RATES OF CHEMICAL REACTIONS

1. EXPRESSING RATES

The rate of a chemical reaction is the basically the speed at which products are formed from reactants. Therefore to express the rate of a reaction, a ratio is used in which Δt is always found in the denominator. The numerator can consist of many different possible forms and is usually expressed in a form that is either observable or very useful. Here are some examples:

rate = $\frac{\Delta V}{\Delta t}$ change in volume over time

rate = $\frac{\Delta P}{\Delta t}$ change in pressure over time

rate = $\frac{\Delta T}{\Delta t}$ change in temperature over time

rate = $\frac{\Delta C}{\Delta t}$ change in concentration over time

rate = $\frac{\Delta m}{\Delta t}$ change in mass over time

rate = $\frac{\Delta pH}{\Delta t}$ change in pH over time

rate = $\frac{\Delta n}{\Delta t}$ change in amount over time

rate = $\frac{\Delta q}{\Delta t}$ change in charge (coulombs) over time

pick the best observable

In fact the change of any observable property (or a related property) over time is an acceptable way of representing a rate. However some ways of expressing the rate may be more practical than others. For example in a simple reaction studied in grade eleven, magnesium metal is allowed to react with hydrochloric acid. The resulting hydrogen gas is collected in a gas measuring tube.

$$Mg(s) + 2HCl(aq) \rightarrow H_2(g) + MgCl_2(aq)$$

$$\text{rate} = \frac{\Delta m(\text{magnesium})}{\Delta t}$$

This would be cumbersome because in order to find the mass of the magnesium you would have to stop the reaction, dry the magnesium and then find its mass. It would be impossible to study the rate during the reaction.

$$\text{rate} = \frac{\Delta C(\text{hydrochloric acid})}{\Delta t}$$

This could not be measured directly. However one could measure the change in pH. This can be measured using a good quality pH meter.

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

The pH of the hydrochloric acid solution will change as hydrochloric acid is consumed. However the change in concentration will be very slight if the acid is in excess of the magnesium. It may be technically difficult to observe.

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

The change in volume of the evolving hydrogen gas is very easy to measure. It is the obvious choice for this reaction.

For a reactions such as:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

$\text{rate} = \frac{\Delta V}{\Delta t}$ or $\text{rate} = \frac{\Delta P}{\Delta t}$ are both practical

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

$\text{rate} = \frac{\Delta Q}{\Delta t}$ or $\text{rate} = \frac{\Delta T}{\Delta t}$ are both very practical

2. RELATIONSHIP BETWEEN DIFFERENT EXPRESSIONS OF A RATE

In the above examples no mention was made of negative rates. for example, if you measured the change in volume for the phosgene gas reaction ($CO(g) + Cl_2(g) \Longrightarrow COCl_2(g)$) you would find that the rate gives a negative answer (i.e. the volume decreases as the reaction proceeds and the $V_f - V_i = V$ will be negative). To avoid this problem you would need to use one of the following:

$$\text{rate} = \frac{-\Delta V}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{|\Delta V|}{\Delta t}$$

Both expressions avoid the negative rate. To expand on this idea, consider the following:

Many reaction rates are expressed as a change in concentration as it is considered be to more useful than other methods of expressing the rate (some conversions may be necessary). For a gas phase reaction such as:

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

The following rates can be stated:

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} \quad \text{rate} = \frac{-\Delta[B]}{\Delta t} \quad \text{rate} = \frac{\Delta[C]}{\Delta t} \quad \text{rate} = \frac{\Delta[D]}{\Delta t}$$

And these relationships between the rate expressions can be gleaned:

$$\frac{\Delta[A]}{\Delta t} = \frac{2(\Delta[B])}{\Delta t} \qquad \frac{\Delta[A]}{\Delta t} = \frac{-2(\Delta[C])}{\Delta t}$$

$$\frac{\Delta[B]}{\Delta t} = \frac{-\Delta[C]}{\Delta t} \qquad \frac{3(\Delta[B])}{\Delta t} = \frac{-\Delta[D]}{\Delta t}$$

$$3\,\frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t} \qquad \frac{3(\Delta[A])}{\Delta t} = \frac{-2(\Delta[D])}{\Delta t}$$

complicated - think about it

You may need to think about these relationships a bit. For example in the first relationship the rate at which A is consumed is twice the rate at which B is consumed. This makes sense in view of the stoichiometry of the equation. The following graph illustrates the likely change in concentrations of A, B, C and D over time.

