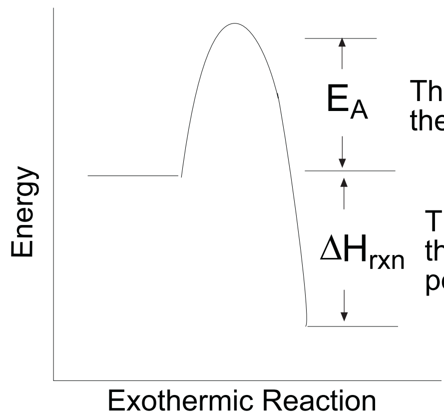
Kinetics: Rate of Reaction: Student Review Notes

- **Kinetics is about how quickly or slowly a reaction occurs.**

- It has **nothing to do with the extent to which a reaction** will occur, that's governed by thermodynamics (thermo is the study of the energy of chemical systems). There's a distinction between the probability that molecules will react when they meet each other and, once they do react, how stable the product of their reaction is. The first, the probability that the reaction will occur, has to do with an energy barrier or activation energy that must be overcome in order for the thing to go. The second, the extent of the reaction has to do with the energy difference between the products and the reactants. You can have very stable products (meaning once the reactants turn into products they won't ever go back), but very slow kinetics. This is because of a high activations energy; i.e., very few reactants have enough energy to get over the hump for the reaction to occur. On the other hand, the kinetics of a reaction can be very fast, but the products may not be very stable; therefore the extent of reaction will be low. The bottom line here is that you have to be able articulate the difference between kinetics and thermodynamics (which you'll do later in the year) and what is happening chemically



This energy difference, the Activation Energy, determines the kinetics of the reaction, how fast or slowly it occurs.

This energy difference, the Heat of Reaction determines the thermodynamics and subsequently the equilibrium position (yield) of the reaction.

- The sign convention can be a little confusing. The rate of a chemical reaction is measured by the decrease in concentration (molar concentration) of a reactant or increase in concentration of a product over a certain period of time.

Change in molar concentration of a product → Δ [product]

Change in molar concentration of a reactant → Δ [reactant]

$$\text{rate} = \frac{\Delta\,[\text{product}]}{\Delta\, t} = -\frac{\Delta\,[\text{reactant}]}{\Delta\, t}$$

Change in time → Δ t

← A rate of reaction can never be negative

- Δ, in case you didn't know, refers to change when it's used in an equation. Furthermore, change is always defined as final - initial. That's important because if you do it the other way around, your sign will be messed up. So in chemistry Δ[A] means change in the molar concentration of species A and ΔH, the heat of reaction, means the change in enthalpy between the products and reactants, etc.

- The reaction rate, r, may be found in terms of any species in a reaction. Rates found for different species are related to each other by the stoichiometry of the reaction. Use stoichiometric ratios to relate rates just like you would relate reactants used or products formed.

  For example, look at how the rates of reaction are related for species in a chemical reaction:

$$2\,A + 3B \;\text{<=====>}\; C + 4D$$

$$r_A = \frac{2}{3} r_B = -2\, r_C = -\frac{1}{2} r_D$$

Factors That Affect the Rate of Reaction

A. Contact/interfacial area. The greater degree to which reactants are exposed to each other, the faster the reaction will proceed. An example is starting a fire (combustion of wood) with kindling instead of logs. In chemistry people try to make chemical reactors that maximize the amount of contact the reactants will have--you know they put a stirrer in the cup or something creative like that. Actually there is this one cool thing called a fluidized bed where you blow a gas up through a bunch of little beads, the beads all become airborne and and the whole system looks like its flowing. It's a way of getting as much gas exposed to the beads as possible.

B. Temperature. Generally, increasing temperature will increase the rate of reaction because of two reasons:

1. At higher temperatures, bonds within the reacting molecules are vibrating with more energy and are closer to the breaking point than at lower temperatures. So the molecues themselves are less stable.

2. At higher temperatures the average velocity of molecules goes up, and therefore when potentially reactive molecules collide there is a greater probability that they will react. Getting over the activation barrier has a lot to do with how hard molecules can slam into each other.

C. Presence of a catalyst. Catalysts increase the rate of reaction by placing one or more of the reactants in an environment in which they are more susceptible to chemical reaction. Catalysts lower the activation energy. Lots of times catalysts are metal surfaces in the reaction vessel. Reactants get close to the metal surface and interact with it. Basically the metal surface and the reactant pull on each other weakening the reactant. Now when another reactant comes along and bumps into the one being pulled on the reaction will occur more easily than if the two reactants just ran into each other in free space.

D. Presence of an inhibitor. Opposite of a catalyst. It does what it says it will do. It inhibits the reaction.

E. Concentration of reactants. This is usually the most important factor. A lot of kinetics is about determining a Rate Law for a specific reaction <-- the rate law is how the reaction rate depends upon concentration of reactants:

For example: $aA + bB \longleftrightarrow cC + dD$

Zero order: $r = k$
First order in A: $r = k[A]$
First order in B: $r = k[B]$
Second order in A: $r = k[A]^2$
Second order in B: $r = k[B]^2$
First order in A, first order in B, second order overall: $r = k[A][B]$

} You have to know how a rate law can be determined form different types of experimental data