Chemical Kinetics

I. Basics-
    A. Chemical Kinetics:
        1. The study of reaction rates.
            a. Factors that affect speeds of reactions and in how reactions can be controlled are the main topics of study.
        2. **Rate of reaction** – the speed with which a reaction's reactants disappear and its products form for a given chemical change.
        3. **Mechanism of the reaction**- the series of individual steps that add up to the overall observed reaction.

II. Factors that affect reaction rates-
    A. Basics:
        1. **Chemical nature of the reaction**- the ease with which the bonds can be broken and formed affects the rate of the reaction. Depending the on the nature of the atoms, the speed at which they are broken and formed will differ.
        2. **Ability of the reactants to meet**- the reactants must collide in order for a reaction to take place. This is why most reactions are carried out in liquid solutions or in the gas phase.
        3. **Homogenous reaction**- a reaction in which all of the reactants are in the same phase.
        4. **Heterogenous reaction**- a reaction in which the reactants are in different phases, and they are able to collide only at the interface between the phases. This area of contact determines the rate of the reaction.
            a. The interface area is controlled by the size of the particles of the reactants/
            b. A solid can be pulverized to dramatically increase the surface area.
        5. **Concentration of the reactants**- directly proportional to the rate of the reaction.
        6. **Temperature of the system**- Increase the temp. → increase the rate for most reactions.
        7. **Catalysts**- substances that increase the rates of chemical reactions without being used up.

III. Rates-
    A. Basics:
        1. A ratio of change, in this case concentration, per unit of time.
        2. By convention always positive whether increasing or decreasing.
        3. One equation is:

$$rate\ with\ respect\ X = \frac{conc(t_2) - conc(t_1)}{t_2 - t_1}$$

The units are mol $L^{-1}s^{-1}$.

B. Rates and coefficients:
   1. If the value of a reaction rate with respect to one species is known, the other rates can be determined using the coefficients of a balanced equation for the reaction.
      a. For instance, consider the following equation:

$$A + 2B \rightarrow C + 3D$$

         i. If the rate of A is known to disappear at a rate of 4 mol per second, then the rate of consumption of B must be twice that of A(8 mol per liter second), due to the coefficient found in the balanced equation.
         ii. By the same rationale, the rate of appearance of D must be three times the rate of A(12 mol $s^{-1}L^{-1}$).
         iii. ***NOTE BOTH ARE POSITIVE; THE DISTINCTION IS MADE BY SAYING FORMATION OF FOR PRODUCTS AND CONSUMPTION OF REACTANTS.***
   2. Most reactions slow down as reactants are used up.
      a. Due to the dependency of the rate on the concentrations of the reactants, the rate is not constant throughout the reaction.
      b. **Instantaneous rate**- the rate at which a reactants are consumed at any particular moment.
         i. The instantaneous rate can be determined by calculating the slope at the time in question.(still must be expressed positively)
         ii. If the initial rate of change at time zero, the time and concentration at zero is used as the initial, but for the other point extend the line to the x-axis, and use this x-intercept as the other point.

IV. Rate laws-
  A. Including all reactants:
   1. Proportional to the product of the molar concentrations of the reactants.
      a. the concentrations are raised to the power found in the coefficients.
(not necessarily from the net mechanisms equations, the half reactions must be observed)
   2. **Rate constant**- a constant that accounts for the proportionality of the rate to the concentrations.
      a. Determined experimentally.
   3. **Rate Law**- an expression that is used to calculated the rate of the reaction at any set of known values of concentrations.
      a. Once the rate constant and the exponents are determined, the rate of the reaction can be determined at any concentration of reactants.
  B. You cannot predict the rate law from the overall reaction:
   1. You must have experimental data in order to predict the number of reactants in the rate law, and their exponents.
   2. **Order of the reaction**- an exponent in the rate law corresponding to the reactant.
      a. Occasionally, there is a negative or fractional exponent.

i. Negative exponents indicate a term that should be in the denominator, which means that as the concentration of the species increases, the reaction rate decreases.

3. **Overall order of a reaction**- the sum of the orders with respect to each reactant in the rate law. Just add the individual orders to get the overall.
4. **Zero order reactions-** reactions that have rates that are independent of concentration of any reactant.
   a. Usually a catalyst that is saturated with reactants.
   b. Rate = k.

C. The reaction order must be determined experimentally:
   1. By looking at the rates associated at the differing concentrations of reactants the rate constant and the orders of the reactants can be determined.

