

AP Chemistry Ultimate Study Guide

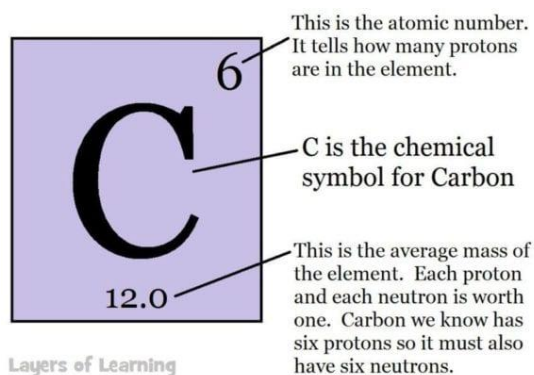
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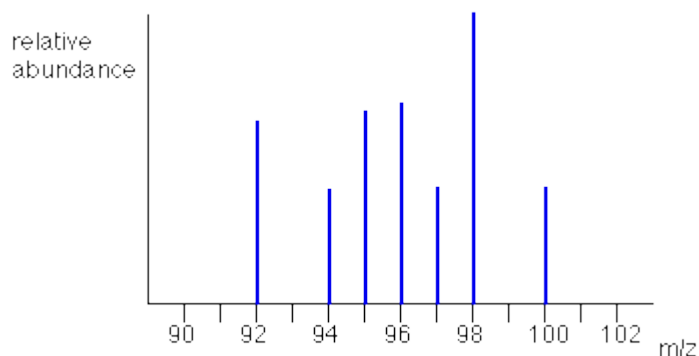
PLEASE, DO NOT LOSE THIS STUDY GUIDE AND REMEMBER TO STILL STUDY YOUR NOTES! I DO NOT KNOW WHAT IS ON THE TEST AND ALL INFORMATION INSIDE IS INCLUDED BASED ON PURE SPECULATION. I AM NOT RESPONSIBLE FOR ANY IRRELEVANT, MISLEADING OR OTHERWISE FALSE INFORMATION!

The Building Blocks of Matter

The Periodic Table



- The horizontal rows of the periodic table are called **periods**
- The vertical columns of the periodic table are called **groups**
- The identity of an atom depends on the number of protons that it has
- An atom's mass number is the sum of its neutrons and protons
- **Isotopes** are elements with different numbers of neutrons



- The abundance of isotopes of an element can be determined via **mass spectrometry**
- The molar mass of an element is the weighted average of its isotopes

Moles

- **Avogadro's number** describes the amount of atoms per a single mole of an element
 - 6.02×10^{23}
- If 1 carbon atom has a mass of 12 amu, then 1 mole of carbon atoms has a mass of 12 grams
- You can use the ideal gas equation to calculate the moles of a gas given its physical properties

$$\text{Moles} = \frac{PV}{RT}$$

- P = Pressure (atm)
- V = Volume (L)
- T = Temperature (K)
- R = Gas constant (0.0821 L*atm/mol*K)
- At **STP**, P = 1 atm and T = 273 K
 - One mole of gas always occupies 22.4 L

$$\text{Moles} = \frac{\text{liters}}{22.4\text{L/mol}}$$

Molarity

- Expresses the concentration of a solution in terms of volume
- Expressed in brackets
 - [O₂]

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

Percent Composition

- Represents the percent mass of each element in a compound
- Calculated by dividing the mass of each element present by the substance's total molar mass

EXAMPLE

Carbon: $6 \times 12.01 = 72.06$

Hydrogen: $12 \times 1.01 = 12.12$

Oxygen: $6 \times 16.00 = 96$

Total: $72.06 + 12.12 + 96 = 180.18 \text{ g/mol}$

C: $72.06/180.18 \times 100\% = 40.00\%$

H: $12.12/180.18 \times 100\% = 6.73\%$

O: $96/180.18 \times 100\% = 53.28\%$

$40.00 + 6.73 + 53.28 = 100.01\%$ (Close enough when accounting for rounding)

Empirical and Molecular Formulas

- The empirical formula represents the simplest ratio of elements in a compound
- The molecular formula represents the most likely formula for the substance

Coulomb's Law

- An atom's positively-charged nucleus is constantly pulling at its negatively charged electrons
 - The farther that an electron gets from the nucleus, the greater that its potential energy is
- The amount of energy that an electron has can be calculated using Coulomb's Law

$$E = \frac{k(+q)(-q)}{r^2}$$

E = Energy

K = Coulomb's constant

+q = Magnitude of positive charge (nucleus)

-q = Magnitude of negative charge (electron)

r = Distance between charges

- The greater the charge of the nucleus, the more energy the electrons will have
- The coulombic potential of a 1s electron is more negative than that of a higher-orbital electron
 - Thus, the amount of energy needed to remove a 1s electron is greater than that needed to remove a more distant one
 - This is the **binding energy**

Electromagnetic Waves

- When atoms absorb electromagnetic radiation, their electrons can jump to higher electron levels
 - When electrons drop from higher to lower energy levels, their atoms give off electromagnetic radiation

$$E = h\nu$$

E = energy charge (J)

h = Planck's constant (6.626×10^{-34} J s)

ν = frequency (s^{-1})

$$c = \lambda\nu$$

c = speed of light (2.998×10^8 ms $^{-1}$)

ν = frequency (s^{-1})

λ = wavelength (m)

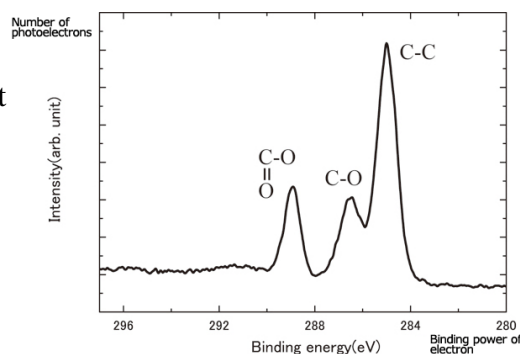
- Higher frequencies and shorter wavelengths = more energy

