change in enthalpy or energy that occurs during a reaction in **Joules** (**J**).If ΔH is negative, heat flows out of the system. This type of reaction gives off heat and the reaction vessel feels warmer. This is called an **exothermic reaction**.

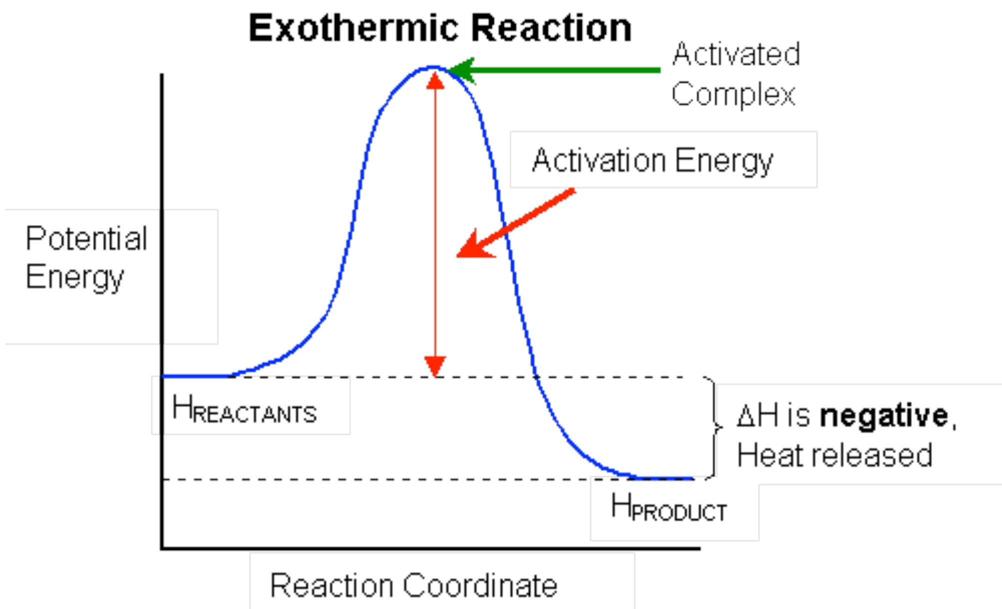
If ΔH is positive , heat is absorbed or flows into the system because the products have more enthalpy than the reactants. The reaction vessel feels cooler as energy is absorbed from the surroundings. This type of reaction is called an **endothermic reaction**.



