

AP Chemistry

Chapter 14 Outline

a. Factors Affecting Reaction Rates

i. Physical state of reactants

1. The more the reactants collide with each other, the faster the reaction rate.
2. If reactants are in different phases, the reaction is limited to the area of contact.
3. [Increasing surface area of a solid](#) increases reaction rate.

ii. [Concentration of reactants](#)

1. If the concentration of one or more reactants is increased, most reactions will go faster, due to an increased frequency of collisions.

iii. Temperature

1. Reactions go faster as [temperature is increased](#).
 - Increasing temperatures increases the kinetic energy of particles.
 - Particles at higher temperatures collide more frequently and with higher energy.

iv. Catalysts

1. Catalysts increase reaction rates without being used up.
2. Catalysts affect the kinds of collisions that lead to reaction.

b. Reaction Rates

i. Reaction rate = the change in concentration of reactants or products per unit time

1. Typical units M/s
2. By convention, reaction rates are always positive

3. For reaction $A \rightarrow B$: *average rate for disappearance of A* = $-\frac{\Delta[A]}{\Delta t}$

ii. Average rate for appearance of B = $\frac{\Delta[B]}{\Delta t}$

iii. Change of rate with time

1. Reaction rates typically slow down as reaction proceeds, because reactant concentrations decrease.
2. [Instantaneous rate](#) = the rate at a particular moment in the reaction = the slope of the curve at the point of interest
3. [Initial rate](#) = the instantaneous rate at $t = 0$

iv. Reaction rates and stoichiometry

1. For reaction $aA \rightarrow bB$: *average rate* = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}$

c. Concentration and Rate

i. To study this, determine the way the initial rate depends on the starting concentrations. ([Method of Initial Rates](#))

1. Hold one reactant constant (ideally, in great excess) and double the concentration of the other reactant, in multiple trials ;

ii. Rate law = shows how rate depends on the concentrations of reactants

1. For reaction $aA + bB \rightarrow cC + dD$
 2. Rate = $k[A]^m[B]^n$
 3. k = rate constant; depends on temperature
- iii. m, n = reaction orders; typically small whole numbers (often 0, 1, or 2) but can be fractional or even negative
1. indicate how the rate is affected by the concentration of each reactant
 2. values of m and n must be experimentally determined
 3. if exponent = 0, then reaction is “zero order” in that reactant
 - changing the concentration of that reactant will have no effect on reaction rate, as long as some of the reactant is present
 4. if exponent = 1, then reaction is “first order” in that reactant
 - if concentration of reactant is doubled, rate will double
 5. if exponent = 2, then reaction is “second order” in that reactant
 - if concentration of reactant is doubled, rate will quadruple
 - overall reaction order = sum of the orders with respect to each reactant
 - Units of rate constants depend on the overall reaction order
 - first order reaction has one “part” to unit: s^{-1}
 - Second order reaction has two “parts” to unit: $M s^{-1}$

d. The Change of Concentration with Time

- i. Rate laws can be converted into equations that give concentrations of reactants or products at any time during the course of the reaction.
- ii. First order reaction of type $A \rightarrow$ products
 1. Rate = $k[A]$
 2. Integrated rate law: $\ln[A]_t = -kt + \ln[A]_o$ MEMORIZE THIS!
 3. **Graphically**: a graph of $\ln[A]_t$ vs. time gives a straight line with a slope of $-k$ and a y intercept of $\ln[A]_o$
 - A reaction that is not first order will not yield a straight line in this graph
- iii. Second order reaction of type $A \rightarrow$ products
 1. Rate = $k[A]^2$
 2. Integrated rate law: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$ MEMORIZE THIS!
 3. **Graphically**: for a second order reaction, a plot of $1/[A]_t$ vs. t will give a straight line with a slope equal to k and a y intercept equal to $1/[A]_o$
- iv. **Half-life** = $t_{1/2}$
 1. Time required for the concentration of a reactant to reach one-half its initial value
 2. Convenient way to describe how fast a reaction occurs, particularly for first order reactions
 - For a first order reaction: $t_{1/2} = \frac{0.693}{k}$ MEMORIZE THIS!
 - The half life of a first order reaction does not change as concentration decreases!