Photoelectron Spectroscopy

- If exposed to enough electromagnetic radiation, electrons can be ejected from an atom
 - The energy needed to do that is the **ionization energy**
 - Ionization energy = binding energy
 - Measured in electronvolts (1.60×10^{-19} J)
- Any energy that does not go towards ejecting the atom is converted into **kinetic energy**
 - The faster the ejected electron is going, the more kinetic energy that it has
- Electrons that are farther away from the nucleus need less energy to be ejected
 - Thus, they will move faster
- Usually, it takes visible or UV radiation to eject electrons

Photoelectron Spectra

- **Photoelectron spectra** chart the ionization energies for all electrons ejected from an atom
- Binding energy decreases from left to right
- Each peak of the spectra represents a different energy level
 - Within each are subshells



Electron Configuration and Subshells

- Although they are portrayed as such in the Bohr model, electrons do not orbit the nucleus as planets orbit the sun
 - Rather, they are found moving about certain areas in space
 - Thus, orbitals represent the probable are in which the electron is
 - This is called the subshell
- There are four different subshells
 - S subshell
 - 2 electrons
 - P subshell
 - 6 electrons
 - D subshell
 - 10 electrons
 - F subshell
 - 14 electrons
- **The Aufbau Principle**
 - When creating an electron configuration of an atom, electrons are placed in orbitals, shells, and subshells in order of increasing energy
- **The Pauli Exclusion Principle**
 - Two electrons sharing an orbital cannot spin in the same direction
- **Hund's Rule**
 - When added to a subshell, an electron will always occupy an empty orbital if one is available
 - Electrons only pair up if no empty orbitals are available

	1s	2s	2p
Boron	↑↓	↑↓	↑
Carbon	↑↓	↑↓	↑↑
Nitrogen	↑↓	↑↓	↑↑↑
Oxygen	↑↓	↑↓	↑↓↑↑
Fluorine	↑↓	↑↓	↑↓↑↓↑
Neon	↑↓	↑↓	↑↓↑↓↑↓

Predicting Ionic Charges

- The most stable configuration is one in which the outermost energy levels are full
 - Totals up to 8 for s p shells (2 in s, 6 in p)
- The electrons in the outermost s and p subshells are called the **valence electrons**
- Elements that are close to having a full energy level tend to gain electrons
 - Others that are farther away from that, such as the alkali metals, tend to lose electrons
- An **ion** is an atom which has lost/gained electrons
 - An **anion** is an atom with more electrons than proton
 - A **cation** is an atom with more protons than electrons
- All transition metals lose electrons to form cations
 - This depends on the compound that they're in
 - Transition metals lose higher-level s electrons before losing lower-level d electrons

Periodic Trends

- **Moving left to right across a period causes the atomic radius to decrease**
 - Protons are added to the nucleus, causing the valence electrons to be more strongly attracted to the nucleus
 - Although electrons are added, they have little shielding effect since they're all in the same shell, the same distance from the nucleus
- **Moving down a group causes the atomic radius to increase**
 - Shells of electrons are added to the nucleus
 - Protons are also added, but the shielding effect of the added electrons cancels out the positive charge
- **Cations are smaller than uncharged atoms**
 - When electrons are removed from an atom to make a cation, the outer shell is lost
 - This causes the cation's atomic radius to decrease
 - Electron-electron repulsions are also reduced, allowing the remaining electrons to get closer to the nucleus
- **Anions are larger than uncharged atoms**
 - When electrons are added to an atom to form an anion, electron-electron repulsions increase
 - This causes the valence electrons to move farther apart, increasing the radius
- **Moving left to right across a period causes ionization energy to increase**
 - As protons are added to the nucleus, its charge is increased
 - This increases the pull on the electrons, increasing the amount of energy needed to eject them
- **Moving down a group causes ionization energy to decrease**
 - Shells of electrons are added to the nucleus
 - Each shell shields the more distant ones, reducing the nucleus' pull

- **The 2nd ionization energy of an atom is greater than its 1st**
 - When an electron is removed from an atom, electron-electron repulsion decreases and the remaining electrons move closer to the nucleus

Electronegativity

- **Electronegativity** refers to the how strongly that an atom's nucleus attracts the electrons of other bonded atoms
- The smaller an atom is, the farther out that its nuclear charge will be felt and the higher its electronegativity will be
- The closer that an element is to having a full energy level, the more likely it is to attract more electrons
- Since helium, neon, and argon do not form bonds, their electronegativity decreases

Bonding and Phases

Ionic Bonds

- Ionic solids are held together by the attractions between ions that are next to each other
 - Held in a lattice structure
- In ionic bonds, electrons are not shared
 - Instead, the cation gives up one or more electrons to the anion
- The two atoms are held together by electrostatic forces
 - These forces are very strong
 - Thus, most substances held together by ionic bonds tend to be solid at room temperature, and have very high boiling/melting points
- Two factors affect the melting points of ionic substances
 - The charge of electrons is a primary factor
 - According to coulomb's law, greater charge = greater bond energy
 - Thus, a compound composed of ions with charges of +2 and -2 will have a higher melting point than a compound with charges of +1 and -1
 - If both compounds are made up of ions with equal charges, then size must be considered
 - Smaller ions will have greater Coulombic attraction
 - Size is inversely proportional to bond energy
- Each electron is localized around a particular atom
 - Electrons do not move about the lattice
 - Thus, the compound is a poor conductor
- However, ionic liquids conduct electricity since the electrons can move around in the liquid phase