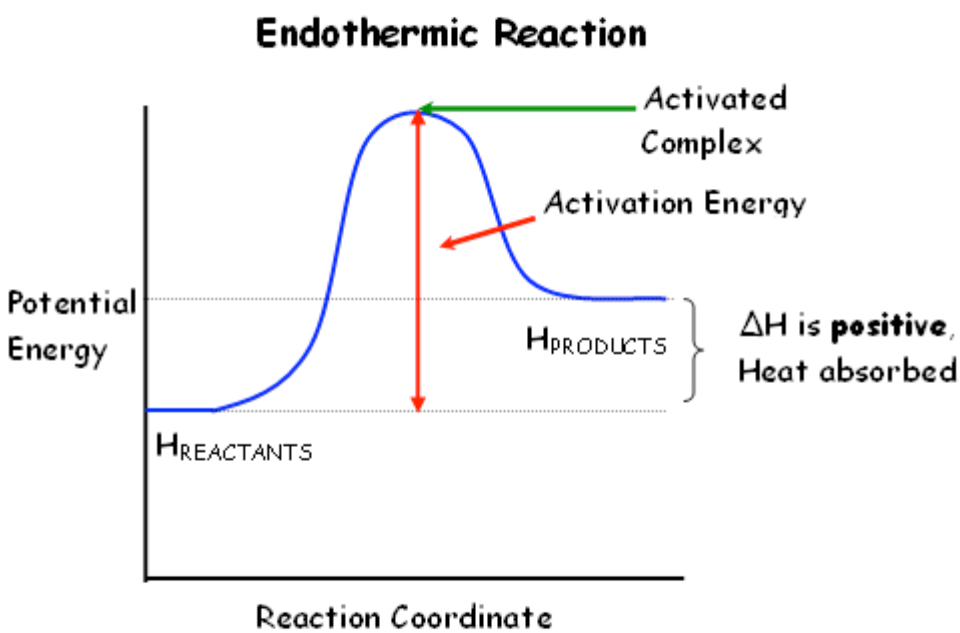


Potential Energy Diagrams

A **reaction coordinate diagram**, or **potential energy (EP) diagram** or **reaction progress diagram** represents the energy change that occurs during a chemical reaction.
In the exothermic reaction, the products possess less energy than the reactants. During the reaction, heat is lost from the system and ΔH is a negative value.



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

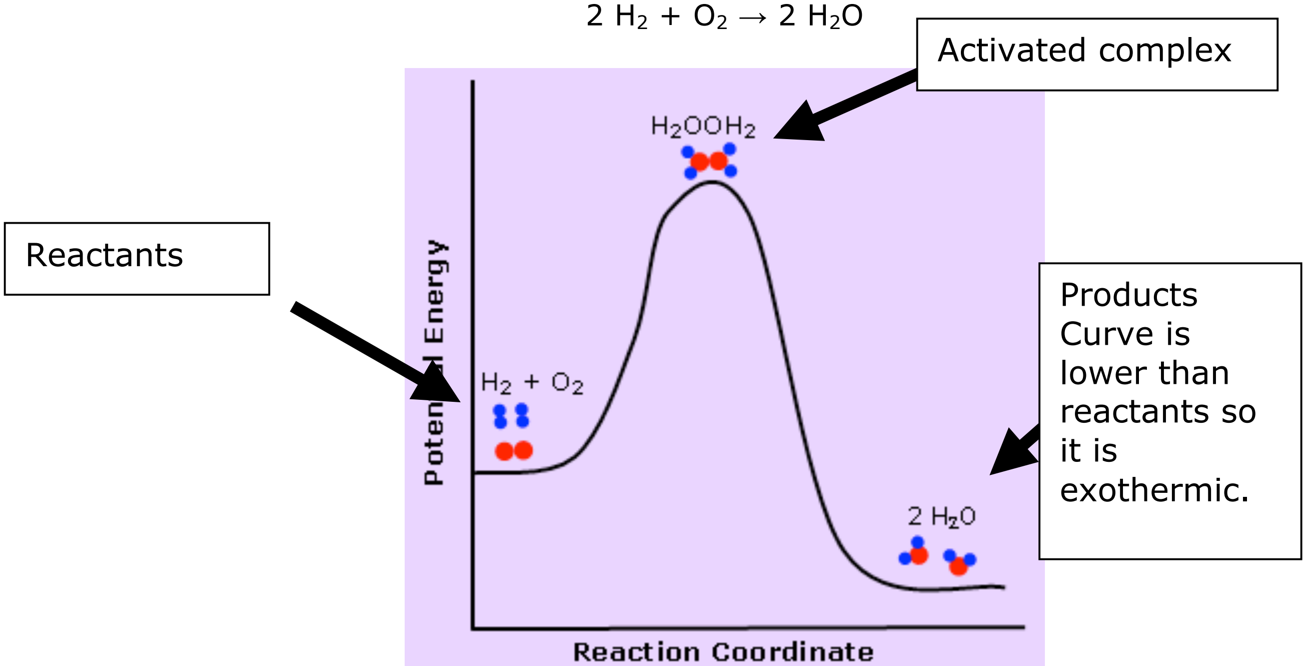


Reaction coordinate or potential energy diagrams provide
- a picture of the energy changes which occur as a chemical reaction proceeds

Example

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.

The activation energy is high because of the need to break covalent hydrogen-hydrogen bonds in hydrogen molecules and oxygen-oxygen bonds in oxygen molecules.

The H_2OOH_2 particle is the intermediate or the activated complex. It must be formed for the reaction to take place.