3. For second order reactions, the half-life changes as the reaction progresses

- For a second order reaction: $t_{1/2} = \frac{1}{k[A]_o}$

e. Temperature and Rate

i. The [rate constant](#), and the rate of the reaction, increases dramatically with temperature—nonlinear!.

ii. Collision theory

1. Molecules must collide to react.

2. As molecules move faster, they collide more forcefully and more frequently.

3. Only a tiny fraction of collisions leads to reaction.

- Molecules must be oriented in a certain way (an “[effective collision](#)”) during a collision in order for a reaction to occur.

- Ineffective collisions do not lead to products.

4. Molecules must possess a [certain minimum amount of energy](#) in order to react.

- Kinetic energy of the molecules can be used to stretch, bend, and break bonds, leading to products.

- Reactants must have a total kinetic energy equal or greater to some minimum energy, called the [activation energy, \$E_a\$](#)

- The value of the activation energy varies for each reaction.

- Activated complex = [transition state](#) = the particular arrangement of atoms at the top of the barrier as bonds are broken and new bonds form

iii. Arrhenius equation—relates activation energy, number of collisions, and fraction of effective collisions

1. $k = Ae^{-E_a/RT}$ MEMORIZE THIS!

- A is the frequency constant—deals with number and effectiveness of collisions—nearly constant with temperature

- Reaction rates decrease as activation energy increases.

- Activation energy can be determined graphically: [plot \$\ln k\$ vs. \$1/T\$](#) :

2. $\ln k = -\frac{E_a}{RT} + \ln A$ MEMORIZE THIS!

i. Measure k at a series of temperatures, calculate E_a from the slope of the resulting line (slope = $-E_a/R$)

f. Reaction Mechanism

i. Reaction mechanism = the process by which a reaction occurs

ii. Elementary reaction = elementary step = processes that occur in a single event or step

1. Molecularity of a reaction = the number of molecules that are reactants in an elementary step

- [Unimolecular](#) = single molecule as reactant

- [Bimolecular](#) = collision of two molecules as reactant

- [Termolecular](#) = simultaneous collision of three molecules; rare!

iii. [Multistep mechanism](#) = sequence of elementary steps

1. The elementary steps must add up to the balanced equation for the overall process

2. Intermediate = formed in one elementary step and consumed in another step
- iv. If we know that a reaction is an elementary step, then we know its rate law!
 1. Unimolecular = first order
 2. Bimolecular = second order
- v. Often, one step in a multi-step mechanism is much slower than the others = [rate determining step](#).
 1. The overall rate of the reaction cannot be faster than its slowest step.
 2. *The rate limiting step governs the rate law for the overall reaction.*
 3. The proposed mechanism must be consistent with the observed rate law!
 4. If the RDS involves an intermediate formed in a previous step, express the concentration of the intermediate in terms of the reactants in that previous step by assuming that an equilibrium is involved

g. Catalysis

- i. [Catalyst](#) = substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself
 1. Homogeneous catalyst = in same phase as the reacting molecules
 2. Catalysts do not appear in the overall balanced chemical equation for the reaction (may be written over the arrow, however); present at the beginning of the reaction
 3. Catalysts may change either the activation energy or the frequency factor in the Arrhenius equation
 - The most dramatic differences come from [activation energy changes](#)
 - i. Usually, by providing a completely different mechanism for the reaction
- ii. Heterogeneous catalyst = exists in a different phase from the reactant molecules; often solids
 1. Initial step = adsorption (binding of molecules to surface), because of unused bonding capacity of atoms or ions at surface of solid
- iii. Enzymes are an important class of proteins that serve as biological catalysts
 1. Selective: only catalyze very specific reactions
 2. Active site = specific location in enzyme where reaction occurs
 3. Lock and key model
 4. [Enzyme-substrate complex](#)
 5. Enzyme inhibitors bind strongly to the active site and block entry of the substrate