Metallic Bonds

- The positively charged core of a metal is usually stationary, while its valence electrons are very mobile
- Metals can bond with one another to form an alloy
 - In **interstitial alloys**, metal atoms with vastly different radii combine
 - In **substitutional alloys**, metal atoms with similar radii combine

Covalent Bonds

- In a covalent bond, two atoms share electrons
 - From this, both achieve complete valence shells
- Although double and triple bonds are stronger than single bonds, they are not twice nor triple the strength

Bond Type	Single	Double	Triple
Designation	1 sigma (σ)	1 sigma (σ) and one pi (π)	1 sigma (σ) and two pi (π)
Order	One	Two	Three
Length	Longest	Immediate	Least
Energy	Least	Immediate	Greatest

Internuclear Distance

- The length of a covalent bond depends on the balance of repulsive and attractive forces
 - The minimum potential energy will occur when both forces are balanced
- When dealing with potential energy, the more negative the value is, the lower the energy
- The bond length of any covalent bond will occur at the point of minimum potential energy

Network/Covalent bonds

- In a network solid, atoms are held together in a lattice of covalent bonds
 - These solids are very hard, and have high melting/boiling points
- Electrons in a network solid are localized in covalent bonds between atoms
 - Thus, they cannot move about the lattice
 - Many network solids are semiconductors
- **Doping** is a process where impurities are adding to a lattice

Incomplete and Expanded Octets

- Some atoms are stable with less than 8 electrons in their outer shell
 - Hydrogen, helium, boron
- All other atoms require a minimum of 8 electrons to be considered stable
- In molecules with available d subshells, the central atom can have more than 8 valence electrons, but never more than 12

Formal Charge

- To calculate formal charge, subtract the number of valence electrons per atom and subtract the number of assigned electrons
- Lone pairs count as two electrons, and bonds count as one
- The total charge for a neutral molecule should be zero

Molecular Geometry

- When atoms bond to form a molecule, the molecule will assume a shape keeping its electron pairs as far apart as possible
 - Valence shell electron-pair repulsion model (**VSEPR**)
- With the VSEPR model...
 - Double and triple bonds are slightly more repulsive than single bonds and thus will occupy more space than single bonds
 - Lone electron pairs have more repulsive strength than bonding pairs, so molecules with lone pairs will have slightly reduced bond angles

Polarity

- Just because electrons are shared equally in covalent bonds doesn't mean that they are shared equally
- In a **polar covalent** bond, electrons are unequally shared
 - This causes the formation of dipoles
- A **dipole** is an area of negative or positive charge, and is based on the likelihood that electrons from a bond will be found around an atom
- If two identical atoms bond, the atoms can be shared equally
 - This creates a **nonpolar** bond, in which no dipoles are present
- In addition to atoms, entire molecules can also be polar
 - The polarity of a molecule depends on the polarity of its bonds and on its geometry
 - Molecules can be shaped in such a way that the direction of each dipole cancels
- If a molecule is made up of different atoms and there are any lone pairs on the central atom...
 - The molecule is asymmetrical and will be polar
- If there are no lone pairs on the central atom...
 - The molecule is symmetrical and will be polar
- In polar molecules, the central atom generally has a positive dipole, and the terminal atoms have negative dipoles
 - An exception to this is molecules with hydrogen as a terminal atom
- The trigonal planar shape is an exception, as it is almost always nonpolar

Intermolecular Forces

- Intermolecular forces are the forces existing between molecules in a covalently bonded substance
- When ionic substances change phase, the bonds between their individual ions are broken
- When covalent substances change phase, the bonds between their individual atoms remain in place
- **Dipole-Dipole Forces**
 - Occur between polar molecules
 - The positive end of one molecule is attracted to the negative end of another polar molecule
 - Molecules with larger dipole moments tend to have higher melting and boiling points
 - Dipole-dipole attractions are relatively weak
- **Hydrogen Bonds**
 - A special type of dipole-dipole attraction in which positively charged hydrogen atoms become attracted to the negatively charged end of a highly electronegative element
 - F O N
 - Much stronger than normal dipole-dipole forces
- **London Dispersion Forces**
 - LDFs occur between all molecules due to the random motions of electrons on atoms
 - They act as a very weak temporary dipole
 - Molecules with more electrons will experience greater LDFs
 - As molecules gain more electrons, their LDFs become more significant
 - As mass increases, so do the number of electrons and therefore, so does the strength of the LDFs

Bond Strength and Phases

- From order to strongest to weakest are...
 - Hydrogen bonds
 - Non-hydrogen bond permanent dipoles
 - London dispersion forces (temporary dipoles)
- Substances that exhibit weak IMFs tend to be gases at room temperature
- Ionic substances don't experience IMFs
 - Their phase is determined by the ionic bond
 - Thus, they are usually solid at room temperature

Vapor Pressure

- Vapor pressure arises from the fact that liquid molecules are constantly in motion
 - If they hit the liquid's surface with enough kinetic energy, they can escape into the gas phase
- No outside energy needs to be added for vaporization to occur
- The higher a liquid's temperature is, the faster its molecules are moving and thus the more likely that they are to break free
- If two liquids are the same temperature, vapor pressure chiefly depends on the strengths of their IMFs
 - The stronger that their IMFs are, the less likely that the molecules are to escape the liquid

Solutes and Solvents

- **Like dissolves like**
 - Polar/ionic solutes dissolve in polar solvents
 - Nonpolar solutes dissolve in nonpolar solvents
- When an ionic substance **dissociates**, it breaks up into ions
 - Free ions in a solution are called electrolytes because they are electrically conductive
- The more ions present in an ionic compound, the greater its conductivity will be post-dissociation