3. AVERAGE RATE VERSUS INSTANTANEOUS RATES

don't really need to know - math joins in

So far all rate expressions have been for average rates. The change in the observable is over a definite time interval, Δt. This gives the average rate of change for the time interval considered. Note however, in the above graph the rates change with time. That is the change in concentrations are greater at the outset of the reaction and less as the reaction nears completion. To get an instantaneous rate you would have to shrink the time interval to a infinitesimally small interval on the graph. This in practice is next to impossible to do. However if you knew an equation that gave the change in a concentration as a function of time you could employ the first derivative of that equation and come up with the instantaneous rate. This is basically finding the slope of the line in the above graph where each curve is defined as a mathematical function in t. The first derivative is the slope. Taking first derivatives one can prove that as the time interval becomes infinitesimally small:

$$\text{rate} = \frac{\Delta[A]}{\Delta t} \quad \text{becomes} \quad \text{rate} = \frac{d[A(t)]}{dt}$$

where [A(t)] represents a function expressing [A] in term of time and d/dt means to take the first derivative [A(t)]

Obviously this whole idea is somewhat above the level of this course and may not make any sense even if you have taken OAC calculus. I wanted you to appreciate that there are well developed links between chemistry and higher levels of mathematics such as calculus and differential equations!!! So if you are willing to appreciate that, don't worry about learning this section.

START HERE

4. COLLISION THEORY OF REACTIONS

The collision theory of reactions states that **ALL REACTIONS ARE THE RESULT OF BIMOLECULAR COLLISIONS**. Bimolecular collisions simply means two molecule collisions. Examples of trimolecular collisions or tetramolecular collisions are virtually unknown. A simple example clearly illustrates a bimolecular collision.

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

this actually happens bimolecular

Here it should make sense that a hydrogen molecule and an iodine molecule collide and the atoms recombine and two hydrogen iodide molecules result. This is a simple bimolecular collision. For more complex reactions such as:

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

the overall equation actually represents the sum of several intermediate reactions, all of which are bimolecular:

#5

$$\begin{array}{l} HBr(g) + O_2(g) \rightarrow HOOBr(g) \\ HOOBr(g) + HBr(g) \rightarrow 2HOBr(g) \\ HOBr(g) + HBr(g) \rightarrow H_2O + Br_2(g) \\ HOBr(g) + HBr(g) \rightarrow H_2O + Br_2(g) \\ \hline 4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g) \end{array}$$

one step is slower determines the overall rate

It is easy to see that the sum of the four bimolecular steps adds together to produce the overall reaction equation. The four bimolecular steps are collectively called the reaction mechanism. Reaction mechanisms are of great importance when trying to understand reaction rates in terms of a rate determining step. More on this later.

The reasoning behind the collision theory of reactions is based on a few simple deductions:

- In order for a reaction to occur, molecules must contact each other, therefore they must collide.
- Energy needed to overcome the activation energy (activation energy will be discussed in detail later) is provided by the kinetic energy of the collision.
- Bimolecular collisions can occur quit easily. Imagine two people playing pool where each person simultaneously shoots a ball from opposite ends of the pool table and the balls collide in the middle.

- Trimolecular collisions are extremely rare. Imagine three people playing pool where each person simultaneously shoots a ball from three different directions such that the balls collide in the middle at exactly the same time (this is difficult, think about it).
- Tetramolecular collisions and above are virtually impossible.