V. Integrated rate laws give concentration as a function of time-
A. Basics:
   1. The relationship between the concentration of a reactant and time can be derived from the rate law by integrating the rate law between zero and some specified time.
      a. **First order**- the integral simplifies to

      $\ln \frac{[A_o]}{[A_t]} = kt$ or can be rearranged to yield **[A$_t$] = [A$_o$] e** $^{-kt}$

         i. If a linear plot is desired for the relationship between the concentration and time, rearrange the equation above, and simplify to obtain:

         Ln [A$_t$] = -kt + ln [A$_o$] which is in the form of y = mx + b
      b. **Second order**- starting with the rate = k [B]^2 the equations can be simplified to:

      $$\frac{1}{[B_t]} - \frac{1}{[B_o]} = kt$$

      which is then rearranged to give $\frac{1}{[B_t]} = \frac{1}{[B_o]} + kt$ **in linear form.**

B. Half Life-
   1. A way to describe how fast it reacts. The amount of time required for half of the reactant to disappear. Proportional to reaction rate.
   2. **First order**- $t_{1/2} = \frac{\ln 2}{k}$
   __Note-the half life of first order reactions are independent of concentration.__

3. **Second order**- Dependent on concentration of the reactants.

$$t_{1/2} = \frac{1}{k[React]_o}$$

VI.   Reaction rate theories-

    A. **Collision theory:**

        1. A postulate that the rate of a reactions proportional to the number of effective collisions per second among the reactant molecules.

           a. Effective collisions- a collision that actually yields a product. Dependent on concentration of reactants, kinetic energy and orientation of collisions.

        2. **Activation Energy, E$_a$**-the minimum amount combined kinetic energy that changes the potential energy as the particles hit each other and chemical bonds become reorganized into those of the products.

           a. The kinetic energy must be strong enough to overcome the repulsion felt from overlapping electron clouds and place the atoms in the right positions for bond breaking and bond forming.

               i.   Otherwise the molecules veer away or bounce apart.

        3. Temperature is proportional to the average kinetic energy.

           a. When the temperature is increased, the fraction of molecules that attain the minimum kinetic energy required for the reaction to occur(activation energy).

    B. **Transition state theory:**

        1. Head on collisions result in the slowing down of the colliding molecules. As this happens the kinetic energy is being transferred into potential energy.

           a. Molecules usually fly apart unchanged,

           b. Some undergo a reaction and then products are formed.

        2. **Potential energy diagram**- a way of visualizing the relationship between the activation energy and the development of total potential energy.

           a. The vertical axis is the change in potential energy.

           b. **Reaction coordinate**- the horizontal axis that represents the extent to which the reactants have changed to products.

           c. the activation energy is represented as a "hill" or barrier for the reactants to overcome to transition into products.

        3. **Exothermic reaction**- because the products have lower potential energy than that of the reactants, there is a release of heat during the reaction, therefore a negative enthalpy.

           a. The potential energy is decreasing during these reactions b/c transferred to kinetic energy of products.

        4. **Endothermic reaction**- the potential energy of the products is higher than that of the reactants. Heat must be put into the system in order for the reactants to attain the necessary activation energy to transition into the products. This results in a negative enthalpy.

5. **Transition state**- the unstable chemical species that results upon a successful collision that momentarily exists with partially formed and partially broken bonds. Sometimes referred to as an activated complex.
   a. Corresponds to the highest point on the potential energy diagram.

VII. Activation Energy equations-
  A. Basics:
   1. Arrhenius equation is an equation that relates the rate constant to the activation energy,

$$k = A\,e^{-E_a/RT}$$

In which A→a proportionality constant called the frequency factor,
R→ Gas constant 8.314 J mol^{-1}K^{-1},
T→ temp in Kelvin
k→ the rate constant
   2. Activation energy can be determined graphically. If you manipulate the above equation with natural logs and a little algebra, the following equation results:

$$\ln k = \ln A - \left(E_A/R\right)\,{}^1\!/_T \quad \text{in which the independent x is 1/T;}$$
$$\text{the dependent y is ln k.}$$
   3. If two rate constants can be obtained at two differing temperatures, activation energy can be calculated using the following equation:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

VIII. Experimental rate laws test validity of proposed mechanisms-
  A. Basics:
   1. **Elementary process**- the reaction whose rate law can be written from its own chemical equation, using the coefficients as the exponents for the concentration terms without requiring experiments.
   2. **Mechanism**- the entire series of elementary processes. Most elementary processes are so fast it is impossible to see the reaction, but a theory on how the molecules are formed is done by chemists.
   The overall rate law derived from the mechanism must agree with the observed rate law for the overall reaction.
      a. The elementary processes must be added together to yield the overall reaction.
  B. Rate law for the slowest step determines the experimental rate law:
   1. **Rate determining step** - Also referred to as the rate limiting step, the slowest step of the reaction. The products cannot form faster than this step.

IX.   How catalysts affect rates-
   A.   Basics:
      1.   A substance that changes the rate of a chemical reaction without itself being used up.
         a.   Can speed up a reaction, **positive catalysis**,
         b.   Can slow down a reaction, **negative catalysis.**
      2.   Reduces the activation energy of the reaction, making it easier for the reactants to change into products, allowing a larger fraction of molecules to attain activation energy.
      3.   **Homogeneous catalysts**- exist in the same phase as the reactants.
      4.   **Heterogeneous catalysts**- the catalyst is in a separate phase than the reactants.