Chromatography

- Through the process of **chromatography**, a mixture is separated by being passed through a medium in which its constituent parts move at different rates
- Most chemical solutions (for example, pen ink) are made up of a number of covalent substances
 - Each substance has its own polarity value
- **Paper Chromatography**
 - A piece of paper is suspended in a solvent
 - The substance in question is dotted onto the paper
 - As it climbs the paper, its different parts move at different rates
 - The farthest substance experienced the strongest attractions and thus was the most polar
 - Paper chromatography is most useful with colored substances
 - The distance traveled is measured by the retention/retardation factor, R_f

$$R_f = \frac{\text{Distance traveled by solute}}{\text{Distance traveled by solvent front}}$$

- **Column Chromatography**

- A column is packed with a stationary substance
- The solution to be separated (the analyte) is injected into the column
 - After it, the eluent is injected
- As the eluent passes through the stationary substance in the column, it attracts the analyte's molecules
 - However, these are attracted at varying strengths
 - The more attracted that the analyte molecules are to the eluent, the faster that they move through and leave the column
- Ideally, each substance will leave the column at a different time, allowing them to be separated

Distillation

- Distillation takes advantage of the differing boiling points of substances to separate them
- Gases run through the condenser, and condense back into liquid form as the distillate
- Since it works off of boiling points, color doesn't matter for distilled solutions
 - However, keeping the flask at a steady, constant temperature can be difficult

Kinetic Molecular Theory

- According to the kinetic molecular theory, the following assumptions about ideal gases can be made
 - An ideal gas' kinetic energy is directly proportional to its temperature
 - Greater temperature = greater average kinetic energy
 - If several different gases are present in the same sample, all will have the same average kinetic energy
 - The volume of ideal gas particles is insignificant compared to the volume of its container
 - There are no attractive forces between ideal gas molecules
 - Ideal gas molecules are constantly in motion, colliding with each other and the walls of their container, yet not losing energy

Average Kinetic Energy of an Ideal Gas Molecule

$$KE = \frac{1}{2}mv^2$$

m = molecular mass (g)

v = molecular speed (m/s)

KE = joules

Effusion

- Effusion is the rate at which a gas will escape from a container through microscopic surface holes
- The rate at which gas particles effuse is dependent on their speed
 - Faster particles are more likely to effuse
 - Gases with lower molar masses are likely to effuse first

The Ideal Gas Equation

The Ideal Gas Equation

$$PV = nRT$$

P = gas pressure (atm)

V = volume of gas (L)

n = moles of gas

R = gas constant (0.0821 L*atm/mol*K)

T = absolute temperature of gas (K)

The Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

P = gas pressure (atm)

V = gas volume (L)

T = absolute temperature of gas (K)

- If volume is constant, as pressure increases, so does temperature
 - As temperature increases, so does pressure
- If the temperature is constant, as pressure increases, volume decreases
 - As volume increases, pressure decreases
 - This is **Boyle's Law**
- If the pressure is constant, as temperature increases, volume increases
 - As volume increases, temperature increases
 - This is **Charles' Law**

Dalton's Law and Density

- States that the total pressure of a gaseous mixture is the sum of the partial pressure of its constituent gases
- Partial pressure is directly proportional the number of moles present
 - This, represented by X, is called the mole fraction

Dalton's Law

$$P_{total} = P_a + P_b + P_c + \dots$$

Partial Pressure

$$P_a = (P_{total})(X_a)$$

$$X_a = \frac{\text{moles of gas A}}{\text{total moles of gas}}$$

Density of a Gas

$$D = \frac{m}{V}$$

D = density

m = mass of gas (g)

V = volume occupied by gas (L)

Reactions and Energy Changes

Types of Reactions

- Synthesis reaction
 - Elements/simple compounds are combined to form a single and more complex compound
- Decomposition
 - A single compound is split into two or more elements/simple compounds
- Acid-base reaction
 - An acid (H⁺) reacts with a base (OH⁻) to form water and salt
- Oxidation-reduction reaction (redox)
 - A reaction resulting in a change of a participating species' oxidation state
- Hydrocarbon combustion
 - When a covalent substance containing C H O is ignited, it reacts with oxygen in the air
 - Present elements other than C and H combine with oxygen to form various gases
- Precipitation
 - An insoluble salt is sometimes created with two aqueous solutions mix
 - **Spectator ions** start out as free ions and end up as free ions
 - Thus, they don't have much of a role and can be excluded from the net-ionic equation
 - Solubility rules followed by compounds in a precipitation reaction include:
 - Alkali metal cation-containing compounds (Na⁺, Li⁺, K⁺) or an ammonium (NH₄⁺) cation are always soluble
 - Compounds with a nitrate (NO₃⁻) anion are always soluble
 - Ionic substances dissolve in water due to attractions of the ions to water dipoles exceeding those of the ions to each other

Enthalpy

- A substance's enthalpy is a measure of the energy released or absorbed when its bonds are broken and formed
 - When bonds are formed, energy is released
 - When bonds are broken, energy is absorbed
- The change in enthalpy occurs over the course of a reaction

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- Exothermic reactions have a negative enthalpy change
- Endothermic reactions have a positive enthalpy change

Catalysts and Energy Diagrams

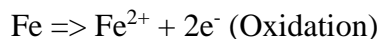
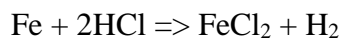
- For the reaction to proceed, the reactants must have enough energy to reach the transition state
 - Activated complex (highest point on the graph)
- The amount of energy needed to reach the activated complex is the **activation energy, E_a**
 - Point with the highest energy and lowest stability
- A catalyst speeds up a reaction by providing the reactants with an alternate pathway that has a lower activation energy
 - The activation energy is lower for a catalyzed reaction
 - However, the catalyst has no effect on the energy of the reactants