5. COLLISION THEORY AND REACTION RATES

Using collision theory a very straight forward equation can be deduced:

$$\boxed{\text{rate} = \begin{bmatrix}\text{\# of collisions}\\ \text{per unit time}\end{bmatrix} \text{x} \begin{bmatrix}\text{fraction of collisions}\\ \text{that are successful}\end{bmatrix}}$$

This equation called **THE GENERAL RATE EQUATION** is simply the product of two factors. Obviously, the more collisions that occur in a given time (the first factor) the faster the reaction. The second factor deals with whether or not the collision actually works. It is very possible to have a collision in which the two colliding molecules simply bounce off one another. It doesn't matter how many collisions you have, if they are not successful, no reaction will occur. This simple equation is extremely important. **In fact all factors that affect the rate of a reaction can be explained by this equation, one way or another. Remember this equation.**

eg Here is an analogy for the general rate equation that takes place at a dance. In order to get dances with people (the desired reaction) two things must happen. First you have to ask people to dance. This is like the collision. Secondly, that person has to accept your offer. This is a successful collision. To increase the number of dances you get in a night, you can ask more people (improve factor #1) but you must also be successful at least some of the time when you ask (factor #2) Your overall success probably has as much to do with how many people you ask as it does with who or how you ask.

6. A COLLISION IN DETAIL

In chemistry, the success of a collision depends on two things:

- The collision must have sufficient kinetic energy to overcome the energy barrier of the activated complex, also known as activation energy.
- The geometry of the collision must be right (i.e, the molecules have to line up right to go on to the next step, the activated complex).

Consider a typical reaction:

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ kinetic energy of the particles

Many collisions between the reactant molecules, hydrogen and chlorine, will be unsuccessful. The reason being that initial repulsive forces between molecules prevent them form coming close enough together to react. Also, the geometry of the collision is wrong. However is the collision is forceful enough (faster moving, therefore more kinetic energy) and the geometry is favourable the initial repulsion between molecules can be overcome. The energy required to overcome the initial repulsion is called the activation energy for the collision and is supplied by the kinetic energy of the collision. If there is sufficient energy in the collision to **meet** or **exceed** the activation energy an activated complex will form. The activated complex is a high potential energy unstable reaction intermediate. Once this activated complex is formed it can either go forward and form products (a successful collision) or simply reform reactants (an unsuccessful collision). The activated complex is often labelled with an * to indicate its high energy temporary existence. The following sequence shows the possible collisions for the above reaction. (==> show direction of motion)

```
H-H        Cl-Cl      unfavourable geometry, collision will
                      not be successful no matter how
 →           ←        energetic
```

```
H          Cl              H-Cl           H-Cl
|          |    becomes    | |   becomes
H          Cl              H-Cl           H-Cl

→          ←                activated       products!!
                             complex
```

In this diagram the geometry was right, energy was sufficient and an activated complex was formed. The activated complex in this case went on to form products!!

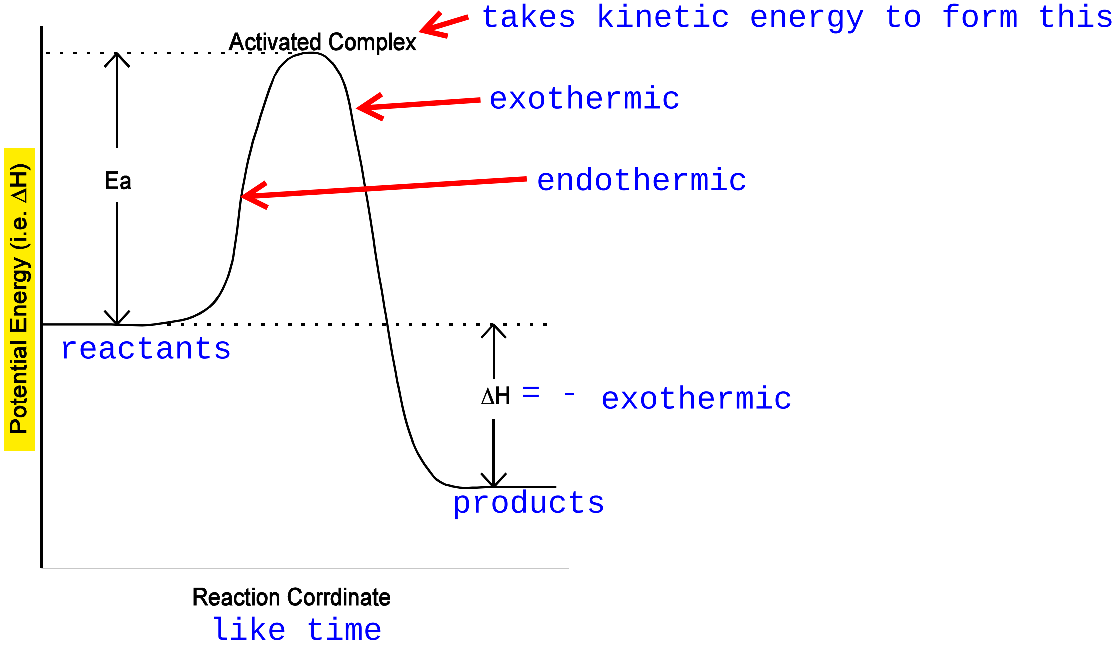
7. POTENTIAL ENERGY DIAGRAM FOR A REACTION

