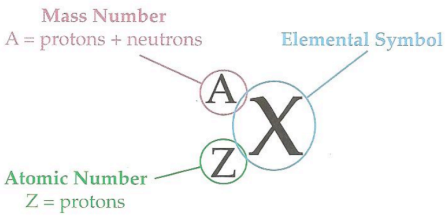
General Chemistry Memorization

CHAPTER 1
Atoms, Molecules and Quantum Mechanics

- Elementary Particles
  - A.

Particle	Charge	Mass (amu)
Proton	Positive (1+)	1.0073
Neutron	Neutral	1.0087
Electron	Negative (1–)	5.5×10^{-4}

- Elemental Descriptions
  - A.



- Isotopes
  - A. Two or more atoms of the same element with different numbers of neutrons
  - B. Same number of electrons
- Nuclide
  - A. Atom of a specific isotope
- Atomic Mass Weight (amu) or Molar Mass (MM)
  - A. Carbon-12 has a mass of 12 amu's
- Moles
  - A. 6.022×10^{23} amu = 1 gram
  - B. Moles = grams/atomic or molecular weight
- Period
  - A. Horizontal row in the periodic table of elements
- Groups/Families
  - A. Vertical columns in the period table of elements
  - B. Atoms tend to make similar bonds and ions
- Metals
  - A. Tend to form positive ions
  - B. Form ionic oxides, i.e. BaO
  - C. Characteristics:
    - 1. Luster
    - 2. Ductile
    - 3. Malleable
    - 4. Thermal conductor
    - 5. Electrical conductor
- Nonmetals
  - A. Lower melting points than metals
  - B. Form negative ions
  - C. Comprise most molecular substances
  - D. Form covalent oxides, i.e.SiO_2
- Metalloids
  - A. Some characteristics of metals and nonmetals
- Alkali Metals, Group 1A
  - A. First family
  - B. Soft, low density and melting point

    - C. Form +1 cations
    - D. VERY reactive
    - E. React with nonmetals to form ionic compounds
    - F. React with hydrogen to form hydrides
- Alkaline Earth Metals, Group 2A
    - A. Second family
    - B. Hard, higher density and melting point (than alkali metals)
    - C. Form +2 cations
    - D. Less reactive than alkali metals
    - E. Within the family, reactivity: heavier > lighter
- Group 4A: Carbon and Rest
    - A. Form 4 covalent bonds with nonmetals
    - B. Only carbon makes triple bonds within this family
- Group 5A: Nitrogen and Rest
    - A. Form 3 covalent bonds
    - B. Except for Nitrogen, all can form 5 covalent bonds (*d* orbitals)
    - C. With a Lewis base, can make 6 bonds
- Chalcogens, Group 6A
    - A. Oxygen reacts with metals to form oxides, i.e. BaO
    - B. Oxygen reacts with alkali metals to form peroxides, i.e. Na_2O_2 and super oxides, i.e. KO_2
- Halogens, Group 7A
    - A. Seventh family (my own interpretation)
    - B. Most are diatomic
    - C. Like to gain electrons
    - D. All react with hydrogen to form gaseous halides
- Noble/Rare/Inert Gases
    - A. Eighth Family (my own interpretation)
    - B. Nonreactive
    - C. All gases at room temperature
    - D. Unlike all other elements, they have endothermic electron affinity values
- Main-Group/Representative Elements
    - A. Section A metals
- Transition Metals
    - A. Section B metals
    - B. When forming ions, lose electrons from *s* subshell first and then *d* subshell and thus can form multiple ions, e.g. Vanadium, V
    - C. Form colored solutions – a result of partially filled *d* orbitals; these electrons can absorb photons and be bumped up to a higher energy orbital
- Diatomics
    - A. Oxygen
    - B. Hydrogen
    - C. Nitrogen
    - D. Halogens
    - E. Heat of Formation
        - 1. The first three and fluorine from the Halogens all have an enthalpy change of zero
- Small atoms
    - A. Tend to be more reactive because they can't stabilize charge
- Cations
    - A. Tend to be smaller
- Anions
    - A. Tend to be larger
- Isoelectric ions
    - A. Same number of ions, different protons
    - B. Get smaller with increasing atomic number (more protons to pull in electrons)

- Density
  - A. The alkali metals have lower density than the alkaline Earth metals (as discussed above)
  - B. In a given sample of elements, the gaseous element will have the smallest density (density = mass/volume)
  - C. When comparing gases, atomic weight and elemental form (single, diatomic, Triatomic, etc) matter
- Periodic Trends
  - A. Decrease across Period; Increase down Group (Max Value: Bottom Left)
    - 1. Atomic Radii
    - 2. Ionic Radii
    - 3. Energy of Valence Electrons
    - 4. Metallic Character
  - B. Increase across Period; decrease down Group (Max Value: Top Right)
    - 1. Effective Nuclear Charge (Z)
    - 2. Electronegativity (X)
    - 3. Ionization Energies (increasingly endothermic)
    - 4. Electron Affinity (increasingly exothermic)
- Atomic Radii
  - 1. Because size gets larger down and to the left, and smaller up and to the right, atoms most similar in size will be down and to the right, or up and to the left
  - 2. Ex: Phosphorous is most similar in size to Selenium
- Effective Nuclear Charge, Z_{eff}
  - A. Because inner electrons shield outer electrons from full force of protons
- Electronegativity
  - A. The tendency of an atom to attract electrons in a bond that it shares with another atom
  - B. Measured in elements partaking in chemical bonds with other elements
- Ionization Energy
  - A. Energy necessary to detach an electron from a nucleus in its gaseous state
- Electron Affinity
  - A. Willingness of an atom to accept an additional electron, i.e. the energy released when an electron is added to a gaseous atom
  - B. Values for noble gases are endothermic
- Bohr's Equation for the Frequency of transmitted light when an electron falls from one orbital of a hydrogen atom to a lower one
  - 1. $E = -A(1/ni^2 - 1/nf^2)$
  - 2. Where A = energy needed to remove an electron from the ground state of a hydrogen atom to an infinite distance from the atom
- Covalent Bond
  - A. Two electrons are shared by two nuclei
- Bond length
  - A. Inversely proportional with bond energy – which is the energy needed to break a bond
  - B. Inversely proportional with bond strength
- Bond dissociation/bond energy
  - A. Energy needed to completely separate two atoms
- Bond Types

HYBRIDIZATION	BOND ANGLES	SHAPE
sp	180°	Linear
sp^2	120°	Trigonal planar
sp^3	109.5°	Tetrahedral, Pyramidal, or Bent
dsp^3	90°, 120°	Trigonal-bypyramidal, Seesaw, T-shaped, Linear
d^2sp^3	90°	Octahedral, Square pyramidal, Square planar

- Compound

- A. Two or more elements in whole number ratios
- Molecules
  - A. The repeating groups of atoms in compounds
  - B. Ionic compounds do not have molecules
- Empirical formula
  - A. Simplest whole number ratio of atoms in a compound
- Molecular Formula
  - A. Representative of all the elemental atoms in a molecule
- Ionic compounds
  - A. Named after their cation or anion, e.g. Copper (II) ion
  - B. Monatomic anions = ide, e.g. Hydroxide
  - C. Polyatomic ions = ite or ate, e.g. NO^{2-} = nitrite and NO^{3-} = nitrate
- Molecular Compounds
  - A. Two nonmetals
  - B. Always has covalent bonds
- Acids
  - A. If name ends in *ide*, it starts with *hydro* and ends in *ic*, e.g. Hydrosulfuric acid
  - B. If an oxyacid, more oxygens = *ic* and less oxygens = *ous*
- Binary molecular compounds
  - A. Compounds with only two elements
  - B. Name begins with element farthest left and down, may get prefix
  - C. Second element gets the *ide*
  - D. Ex: Dinitrogen Tetroxide, N_2O_4
- Physical Reaction
  - A. Maintains the molecular structure
  - B. Ex: melting, evaporation, dissolution, rotation of light
- Chemical Reaction
  - A. Molecular structure changes
  - B. Ex: Combustion, metathesis, redox
- Run to completion
  - A. Moves to the right until the supply of at least one reactant is gone
  - B. Reactions often don't do this because they reach equilibrium first
- Limiting Reagent
  - A. reactant that is completely used up in a reaction and determines when a reaction stops and how much products are made
  - B. Ex: alcohol on spring break
- Theoretical Yield
  - A. The amount of product produced when a reaction runs to completion
- Actual Yield
  - A. The actual amount of product collected
- Percent Yield
  - A. Actual/theoretical x 100% = percent
- Reaction types
  - A. Combination: A + B → C
  - B. Decomposition: C → A + B
  - C. Single Displacement: A + BC → B + AC
  - D. Double Displacement/Metathesis: AB + CD → AD + CB
- Bonding in solids: Crystalline
  - A. Sharp melting point
  - B. Characteristic shape with repeating units
  - C. Classified:
    1. Ionic: electrostatic forces, e.g. salts
    2. Network covalent: infinite network of covalent crystals, e.g. diamond
    3. Metallic: metal atoms bound together by delocalized electrons, e.g. any metal
    4. Molecular: individual atoms held by intermolecular bonds, e.g. ice
- Bonding in solids: Amorphous
  - A. No characteristic shape or melting point (has a melting *range*, not point), e.g. glass
- Polymers

- **A.** Can be crystalline or amorphous, e.g. DNA

- Valence Electrons
  - **A.** Contribute most to an element's chemical properties
  - **B.** Located in the outermost shell of an atom
  - **C.** Most of the time (but no always), only electrons from *s* and *p* subshells are considered valence
- First Quantum Number: Principle Quantum Number, *n*
  - **A.** Designates the shell level
  - **B.** The greater the quantum number, the greater the size and energy of the electron orbital
  - **C.** For the representative elements, the principal quantum number for electron in the outer most shell is given by the period in the periodic table
  - **D.** For the transition elements, the principal quantum number for electron in the outer most shell is given by the period in the periodic table minus one
  - **E.** For the lanthanides and actinides elements, the principal quantum number for electron in the outer most shell is given by the period in the periodic table minus two
- Second Quantum Number: Azimuthal Quantum Number, *l*
  - **A.** Designates the subshell of a given shell
  - **B.** For each new shell, there exists an additional subshell with the Azimuthal quantum number $l = n - 1$
  - **C.** Ex: $n = 1$; $l = 0 = s$ subshell; $l = 1 = p$ subshell; d = 2; f = 3
  - **D.** Subshells: *s*, *p*, *d* and *f*
  - **E.** In each subshell there is a 90% chance of finding the electron inside that shape
  - **F.** Note: *s* subshells are spheres and *p* subshells are dumbbells
- Third Quantum Number: Magnetic Quantum Number, m_l
  - **A.** Designates the orbital of a given subshell of a given shell
  - **B.** Each subshell has orbitals with magnetic quantum numbers from $-l$ to $+l$
  - **C.** Ex 1: $n = 1$, $l = 0$, $m_l = 0$
  - **D.** Ex 2: $n = 2$, $l = 1$, $m_l = -1, 0, 1$
  - **E.** Ex 3: $n = 3$, $l = 2$, $m_l = -2, -1, 0, 1, 2$
- Fourth Quantum Number: Electron Spin Quantum Number, m_s
  - **A.** Designates the direction of spin of the electron in a given orbital of a given subshell of a given shell
  - **B.** m_s can have values of -1/2 or +1/2
  - **C.** Any orbital can hold up to two electrons but no more
  - **D. Pauli Exclusion Principle:** no two electrons in the same atom can have the same four quantum numbers. If two electrons occupy the same orbital, they have the same first three quantum numbers, and thus must have different electron spin quantum numbers
  - **E. Paired**: when electrons are in the same orbital they must have opposite spins
  - **F. Parallel spins**: when electrons in different orbitals happen to have the same m_s value
- Calculations
  - **A.** The number of total orbitals within an atom is equal to n^2
  - **B.** Two electrons in each orbital, so total electrons is equal to $2n^2$
  - **C.**

Number	Character	Symbol	Value
1st	Shell	n	n
2nd	subshell	ℓ	from zero to $n-1$
3rd	orbital	m_l	between ℓ and $-\ell$
4th	spin	m_s	$\frac{1}{2}$ or $-\frac{1}{2}$

- Heisenberg Uncertainty Principle

- **A.** The dual nature (wave-particle) of matter says that there is an inherent uncertainty in the product of the position of a particle and its momentum, and this uncertainty is on the order of Planck's constant $\Delta x \Delta p \oplus h$
- **B.** That is, the more we know about it's <u>position</u>, the less we know about it's <u>momentum</u>

- Aufbau Principle
  - **A.** With each new proton added to create a new element, a new electron is added as well
  - **B.** Because a lower energy system is more stable, a new electron will add to the lowest energy orbital in the lowest subshell
  - **C.** Electrons are attracted to the nucleus → a force has to separate them → requires the transfer of energy into the system → the farther away the electrons, the less energy is needed → the energy of the system moves from negative to zero as the electron moves infinitely far away
- Electron Configuration
  - **A.** List the shells and subshells in order from lowest to highest energy level and add a subscript to show the number of electrons in each subshell
  - **B.** Transition elements have *degenerate* orbitals (same energy level) and thus, with 4s and 3d, may occupy either or; just remember that transition metals don't always follow the given rules
  - **C.** An electron can momentarily absorb energy and jump to a higher energy level creating an atom in an excited state
- Hund's Rule
  - **A.** Electrons will not fill up any orbital in the same subshell until all orbitals in that subshell contain at least one electron and the unpaired electrons have parallel spins
- Planck's Quantum Theory
  - **A.** Electromagnetic energy is quantized
  - **B.** Thus, photons and electrons have quantized energy level
  - **C.** When an electron emits a photon, it falls an energy rung; when it absorbs a photon, it goes up an energy rung; if the photon doesn't have enough energy ($E = hf$), the photon is deflected away and electron stays in its current rung
  - **D.** If a photon doesn't have sufficient frequency, it will never eject an electron, regardless of the number of photons
- Work Function, Φ
  - **A.** The minimum amount of energy required to eject an electron
  - **B.** Kinetic Energy of the ejected electron is given by the energy of the photon minus the work function: $K.E._{electron} = hf - \Phi$