Oxidation States

- To determine whether each reactant is gaining or losing electrons, we use an **oxidation state**
- Oxidation state rules:
 - Neutral atoms not bonded to atoms of other elements have oxidation states of zero
 - The oxidation state for any ion is equal to its charge
 - Most of the time, oxygen is -2
 - However, in hydrogen peroxide (H_2O_2), oxygen is -1
 - When bonded to a nonmetal, hydrogen is +1
 - When bonded to a metal, hydrogen is -1
 - If in the absence of oxygen, the oxidation state of the most electronegative element in a substance will take on that of its common charge
 - The combined oxidation states of all elements in a neutral compound must add up to zero

Redox Reactions

- In a redox reaction, electrons are exchanged by reactants as some of their oxidation states change
 - When an atom gains electrons, it is “reduced” and its oxidation number decreases
 - When an atom loses electrons, it is “oxidized” and its oxidation number increases
- If one atom loses electrons, then another must gain them
- A redox reaction can also be written as two **half reactions**
 - One for the reduction, and one for the oxidation



Redox Titrations

- In a titration, a solution at a known concentration is slowly added to another of an unknown concentration
 - To determine the titration's endpoint, a color-changing titrant is often used
- Potassium permanganate, KMnO_4 is commonly used as a titrant
 - Once the compound being oxidized runs out, there are no more electrons left for the titrant to take
 - Thus, any extra ions added remain unreduced

Reduction Potentials

- Every half-reaction has an electric potential
 - Always given as reduction half-reactions, but can be flipped to get oxidation potentials
- When calculating the potential of a redox reaction...
 - Add the potential for the oxidation half-reaction to that of the reduction half-reaction
 - Never multiply the half-reaction's potential by a coefficient

Galvanic Cells

- In **galvanic cells**, favored redox reactions are used to generate a flow of current
- In the cell, the two half-reactions take place in separate chambers
 - The released electrons are sent to the chamber where they are consumed via a wire
- **Current** is the flow of electrons from one place to another
- Oxidation takes place at the **anode** electrode
- Reduction takes place at the **cathode** electrode
- The salt bridge maintains electrical neutrality within the cell
 - Removing the bridge would cause the solutions to become electrically imbalanced and the voltage would drop to 0
 - Through the salt bridge, the ions flow into the cell where they're consumed
- Under standard conditions, the cell's voltage equals the total of its redox reaction

Electrolytic Cells

- In electrolytic cells, outside voltage is used to force an unfavored redox reaction to take place
- Most electrolytic cells occur in aqueous solutions
- The anode and cathode are usually conductive metal bars, and thus do not take part in the reaction
- The total cell potential of an electrolytic reaction, E , is always negative

Electroplating

- Electrolytic cells are also used for electroplating
- To solve an electrolysis problem...
 - Calculate the charge in coulombs if the current and time is known
 - Once you know the charge, find the moles of electrons involved
 - Once you know the moles of electrons and know the half electron, you can find out the moles of metal plated out
 - With the moles of metal plated out, you can use stoichiometry to calculate the grams of metal

Current

$$I = \frac{q}{t}$$

I = current (A)

q = charge (C)

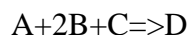
t = time (s)

$$\text{Moles of electrons} = \frac{\text{coulombs}}{96,500 \text{ coulombs/mol}}$$

Reactions and Rates

Rate Law Using Initial Concentrations

- The rate law of a reaction describes the dependence of the initial rate on the concentration of its reactants
 - Includes the Arrhenius constant, k
 - Takes activation energy and temperature into account
- The rate of a reaction is in terms of the rate of appearance of products and the rate of disappearance of reactants



Experiment	Init. Conc. [A]	Init. Conc. [B]	Init. Conc. [C]	Init. Form rate D
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

$$\text{Rate} = k[A]^x[B]^y[C]^z$$

- The greater the value of a reactant's exponent, the more that a change in its concentration will affect the reaction rate
- The easiest way to find the exponents XYZ is to see what happens to the rate when the concentration of each reactant is doubled

Rate Law Using Concentration and Time

- The rate laws will be different depending on the reaction's order
- Zero-Order**
 - The rate of a zero-order reaction doesn't depend on concentration, and it will always be the same at a given temperature
 - A graph of the change in concentration of reactants for a zero-order reaction versus time will be a straight line with a slope equal to $-k$
 - Rate = k
- First-Order**
 - The rate of a first-order reaction depends on the concentration of a single reactant raised to the first power
 - Rate = $k[A]$
 - The rate law uses natural logarithms
 - The slope of the line is $-k$ and the y intercept is $\ln[A]_0$

First-Order Rate Law

$$\ln[A]_t = -kt + \ln[A]_0$$

$[A]_t$ = concentration of reactant A at time t

$[A]_0$ = initial concentration of reactant A

k = rate constant

t = time elapsed

- **Second order**

- The rate of a second-order reaction depends on the concentration of a single reactant raised to the second power
 - $\text{Rate} = k[A]^2$
- The use of inverses creates a linear graph comparing concentration and time
- The slope is given by k and the y-intercept is given by $\frac{1}{[A]_0}$

Second-Order Rate Law

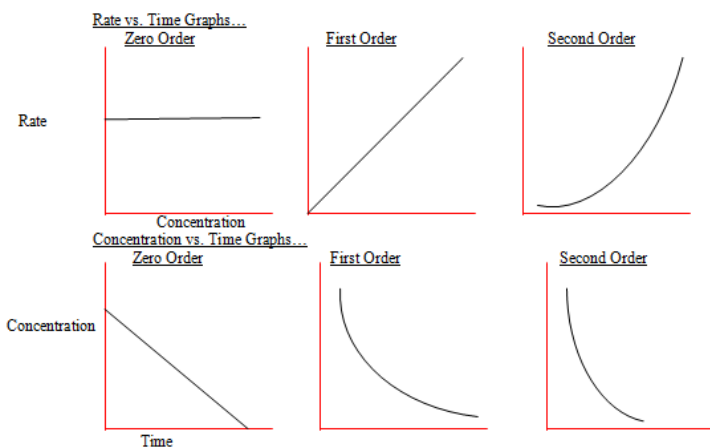
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$[A]_t$ = concentration of reactant A at time t