4. a) b) c)

A potential energy diagram is used to illustrate the change in potential energy involved in a reaction including the activated complex and the overall enthalpy. These diagrams are usually sketches and do not require a scaled axis. The vertical axis is always potential energy and increases as you go up the axis. The horizontal axis is called the reaction coordinate. This axis is something like time. The actual time involved in a reaction is too short to measure. The reaction coordinate then basically follows the reaction through from reactants to activated complex and then to products.

Potential Energy Curve

(exothermic reaction/high activation energy)

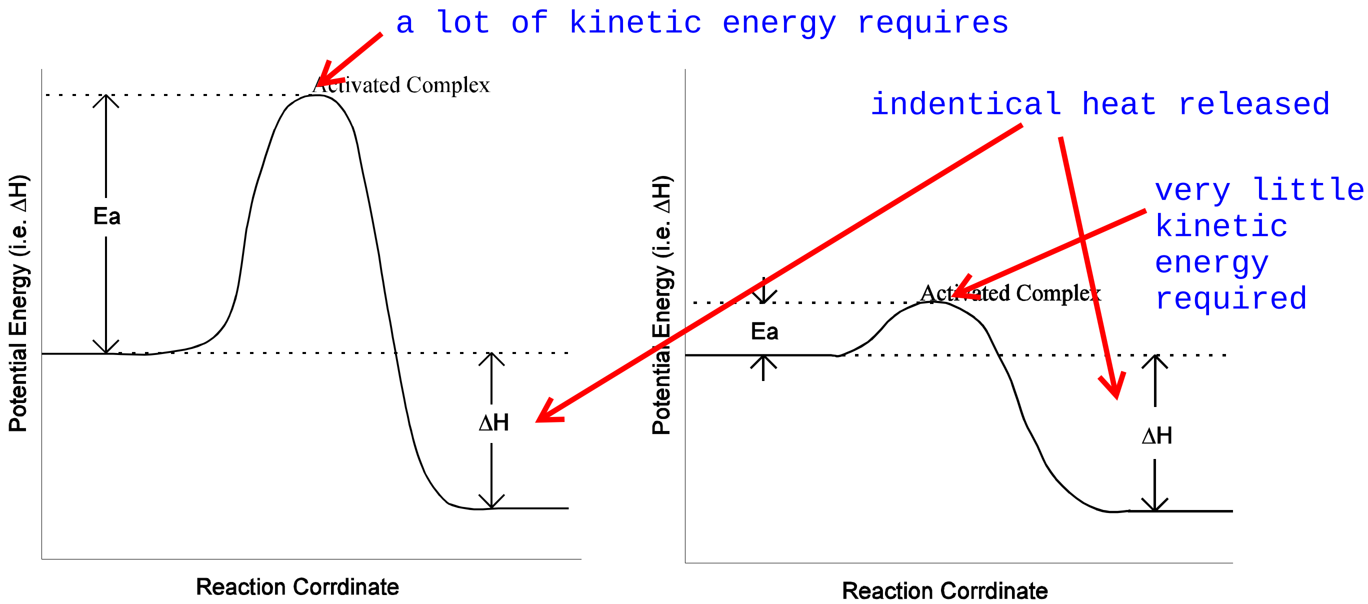


In the above sketch, E_A is used to represent activation energy (E_A = energy of activation), ΔH is used to show the change in potential energy (this is the same ΔH you have already studied) and details such as the reactants, activated complex and products are usually included.