<u>CHAPTER 2</u>
<u>Gases, Kinetics and Chemical Equilibrium</u>

- Standard Temperature and Pressure (STP)
  - A. 0°C and 1 atm
  - B. Speeds at STP are hundreds of meters per second, e.g. oxygen = 481 m/s
- Standard Molar Volume
  - A. One mole of any ideally behaving as will occupy 22.4 liters at STP
- Mean Free path
  - A. Distance traveled by a gas molecule between collisions
  - B. About 1/10,000 of a millimeter
  - C. Billions of collisions per second
- Mixtures
  - A. Unlike liquid, regardless of polarity differences, two different gaseous substances will form a homogenous mixture
  - B. At lower temperatures, gravity will cause the heavier molecules to settle below the lighter molecules
- Ideal Gases: Kinetic Molecular Theory
  - A. Describes the characteristic of an **ideal gas**, like **ideal liquids**, they do not perfectly reflect real gases.
  - B. Mixtures of gases
    - 1. The laws do not change for different gases.
    - 2. Contribute to the pressure in the same proportions as it contributes to the number of moles of gas
  - C. Characteristics of an Ideal Gas
    - 1. Gas molecules have zero volume
    - 2. Gas molecules exert no forces other than repulsive forces due to collisions
    - 3. Gas molecules make completely elastic collisions
    - 4. The average translational kinetic energy of gas molecules is directly proportional to the temperature of the gas; K.E. = 3/2R.T.
  - D. Ideal gas obeys the **Ideal Gas Law:** PV = nRT
    - 1. P = pressure in atm; related to the K.E. per volume
    - 2. T = temperature in Kelvin; related to the K.E. per mole
    - 3. n = number of moles of gas
    - 4. V = volume in liters
    - 5. R = universal gas constant: 0.08206 L*atm/K*mol or 8.314 J/K*mol
    - **Note:** Why can increasing the volume of a gas cool it, when PV = nRT shows that it should heat up? Because the pressure decreases by two as the volume doubles by two. Pressure is related to K.E., so if K.E. also decreased by two, pressure would decrease by more than a factor of two. Thus temperature decreases to maintain equality in PV = nRT.
- Ideal Gases: Special Cases of the Ideal Gas Law

Boyle's Law	Charles's Law	Avogadro's Hypothesis	General Gas Law	Ideal Gas Law
$V \propto (1/P)$	$V \propto T$	$V \propto n$	$P_1V_1/T_1 = P_2V_2/T_2$	$PV = NRT$
(Constant T, n)	(Constant P)	(Constant T, P)	(Constant n)	

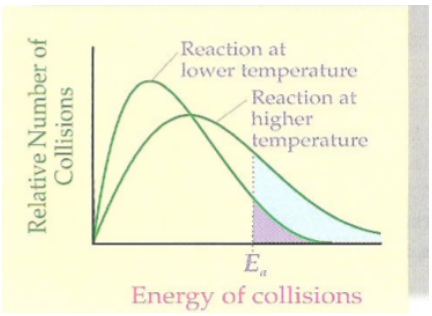
- Ideal Gases: Partial Pressure
  - A. Partial pressure of a particular gas is the total pressure of the gaseous mixtures times the mole fraction of the particular gas
  - B. $P_a = \chi_a P_{total}$
  - C. P_a = partial pressure of gas 'a'
  - D. χ_a = mole fraction of gas 'a' (# moles gas 'a' divided by total # moles of gas in the sample)
- Ideal Gases: Dalton's Law
  - A. Total pressure exerted by a gaseous mixture is the sum of the partial pressures of each of its gases
  - B. $P_a = P_1 + P_2 + P_3 \ldots$
- Ideal Gases: Average Translational Kinetic Energy

- A. $K.E._{avg} = 3/2RT$
- B. Average translational kinetic energy is found from the root-mean-square (rms) velocity = square root of the average of the squares of the molecular velocities
- C. rms velocity slightly > average speed
- D. The Kinetic Energy is inversely related to the temperature; the speed is directly proportional to the square root of the kinetic energy
  - 1. KE = 3/2RT, and…
  - 2. V = sqrt(K.E.)
- E. Remember, this is the *average* K.E. of gas molecule; little to no molecules could have this energy, they vary widely

- Ideal Gases: Graham's Law
  - A. Same temperature means different molecules in a mixture have the same average K.E. but, because they have different masses, they have different rms velocities.
  - B. Setting the two K.E. equal to each other, one can determine the relationship between their rms velocities; more specifically, the ratio
  - C. $V_1/V_2 = sqrt(m_2)/sqrt(m_1)$
    - 1. Dependent upon:
      - a. Molecular weight (directly proportional to effusion rate)
      - b. Pressure
  - D. Pressure vs. Time graph: effusion rate is the slope
  - E. Graham's Law provides information about two types of gaseous spreading: effusion and diffusion
- Ideal Gases: Effusion
  - A. Definition: spreading of a gas from high pressure to very low pressure through a pinhole, an opening much smaller than the average distances between the gas molecules
  - B. Molecules with higher rms velocities will effuse faster
  - C. Calculated: $(\text{effusion rate}_1/\text{effusion rate}_2) = sqrt(m_2)/sqrt(m_1)$
- Ideal Gases: Diffusion
  - A. Definition: the spreading of one gas into another gas or into empty space
  - B. Diffusion rate is much slower than rms velocity because gas molecules collide with each other as they diffuse
  - C. Calculated: $(\text{diffusion rate}_1/\text{diffusion rate}_2) = sqrt(m_2)/sqrt(m_1)$
- Real Gases: Van der Waals Equation
  - A. Predicts how real gases deviate from ideal behavior
  - B. Calculated: $[P + a(n/V)^2](V - nb) = nRT$
  - C. b = measure of the actual volume occupied by a mole of gas
  - D. a = strength of intermolecular attractions
  - E. Values of a and b (usually) increase with the molecular mass of a gas and molecular complexity of a gas
- Real Gases: Deviations
  - A. Volume: Real gas molecules do have volume
    - 1. $V_{real} > V_{ideal}$
    - 2. V_{ideal} is calculated from PV = nRT
  - B. Forces: Real gas molecules exhibit forces on each other
    - 1. Repulsive when very close (minor)
    - 2. Attractive when far apart (major) and are thus pulled toward the center of the container, causing them to slow before they hit the wall (think harmonic motion – kinda) and thus have less pressure: $P_{real} < P_{ideal}$
    - 3. P_{ideal} is calculated from PV = nRT
- Real Gases: Facts
  - A. Deviate from ideal behavior when their molecules are close together
  - B. High pressures (+10 atm) push gas molecules together
  - C. Low temperatures (~boiling points) cause gas molecules to settle close together
- Real Gases: Deviations Explained Even More
  - A. Deviations
    - 1. $V_{real} > V_{ideal}$
    - 2. $P_{real} < P_{ideal}$

- B. Pressure: $P_{real} < P_{ideal}$
  - 1. High pressures (+10 atm) push gas molecules together, causing them to exert weaker outward forces on the container
  - 2. Low temperatures (~boiling points) cause gas molecules to settle close together and thus exert weaker outward force on the container
- C. *MY THEORY, NOT SURE IF TRUE*: Volume: $V_{real} > V_{ideal}$
  - 1. Higher pressures (+100 atm) push gas molecules so close that the actual volumes begin to touch, causing it to resist compression relative to what was predicted
  - 2. Higher temperatures (>>>>boiling points) cause gas molecules to move around so violently they push the container outward farther than what was calculated
- D. Similarity, NOT Deviation
  - 1. RMS velocity of real and ideal gas molecules is directly proportional to the temperature
- E. Remember
  - 1. In a PV/RT = n graph, the numerator is the product of volume and pressure
  - 2. Thus, the deviations will be less or greater than ideal at some points to either $V_{real} > V_{ideal}$ or $P_{real} < P_{ideal}$
  - 3. Positive deviation = molecular volume, very high temperature and pressure, $V_{real} > V_{ideal}$
  - 4. Negative deviation = intermolecular attractions, very low temperature and moderately high pressure, $P_{real} < P_{ideal}$

- Chemical Kinetics
  - A. Definition: study of reaction mechanisms and rates
  - B. Equilibrium:
    - 1. Kinetics deals with the rate of a reaction as it moves *toward* equilibrium...thermodynamics deals with the balance of reactants and products *after* they have achieved equilibrium
    - 2. Kinetics deals with how *fast* equilibrium is achieved…thermodynamics deals with what equilibrium *looks* like
- Collision Theory: Collision Model
  - A. Reacting molecules must collide, but not every collision results in a reaction
  - B. Two requirements:
    - 1. Activation energy: threshold kinetic energy due to relative velocity *only*; that is, velocity away from another molecule decreases the kinetic energy of a collision
    - 2. Spatial Orientation: molecules have to collide just right
- Collision Theory: Arrhenius Equation
  - A. $k = zpe^{-Ea/RT}$ (zpe is often written as Ae)
  - B. z = collision frequency
  - C. p = "steric factor:" fraction of collisions having the effective spatial orientations
  - D. $e^{-Ea/RT}$ = fraction of collisions having sufficient relative energy (where E_a = activation energy)
  - E. k = rate constant of a reaction, dependent on:
    - 1. Pressure – usually negligible
    - 2. Catalysts – [fill in]
    - 3. Temperature – 10°C increase = double or triple of rate constant, thus the rate of a reaction increases with temperature

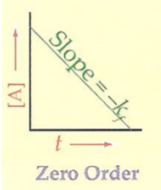
- F. 

- Reaction Rate Equations
  - A. Rate of a reaction says how quickly [product] or [reactant] is changing
  - B. Given in molarity per second, mol/L*s
  - C. Factors affecting reaction rates:
    - 1. Temperature
    - 2. Pressure – usually negligible
    - 3. [substances]
- Reaction mechanisms
  - A. How the molecules collide
- Reaction order
  - A. Reaction order = sum of all exponents of the concentration variables in the rate law.
  - B. Reaction order in A = the exponent of [A]
- Reaction rates
  - A. Depends on multiple factors
- Rate constant
  - A. The k in the rate law is the rate constant.
  - B. The rate constant is an empirically determined value that changes with different reactions and reaction conditions.
  - C. Within a given equation:
    - 1. Independent of:
      - a. [product]
      - b. [reactant]
    - 2. Dependent on:
      - a. Temperature
      - b. Catalyst
- Rate law
  - A. The equation that describes the rate = the product of reactants raised to some exponents
- Equilibrium constant
  - A. The balance of products and reactants at equilibrium

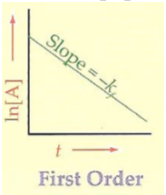
- Reaction Rate Equations: Example
  - A. aA + bB → cC + dD
  - B. Lower case letters are stoichiometric coefficients
- Reaction Rate Equations: Types
  - A. **Molecularity:** the number of molecules colliding at one time to make a reaction
  - B. **Elementary Reaction:** occur in a single step; only here can the coefficient of the balanced equation serve as the exponent in the rate law
  - C. **Unimolecular**: one molecule colliding
  - D. **Bimolecular:** two molecules colliding
  - E. **Termolecular:** three molecules colliding
- Reaction Rate Equations: Intermediates
  - 1. Intermediates: species that are products of one reaction and reactants of a later reaction in a reaction chain
  - 2. Concentrations are often very low because they are both unstable and used up quickly
- Reaction Rate Equations: Directions
  - 1. Reaction rates are reversible; that is, as products are formed, products begin to react to form reactants
- Reaction Rate Equations: Rate Law
  - A. **Rate law:** considering the forward reaction only
  - B. $Rate_{forward} = k_f[A]^{\alpha}[B]^{\beta}$
  - C. k_f = **rate constant** for the forward reaction
  - D. α and β = **order** of each respective reactant
  - E. $\alpha + \beta$ = **overall order** of the reaction
- Rate Law Experimental Determination

Trial	$[A]_{initial}$ (M)	$[B]_{initial}$ (M)	$r_{initial}$ (M/sec)
1	1.00	1.00	2.0
2	1.00	2.00	8.1
3	2.00	2.00	15.9

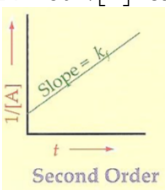
  - A. Info:
    - 1. Trial 1: $r_1 = k[A]^x[B]^y = k(1.00)^x(1.00)^y$
    - 2. Trial 2: $r_2 = k[A]^x[B]^y = k(1.00)^x(2.00)^y$
  - B. Divide the second equation by the first
    - 1. $r_2/r_1 = 8.1/2.0 = k(1.00)^x(2.00)^y/k(1.00)^x(1.00)^y = (2.00)^y$
    - 2. $4 = (2.00)^y$
    - 3. $y = 2$
  - C. Repeat for other trials
  - D. $r = k[A][B]^2$
    - 1. Reaction order with respect to A = 1
    - 2. Reaction order with respect to B = 2
    - 3. Overall reaction order: 1 + 2 = 3
  - E. Calculate k: substitute the values from any one of the above trials into the rate law, e.g.
    - 1. $2.0M/sec = k \times 1.00\ M \times (1.00M)^2$
    - 2. $k = 2.0M^{-2}\ sec^{-1}$
  - F. Thus, the rate law: $r = 2.0M^{-2}\ sec^{-1}\ [A][B]^2$
  - G. Note: increasing the concentration of reactants will result in more collisions which will increase the reaction rate
- Reaction Orders: Irreversible Zeroth Order
  - A. Plot [A] with respect to time t results in a straight line with slope = $-k_f$



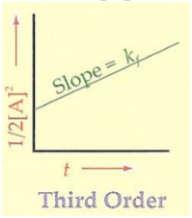
- Reaction Orders: Irreversible First Order
  - A. A → products, rate = k_f[A]
  - B. [A] decreases exponentially
  - C. Plot ln[A] with time *t* results in straight line with a slope = $-k_f$



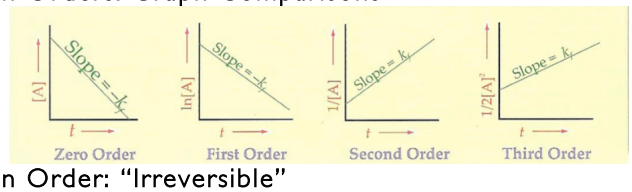
  - D. Half life: constant and independent of [A]
  - E. Pseudo-first order kinetics: first order reaction means no collision takes place; only one molecule reacting. New theory suggests a second molecule bumps the first one into a higher energy state, but the reaction still exhibits first-order kinetics
- Reaction Orders: Irreversible Second Order with a Single Reactant
  - A. 2A → products, rate = $k_f[A]^2$
  - B. Plot 1/[A] results in a straight line with slope = k_f



  - C. Half life: dependent on [A] and the rate changes with time, i.e. each consecutive half-life is twice as long as the last
- Reaction Orders: Irreversible Second Order with Two Reactants
  - A. A + B → products, rate = k_f[A][B]
  - B. Different graph, different slope
  - C. Half life: not easily predictable
- Reaction Orders: Irreversible Third Order with a Single Reactant
  - A. 3A → products, rate = $k_f[A]^3$
  - B. Plot ½$[A]^2$ results in a straight line with slope = k_f

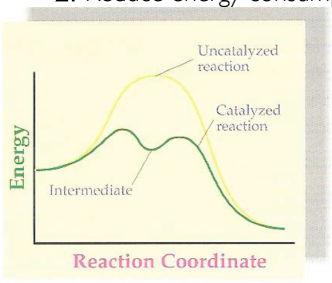


- Reaction Orders: Graph Comparisons



- Reaction Order: "Irreversible"
  - A. Initial Rates: a technique employed to avoid complications with reverse reactions; in the initial moments of a reaction starting with all reactants and no products, the rate of the reverse reaction is zero.