$[A]_0$ = initial concentration of reactant A

k = rate constant

t = time elapsed



Half-Life

- The half-life of a reactant is the time that it takes for half the substance to react
 - Initial = 100%
 - 1 half-life = 50%
 - 2 half-lives = 25%
 - 3 half-lives = 12.5%

- For a first order reactant, half-life remains constant

$$\text{Half-life} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- For zero/second order reactants, half-life is not constant
 - Their half-lives vary over the course of the reactions
 - You can only use the half-life equation for the first order

Collision Theory

- Collision theory is the idea that chemical reactions occur due to constantly moving reactants colliding with one another
- When reactants collide with enough energy (activation energy, E_a), a reaction occurs
 - Effective collisions lead to chemical reactions
 - Ineffective collisions do not lead to chemical reactions
- At any time during a chemical reaction, a certain fraction of reactants will collide with enough energy to cause a reaction
- For gaseous/aqueous reactants, with increased concentration comes an increased rate of reaction
 - More molecules = higher likelihood of a collision
- For solid reactants, with increased surface area comes an increased rate of reaction
- Stirring can also increase the rate of reaction
 - However, it only increases the reaction rate in a heterogeneous mixture
 - In a **heterogeneous mixture**, all portions are not identical
 - In a **homogeneous mixture**, all portions are identical
- Reaction rate increases with temperature since as temperature increases, so do the speeds of the molecules
 - Thus, the molecules have a greater average kinetic energy
 - At higher temperatures, a larger fraction of reactant molecules have enough energy to exceed the activation energy barrier
- Reactions only occur if reactants collide with the correct orientation

Beer's Law

- You can use a spectrophotometer to measure the concentration of a solution over time
 - It measures the amount of light at a given wavelength absorbed by a solution
 - Absorbance can be calculated via Beer's Law

$$A = abc$$

A = absorbance

a = molar absorptivity

b = path length

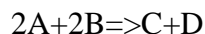
c = concentration

- Beer's law is often interpreted as a direct relationship between absorbance and the concentration of the solution
- Beer's law is most effective with solutions that visible change color over the reaction's course
- A colorimeter is similar to a spectrophotometer, except it can only emit light at specific frequencies

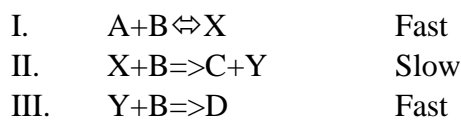
Reaction Mechanisms

- Often, the balanced equation of a reaction is the sum of a series of individual steps, called **elementary steps**
 - An elementary step with two reactants is bimolecular
 - An elementary step with one reactant is unimolecular

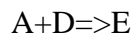
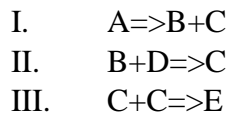
Example



$$\text{Rate} = k[A]^2[B]$$



- Species X and Y are reaction **intermediates** because while they are produced, they are fully consumed over the course of the reaction
 - They also cancel out when adding up the elementary steps in a reaction



- By adding up the elementary steps, you end up with a balanced overall equation
- The speed of the process cannot be faster than that of its slowest step
 - Thus, the slowest step is called the **rate-determining step**

Example

I.	$A + A \rightleftharpoons X$	Rate = $k[A]^2$	Fast
II.	$X + B \Rightarrow Y$	Rate = $k[X][B]$	Slow
III.	$Y + B \Rightarrow D$	Rate = $k[Y][B]$	Fast

- The reaction's rate law is equal to that of its slowest elementary step
- $[X]$ is equivalent to $[A]^2$
- If $[A]^2$ is substituted for $[X]$, step II's rate law becomes Rate = $k[A]^2[B]$
 - This is the overall rate for the reaction
- You can only use the coefficient method to determine the rate law of elementary steps
 - The only way to use this method for the full reaction is by knowing which elementary step is the slowest, and applying the method to that step

Energy Diagrams and Catalysts

- Energy diagrams are graphical representations that show the energy levels of the products and reactants, along with the required activation energy for the reaction to occur
 - Can be broken down to examine the energy change for each step
- Catalysts increase the rate of reaction without being consumed
 - They are present both before and after the overall reaction
 - They cancel out of the overall reaction, but are present in elementary steps

Thermodynamics and Change

Heat and Temperature

- Temperature represents the average kinetic energy of a substance
- Heat represents the flow of energy between two substances of varying temperatures
- According to the **first law of thermodynamics**, energy cannot be created, nor can it be destroyed
- In an exothermic process, energy is released from the reaction into its surroundings
- In an endothermic process, energy is taken in by the reaction from its surroundings

State Functions and Standard State Conditions

- **State functions** depend only on the change between the initial and final states of a system, not on the process by which it occurs
 - This includes enthalpy change (ΔH), entropy change (ΔS), and free-energy change (ΔG)
- Standard state conditions:
 - All gases are 1 atm
 - All liquids and solids are pure
 - All solutions are at 1M concentration
 - The energy of formation of an element in its normal state is zero
 - The temperature used is almost always room temperature (25°C, 298K)
- A thermodynamic quantity under standard conditions is indicated by a superscript circle
 - ΔH°

Enthalpy of Formation (ΔH_f°)

- Enthalpy of formation is the energy change produced when one mole of a compound is formed from its pure components under standard state conditions