The two examples bellow show:

- a fairly exothermic reaction with a large activation energy
- the same reaction with the addition of a catalyst.

The addition of a catalyst lowers the activation energy E_A but has no effect on the enthalpy, ΔH.


a lot of kinetic energy requires

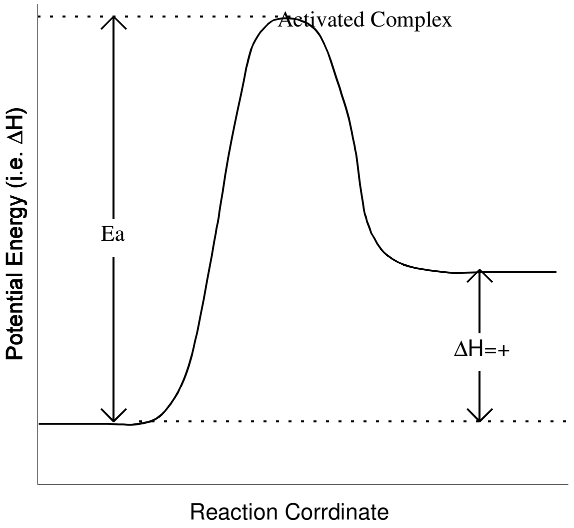
indentical heat released

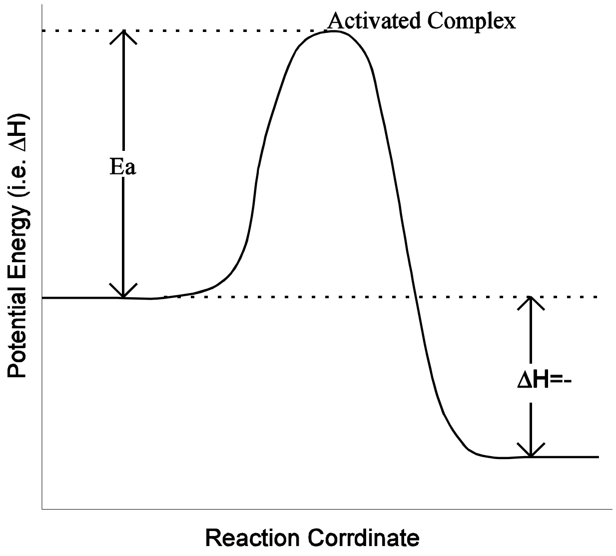
very little kinetic energy required

The next two examples show:

- an endothermic reaction with a large activation energy
- the reverse of the first reaction

Notice that the enthalpies are of equal magnitude but opposite sign. The activation energies are quite different.