- Reversible Reactions: Rate Determining Step
  - A. **Rate determining step:** If a complex reaction is separated into elementary steps, the rate of slowest step determines the rate of the overall reaction
  - B. If the slow step is the first step, the rate law can be derived directly from this step and no other
  - C. If the slow step is other than the first step, the slow step is still the rate-determining step, but steps prior to the slow step will contribute to the rate law.
  - D. Steps after the slow step make contribution to the rate law
- Reversible Reaction Rates: First Step Rate-Determining Example
  - 1. $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ slow step
  - 2. $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO2(g)$ fast step
  - 3. *Rate* = $k_1[NO_2]^2$
- Reversible Reaction Rates: Second Step Rate-Determining Example
  - 1. $2NO(g) + Br_2(g) \rightarrow NOBr_2$ fast step
  - 2. $NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$ slow step
  - 3. *Rate* = $k_2[NOBr_2][NO]$
  - 4. $[NOBr_2]$ depends upon the first step; if we assume it reaches equilibrium very quickly, $[NOBr_2]$ can be written in terms of the equilibrium constant K_c for step 1, $[NOBr_2] = K_c[NO][Br_2]$
  - 5. *Rate* = $k_c[NO][Br_2]k_2[NO] = k_ck_2[NO]^2[Br_2]$
  - 6. Or we can use *Equilibrium Approximation*
- Reversible Reaction Rates: Equilibrium Approximation
  - A. **Equilibrium approximation** assumes all steps prior to the rate-limiting step are in equilibrium
  - B. It requires that the slow step be significantly slower than the fast steps
  - C. Example
    - 1. Since the first step is considered to be in equilibrium, set the forward reaction rate equal to the reverse reaction rate: $k_1[NO][Br_2] = k_{-1}[NOBr_2]$, and then solve for $[NOBr_2]$
    - 2. $[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$
    - 3. Rate law: *rate* = $k_1/k_{-1}[NO][Br_2]k_2[NO] = k_2k_1/k_{-1}[NO]^2[Br_2]$
    - 4. $k_2k_1/k_{-1} = k_{observed}$
  - D. If there is not a step that is significantly slower than the others, use *Steady State Approximation*
- Reversible Reaction Rates: Steady State Approximation
  - A. **Steady State Approximation:** the concentration of the intermediate is considered to be small and hardly changing; it leads to the same result as equilibrium concentration
- Catalysis
  - A. **Catalyst:** substance that increases the rate of reaction, and creates an intermediate, without being consumed or permanently altered, by:
    - 1. Enhance product selectivities – increase the steric factor, *p*
    - 2. Reduce energy consumption – lower the activation energy, E_a



A catalyst creates a new reaction pathway which typically includes an intermediate.

  - B.
  - C. Catalysts work by providing an alternative reaction mechanism that competes with the uncatalyzed mechanism

- **D. Cannot** alter the equilibrium constant, Kc, of a reaction or the composition of the mixture at equilibrium, thus it increases the rate of the forward and reverse reactions
- **E.** Types: heterogeneous and homogeneous
- **F.** Since they alter reaction mechanisms, they require separate rate constants
- **G.** Turnover Number: the number of reactions occurring at one active site on one enzyme

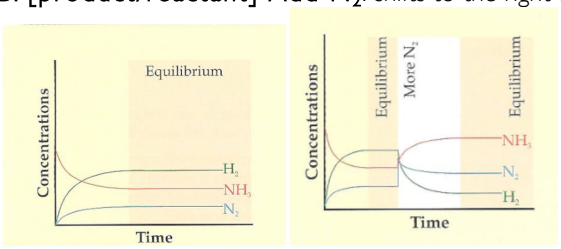
- **Catalysis: Heterogeneous Catalysts**
  - **A. Heterogeneous Catalyst:** in a different phase than the reactants and products
  - **B.** Usually solids while the reactants and products are liquids and gases
  - **C.** Reactants adsorb (binding of molecules to the surface), not absorb (uptake of molecules into the interior) to the solid catalyst
    - **1.** Physically adsorb via Van der Waals forces (minor)
    - **2.** Chemically adsorb via covalent bonds (major)
  - **D.** Reactants bind to the surface because the catalyst molecules there have unfilled valence electrons and this process is always exothermic
  - **E.** Binding strengths determine the rate of catalysis
    - **1.** Too weak: not enough adsorption, doesn't speed up enough
    - **2.** Too strong: requires too much energy to remove, cancels out effects
  - **F.** Reaction rate can be enhanced by increasing the surface area of the catalyst
- **Catalysis: Homogeneous Catalysts**
  - **A. Homogeneous Catalysts:** the same phase as the reactants and products, usually a gas or liquid, e.g. aqueous acid or base solutions are homogenous catalysts
  - **B. Autocatalysis:** when reactions generate a catalyst as a product
  - **C.** Concentration: usually small compared to [reactant] and [product]; increasing [catalyst] will increase the rate of reaction
  - **D.** Concentration: if large compared to [product] and [reactant], changing it won't do much to the rate of reaction
- **Effects of Solvent on Rate**
  - **A.** Liquid molecules make ~100 times more collisions per second that gas molecules because of the closer proximity; however, most are between solvent molecules and thus don't result in a reaction
  - **B.** Rate constant, *k*, in liquid is affected by both:
    - **1.** Solvent
      - **a.** Solvent-reactant bonds
      - **b.** Electrical insulation
      - **c.** Solvent viscosity
    - **2.** Temperature
- **Effects of Solvent on Rate: Solvent-Reactant Bonds**
  - **A.** Reactants in liquid are solvated and these reactant-solvent bonds must be broken before the reaction can take place
  - **B.** Reactant-solvent bonds can also stabilize an intermediate
  - **C.** Degree of solvation affects *k*
- **Effects of Solvent on Rate: Electrical Insulation**
  - **A.** Solvents can electrically insulate reactants, reducing the electrostatic forces between them
  - **B.** Dielectric constant of the solvent affects *k*
- **Effects of Solvent on Rate: Viscosity**
  - **A.** Viscosity affects *k* by the *cage effect*
  - **B.** Cage effect: solvent molecules form a 'cage' around the solute
    - **1.** The solute bounces around until it escapes the cage, where it then enters another cage.
    - **2.** If the other reactant molecule is in the cage, they will react.
    - **3.** Because so few of the collisions are between reactants, and because liquids collide roughly 100 times as frequently, it is fair to say that **liquid and gaseous reactants collide at the same rate**
- **Equilibrium: Chemical Equilibrium**
  - **A. Chemical equilibrium**: the condition where the forward reaction rate equals the reverse reaction rate; it is the point of greatest entropy

- B. No change in [product] or [reactant]

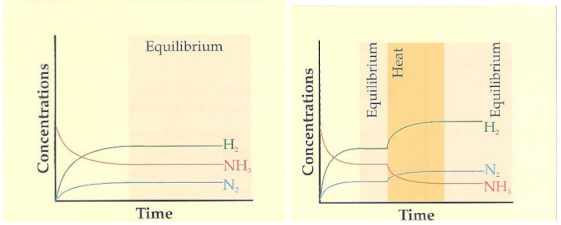
- **Equilibrium: Equilibrium Constant, K**
  - **A. Equilibrium Constant** = K (where *rate* constant is 'k')
  - **B.** Equilibrium constant for the reverse reaction is the reciprocal of the forward reaction
  - **C.** Equilibrium constant for a series of reactions is equal to the product of the equilibrium constant for each of its elementary steps
  - **D.** Since the rate constant depends upon temperature, so does the equilibrium constant
  - **E.** K has no dimensions because the concentrations are approximations for a dimensionless quantity called **activity**
- **Equilibrium: Equilibrium Constant, K; Example**
  - **A.** $aA + bB \rightarrow cC + dD$ [elementary reaction]
  - **B.** $Rate_{forward} = k_f[A]^a[B]^b$
  - **C.** $Rate_{reverse} = k_r[C]^c[D]^d$ (remember, we can only use the coefficients as exponents because we know it is an elementary reaction]
  - **D.** For equilibrium conditions only, set the two rates equal to each other:
    - **1.** $k_f[A]^a[B]^b = k_r[C]^c[D]^d =$
    - **2.** $k_f/k_r = [C]^c[D]^d/[A]^a[B]^b$
  - **E.** $k_f/k_r = K$ (this relationship only holds true for elementary reactions)
- **Equilibrium: Equilibrium Constant, K, and the Law of Mass Action**
  - **A. Law of Mass action:** $K = [C]^c[D]^d/[A]^a[B]^b = Products^{coefficients}/Reactants^{coefficients}$
  - **B.** The Law of Mass Action is good for all chemical equations, including non-elementary equations; **NOTE:** this means you CAN use the balanced equation stoichiometric coefficients as exponents of the concentrations, regardless of molecularity (i.e., not just elementary reactions)
  - **C.** Although pure solids and liquids (including solvents, which are considered to be ideally dilute on the **exam**) are present and necessary for equilibrium to exist, they are given values of 1 in the equilibrium expression and thus **are not used in the Law of Mass Action**.
- **Partial Pressure Equilibrium Constant: The Principle for Detailed Balance**
  - **A. Principle for Detailed Balance**: at equilibrium, for reactions with more than one pathway/step, the forward and reverse reactions rates for each step must be equal
  - **B.** Also, any two + reactions or series of reactions resulting in the same products from identical reactants must have the same equilibrium constant for a given temperature
- **Partial Pressure Equilibrium Constant: Equilibrium of Gases**
  - **A.** Reactions with gases: equilibrium constant is written in terms of partial pressures
  - **B. NOTE:** the concentration equilibrium constant and the partial pressure equilibrium constant **do not have the same value**
  - **C.** However, both constants can be used in the same equation; it will just result in different values of K
  - **D.** The two constants are related by the equation
    - **1.** $K_p = K_c(RT)^{\Delta n}$
    - **2.** K_p = partial pressure equilibrium constant
    - **3.** n = sum of the coefficients of the products minus the sum of the coefficients of the reactants (equation next bullet)
    - **4.** Visualized: X[product 1] + Y[product 2] → A[reactant 1] + B[reactant 2] would be written as: $n = \Sigma_{x+y} - \Sigma_{a+b}$
- **Reaction Quotient, Q**
  - **A.** Describes reactions not at equilibrium
  - **B.** $Q = Products^{coefficients}/Reactants^{coefficients}$
  - **C.** Q is not constant; it can have any positive value
  - **D.** Since reactions *always* move towards equilibrium, Q always changes toward K
- **Reaction Quotient, Q: Predictions**
  - **A.** Q = K: reaction at equilibrium
  - **B.** Q > K: [product] > [reactant] then at equilibrium; thus it will shift towards the reactant side, called a **leftward shift**

- **C.** Q < K: [product] < [reactant] then at equilibrium; thus it will shift towards the product side, called a **rightward shift**

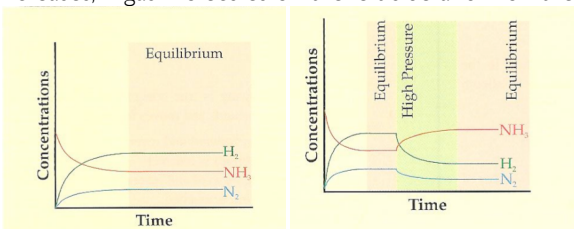
- Le Chatelier's Principle
  - **A.** When a system at equilibrium is stressed, it will shift in whatever direction reduces said stress
  - **B.** 3 stresses that obey Frenchie:
    - **1.** +/- [reactant] or [product]
      - **a.** Unless: you have a solid reactant and gaseous products. Then, increasing [solid] will not shift the equilibrium (Exam Krackers problem 287)
    - **2.** ΔPressure
    - **3.** ΔTemperature
      - **a.** The reaction <u>rate</u> (forward and reverse) is *always* increased with increased temperature, even if the reaction is exothermic (Exam Krackers problem 289)
    - * Solvation reactions
    - ** Pressure increase due to addition of nonreactive gases
- Le Chatelier's Principle: Haber Process Example
  - **A.** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + Heat$
  - **B. [product/reactant] Add N_2:** shifts to the right to reduce partial pressure of N_2



  - **C. [Heat] Add heat:** reaction pushed to the left



  - **D. [Pressure] Reduce size of container at constant temperature:** Pressure increases; 4 gas molecules on the left side and 2 on the right, so shifts to the right



- Le Chatelier's Principle: Special Exceptions
  - **1. Solvation reactions:** the solubility of salts increases with temperature regardless if its exothermic, i.e., if the salt is on the left, it will dissolve when heat is added even if heat is on the right; this is because entropy increases with dissolution and the **entropy factor becomes more important as the temperature increases; TΔS**
  - **2. Pressure increase due to the addition of a nonreactive gas:** Add He to the Haber system, the total pressure will increase but the partial pressures of the other gases will not, so **no equilibrium shift occurs**

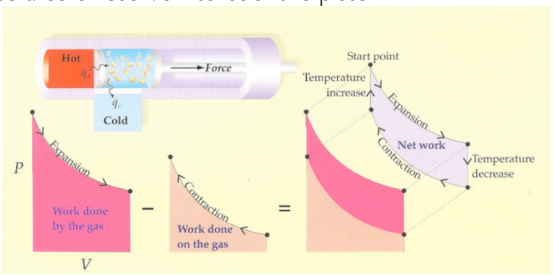
- REVIEW
  - Enthalpy, H
    - A. $H = U + PV$
    - B. At constant pressure, $\Delta H = \Delta U + P\Delta V$
    - D. ΔH = change in heat of a reaction
    - C. $\Delta H = q$, at:
      - 1. Constant pressure
      - 2. Closed system at rest
      - 3. *PV* work only
  - Entropy: Extensive
    - A. Increases with:
      - 1. Number
        - A. When comparing a sample of gases, the highest number of molecules has the highest entropy value
        - B. When the number of molecules are equal, must compare bonds, e.g. O(g) > O_2(g) because O(g) has no chemical bonds
      - 2. Volume
      - 3. Temperature
        - 1. Entropy change always increases with temperature
        - 2. Due to $\Delta S = dq_{rev}/T$, the *rate* of energy change increases with decreasing temperature, but the rate is still going forward
    - B. If a reaction increases the number of gaseous molecules, entropy = positive (for the reaction system, not necessarily the surroundings or universe)
    - C. Greater temperature = greater entropy
  - Gibbs Free Energy: Equations
    - A. $\Delta G = \Delta H - T\Delta S$
      - 1. Every variable above refers to the system and **not** the surroundings
      - 2. Only good for constant temperature reactions
    - B. $\Delta G = 0$ = equilibrium at:
      - 1. Constant temperature
      - 2. PV work only
      - 3. Reversible process
    - C. ΔG = positive
      - 1. The smaller the K for the reaction (with the positive ΔG)
    - D. ΔG = negative
      - 1. Increase $\Delta S_{universe}$
      - 2. Spontaneous only if
        - a. Constant temperature
        - b. Constant pressure
  - Internal Energy: Definition
    - A. Definition: the collective energy of molecules on a microscopic scale
      - 1. Vibrational
      - 2. Rotational
      - 3. Translational
      - 4. Electronic
      - 5. Intermolecular
      - 6. Rest mass
    - B. Internal energy does not include mechanical energy; that is, it is all possible forms of energy on the molecular scale
    - C. A closed system at rest with no electrical or magnetic fields can only have energy change from ΔU
    - D. First law of thermodynamics rewritten: $\Delta U = q + w$
    - E. Reaction in such a system, with no change in volume, there is no work and $\Delta U = q$
  - Work: PV Work
    - A. Constant pressure times the change in volume: $P\Delta V$

        - B. Occurs in a *system at rest*: no gravitational potential energy, no kinetic energy
        - C. Work is a path function
        - D. PV work takes place when a gas expands against a force regardless of whether or not the pressure is constant