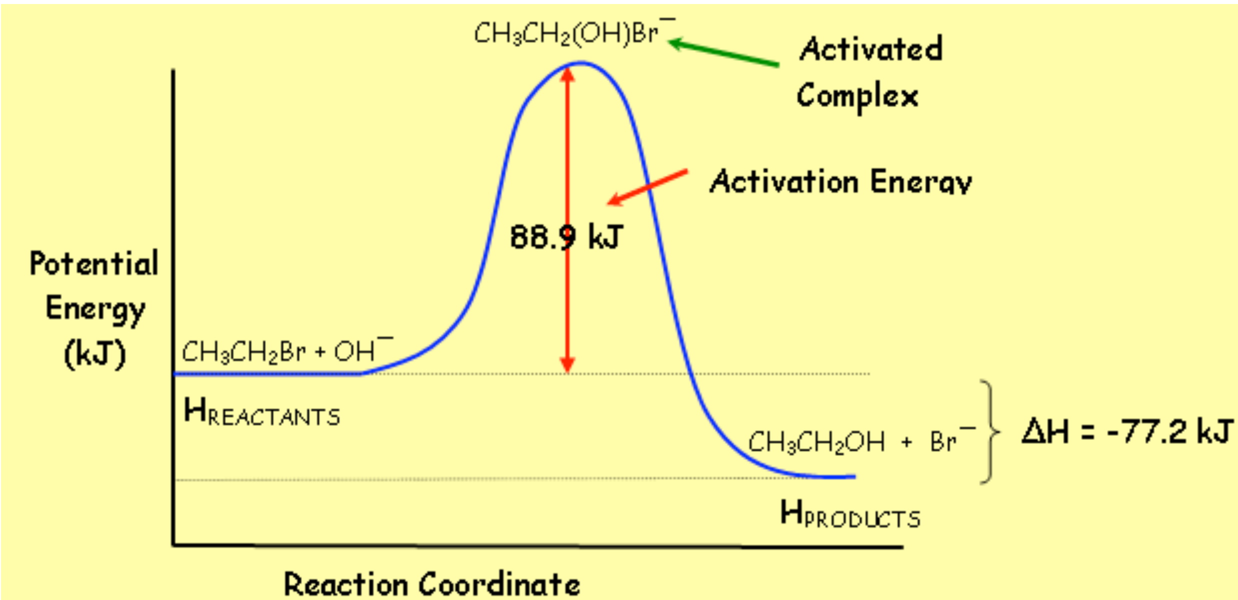
The enthalpy is negative, so energy is lost in the formation of water is released in the form of heat and light energy. All combustion reactions are exothermic.

Example 2

In the reaction,

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

the **reaction coordinate diagram** is shown below:



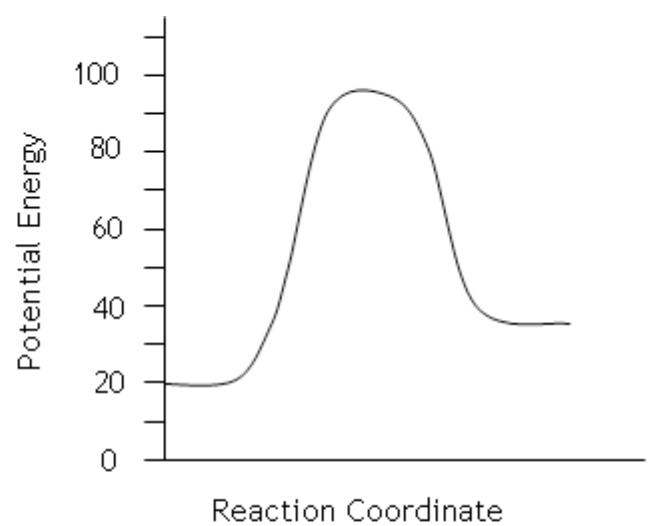
The activated complex in this reaction is $CH_3CH_2(OH)Br^-$. It is a single particle formed by the all the reactant particles.

The activation energy is 89.5 kJ per mole of CH_3CH_2Br.

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

Example:

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?



Summary

In this lesson you have learned:

- The collision theory is used to explain why chemical reactions occur.
- 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 frequency (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 enthaply of the products (final) and the enthalpy of the reactants (initial)..
- A reaction coordinate diagram provides a visual representation of energy changes that occur during a chemical reaction.