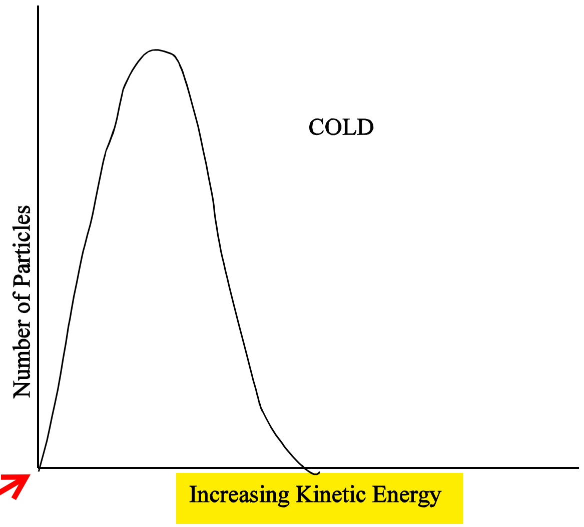


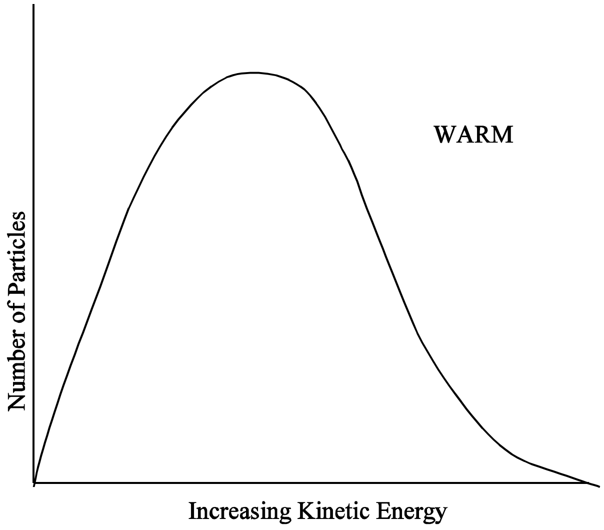


8. KINETIC ENERGY DISTRIBUTIONS

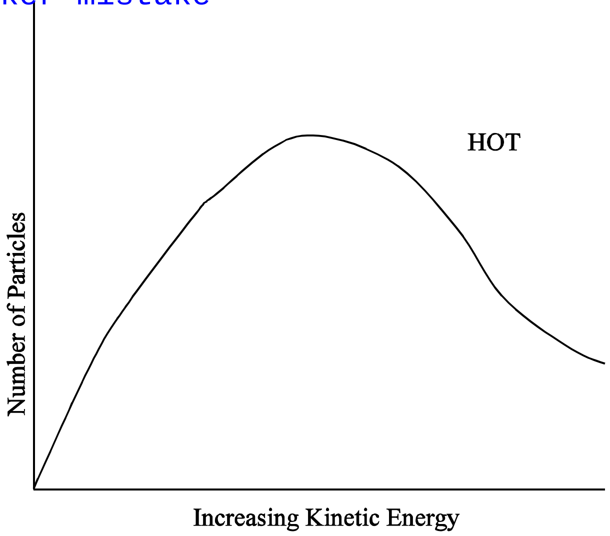
4. d) e) f)

Whether or not there is sufficient energy to from an activated complex depends on the kinetic energy of the reactants before a collision. The temperature of the reactants gives an average of all kinetic energies. There is actually a distribution of kinetic energies which follows a well defined curve known as a Boltzmann's Distribution. The shape of the curve is an inverted parabola, slightly skewed to the right and with a tail on the far right. The three diagrams bellow are all at different temperatures. The vertical axis represents number of molecules with a given energy or the number of collisions with a given energy. The horizontal axis represents the kinetic energy. The temperature which is shown on each sketch. Remember that temperature is the average of the kinetic energy and should be slightly to the left of the highest spot of the curve.