---

- First Law of Thermodynamics
    - A. Definition: energy of a system and surrounding is always conserved
    - B. Thus, any energy change to a system must equal the heat flow into the system plus the work done on the system: $\Delta E = q + w$
        - 1. Note: this convention is where work *on* the system is positive
        - 2. If it were work *by* the system were positive, it'd be: $\Delta E = q - w$
- Second Law of Thermodynamics
    - A. Definition: Heat cannot be changed into work in a cyclical process
    - B. Definition 2: entropy of an isolated system will never decrease
    - C. Definition 3: 2nd law generally deals with irreversibility
- Third Law of Thermodynamics
    - A. Assigns a zero entropy value to any pure substance (element or compound) at absolute zero and in internal equilibrium
    - B. Entropy change = tiny change in heat per Kelvin in a reversible process
        - 1. $\Delta S = dq_{rev}/T$
- Zeroth Law of Thermodynamics
    - A. Definition: Two systems in thermal equilibrium with a third system are in equilibrium with each other
    - B. That is, two bodies in thermal equilibrium share a thermodynamic property, which must be a state function; its called Temperature
- Thermodynamics
    - A. Thermodynamics: the study of energy and its relationship to macroscopic properties; based on probabilities and thus really only work for macroscopic complex systems with a lot of molecules and cannot be applied to the microscopic systems; indeed, it is the opposite of quantum mechanics
- Thermodynamics: Division of the Universe
    - A. System: macroscopic body under study; three types
        - 1. Open: exchange both mass and energy with their surroundings
        - 2. Closed: exchange energy but not mass with their surroundings
        - 3. Isolated/adiabatic: do not exchange energy or mass
    - B. Surroundings: everything other than the macroscopic body under study
- State Functions: State Function
    - A. State: physical condition of a system described by a specific set of thermodynamic properties
    - B. State Function: When a state can be described by 3 properties and is independent of the path of its' formation (think: conservative forces), which can also be stated as "It can be measured without knowing any of its' history"
        - 1. Note: the macroscopic-state-of-any-one-component-fluid-system-in-equilibrium can be described by at least 3 properties; 1 must be extensive
        - 2. If you have at least 3 properties, all others can be specified
    - E. Two Types: quack
        - 1. Extensive
            - A. Definition: proportional to the size of the system
            - B. If you combined two identical systems, an extensive property would double
            - C. Divide one extensive property by another = intensive property
            - D. Examples:
                - 1. Volume, *V*
                - 2. # of moles, *n*
                - 3. Enthalpy
                - 4. Entropy

        - 5. Gibbs
        - 6. Specific Heat
        - 7. Internal Energy
        - 8. Energy
    - 2. Intensive
        - A. Definition: independent of the size of the system
        - B. If you combined two identical systems, an intensive property would not change
        - C. Examples
            - 1. Pressure, *P*
            - 2. Temperature, *T*
            - 3. Reduction Potentials, $E°$
            - 4. Molar heat capacity
            - 5. Density
- Path Functions
    - A. Definition: Properties that do not describe the state of a system and are dependent upon the pathway used to achieve (think nonconservative forces)
    - B. Examples of Path Function:
        - 1. Work
        - 2. Heat
- Heat: Energy Transfer
    - 1. Only two ways to transfer energy between systems
        - 1. Heat, *q*: the natural transfer of energy from warmer to cooler body; types: conduction, convection and radiation
        - 2. Work, *w*: any energy transfer that is not heat
- Heat: Conduction
    - A. Definition: thermal energy transfer via molecular collisions, i.e. higher energy molecules collide with lower energy molecules
    - B. Requires: direct physical contact
    - C. Thermal Conductivity, k: object's ability to conduct heat: $Q/t = kA[(T_h - T_c)/L]$
        - 1. A = face area
        - 2. L = length
        - 3. *k* = thermal conductivity
        - 4. Q = heat
        - 5. T_h = hot body
        - 6. T_c = cold body
        - 7. *t* = time
        - 8. ΔT = change in temperature
    - E. Resistance to heat flow, R: $R = L/kA$
    - D. Rate of Heat Flow, or Heat current, I: $I = Q/t$
    - F. Heat Flow: $\Delta T = IR$
        - 1. Think: Ohm's Law, rate of ideal fluid flow, electric current flow through resistors in series
        - 2. In a steady state system, rate of heat flow is constant across any number of slabs between two heat reservoirs
        - 3. That is, if a series of slabs of different lengths, thicknesses and thermal conductivities, or even order of slabs, were lined up between hot and could sources, the rate, *I*, would be the same.
        - 4. Why? Got to be. If one was too cool, it would not continue transferring heat to warmer bodies
        - 5. Note: Higher conductivity results in lower temperature difference between any slab of a given length
- Heat: Convection
    - A. Definition: thermal energy transfer via fluid movements
    - B. Differences in pressure or density drive warm fluid in the direction of cooler fluid, like hot air above the beach rising faster than cooler air above the ocean

- Heat: Radiation
  - A. **Definition:** thermal energy transfer via electromagnetic waves; it is the only type of heat that transfers through a vacuum
  - B. When metal is hot, it goes red → yellow → white → blue…it's radiating visible electromagnetic waves
  - C. All objects above 0K radiate heat
  - D. **Power (rate of electromagnetic radiation)**, $P = \sigma\varepsilon AT^4$
    - 1. A = surface area
    - 2. T = temperature in K
    - 3. ε = emissivity of the object's surface, value of 0 to 1
    - 4. σ = Stefan-Boltzmann constant: 5.67×10^{-8} W/m^2K^4
      - a. **Black body radiator:** emissivity of 1; only in theory
      - b. **Dark colors**: radiate and absorb more, reflect less
      - c. **Light colors**: reflect more, radiate and absorb less
  - E. Emissivity example: better to paint your house white: reflects more heat in the summer (your house is cooler than the environment), radiates less heat in winter (house is warmer than environment)
  - F. **Rate at which object absorbs radiant heat from its environment**: $P = \sigma\varepsilon A(T_e^4 - T_o^4)$
    - 1. T_o = temperature of object
    - 2. T_e = temperature of environment
  - G. **Newton's Law of Cooling:** the rate of cooling of a body is proportional to the temperature difference between it and the environment
- Work
  - A. **Definition**: any transfer of energy that is not heat
  - B. Whereas in physics it's the change to a motion or position of body, in chemistry it's the change in size and/or shape of a system at rest
- Work: PV Work
  - A. Constant pressure times the change in volume: $P\Delta V$
  - B. Occurs in a *system at rest*: no gravitational potential energy, no kinetic energy
  - C. Work is a path function
  - D. PV work takes place when a gas expands against a force regardless of whether or not the pressure is constant
- Heat engines
  - A. Turn a piston on its side (to remove gravity), at heat (not temperature), and the energy is changed "entirely" into PV work as force against the piston
  - B. Not *all* heat is turned into work
    - 1. Piston hits a max, we have to push it back in
    - 2. The process of pushing it back in increases temperature
    - 3. This requires more work to compress it than was expended to expand it
    - 4. So we use a cold reservoir to cool the piston
    - 5. Diagram 

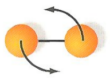
    - 6. Diagram explained: Due to the conservation of energy, heat entering the engine, q_h, must equal net work done on the engine w plus the heat leaving the engine q_c
      - a. $q_h = w + q_c$
- Second Law of Thermodynamics
  - A. **Definition:** Heat cannot be changed into work in a cyclical process

- **B. Definition 2:** entropy of an isolated system will never decrease

- **Second Law of Thermodynamics: Applied**
  - **B. Heat engine** converts heat into work
  - **C. Refrigerator** is the opposite of a heat engine
  - **D. Carnot Engine:** the most efficient hypothetical heat engine, $e = 1 - T_c/T_h$, that becomes more efficient with the increase in difference between the two reservoirs
    - **1.** e = efficiency; the fraction of heat that can be converted to work
    - **2.** T_h = temperature of the hot reservoir
    - **3.** T_c = temperature of the cold reservoir
- **Thermodynamic Functions: Seven State Functions**
  - **1.** Internal energy = U
  - **2.** Temperature = T
  - **3.** Pressure = P
  - **4.** Volume = V
  - **5.** Enthalpy = H
  - **6.** Entropy = S
  - **7.** Gibbs Energy = G
- **Internal Energy: Definition**
  - **A. Definition:** the collective energy of molecules on a microscopic scale
    - **1.** Vibrational
    - **2.** Rotational
    - **3.** Translational
    - **4.** Electronic
    - **5.** Intermolecular
    - **6.** Rest mass
  - **B.** Internal energy does not include mechanical energy; that is, it is all possible forms of energy on the molecular scale
  - **C.** A closed system at rest with no electrical or magnetic fields can only have energy change from ΔU
  - **D.** First law of thermodynamics rewritten: $\Delta U = q + w$
  - **E.** Reaction in such a system, with no change in volume, there is no work and $\Delta U = q$
  - **F. Note:** for an ideal gas, internal energy only depends on temperature
- **Internal Energy: Types**
  - **Note**: The first three are kinetic, the last three are potential
  - **1. Vibrational energy:**
    - **a.** Atoms vibrating in a molecule
    - **b.**

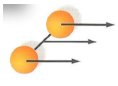
Vibrational

  - **2. Rotational energy**
    - **a.** Molecular movement where the spatial orientation of the body changes, while the center of mass remains fixed and each point within a molecule remains fixed relative to all other points
    - **b.**



Rotational

  - **3. Translational energy**
    - **a.** Movement of the center of mass of a molecule
    - **b.**



Translational

- 4. Electronic energy
  - a. Potential electrical energy created by the attractions between the electrons and their respective nuclei

Electronic

  - b.
- 5. Intermolecular potential energy, also called bond energy
  - a. Energy created by the intermolecular forces between molecular dipoles

Intermolecular potential

  - b.
- 6. Rest mass energy
  - a. Energy predicted by $E = mc^2$

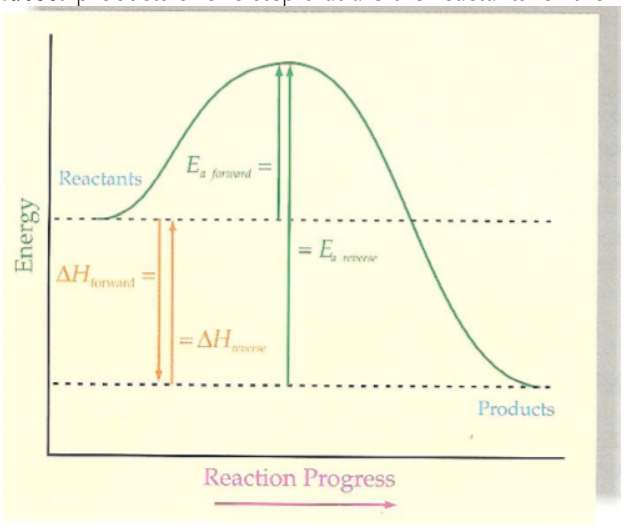

Rest mass

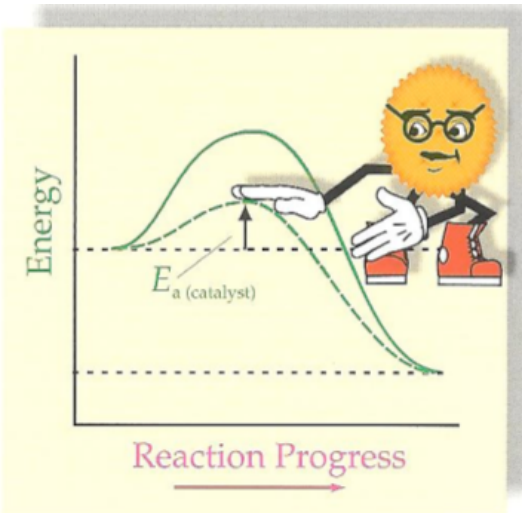
  - b.

- Zeroth Law of Thermodynamics
  - A. Definition: Two systems in thermal equilibrium with a third system are in equilibrium with each other
  - B. That is, two bodies in thermal equilibrium share a thermodynamic property, which must be a state function; its called Temperature
- Temperature
  - A. Temperature increases with an increase in thermal energy
  - B. Thermal energy: the sum of Internal kinetic energy
    - 1. Translational energy
    - 2. Rotational energy
    - 3. Vibrational energy
  - C. Remember: extensive/extensive = intensive; energy/#moles = temperature
- Temperature: Measurements
  - A. Celsius: at 1 atm, water freezes at 0°C and boils at 100°C
  - B. Kelvin: Celsius – 273; lowest possible temperature ever = 0K
  - C. Increase of 1°C = increase of 1K
- Enthalpy, H
  - A. $H = U + PV$
  - B. At constant pressure, $\Delta H = \Delta U + P\Delta V$
  - C. $\Delta H = q$, at:
    - 1. Constant pressure
    - 2. Closed system at rest
    - 3. PV work only
  - D. Enthalpy is not a measurement of some intuitive property;
  - E. Enthalpy is not conserved like energy; universal enthalpy does not remain constant
  - F. Differs from energy in that enthalpy assumes no work was done by the gas
  - G. Extensive property
  - H. Units: J/mol
  - I. Note: for an ideal gas, enthalpy only depends on temperature
- Enthalpy: Standard States
  - A. Again, there are not actual objective values for enthalpy, so scientists made it up:
    - 1. Chosen temperature, T
    - 2. Pressure 1 bar = 750 torr or 10^5 pascals
  - B. Element in the above standard state usually at 25°C, but can be any value: enthalpy = 0 J/mol
- Enthalpy: Standard Enthalpy of Formation, ΔH_f°

- A. $\Delta Hf°$ = change in enthalpy for the formation of a compound from it's raw elements in their standard state

- Enthalpy: Heat of Reaction, $\Delta H°$
  - A. Change in enthalpy from reactants to products
    - 1. $\Delta H°_{reaction} = \Delta Hf°_{products} - \Delta Hf°_{reactants}$
  - B. Because this is a state function, the path to get here doesn't matter
  - C. **Endothermic**: enthalpy change is positive; heat flow to the system (in a constant pressure reaction)
  - D. **Exothermic**: enthalpy change is negative; heat flow to the surroundings (in a constant pressure reaction)
- Exothermic Reactions
  - A. The energy released comes from the intermolecular potential energy of the bonds, **not** the kinetic energy
  - B. Forming bonds is ALWAYS exothermic
  - C. Breaking bonds is ALWAYS endothermic
- Enthalpy: Hess's Law
  - A. **Hess's Law:** Sum of the enthalpy changes for each step is equal to the total enthalpy change regardless of the path chosen
  - B. Forward reaction has the exact opposite change in enthalpy as the reverse
- Enthalpy: Reactions
  - A. **Activation energy:** minimum kinetic energy threshold to collide molecules and make babies
  - B. **Transition state:** the highest energy point in a reaction where old bonds are breaking and new bonds are forming; **not** the same as intermediates
  - C. **Intermediates:** products of one step that are the reactants for the next step
  - D. Diagram 1





