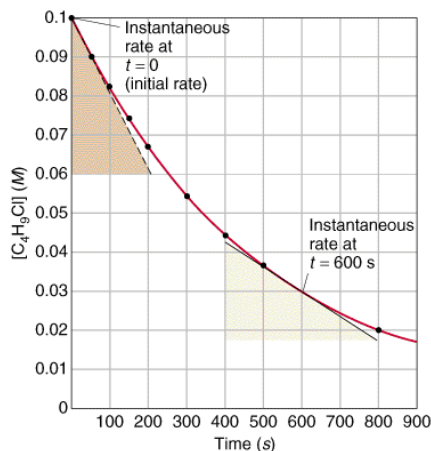


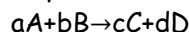
Kinetic!!!!

Reaction Rates:

- The rate of a reaction is customarily taken to mean the change in the concentration of a chemical species over a time interval. The instantaneous rate would correspond to the slope of the tangent line at a particular point of a concentration vs. time plot.



- When chemists say "reaction rate" without saying "respect to" a particular chemical species, they mean it in the way described by this equation, which takes stoichiometric ratios into account:



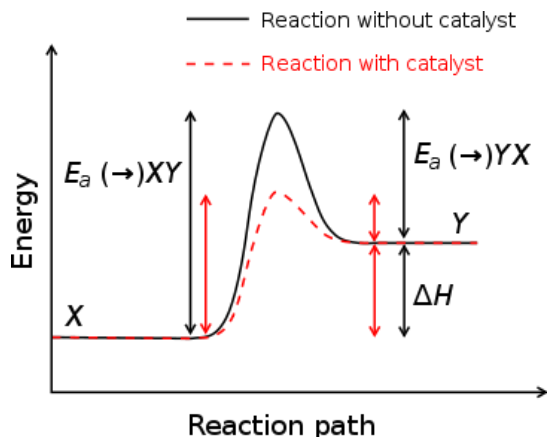
$$\text{Reaction Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Concentration and Rate:

- General form of a rate law: $\text{rate} = k[A]^m[B]^n$
- k is the rate constant, A and B are the reacting species, and m and n are the reaction orders with respect to A and B ; $m+n$ gives the overall reaction order.
- k is temperature dependent.
- Rate laws **MUST** be determined experimentally, or through knowledge of the reaction mechanism.
- In a sense, the rate law is a differential equation that can be solved by the methods of calculus to obtain equations that express concentration as a function of time.
- For first order reactions, the equation is: $\ln[A]_t = -kt + \ln[A]_0$
 $[A]_t$ refers to the concentration at time t , $[A]_0$ is the initial concentration.
- For working with half-life (the time it takes half of a reactant sample to be consumed), solving the above equation gives: $t_{1/2} = \frac{0.693}{k}$
- For a first order reaction, the half-life is independent of initial concentration.
- The equation for a second-order reaction is: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
- For half-life we obtain: $t_{1/2} = \frac{1}{k[A]_0}$
- Here half-life is dependent on initial concentration.

Collision Model:

- Reactions occur as the result of collisions between molecules that utilize their kinetic energy to overcome the activation energy necessary for the reaction.
- Temperature and activation energy both affect the value of the rate constant.
- The fraction of molecules in a sample that possess the necessary activation energy is given by $f = e^{-E_A/RT}$
- R is the ideal gas constant, t is absolute temperature, and E_A is activation energy.
- Also, only some of the colliding molecules will be suitably oriented for reaction to occur. All these variables are taken into account in the Arrhenius equation $k = Ae^{-E_A/RT}$ (A is the frequency factor). Taking the natural log of both sides of this equation, we obtain: $\ln k = -\frac{E_A}{RT} + \ln A$



- To express the relationships between temperature change and the magnitude of the rate constant, use $\ln \frac{k_1}{k_2} = \frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$, where k_1 and k_2 are the two rate constants, and T_2 and T_1 are the two temperatures.

Reaction Mechanisms:

- It is easy to write rate laws for elementary steps; here we CAN use stoichiometric coefficients.
- For multistep mechanisms, you will need to know the slowest elementary step in the reaction; it will be the rate determining step and will dictate the rate law.
- For multistep reactions that have a fast first step and have a rate determining step involving intermediates, assume that equilibrium is established in the fast step. Then, express the concentration of the intermediate in terms of other chemical species.

Catalysts:

- Catalysts are never consumed in chemical reactions.
- Catalysts speed up reactions by lowering activation energy. They can do this in a variety of ways such as providing a completely different mechanism, providing a site for a reaction to occur, stretching bonds, or distorting the charge distribution on a reactant.

Tips:

- Never write a rate law solely based on stoichiometric coefficients.
- Do NOT confuse reaction rate with how thermodynamically favored a particular reaction is. A reaction could have an incredibly negative change in Gibbs free energy, yet still take a long time to occur.
- Termolecular steps (elementary steps involving the collision of three reactant molecules) are very rare and do not often occur.
- Memorize the basic forms of equations. Some other forms can be quickly derived by just taking the log of both sides. Also, many equations can be found in the AP packet.