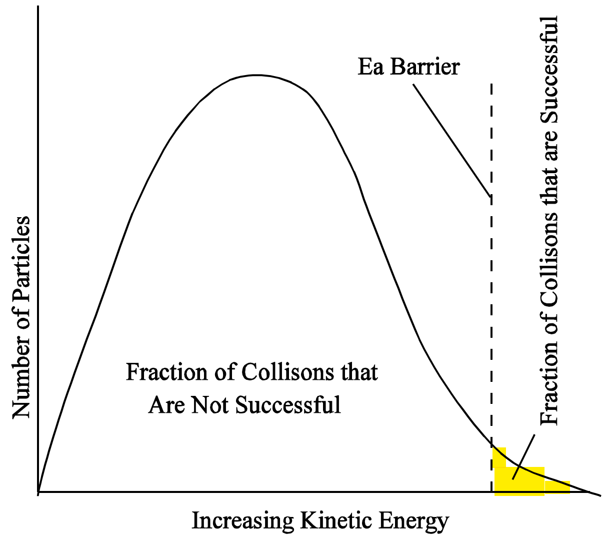
not an origin - Schlenker mistake

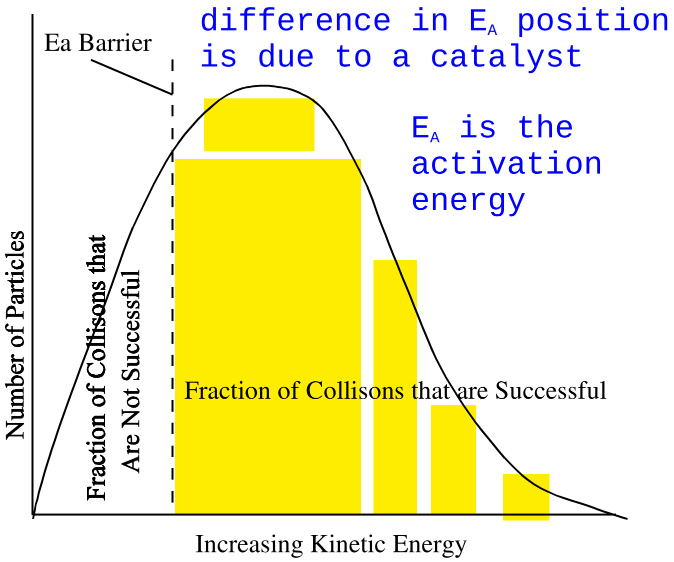


The best use for kinetic energy distributions is to help visualize the fraction of collisions that can be successful. This goes back to the second factor in the general rate equation (see section #5. The two examples below show:

- an example where the activation energy is so high that no collisions can not be successful at the given temperature
- the same reaction with the addition of a catalyst

The catalyst lowers the activation energy so that a substantial fraction of the collisions will be successful. Notice that the two curves have exactly the same shape. The temperature has not changed and the shape of the curve is based on temperature alone!!!



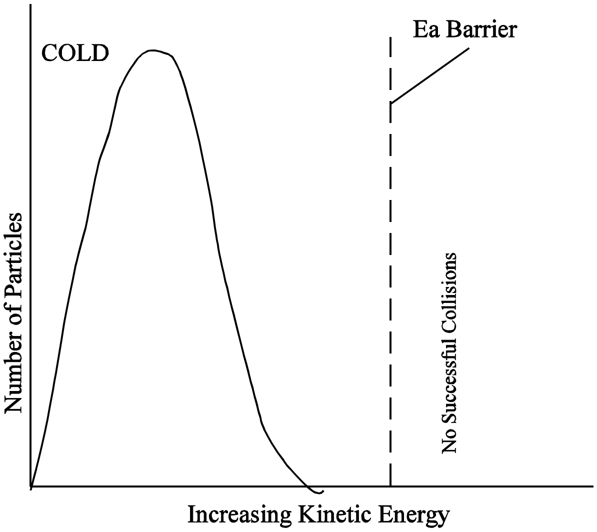

difference in E_A position is due to a catalyst

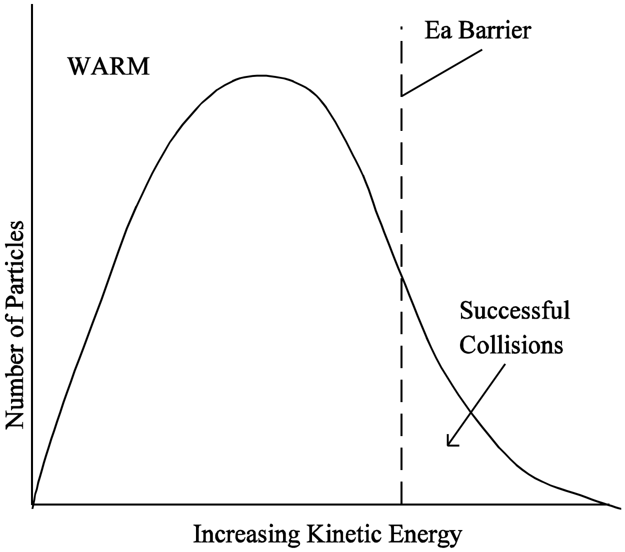
E_A is the activation energy

The next two examples show:

- an example where no collision are successful
- the same reaction (activation energy is unchanged) but at a higher temperature (note the different shapes of the curves)

These two diagrams help explain why an increase in temperature has a marked effect on reaction rate.