    - E. Diagram 2
- Entropy, S
    - A. **Definition:** nature's tendency to create the most probable situation that can occur within a system, like a room getting dirty
    - B. **Definition 2:** Nature's way of spreading energy evenly between systems
    - C. Extensive property
    - D. State function
    - E. Units = J/K
    - F. Ex: 4 mexican jumping beans with two containers; most probable situation is 2 in each container, with six probabilities; least probable is all 6 in one container, with one probability
    - G. $\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{universe} \geq 0$
        - 1. So the entropy of a system can decrease only if the entropy of the surroundings increase by a greater or equal magnitude
    - H. Entropy change of forward reaction equals that of the reverse reaction **only** if the reaction has zero universal entropy change; these are ideal reactions
    - I. Real reactions are irreversible
- Entropy: Reaction Determinations
    - A. Because nature likes to lower the energy of a system that is higher energy than its' surroundings, and vice versa, **entropy, not energy, dictates the direction of a reaction**
    - B. That is, a reaction can be unfavorable in terms of enthalpy and/or energy and still proceed, but never unfavorable in terms of entropy
    - C. Equilibrium = maximum universal entropy
- Entropy: Extensive
    - A. Increases with:
        - 1. Number
        - 2. Volume
        - 3. Temperature
    - B. If a reaction increases the number of gaseous molecules, entropy = positive (for the reaction system, not necessarily the surroundings or universe)
    - C. Greater temperature = greater entropy
- Third Law of Thermodynamics
    - A. Assigns a zero entropy value to any pure substance (element or compound) at absolute zero and in internal equilibrium
    - B. Entropy change = tiny change in heat per Kelvin in a reversible process
        - 1. $\Delta S = dq_{rev}/T$
- Gibbs Free Energy:
    - A. Maximum non-PV work available from a reaction
    - B. An extensive property
    - C. Not conserved in the sense of energy conservation; i.e. an isolated system can change its Gibbs energy

- Gibbs Free Energy: Equations
  - A. $\Delta G = \Delta H - T\Delta S$
    - 1. Every variable above refers to the system and **not** the surroundings
    - 2. Only good for constant temperature reactions
  - B. $\Delta G = 0$ = equilibrium at:
    - 1. Constant temperature
    - 2. Constant pressure
    - 3. PV work only
    - 4. Reversible process
  - C. ΔG = negative
    - 1. Increase $\Delta S_{universe}$
    - 2. Spontaneous
- Gibbs Free Energy: Spontaneity
- Remember:
  - A. Enthalpy = KJ
  - B. Entropy = J

ΔH	ΔS	ΔG	Spontaneity
Negative	Positive	Negative	All temperatures
Negative	Negative	Negative (low T); Positive (high T)	Low temperatures
Positive	Positive	Negative (high T); positive (low T)	High temperatures
Positive	Negative	Positive	Not spontaneous

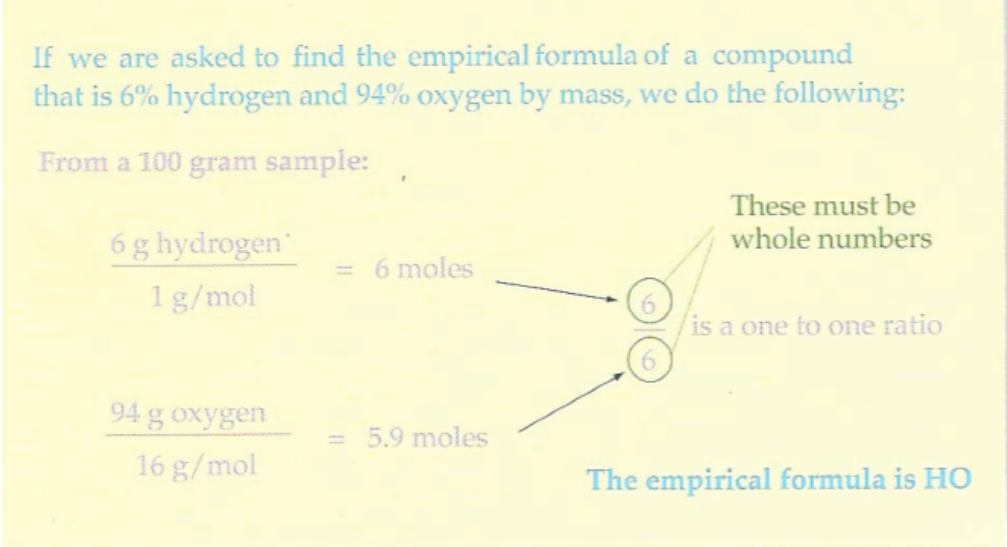
CHAPTER 4
Solutions

- Solution: Definition
  - A. Solution: a homogenous mixture of two or more compounds in a single phase, such as solid, liquid or gas
  - B. Solvent: In a solution, the compound with greater concentration
  - C. Solute: In a solution, the compound with less concentration
  - D. If concentrations are equal, both are referred to as solvents
  - E. Types of solutions
    - 1. Ideal solution
    - 2. Ideally dilute solutions
    - 3. Nonideal solutions
- Solutions: Ideal Solutions
  - A. Ideal solutions: solutions made from compounds with similar properties
  - B. That is, the compounds can be interchanged without changing:
    - 1. Spatial arrangement of molecules
    - 2. Intermolecular attractions
- Solutions: Ideally Dilute Solutions
  - A. Ideally Dilute Solutions: solute molecules are completely separated from one another by solvent molecules so they have no interactions
  - B. On exam,:you can assume it is ideally dilute, but you cannot automatically assume its ideal
- Solutions: Nonideal solutions
  - A. Nonideal solutions: violate the tenets of both ideal solutions and ideally dilute solutions
- Colloids: Definition and Properties
  - A. When particles larger than small solute molecules form a mixture but are too small to settle out due to gravity or be filtered out; it's a sort of middle ground
    - 1. Coagulation: (1) heated or (2) mixed with electrolytes → colloid particles clump together
    - 2. Dialysis: the third (3) way to separate colloids
    - 3. Cannot use simple filtration
  - B. Tyndall effect
    - 1. When colloidal suspensions scatter light
    - 2. That is, if light is shone through a colloid first with a solution behind it, the light will be visible in the colloid but not visible in the solution.
  - C. Dispersion medium: analogous to solvent
    - 1. Lyophilic: colloids are attracted to the dispersive medium
    - 2. Lyophobic: colloids are repelled by the dispersive medium
- Colloids: Types
  - A. Aside from gas-gas,, a colloid can be any combination of phases:
    - 1. Aerosol: liquid or solid particles in gas, e.g. fog
    - 2. Foam: gas particles in a liquid, e.g. whipped cream
    - 3. Emulsion: liquid particles in liquid, e.g. milk, or liquid particles in solid, e.g. butter
    - 4. Sol: solid particles in a liquid, e.g. paint
- Solutions: "Likes dissolve likes"
  - A. Polar molecules: polar solute particles are strong enough to separate polar solvent molecules, due to their permanent dipole moments
  - B. Nonpolar molecules: nonpolar solutes are only strong enough to mess up nonpolar solvent, due to their London dispersion forces
- Solutions: Solvation
  - A. Solvation: when ionic compounds break into their respective ions, polar molecules use their dipole moments to attract the ions
- Solvation: Hydration
  - A. Hydration: When several solvent molecules surround an ion
  - B. Aqueous Phase: Something that is hydrated
  - C. Hydration number

        - 1. Number of water molecules needed to surround an ion
        - 2. Varies with size and charge of the ion
        - 3. Usually has values between 4 and 6
- Electrolyte
    - A. A compound which forms ions in aqueous solutions
    - B. **Strong electrolytes**: create solutions conduct electricity
        - 1. Salts
        - 2. Strong bases
        - 3. Strong acids
    - C. **Weak electrolytes:** compounds that form few ions in solution
- Names You Need to Know

Name	Formula
Nitrite	NO_2^-
Nitrate	NO_3^-
Sulfite	SO_3^{2-}
Sulfate	SO_4^{2-}
Hypochlorite	ClO^-
Chlorite	ClO_2^-
Chlorate	ClO_3^-
Perchlorate	ClO_4^-
Carbonate	CO_3^{2-}
Bicarbonate	HCO_3^-
Phosphate	PO_4^{3-}

- Units of Concentration
    - 1. **Molarity (M) =** (moles of solute)/(volume of solution)
        - 1. Temperature dependent because it is per *liter* of solution and density changes with temperature
    - 2. **Molality (m) =** (moles of solute)/(kilograms of solvent)
        - 1. Temperature independent
    - 3. **Mole fraction (χ)** = (moles of solute)/(total moles of all solutes and solvent)
        - 1. Temperature independent
    - 4. **Mass percentage** = (mass of solute)/(total mass of solution) x 100%
    - 5. **Parts per million (ppm)** = (mass of solute)/(total mass of solution) x 10^6
    - ***Normality:** the "equivalents" of a solution; depends on the type of reaction taking place; e.g. H_2SO_4 has two equivalents in an acid-base reaction because it can donate two protons
- Problem Strategy



- Solution Formation: 3 steps
  - 1. Breaking intermolecular solute bonds; endothermic
  - 2. Breaking intermolecular solvent bonds; endothermic
  - 3. Formation of intermolecular bonds between the solvent and solute molecules; exothermic
- Solution Formation: Enthalpy
  - A. Because at constant pressure enthalpy change = heat: $\Delta H = q$
  - B. $\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3$
- Solution Formation: Heat of Solution & Heat of Hydration
  - A. Heat of Solution: measures the energy absorbed in:
    - 1. Breaking of solute-solute bonds
    - 2. Breaking of solvent-solvent bonds
    - 3. Positive or negative
  - B. Heat of Hydration: measures the energy releases in:
    - 1. Formation of solute-solvent bonds
    - 2. ALWAYS negative because it releases energy
  - C. Exothermic:
    - 1. Enthalpy change is negative
    - 2. Solution gives off heat; temperature of solution is seen to rise
    - 3. New intermolecular bonds are more stable than the old
    - 4. New bonds are stronger than the pure substance
  - D. Endothermic:
    - 1. Enthalpy change is positive
    - 2. Solution absorbs heat; temperature of solution is seen to drop
    - 3. New intermolecular bonds are less table
    - 4. New bonds are weaker than pure substance
  - E. Solution formation always has positive entropy
- Vapor Pressure: Explanation
  - 1. Explanation
    - A. A pure liquid in a vacuum-sealed container
    - B. Some of the molecules are liquid, and some have enough kinetic energy (from temperature) to break free from the surface and fly into open space → gas molecules
      - 1. Note: rate of evaporation is temperature dependent and thus stays constant, while condensation rates rise to equilibrate
      - 2. That is, unlike other reactions, equilibrium is **not achieved** by the forward rate slowing down and the reverse rate speeding up

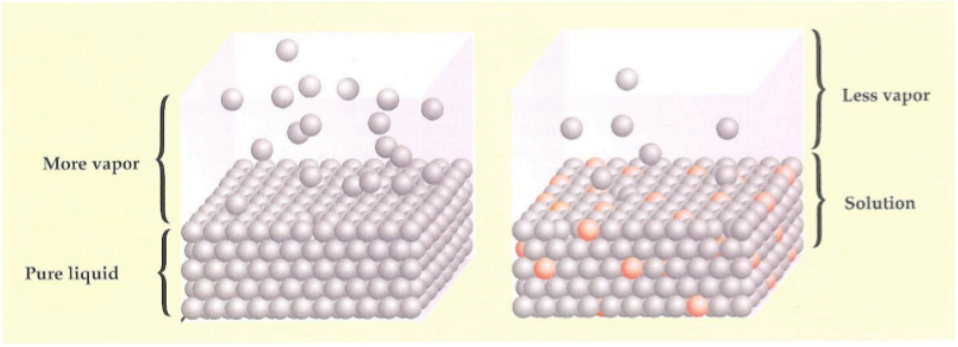
(?)

- 3. So, the forward (evaporation) stays constant while the reverse (condensation) speeds up
- C. Some gas molecules crash back into the liquid
- D. At some point, the rate of molecules flying into open space equal the rate of molecules crashing into the surface of the liquid

- 2. Definition:
  - A. **Vapor Pressure:** At this equilibrium point, the dynamic equilibrium concentration of molecules in the open space creates an air pressure
  - B. This pressure is due to air molecules only, not surrounding atmosphere
  - C. Vapor Pressure: ALWAYS increases with temperature
  -

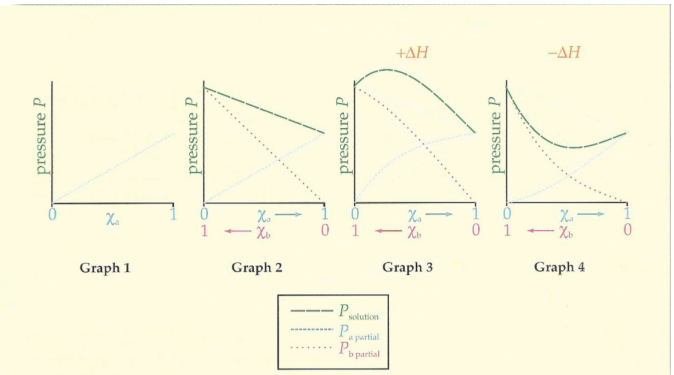
(any eqn?)

- Vapor Pressure: Kinetic Energy Relations; The Clausius-Clapeyron Equation
  - A. Vapor pressure is related to the kinetic energy of the molecules and is thus a function of temperature
  - B. $\ln(P_v) = -(\Delta H_{vap}/RT) + C$ (look into this)
    - 1. H_{vap} = heat of vaporization
    - 2. C = constant specific to the compound
    - 3. Note: slope is equal to vapor pressure
  - C. Because vaporization is an endothermic process, the equation shows that **vapor pressure increases with temperature**
- Vapor Pressure: Phase Changes
  - A. Boiling point:
    - 1. When vapor pressure of a liquid phase equals local atmospheric pressure
    - 2. Local atmospheric pressure = total pressure of the gas above it
      - 3. Note: gaseous water can exist at a wide range of temperatures (due to equilibrium), but at boiling point **it cannot exist**
      - 4. That is, vapor can exist below the boiling point, but no liquid can exist above the boiling point
  - B. Melting point:
    - 1. When vapor pressure of a solid phase equals the vapor pressure of the liquid phase
      - A. Above melting point: liquid vapor pressure is greater than that of the solid vapor pressure
      - B. Below the melting point: liquid vapor pressure is less than that of the solid vapor pressure
  - C. Sublimation:
    - 1. When vapor pressure of the solid must be greater the partial pressure of the gas above it, **not** the total pressure
    - 2. That is, the rate of solid → gas > gas → solid
- Vapor Pressure: Nonvolatile Solutes in Ideal Solutions
  - A. **Nonvolatile solute:** solute with no vapor pressure
    - 1. A pure liquid has a greater vapor pressure than a solution
      - a. Depending on the solute added, however, the solution could have a greater or lesser vapor pressure.
    - 2.