- In any enthalpy formation equation, there is always exactly one mol of product
 - If the product contains an odd number of atoms for a naturally diatomic element, you should use halves to balance the equation
- ΔH_f° for a pure element is zero
 - If ΔH_f° for a compound is negative, energy is released when it is formed from pure elements
 - The product is more stable than its constituent elements
 - Exothermic

- If ΔH_f° for a compound is positive, energy is absorbed when it formed from pure elements
 - The product is less stable than its constituent elements
 - Endothermic

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants}$$

- ΔH describes the energy change in a reaction when it goes to completion
 - Commonly written in $\text{kJ/mol}_{\text{rxn}}$
 - Negative when releasing heat (exothermic)
 - Positive when absorbing heat (endothermic)
- Combustion is always an exothermic process
 - The enthalpy of combustion describes the amount of energy released when one mole of a hydrocarbon combusts
 - Once more, we use halves to balance odd diatomic elements

Bond Energy and Hess' Law

- Bond energy is the amount of energy needed to break a bond
 - This number is always positive, since the breaking of bonds is an exothermic process
- When a bond is formed, energy equal to its bond energy is released

$$\Delta H^\circ = \Sigma \text{Bond energies of bonds broken} - \Sigma \text{Bond energies of bonds formed}$$

- Hess' Law states that if a reaction can be described as a series of steps, then its overall ΔH is simply the sum of the ΔH values for every step

Enthalpy of Solution

- Whenever an ionic substance dissolves in water, it emits or absorbs a certain amount of heat
 - Energy is required to break the bond between the anion and the cation
 - Energy is released when ions form new attractions to the water dipoles
- This process can be broken into three steps
 - Breaking solute bonds
 - Bonds between Na^+ and Cl^- ions must be broken
 - The energy needed for this is equal to the lattice energy
 - Since energy is needed to break the bonds, this step's ΔH value is always positive
 - Separating solvent molecules
 - Water molecules must spread out to make room for the ions
 - Since this requires energy for the bonds to weaken, ΔH is positive

- Creating new attractions
 - Free floating ions are attracted to water dipoles
 - Even though no bonds are formed, energy is still released, resulting in a negative ΔH
- The energy values for steps 2-3 are combined as the **hydration energy**
 - This is always negative
 - Since it is also a coulombic energy, hydration energy increases as the ions increase in charge, or decrease in size
- If you add the enthalpy values for all three steps together, you can determine the solution's enthalpy

Thermodynamics of Phase Change

- Phase changes occur due to changes in temperature and pressure
 - They are always physical, and do not involve the creation of new substances or the breaking of bonds
- The pressure exerted by molecules escaping a liquid/solid solution to the gas phase is the **vapor pressure**
 - When the liquid/solid phase of a substance is in equilibrium with the gas phase, the gas' pressure will equal the vapor pressure
 - Vapor pressure increases with temperature

<i>Solid to liquid</i>	Melting
<i>Liquid to solid</i>	Freezing
<i>Liquid to gas</i>	Vaporization
<i>Gas to liquid</i>	Condensation
<i>Solid to gas</i>	Sublimation
<i>Gas to solid</i>	Deposition

Heat of Fusion/Vaporization

- The **heat of fusion** is the energy needed to melt a solid
 - This is needed to overcome the forces holding the solid together
 - Alternatively, it's the heat given off by a solution when it freezes
- The **heat of vaporization** is the energy needed to turn a liquid to a gas
 - This is needed to overcome the forces holding the liquid together
 - It is alternatively the heat given off by a solution when it condenses
 - When a gas condenses into a liquid, intermolecular forces become stronger and energy is released

Calorimetry

- The **specific heat** of a substance is the amount of heat needed to raise the temperature of one gram of the substance by one degree Celsius
- Substances with high specific heats can absorb lots of energy without changing much in temperature

Specific Heat

$$q = mc\Delta T$$

q = heat added (J or cal)

m = substance mass (g or kg)

c = specific heat

ΔT = temperature change (K or C)

- **Calorimetry** is the measurement of heat changes during a chemical reaction
 - Determining heat transfer can lead to determining a reaction's enthalpy

Entropy

- **Entropy** is the measure of disorder in a system
 - Greater disorder = greater entropy
 - All substances have an entropy value greater than zero

$$\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

- Entropy rules
 - Liquids have higher entropy than solids
 - Gases have higher entropy than liquids
 - Particles in a solution have higher entropy values than solids
 - Two moles of a gaseous substance have a higher entropy than one

Free Energy

- The **Gibbs free energy** of a process of whether or not it can proceed without the input of outside energy
 - A process that doesn't need outside energy to complete is thermodynamically favored (spontaneous)
 - A process that needs outside energy to complete is thermodynamically unfavored (nonspontaneous)
- The standard free energy of a reaction can be calculated from the standard free energies of formation (ΔG°_f)

$$\Delta G^\circ = \Sigma \Delta G^\circ_{f\text{products}} - \Sigma \Delta G^\circ_{f\text{reactants}}$$

- If ΔG is negative, the reaction is thermodynamically favored
- If ΔG is positive, the reaction is thermodynamically unfavored
- If $\Delta G = 0$, the reaction is at equilibrium

Free Energy, Enthalpy, and Entropy

- Reactions generally move towards a state of low energy and high disorder over time
 - Thus, thermodynamically favored processes must result in a decrease in enthalpy, an increase in entropy, or both
- At low pressure, enthalpy is dominant
- At high temperature, entropy is dominant

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

T = absolute temperature (K)

ΔH	ΔS	T	ΔG	Favorability
-	+	Low High	- -	Always favored
+	-	Low High	+ +	Never favored
+	+	Low High	+ -	Not favored at low temperatures Favored at high temperatures
-	-	Low High	- +	Favored at low temperatures Not favored at high temperatures