9. SIX FACTORS THAT AFFECT REACTION RATES

#3

This last section pulls together the ideas in the previous sections. The idea is to be able to explain all six factors using the general rate equation, potential energy diagrams and kinetic energy distributions. The six factors are

1. Nature of the Reactants
2. Concentration of the Reactants
3. Temperature
4. Catalysts
5. Surface Area Contact
6. Nature of the Reaction - Rate Determining Step

hard to do

Nature or the Reactants:

The greater the number of bonds that must be broken the slower the reaction. The breaking of bonds must be supplied by the activation energy of bimolecular collisions. Hence the greater the number of bonds to break, the greater the activation energy that is required and the smaller the fraction of collisions on the kinetic energy distribution that have sufficient kinetic energy. This affects the second term in the general rate equation.

eg $10Fe^{2+}(aq) + 2MnO_4^{1-}(aq) + 16H^{1+}(aq) \rightarrow$

(fast) $10Fe^{3+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

no bonds to break

versus

bonds to break

$5C_2O_4^{2-}(aq) + 2MnO_4^{1-}(aq) + 16H^{1+}(aq) \rightarrow$

(slow) $10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

The first reaction is very fast, while the second reaction is fairly slow. The only difference between these two reactions in that the second reaction requires the breaking of bonds in the $C_2O_4^{2-}(aq)$ reactant, while the first reaction used $Fe^{2+}(aq)$ with no bonds to break.

eg $C_{48}H_{100} + 73O_2 \rightarrow 48CO_2 + 50H_2O$ (slow)

versus

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (fast)

The first reaction is the burning of candle wax which as you know is slow. The second reaction is the burning of methane which can be extremely fast. The only difference is the number of bonds that must be broken in the hydrocarbon reactant.

Concentration of Reactants:

The greater the concentration of the reactants, the faster the reaction. A greater concentration of reactants simply improves the number of collisions per unit time (the first factor in the general rate equation). Assuming the fraction that is successful doesn't change, the more collisions, the faster the reaction

eg. Consider the burning of any substance in air (20 % oxygen) versus pure oxygen!!

Temperature:

An increase in temperature will have a marked effect on the overall rate of a reaction. Both factors from the general rate equation come into play. Higher temperature means more kinetic motion and therefore more collisions (first factor). Higher temperatures means a greater fraction of collisions will have sufficient energy to overcome the activation energy and be successful (second factor). Consider the shift in the kinetic energy distribution as temperature increases (see #8 above). The increase of the second factor is much more significant than the increase of the first factor.

eg A mixture of methane and oxygen will not react at room temperature. However, once a spark is supplied a violent explosion occurs (a fast reaction!!). The spark supplies heat to molecules in the location of the spark. These molecules now have enough kinetic energy to overcome the activation energy barrier. The heat produced from the reaction of a few molecules now provides heat for more molecules etc. A rapid chain reaction occurs leading to the explosion. In general reactants that have a high activation energy but are very exothermic make good explosives.

Catalysts:

A catalyst is a substance that alters the rate of a reaction without itself being consumed. A Catalyst lowers that activation energy for a reaction. This means that a greater fraction of collisions will now have adequate energy to create the activated complex (the second factor). See the kinetic energy distribution in #8 above. Notice that the shape of the kinetic energy distribution does not change, only the position of the E_A barrier. Also notice that the potential energy distribution for a catalyzed reaction has a different shape with a lower energy barrier (see #7 above). The catalyst is said to offer a lower energy route for the reaction.

Surface Area:

The four factors discussed above are all factors that influence the rate of homogeneous reactions (one phase reactions) In a heterogenous reaction (two phases) the surface area of contact between reactants plays a very important role. Since two phase reactions can occur only at the interphase between the two phases, an increase of surface area greatly improves the reaction rate. This is related to the first factor in the general rate equation - the number of collisions.

eg Consider the burning of a log that is in one piece versus the same log if it has been split into many small pieces.

Nature of Reaction:

rate determining step

The nature of the reaction is based on the reaction mechanism. When trying to determine the reaction rate based on a reaction mechanism, one must only consider the slowest step in the entire reaction mechanism. This step is called the rate determining step. It will have the highest activation energy of all of the steps and hence limits the reaction rate according to the second factor in the general rate equation etc.