- B. When added to a liquid, some will reach the surface of the solution and reduce the amount of surface are available for the liquid molecules
- C. That is, theys use up prime real-estate but don't break free into the gaseous phase.
- D. Less prime real-estate = less molecules breaking free while the (1) surface area of the surface and (2) volume above stay the same, so…
- E. From PV = nRT, we know that if *n* decreases at constant volume and temperature, then pressure *P* has to decrease proportionally; and it does by Raoult's Law
- F. Raoult's Law: $P_v = \chi_a P_a$
    - 1. P_v = vapor pressure of the solution
    - 2. χ_a = mole fraction of the liquid
    - 3. P_a = vapor pressure of the pure liquid

- Vapor Pressure: Volatile Solutes in Ideal Solutions
    - A. Volatile Solute: A solute with vapor pressure
    - B. Like nonvolatile solutes, it will compete for the surface area, the "prime real-estate"
    - C. Unlike nonvolatile solutes, some of the volatile solute molecules *will* escape from the surface and contribute to the vapor pressure
    - D. If the solution is ideal (solvent and solute have similar properties), Raoult's Law can be used to find the partial pressures of both the solvent and the solute
    - E. Raoult's Law: $P_v = \chi_a P_a + \chi_b P_b$
        - 1. P_v = total vapor pressure of the solution
        - 2. $P_a \chi_a$ = partial pressure contributed by the respective solvent
- But wait, bitches. It doesn't stop here. What if the solution isn't ideal?
- Vapor Pressure: Nonideal Solutions
    - 1. If the solution is not ideal, the intermolecular forces between molecules will be changed
    - 2. Whereas with nonvolatile and volatile solutes in ideal solutions, it was a simple "the added solute it takes up space and doesn't evaporate, or it does," here, the added solutes alter the energies of the original molecules themselves.
    - 3. Why? Because this means either *less* or *more* energy will be needed by the molecules to break free into the gaseous phase, causing huge deviations from what Raoult's Law predicted.
- Vapor Pressure: Raoult's Law Recap
    - 1. Nonvolatile Solutes, Ideal Solutions: If 97% of the solution is solvent, then the vapor pressure will be 97% of the vapor pressure of the pure solvent
    - 2. Volatile Solutes, Ideal Solutions: If 97% of the solution is solvent, then vapor pressure will be 97% of the vapor pressure of the pure solvent PLUS 3% of the vapor pressure of the pure solute
    - 3. Nonideal Solutions
        - 1. Negative (Exothermic) Heat of Solution
            - a. Stronger bonds are formed
            - b. Fewer bonds are able to break free from the surface
            - c. Negative deviation of the vapor pressure from Raoult's law
        - 2. Positive (Endothermic) Heat of Solution
            - a. Weaker bonds are formed
            - b. More bonds are able to break free from the surface
            - c. Positive deviation of the vapor pressure from Raoult's law
    - 4. Graphical Representation



- A. Lines
  - 1. **Straight lines**: Raoult's Law predictions
  - 2. **Curved lines:** Actual pressures
- B. Graphs
  - 1. **Graph 2:** ideal solution
  - 2. **Graph 3 & 4:** Nonideal solution

- Solubility
  - A. **Solubility:** solute's tendency to dissolve in a solvent
- Solubility: Precipitation
  - A. **Precipitation:** the reverse of dissolution
  - B. Slow at first, then equilibrates with dissolution
  - C. Exothermic most of the time
- Solubility: Saturated
  - A. **Saturated:** when a dynamic equilibrium (concentrations don't change, but the forward and reverse reactions are still occurring at equal rates) has been established and the concentration of dissolved salt has reached a maximum
- Solubility: Equilibrium
  - A. **Solubility product K_{sp}:** used the same way as any other equilibrium constant
  - B. Set equal to products over reactants, raised to their respective coefficients
  - C. Leave out pure solids and pure liquids
- Solubility vs. Solubility product
  - A. They are **not** the same thing
  - B. Solubility: (molar solubility)
    - 1. Number of moles of solute per liter of a solution that can be dissolved in a given solvent
    - 2. Dependent upon common ions
    - 3. Dependent upon temperature; thus a saturated solution can become unsaturated with additional temperature
    - 4. Found from the solubility product
  - C. Solubility Constant
    - 1. Independent from common ions
    - 2. Dependent on temperature
    - 3. Found from a reference book
    - 4. Is unitless (really?)
- Solubility: Product Constant Example
  - A. BaF_2 (s) ⇔ Ba^{2+}(aq) + $2F^-$(aq)
  - B. $K_{sp} = [Ba^{2+}][F^-]^2$
  - C. Reference value of K_{sp} for $BaF_2 = 2.4 \times 10^{-5}$ at 25°C
  - D. x moles per liter of BaF_2 dissolve, then there are x moles of Ba^{2+} and 2x moles of F^-
  - E. Plug in:
    - 1. $2.4 \times 10^{-5} = (x)(2x)^2$
    - 2. $4x^3 = 2.4 \times 10^{-5}$
    - 3. $x = 1.8 \times 10^{-2}$ = solubility of BaF_2 in one liter of water at 25°C

- Solubility: Product Constant Example [Continued}
  - A. Okay, but what if we dissolve 1 mole of NaF? It would completely dissociate
  - B. Spectator ions: [Na^+] ions have that no effect on equilibrium (ideally)
  - C. Common ion effect: when ions that may or may not be from the same source cause an equilibrium shift in accordance with Le Chatelier's principle, but does **not** affect K_{sp}
    - 1. F^- ions do affect equilibrium
    - 2. By Le Chatalier's principle, the reaction will shift in the direction that reduces the F^- ion, which is the left
    - 4. This reduces the solubility of BaF_2
    - 5. $2.4 \times 10^{-5} = (x)(2x + 1)^2$
    - 6. Because the equilibrium is shifting to the left, x (and even 2x) is going to be much smaller
    - 7. Drop the 2x and solve for just x^2
    - 8. $x = 2.4 \times 10^{-5}$
- Solubility Guidelines
  - A. Insoluble: compound with water solubilities of less than 0.01 mol L^{-1}
  - B. Ionic compounds are soluble that contain
    - 1. Nitrate (NO_3^-)
    - 2. Ammonium (NH_4^+)
    - 3. Alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+)
    - 4. Halogens (Cl^-, Br^-, I^-)
  - C. Ionic Compounds are insoluble, that contain
    - 1. Silver, mercury and lead compounds (Ag^+, Hg_2^{2+}, Pb^{2+})
  - D. Sulfate Compounds (SO_4^{2-}) are soluble, but are insoluble if they contain
    - 1. Mercury, lead and the heavier Alkaline Earth metals (Hg_2^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+})
  - F. The heavier alkaline metals (Ca^{2+}, Sr^{2+}, Ba^{2+}) are soluble when they contain
    - 1. Sulfides (S^{2-})
    - 2. Hydroxides (OH^-)
  - G. Generally insoluble compounds, except for the cases mentioned above, are:
    - 1. Carbonates, phosphates, sulfides and hydroxides (CO_3^{2-}, PO_4^{3-}, S^{2-}, OH^-)
- Gas Solubility
  - A. Temperature (look into this, graph?)
    - 1. Solubility is inversely proportional to temperature at low temperatures (increasing the temp decreases the solubility)
    - 2. At higher temperatures, the entropy factor takes over $\Delta G = \Delta H - T\Delta S$
  - B. Pressure
    - 1. Solubility is directly proportional to pressure
  - C. Shaking causes bubbles to coalesce, decreasing solubility (They escape the solution)
  - D. Salt nucleates gas bubbles and causes them to coalesce, decreasing solubility (They escape the solution) *
- Solubility Factors
  - 1. Solubility is affected by:
    - A. Pressure
    - B. Temperature
  - 2. The solubility of liquids and solids are not largely affected by the above factors
- Solubility Factors: Henry's Law
  - A. Henry's Law
    - 1. Gases in an ideally dilute solution: increase in pressure of gas *a* over a solution is directly proportional to the solubility of gas *a* if the gas does not react with, or dissociate in, the solvent.
    - 2. Holds true when pressure is low
  - B. Equation 1: $C = k_{al}P_v$
    - 1. C = solubility of the gas *a* (in moles per liter)
    - 2. k_{al} = Henry's Law constant, which varies
    - 3. P_v = vapor partial pressure of gas *a* above the solution

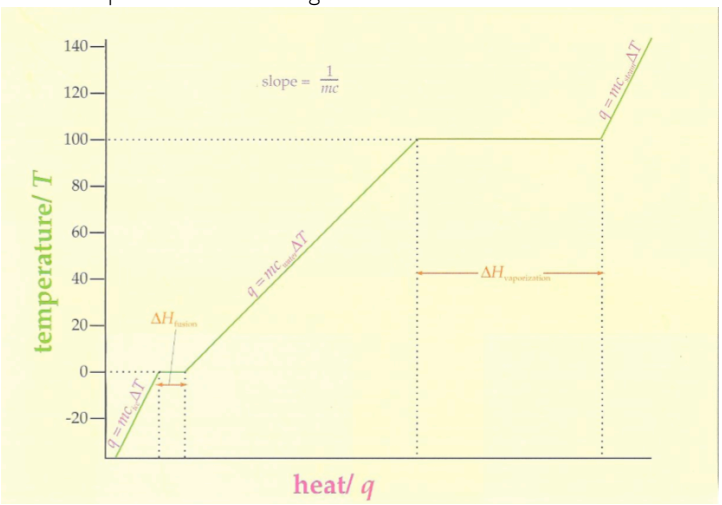
- C. Equation 2: $P_v = \chi_a k_{a2}$
  - 1. χ_a = mole fraction of gas *a* in solution
  - 2. P_v = vapor partial pressure of gas a
  - 3. k_{a2} = Henry's law constant
- D. Henry's Law constant
  - 1. Is different from equation 1 to equation 2
  - 2. Compare to Raoult's Law: $P_v = \chi_a P_a$; unless P_a has the same value as k_{a2}, they appear to conflict
  - 3. Bingo! They do NOT agree; both are approximations

- Solubility Factors: Raoult's Law vs. Henry's Law
  - A. Raoult's Law is more accurate when looking at the vapor partial pressure of a solvent with high concentration; think $P_v = \chi_a P_a$
  - B. Henry's Law is more accurate when looking at the vapor partial pressure of a volatile solute where the solute has a low concentration; think $C = k_{a1} P_v$ and $P_v = \chi_a k_{a2}$
  - C. Summary: In an ideally dilute solution:
    - 1. Solvent obeys Raoult's law
    - 2. Solute obeys Henry's law
  - D. How to Remember Raoult's Law
    - 1. When solvent concentration is high, its surrounded by other solvent molecules
    - 2. This makes it so it behaves more like a pure solvent
    - 3. Thus the solvent vapor partial pressure is proportional to its vapor pressure as a pure liquid; Raoult's Law!
  - E. How to Remember Henry's Law
    - 1. When the volatile solute concentration is low, its surrounded by solvent molecules, creating a …
    - 2. Deviation from the behavior of the pure volatile solute
    - 3. Thus, the volatile solute vapor partial pressure is **not** proportional to its vapor pressure as a pure substance (i.e., Raoult's Law does not work here)…
    - 4. But **is** proportional to some constant; Henry's Law!

CHAPTER 5
Heat Capacity, Phase Change and Colligative Properties

- Phases
  - A. Homogenous: If all the intensive macroscopic properties of a system are constant
  - B. Phase: Any part of a homogenous system and is uniform throughout with respect to chemical composition and physical state; ex:
    - 1. Crystalline solid
    - 2. Amorphous solid
    - 3. Aqueous
    - 4. Pure liquid
    - 5. Vapor
  - C. Differences: a system can have multiple solid and liquid phases but usually only one gaseous phase
  - D. Pure substances: usually only have one gaseous phase and one liquid phase
- Heat Capacity: Phase Changes
  - A. Phase Change: changes in the manner in which internal energy is distributed over molecules and space
  - B. Phase changes arise from
    - 1. Molecules gaining or losing energy
    - 2. Space around molecules reducing or enlarging
  - C. Phase changes are achieved by either:
    - 1. Heat
    - 2. Work
- Heat Capacity, C
  - A. Heat Capacity, C: a measure of the energy change needed to change the temperature of a substance, defined:
    - 1. $C = q/\Delta T$
  - B. Value: always positive; temperature always increases when energy is added to a substance, regardless if at constant volume or constant pressure
  - B. Be aware: heat capacity is a tricky name because heat is a transfer of energy and cannot be stored
    - 1. The temperature of a substance at constant internal energy can be changed only by changing the volume
    - 2. Isothermal expansion of gas: gas can be expanded at constant temperature by adding heat
- Heat Capacity: Types
  - A. Types of Heat Capacity
    - 1. C_V: constant volume heat capacity
      - a. No PV work can be done; all energy change must be in the form of heat, usually temperature
      - b. Less than C_P
    - 2. C_P: constant pressure heat capacity
      - a. Some energy can do PV work and there is less change in temperature because PV work can "absorb" the energy
      - b. Greater than C_V
- Heat Capacity: Incompressible phases
  - A. Solids and liquids have much stronger intermolecular forces than gases, because they are incompressible
  - B. Thus, even small changes in the intermolecular distances results in huge change in intermolecular potential energy
  - C. Intermolecular P.E. does not affect temperature: heat is absorbed at constant pressure with less temperature change than when heat is absorbed at constant volume; $C_P > C_V$
- Heat Capacity: System
  - A. $q = C\Delta T$
  - B. Units: J/K or cal/°C
- Heat Capacity: Specific Heat Capacity, c (lower case)
  - A. Specific: divided by mass; thus it is the heat capacity per unit mass
  - B. $q = MC\Delta T$

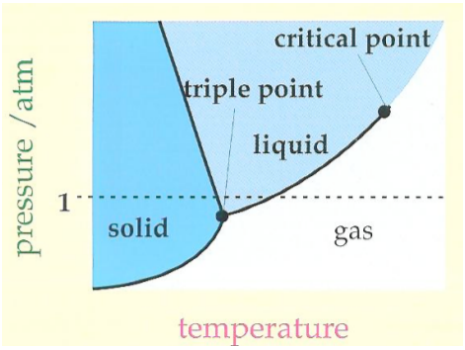
        - 1. m = mass **not** molality
    - C. Units: J/K*kg or cal/°C*g
- Heat Capacity: Water
    - A. Water specific heat capacity: 1 cal/1°C*1g
    - B. The old definition of a calories (new is 4.184 J)
- Calorimeters
    - A. **Calorimeter:** device that measures energy change
    - B. Two types:
        - 1. Constant pressure – coffee cup
        - 2. Constant volume – bomb
- Calorimeters: Constant Pressure
    - A. Used to measure **heats of reaction**
    - B. Reaction takes place with open top at atmospheric pressure…thus expanding gases cannot be contained = constant pressure
    - C. Recall: at constant pressure: $q = \Delta H$
    - D. Thus from $q = MC\Delta T$; q = change in heat
- Calorimeter: Constant Volume
    - A. Used to measure the **change in internal energy of a reaction**, at
        - 1. Condensed phases
        - 2. Not high pressures
    - B. Recall: at constant volume: $q = \Delta U$
    - C. The steel vessel heats up the water around it…
    - D. Thus from $q = MC\Delta T$; q = change in internal energy
- Phase Change: Water Example
    - A. Water at constant pressure of 1 atm
        - 1. -10°C and add heat: molecules vibrate and temperature rises
        - 2. 0°C: temperature stops rising with additional heat because bonds are breaking and ice is melting
        - 3. 0°C+: temperature starts rising with additional heat as molecules vibrate
        - 4. 100°C: temperature stops rising with additional heat because bonds are breaking and water is boiling
        - 5. 100°C+: temperature starts rising with additional heat as molecules vibrate
    - B. Diagram:



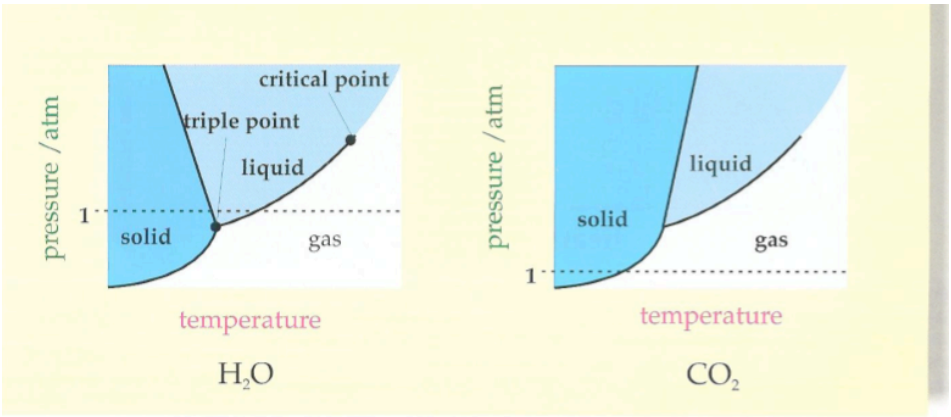
- Phase Changes: Normal Melting/Boiling Point
    - A. **Normal melting point:** at 0°C the heat capacity is infinite
    - B. **Normal boiling points:** at 100°C the heat capacity is infinite
    - C. "Normal:"
        - 1. Indicates pressure = 1 atm
        - 2. Constant pressure: $q = \Delta H$
- Phase Changes: Heating Curve Slope

    - A. Slope: when not zero, is inversely proportional to specific heat only (not mass)
- B. Mass: does not change during phase change Phase Changes: Heat of Fusion and Vaporization
    - A. Heat of fusion:
        - 1. Enthalpy changes associated with melting
        - 2. Endothermic (positive enthalpy values)
        - 3. Increases volume
        - 4. Increases molecular movement
        - 5. Increase entropy (positive values)
    - B. Heat of vaporization: enthalpy change associated with boiling; endothermic
        - 1. Enthalpy changes associated with boiling
        - 2. Endothermic (positive enthalpy values)
        - 3. Increases volume
        - 4. Increases molecular movement
        - 5. Increase entropy (positive values)
- Phase Changes: Freezing and Condensation
    - A. Heat of freezing:
        - 1. Enthalpy changes associated with freezing
        - 2. Exothermic (negative enthalpy values)
        - 3. Decreases volume
        - 4. Decreases molecular movement
        - 5. Decrease entropy (negative values)
    - B. Heat of condensation:
        - 1. Enthalpy changes associated with condensation
        - 2. Exothermic (negative enthalpy values)
        - 3. Decreases volume
        - 4. Decreases molecular movement
        - 5. Decrease entropy (negative values)
- Phase Changes: Water
    - 1. Liquid water can absorb more energy with less temperature change than either ice or gaseous water.
- Phase Changes: Enthalpy Review
    - A. Enthalpy is a state function: thus, the exact same amount of heat is absorbed/released for reversible processes, e.g. melting-freezing, vaporization-condensation, and sublimation-deposition
    - B. $\Delta G = \Delta H - T\Delta S$; thus temperature determines what phase change is favored (spontaneous)
- Phase Diagrams
    - A. Phase Diagram: Indicates the phase of a substance at different pressures and temperatures
    - B. Each section represents a phase
    - C. The lines marking the boundaries indicate where phases are in dynamic equilibrium
        - 1. Note: solid and liquid phases can be in equilibrium with the vapor phase regardless of pressure or temperature
        - 2. Thus, all 3 phases of water can exist at 1 atm and 0°C (which a phase diagram wouldn't seem to agree with)
- Phase Diagrams: Descriptions
    - A. Triple point: where solid, liquid and gas are in dynamic equilibrium
    - B. Critical Temperature: temperature above which a substance cannot be liquefied no matter how much pressure is applied
    - C. Critical Pressure: the pressure necessary to produce liquefaction while the substance is at the critical temperature (Edit: The critical temperature is the temperature *above* which liquefaction cannot be achieved, but still can be achieved *at* the critical temperature)
    - D. Critical Point: Critical temperature and critical pressure

- **E. Supercritical fluid:** beyond the critical point, a fluid has characteristics of both gas and liquid
- **F. Diagram:**



- **Phase Diagrams: Water vs. Carbon dioxide**
  - **A.** 1 atm can be determined without labels
    - **1.** Water at 1 atm exists in all three phases at different temperatures; thus the 1 atm line must be above the triple point
    - **2.** Carbon dioxide at 1 atm sublimes; thus the 1 atm line must be below the triple point
  - **B.** Compare the equilibrium lines separating the liquid and solid phases
    - **1.** Water = negative slope = ice floats
      - **a.** Why? Increasing pressure = decreasing volume; thus, liquid water density > solid water density
    - **2.** Carbon dioxide = positive slope
  - **C. Check this out:**



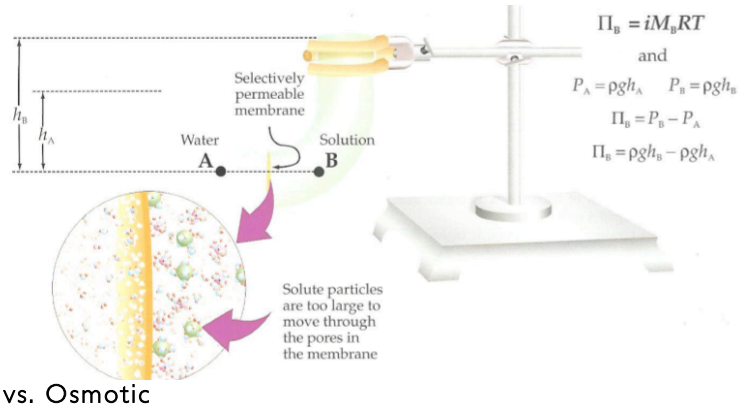
- **Colligative Properties**
  - **A. Colligative properties:** Depend solely on the number of particles, regardless of the type of particle
  - **B. Four colligative properties of solutions:**
    - **1.** Vapor pressure
    - **2.** Boiling point
    - **3.** Freezing point
    - **4.** Osmotic pressure
- **Colligative Properties: Boiling Point Elevation for Nonvolatile Solutes**
  - **A.** From Raoult's law: adding nonvolatile solute decreases vapor pressure…and we know when vapor pressure equals local atmospheric pressure = boiling; thus, addition of a solute increases the boiling point (need more heat addition to boil)
  - **B. Equation (for an ideally dilute solution):** $\Delta T = k_b mi$
    - **1.** ΔT = temperature change
    - **2.** k_b = specific constant of the substance being boiled
    - **3.** m = molality **not** molarity **or** mass

        - 4. i = **van't Hoff factor** = # of particles which a single solute particle will dissociate into when added to solution
    - C. van't Hoff factor:
        - 1. Expected value:
            - a. Doesn't take ion pairing into account
        - 2. Observed value:
            - a. Does take ion pairing into account
        - 3. Ion Pairing:
            - a. **Ideally dilute solution:** # ions upon complete dissociation (e.g., NaCl = 2; $MgCl_2$ = 3)
            - b. **Nonideal solutions:** not due to the solute incompletely dissolving, but rather momentary aggregations of two or more ions into a single particle, caused by electrostatic attractions
- Colligative Properties: Boiling Point Elevation for Volatile Solutes
    - A. Boiling point elevation can only be applied to nonvolatile solutes, **not** volatile solutes
    - B. Why? Because volatile solutes can *increase* (or decrease) vapor pressure and thus *decrease* (or increase) boiling point, respectively
    - C. However, **if you know the heat of solution**, predictions can be made on what will happen to the boiling point when volatile solutes are added,
    - D. Predictions:

Nice! 

        - 1. **Endothermic (positive) heat of solution**: weaker bonds → higher vapor pressure → decreased boiling point
        - 2. **Exothermic (negative) heat of solution**: stronger bonds → lower vapor pressure → increased boiling point
- Colligative Properties: Freezing Point Depression
    - A. Is related to **crystallization**, not vapor pressure
    - B. Impurities (the solute) interrupt the crystal lattice and lower the freezing point by **messing** up the ability of the dipoles to neatly arrange
    - C. Equation (for an ideally dilute solution): $\Delta T = k_f m i$
        - 1. ΔT = temperature change
        - 2. k_f = specific constant of the substance being frozen
        - 3. m = molality **not** molarity **or** mass
        - 4. i = **van't Hoff factor** = # of particles which a single solute particle will dissociate into when added to solution
    - D. Process:
        - 1. Add liquid solute A (impurity) to liquid solvent B = lower melting point
        - 2. More liquid solute A added = increase mole fraction of solute A = becomes the solvent and the original solvent B becomes the solute (impurity)
        - 3. Add more liquid (now) solvent A = decrease mole fraction of solute B (impurity) = freezing point rises
- Colligative Properties: Osmotic Pressure
    - A. **Osmotic Pressure:** measure of the tendency of some solvent to move into solution via osmosis
    - B. Thus, it is the force, created as a by-product during an entropy-driven quest for osmosis, that eventually prevents further osmosis.
    - C. Osmotic pressure is only relevant when comparing one solution to another.
    - D. **Summary**: It's the force needed to counteract the entropy-driven osmosis, and thus is a measure of how "strongly" osmosis is pushing
    - E. Like torturing a terrorist until he finally admits where the nuke is; you can find how badly he "wanted it" until he finally broke
- Colligative Properties: Flow
    - A. Osmotic Pressure
        - 1. Lower pressure → higher pressure How?
    - B. Osmotic Potential
        - 1. Higher pressure → lower pressure

    - C. Water potential
        - 1. Higher pressure → lower pressure
- Colligative Properties: Osmotic Pressure Explained
    - A. Explained:
        - 1. Divide pure water by a membrane permeable **only** to water and **not** the solute
        - 2. Add solute to one side; it cannot permeate the barrier
        - 3. Entropy forces water to move to the other side to equilibrate the solution; let's say it achieves a perfect equilibrium
        - 4. Keep adding solute
        - 5. Water will keep migrating to make a dilute solution but think: the more and more water that moves over → the higher the liquid on that side of the tube will rise → pressure increases ($P = \rho g \Delta y$)
        - 6. Eventually a balance is struck between: entropy vs. pressure
        - 7. **Osmotic Pressure** is the extra pressure on the solution (compared to other side of the tube)
    - C. Analogy: osmotic pressure is the force pulling water into the solution whereas hydrostatic pressure is the force pushing it out (not technically correct because pressure Is a scalar and has no direction, but a good analogy nonetheless)
    - D. Equation: Π = iMRT
        - 1. M = molarity, **not** molality **or** mass (which is opposite of boiling point elevation and freezing point depression)
    - E. Osmotic Potential
        - 1. Definition: *partial* measurement of a system's free energy
            - a. Pure water is not itself "targeted" for osmosis because it is completely dilute – why would solvents move against their gradients to "dilute" it further?
            - b. Since free energy is in part a measurement of entropy, something that is completely dilute has zero "potential entropy," i.e. there is no chance some solvent is going to dilute it, cause dissolution, and increase entropy
        - 2. Pure water: [arbitrarily] assigned an osmotic potential value of zero
        - 3. Solute added: osmotic potential becomes negative
            - a. Solution now has "potential" to be diluted in an entropy driven manner
        - 4. At constant temperature and constant pressure….
            - a. Constant temperature and pressure means entropy is the only force at work
        - 5. …. water flows from higher osmotic potential to lower osmotic potential
            - a. Entropy is increased
    - F. Water Potential
        - 1. Definition: The potential of water molecules to move from a hypotonic solution (more water, less solute) to a hypertonic solution (less water, more solutes); *essentially* the same as free energy
        - 2. Is a function of
            - a. Temperature (does not have to be constant)
            - b. Pressure (does not have to be constant)
            - c. Solute concentration
        - 3. Water moves from higher water potential to lower water potential when two solutions are separated by a membrane permeable to water but not solute
        - 4. Diagram explanation: when at equilibrium, points A (pure water) and B (solution) have the same water potential, but point B has "less" (more negative) osmotic potential than point A
        - 5. Diagram:



- G. Water vs. Osmotic
  - 1. Osmotic: water flows from higher osmotic potential to lower osmotic potential
  - 2. Water: water flows from higher water potential to lower water potential

---

CHAPTER 6
Acids and Bases

Equation Review

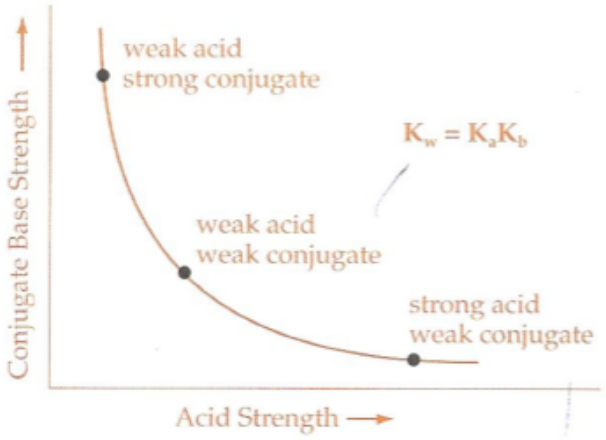
- K_a
  - 1. Acid dissociation constant for HA
    - a. $K_a = [H^+][OH^-]/[HA]$
  - 2. Conjugate Base constant for A^-:
    - a. $K_b = [OH^-][HA]/[A^-]$
      - a. Important Note: The reaction for K_b is the reaction of the conjugate base with water, **not** the reverse of K_a
  - 3. Products of Equilibrium Constants:
    - a. $K_a * K_b = K_w$
- pK
  - 1. $-\log[K_a] = pK_a$
  - 2. $-\log[K_b] = pK_b$
  - 3. At 25°C: $pK_a + pK_b = pK_w = 14$, which is the same as…
  - 4. Aqueous solutions at 25°C: pH + pOH = 14
- Titrations: Henderson-Hasselbalch Equation
  - A. Equation: $pH = pK_a + \log([A^-]/[HA])$
- Titrations: Henderson-Hasselbalch How to Find pH at Half Equivalence Point
  - A. Henderson-Hasselbalch is simply a form of the equilibrium expression K_a:
    - 1. $K_a = ([H^+][A^-]/[HA])$
    - 2. $K_a = [H^+]([A^-]/[HA])$
    - 3. Log rule: $-\log(K_a) = -\log[H^+] - \log([A^-]/[HA])$
    - 4. $pK_a = pH - \log([A^-]/[HA])$
    - 5. $pH = pK_a + \log([A^-]/[HA])$
- Titrations: Henderson-Hasselbalch How to Find pH at Equivalence Point
  - A. Cannot use H.H. to find the pH at the equivalence point
  - B. Must use K_b of conjugate base:
    - 1. Find K_b from K_a and K_w
    - 2. At equivalence point: [Conjugate base] = (# moles acid/volume acid) + (volume of base used to titrate)
    - 3. (*Unless* the base has no volume) volume of base: [Conjugate base at equivalence point] **will not be equal to** [original acid]
  - c. Equivalence point
    - 1. $K_b = K_w/K_a$
    - 2. Equilibrium expression: $K_b = [OH^-][HA]/[A^-]$
    - 3. $[OH^-] = (K_b)[A^-]/[HA]$
    - 4. $-\log[OH^-] = pOH$
    - 5. 14 – pOH = pH
- Equilibrium Constants: Water
  - a. [Water] = 55.6 mol/L
  - b. K_w water = $[H^+][OH^-] = [1 \times 10^{-7}][1 \times 10^{-7}] = [10^{-14}]$
  - c. K_a water = $[H^+][OH^-]/[H_2O] = [1 \times 10^{-7}][1 \times 10^{-7}]/[55.6] = 1.8 \times 10^{-16}$
  - d. pK_a water = $-\log[K_a]$ water = $-\log[1.8 \times 10^{-16}] = 15 - 16$