Voltage and Favorability

- A redox reaction will be favored if its potential is positive
- A reaction that is favored has a negative value for free energy change

$$\Delta G^\circ = -nFE^\circ$$

ΔG° = Standard Gibbs free energy change (J/mol)

n = moles of electrons exchanged in rxn (mol)

F = Faraday's constant (96,500 coulombs/mol)

E° = Standard reduction potential (V, J/C)

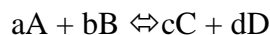
- If E° is positive, ΔG° is negative and the reaction is thermodynamically favored
- If E° is negative, ΔG° is positive and the reaction is thermodynamically unfavored

Equilibrium, Acids and Bases, Titrations, and Solubility

The Equilibrium Constant, K_{eq}

- A reaction is at equilibrium when the rate of the forward reaction is equal to that of the reverse reaction
- The relationship between the concentrations of reactants and products in a reaction at equilibrium is represented by the **equilibrium expression**
 - This is also known as the **Law of Mass Action**
 - It tells you the relative amounts of products and reactants at equilibrium

The Equilibrium Expression



$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Expression rules:
 - [A], [B], [C], and [D] are molar concentrations/partial pressures at equilibrium
 - Products are in the numerator, reactants are in the denominator
 - Coefficients in the balanced equation become exponents in the equilibrium expression
 - Solids and pure liquids are not included since they cannot change in concentration
 - Only gaseous and aqueous species are used
 - Units are not given for K_{eq}
- Other equilibrium constants
 - K_c is the constant for molar concentrations
 - K_p is the constant for partial pressures
 - K_{sp} is the solubility product
 - Has no denominator, since the reactants are solids
 - K_a is the acid dissociation constant for weak acids
 - K_b is the base dissociation constant for weak bases
 - K_w is the ionization value for water (1×10^{-14})
- You can determine K_{eq} for a reaction by manipulating reactions with known K_{eq} values
 - If you flip a reaction, take the reciprocal of K_{eq} to get the new constant
 - If you multiply a reaction by a coefficient, take K_{eq} to that power to get the new constant
 - If you add two reactions, multiply the constants of those reactions to get the new constant

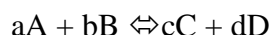
Le Châtelier's Principle

- States that whenever a stress is placed on a system at equilibrium, it will shift in response
 - If the forward rate increases, the reaction has shifted **right**, which will create more products
 - If the reverse rate increases, the reaction has shifted **left**, which will create more reactants
- Concentration
 - When the concentration of a reactant or product is increased, the reaction will shift in the direction that allows it to use up the added substance
 - When the concentration of a reactant or product is decreased, the reaction will shift in the direction that allows it to create more of the removed substance
- Pressure
 - When the external pressure on a system is increased, it will increase the partial pressures of all the gases, and cause a shift to the side with less gas molecules
 - Decreasing the pressure would have the opposite effect
 - Commonly, pressure is changed by increasing or decreasing the size of the container in which the reaction is occurring
 - The partial pressure of a gas can be changed by adding another gas to the container, while also maintaining the total pressure
 - A decreased mole fraction causes a decreased partial pressure, which causes a shift to the left
- Temperature
 - To figure out what happens when the temperature changes, first rewrite the equation to include heat energy on the side that it'd be present on
 - If temperature goes up, the reaction will proceed in the reverse direction
 - This causes a shift away from the added energy
 - Endothermic
 - If temperature goes down, the reaction will proceed in the forward direction
 - This will create more energy
- Dilution
 - For an aqueous equilibrium, diluting it with water can cause a shift
 - This will cause a shift to the side with more aqueous species
 - If water were removed, the reaction would shift to the side with less aqueous species
- Shifts caused by concentration or pressure are temporary
 - Eventually, the concentrations of products and reactants will establish the same ratio that they previously had at equilibrium
- However, shifts caused by temperature changes are different
 - A change in temperature will affect the equilibrium constant for the reaction itself, in addition to causing a shift
 - Thus, increasing temperature decreases the value of K_{eq}
 - The reverse would be true for a temperature decrease

The Reaction Quotient, Q

- The reaction quotient is the quantitative application of Le Châtlier's Principle
 - It is determined using the Law of Mass Action
- The value of Q can be compared to K_{eq} to predict the shift direction of a reaction given its initial conditions

The Reaction Quotient

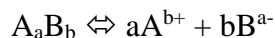


$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- [A], [B], [C], and [D] are initial molar concentrations or partial pressures
- If Q is less than K, the reaction shifts right
- If Q is greater than K, the reaction shifts left
- If Q = K, the reaction is already at equilibrium

The Solubility Product, K_{sp}

- Slightly-soluble and insoluble salts still dissociate to an extent
 - K_{sp} is the measure of the extent of a salt's dissociation in a solution
- The greater the value of K_{sp} , the more soluble that the salt is



$$K_{sp} = [A^{b+}]^a [B^{a-}]^b$$

- The solubility of salts can be described by K_{sp} or by molar solubility
 - Molar solubility describes the number of moles of salt that can be dissolved per liter of solution
- The molar solubility of a salt will also equal the concentration of any ion that occurs in a 1:1 ratio with the salt
- Typically, molar solubility increases with temperature
- According to the **common ion effect**, newly added ions will affect the equilibrium of a solution, even if they didn't come from the original molecule
- In general, when two salts sharing a common ion are mixed, the one with the lower K_{sp} will precipitate first

Standard Free Energy and K_{sp}

- If you know the equilibrium constant expression for a reaction, you can find the amount of Gibbs free energy

$$\Delta G^\circ = -RT \ln K$$

R = gas constant (8.31 J/mol*K)

T = absolute temperature (K)

K = the equilibrium constant

- If ΔG° is negative, K is greater than 1, and the products will be favored at equilibrium
- If ΔG° is positive, K must be less than 1, and the reactants will be favored at equilibrium