Worked Examples:

- Consider the combustion of $H_2(g)$: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$. If hydrogen is burning at the rate of 4.6 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor?
 Using our equation, reaction rate = $-\frac{1}{2} \frac{\Delta[H_2]}{\Delta t} = \frac{-\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[H_2O]}{\Delta t}$
 We can see that the rate of disappearance of oxygen is one half the rate of disappearance of hydrogen; therefore the rate of consumption of oxygen = $4.6 \text{ mol/s} (0.5) = 2.3 \text{ mol/s}$. We can also see that the rate of appearance of H_2O is the same as the rate of disappearance of H_2 . Therefore, the rate of appearance of water = 4.6 mol/s .
- Consider the following reaction: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + H_2O(g)$. a.) The rate law for this reaction is first order in H_2 and second order in NO . Write the rate law. b.) If the rate constant for this reaction at 1000K is $6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$, what is the reaction rate when $[NO] = 0.050\text{M}$ and $[H_2] = 0.010\text{M}$?
 a.) Using the definition of a rate law, rate = $k[H_2]^1[NO]^2$.
 b.) We can simply plug values into the rate law: rate = $6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}(0.010\text{M})(0.050\text{M})^2$. We obtain a reaction rate of 1.5 M/s .
- The first-order rate constant for the decomposition of N_2O_5 , $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2$, at 70°C is $6.82 \times 10^{-3}\text{s}^{-1}$. Suppose we start with 0.0300 mol of $N_2O_5(g)$ in a volume of 2.5 L. a.) How many moles of N_2O_5 will

remain after 2.5 minutes? b.) How many minutes will it take the quantity of N_2O_5 to drop to 0.005 mol? c). What is the half-life of N_2O_5 at 70°C ?

- a.) Using the equation $\ln [A]_t = -kt + \ln[A]_0$, we can plug in values. $0.0300 \text{ mol } \text{N}_2\text{O}_5 / 2.5 \text{ L} = 0.0120 \text{ M } \text{N}_2\text{O}_5$, and we have the magnitude of the rate constant. $2.5 \text{ minutes} \times 60 \text{ seconds}/1 \text{ minute} = 150 \text{ seconds}$. Thus, $\ln [A]_t = -(6.82 \times 10^{-3} \text{ s}^{-1})(150 \text{ s}) + (\ln(0.0120 \text{ M}))$. $\ln [A]_t = -5.446 \text{ M s}^{-1}$. Taking base e to both sides, we obtain $[A]_t = 0.0043 \text{ M s}^{-1}$. Multiplying by 2.5 liters, we obtain 0.0108 mol.
- b.) Here we use the same equation, but this time we are solving for t . $0.005 \text{ mol}/2.5 \text{ L} = 0.002 \text{ M}$. $\ln(0.002 \text{ M}) = -(6.82 \times 10^{-3} \text{ s}^{-1})(x \text{ seconds}) + (\ln(0.0120 \text{ M}))$. Solving this equation, we obtain a value of 262.7 seconds, which is equivalent to 4.379 minutes.
- c.) Using the equation for half-life, $t_{1/2} = 0.693 / 6.82 \times 10^{-3}$. The half-life is 101.61 seconds, or 1.69 minutes.
4. Calculate the fraction of atoms in a sample of argon gas at 400K that have an energy of 12.5 kJ or greater. We need to use the equation $f = e^{-E_A/RT}$. $12.5 \text{ kJ} \times 1000 \text{ J}/1 \text{ kJ} = 12,500 \text{ J}$. $f = e^{-12,500 \text{ J}/(8.314 \text{ J/mol}\cdot\text{K})(400 \text{ K})}$. $f = 0.0233$.

Vocab:

Kinetics: study of rates or speeds at which reactions occur.

Reaction rate: the change in concentration of chemical species over time.

rate law: an expression that shows how a reaction rate depends on the concentrations of reactants.

rate constant: the factor in the rate law that is constant (k)

reaction order: the exponents in the rate law

overall reaction order: sum of the exponents in the rate law

first order reactions: a reaction whose rate depends on the concentration of a single reactant raised to the first power.

second order reactions: a reaction whose rate depends on the reactant concentration raised to the second power or on the concentration of two different reactants.

The collision model: a model that explains reaction rates based on kinetic molecular theory in which molecules must collide with sufficient kinetic energy for a reaction to occur.

Activation energy: a minimum energy required to initiate a chemical reaction

Activated complex: the particular arrangement of atoms at the point of highest energy along the entire reaction path.

Frequency factor: the constant term in the Arrhenius equation related to the frequency of collisions and the probability that collisions are favorably oriented.

reaction mechanism: the process by which reactions occur.

elementary steps: reaction processes that occur in a single event or step.

Molecularity: the number of molecules that participate as reactants in an elementary step.

Rate determining step: the step that limits the overall reaction rate

Homogeneous catalyst: a catalyst that is present in the same phase as reacting molecules.

Heterogeneous catalyst: a catalyst that is present in the different phase as reacting molecules.

adsorption: the binding of molecules to a surface.

Active sites: the places where reactant molecules can become adsorbed

Enzyme: a protein molecule that is biological catalyst.

substrate: a substance that undergoes reaction at an enzyme's active site.

Lock-and Key Model: a model of enzyme activity in which the specific shape of the substrate is complementary to the active site so it fits in much like a key fits into a lock.

Sources:

Brown and LeMay Textbook-examples

Images: http://itl.chem.ufl.edu/4411/2041/lec_k.html and http://en.wikipedia.org/wiki/Activation_energy