- Definitions: Three **to know!**
  - 1. Arrhenius
  - 2. Bronsted-Lowry
  - 3. Lewis
- Definitions: Acid and Base
  - A. Acids: taste sour
  - B. Bases: taste bitter and are slippery
- Definitions: Arrhenius
  - A. Arrhenius acid: anything that produces hydrogen ions in aqueous solution

- B. **Arrhenius base:** anything that produces hydroxide ions in aqueous solution
- C. **Only for aqueous solutions!**

- Definitions: Bronsted-Lowry
  - A. **Bronsted Acid:** anything that that donates a proton
  - B. **Bronsted Base:** anything that accepts a proton
- Definitions: Lewis
  - A. **Lewis acid:** anything that accepts a pair of electrons
  - B. **Lewis base:** anything that donates a pair of electrons
  - C. **Lewis acids include:**
    - 1. **Incomplete octets:**
      - a. $AlCl_3$
      - b. BF_3
    - 2. **All simple cations, except:**
      - a. Alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+)
      - b. Heavier Alkaline Earth metal cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+})
    - 3. **Every Bronsted acid**
  - D. **Lewis acid strength**
    - 1. Strong = smaller cation, higher charge = less stable = wants an electron more
    - 2. Weak = larger cation, lower charge
  - E. **Note!** Lewis acids are not necessarily all Bronsted or Arrhenius acids
- pH
  - A. Measure of hydrogen ion concentration
  - B. p(x) is a function of any x; p(x) = -log(x)
  - C. Measuring hydrogen ion concentration in moles per liter $[H^+]$:
    - 1. $pH = -\log[H^+]$
- pH: Concentrations
  - A. Usually 0 – 14; any $[H^+]$ is possible though
  - B. 25°C, pH =
    - 1. 7 = neutral
    - 2. >7 = basic
    - 3. <7 = acidic
  - C. pH change of 1 is a 10 fold increase in $[H^+]$
- pH: Estimations
  - A. **Example 1:**
    - 1. $10^x = 3.16$
    - 2. $x = \log(3.16)$
    - 3. Why? $10^0 = 1$ and $10^1 = 10$; so x must be between 0 and 1
    - 4. $x = 0.5$
  - B. **Example 2:**
    - 1. $[H^+] = 10^{-3}$
    - 2. $\log(10^{-3}) = -3$
    - 3. $-\log(10^{-3}) = 3$
    - 4. Thus, pH = 3
  - C. **Example 3:**
    - 1. Little more than 10^{-3}; say, 4×10^{-3}
    - 2. Solution must be a little more acidic; pH ~ 2.4
    - 3. Notice: $4 \times 10^{-3} < 10^{-2}$; so 3 > pH > 2
- pH: Conjugates
  - A. $HA + H_2O \rightarrow A^- + H_3O^+$
  - B. **Conjugate acid:** when the original base gained a proton
  - C. **Conjugate base**: when the original acid loses a proton
- pH: Conjugate Strengths
  - A. Stronger acid = weaker conjugate base
  - B. Stronger base = weaker conjugate acid

- C. **WARNING:** this does not mean that weak acids have strong conjugate base; it may be weak **or** strong. The weaker the acid, the stronger it's conjugate base, but that doesn't mean it is a strong base.
- D. **Check this diagram:**



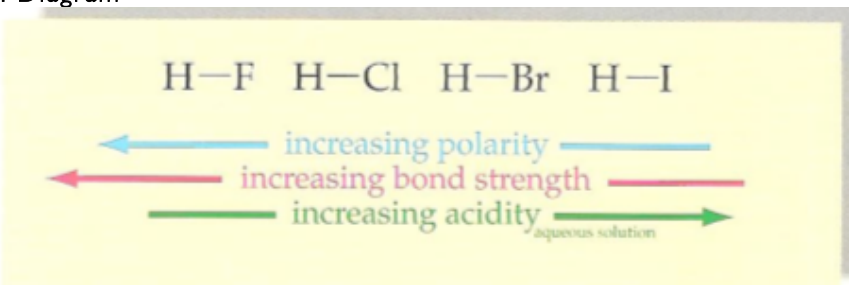
- 1.

- Strong Acids and Bases
  - A. Strong acid: stronger than hydronium
    - 1. Strong base: stronger than hydroxide (I think?)
  - B. Weak acid: weaker than hydronium
    - 1. Weak base: weaker than hydroxide (I think?)

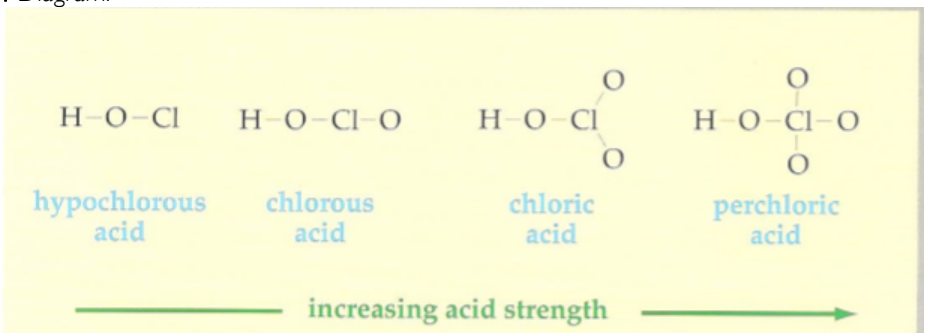
Strong Acid	Formula	Strong Base	Formula
Hydroiodic acid	HI	Sodium hydroxide	NaOH
Hydrobromic acid	HBr	Potassium hydroxide	KOH
Hydrochloric acid	HCl	Amide ion	NH_2^-
Nitric acid	HNO_3	Hydride ion	H^-
Perchloric acid	$HClO_4$	Calcium hydroxide	$Ca(OH)_2$
Chloric acid	$HClO_3$	Sodium oxide	Na_2O
Sulfuric acid	H_2SO_4	Calcium oxide	CaO

- pH: Conjugates Continued
  - A. **Amphoteric:** substance that can act as either an acid or a base, depending on the environment
  - B. **Polyprotic acids:** can donate more than one proton
  - C. **Diprotic**:
    - 1. Donate just two protons
    - 2. Can also be called polyprotic
    - 3. Second proton is so weak that it's effect on pH is negligible (rule: if the K_a values differ by more than 10^3)
    - 4. It should be noted that percent dissociation decreases with increasing acidity; this means acids dissociate less in more concentrated solutions (Le Chatelier's)
    - 5. This does **not** mean that concentrated solutions are less acidic
  - D. **Say it again:**
    - 1. **Acid dissociation** decreases with increasing acid concentration
    - 2. **Acid strength** increases with acid concentration

        - 3. Example:
            - a. 100 acid molecules in a given volume of water → 50 dissociate → 50% dissociation → 50 hydrogen ions
            - b. 1000 acid molecules in the same volume of water → 400 dissociate → 40% dissociation → 400 hydrogen ions → more hydrogen ions in same amount of water = more acid strength, less % dissociation
            - c. **Impact of this:** increasing [weak acid] by 10x does NOT result in 10x hydrogen ion concentration; the acid *strength* increases, but the percent dissociation decreases
- Percent Ionization of an Acid
    - A. Factors affecting percent ionization of an acid
        - 1. Temperature of solution
        - 2. Identity of acid
        - 3. Concentration of acid
- Molecular Structure and Acid Strength: Halides
    - A. Three factors Determine if a Compound Will release its' proton: strength, polarity and stability
        - 1. Strength of the bond holding the hydrogen to the molecule
            - a. HF is the most polar (good) but also the strongest (bad)
        - 2. Polarity of the bond
            - a. HCl is acidic while CH (methane) is not
        - 3. Stability of the conjugate base
            - a. HF is the most polar (good), but F is the smallest (bad) and thus the most unstable (bad)
        - 4. Diagram



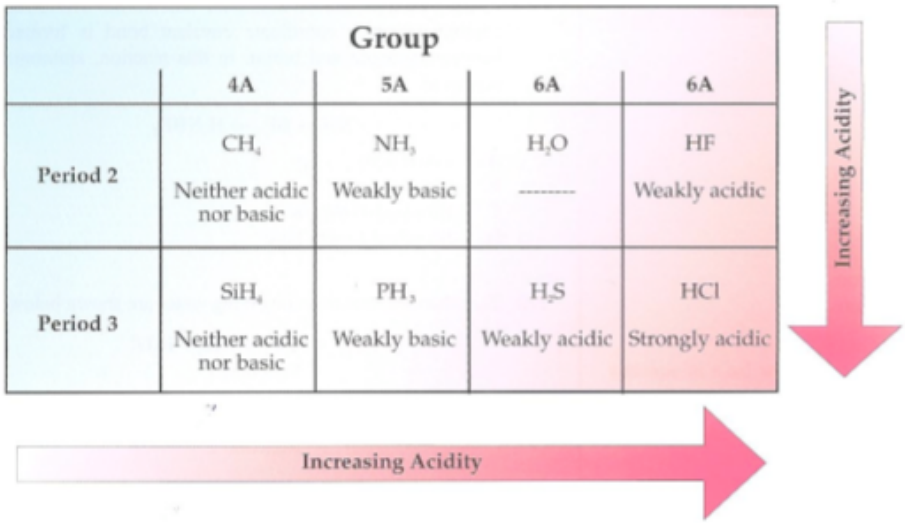
- Molecular Structure and Acid Strength: Oxyacids
    - A. **Polarity:** Increasing electronegative oxygens increases polarity
    - B. **Stability:** the multiple oxygens can stabilize the bonds
    - C. **Oxidation number of central atom:** acidity increases proportionally with the oxidation number of the central atom
    - D. **Summary:** Oxygens ↑ acidity ↑
    - E. **With different central atoms but same number of oxygens:** central atom with highest electronegativity is the most acidic compound
        - 1. HClO > HBrO > HIO
    - F. Diagram:



- Hydrides

- **A. Binary compounds:** contain only two elements and if one is hydrogen are called **hydrides**
- **B. Hydrides** can be: basic, acidic or neutral
  - **1.** Basic
    - **a.** Left on the periodic table, e.g. NaH
    - **b.** Metal hydrides
  - **2.** Acidic:
    - **a.** Right on the periodic table, e.g. H_2S
    - **b.** Nonmetal hydrides
  - **3.** Neutral
    - **a.** Metal hydrides
    - **b.** Nonmetal hydrides
- **C. Metal Hydrides:** basic or neutral
- **D. Nonmetal hydrides:** acidic or neutral, with the exception of Ammonia, NH_3 (which I'm guessing is basic)
- **E. Acidity of hydrides**:
  - **1.** Increases going down the period table
  - **2.** $H_2O < H_2S < H_2Se < H_2Te$

- **Hydrides: Diagram**
  - **A.**



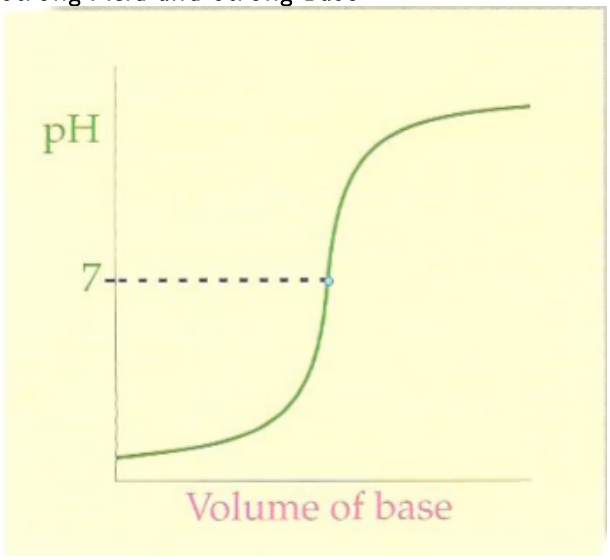
- **Equilibrium Constants for Acid-Base Reactions**
  - **A.** Pure water reacts with itself to form hydronium and hydroxide
    - **a.** $H_2O + H_2O \rightarrow H_3O + OH^-$
  - **B.** This is called **Autoionization**
- **Equilibrium Constants: Water**
  - **a.** [Water] = 55.6 mol/L
  - **b.** K_w water = $[H^+][OH^-] = [1 \times 10^{-7}][1 \times 10^{-7}] = [10^{-14}]$
  - **c.** K_a water = $[H^+][OH^-]/[H_2O] = [1 \times 10^{-7}][1 \times 10^{-7}]/[55.6] = 1.8 \times 10^{-16}$
  - **d.** pK_a water = $-\log[K_a]$ water = $-\log[1.8 \times 10^{-16}] = 15 - 16$
- **Equilibrium Constants for Acid-Base Reactions: Autoionization**
  - **A.** $K_w = [H^+][OH^-]$
  - **B. Equilibrium**: lies far to the left; $K_w = [10^{-14}]$
  - **C. Neutral aqueous solutions, 25°C**:
    - **1.** $[H^+]$ and $[OH^-] = 10^{-7}$ mol/L
    - **2.** pH = 7
  - **D. Add Acid:**
    - **1.** Changes: $[H^+]$ and $[OH^-]$
    - **2.** Remains the same: $K_w = 10^{-14}$
  - **E. Example:** pH = 2

        - 1. $[H^+] = 10^{-2}$ mol/L
        - 2. $[OH^-] = 10^{-12}$ mol/L
        - 3. p(x) function and the log rule: log(AB) = log(A) + log(B) gives an important equation
- Equilibrium Constants: Equations
    - A. pH + pOH = pK_w
    - B. Aqueous solutions at 25°C: pH + pOH = 14
- Equilibrium Constant: Acid dissociation constant, K_a
    - A. Hypothetical reaction: $HA + H_2O \rightarrow H_3O^+ + OH^-$
    - B. Acid dissociation constant for HA
        - 1. $K_a = [H^+][OH^-]/[HA]$
- Equilibrium Constant: Conjugate Base Constant in Water, K_b
    - A. For every K_a there is a corresponding K_b
    - B. Hypothetical reaction: $A^- + H_2O \rightarrow OH^- + HA$
    - C. Conjugate Base constant for A^-:
        - 1. $K_b = [OH^-][HA]/[A^-]$
    - D. Important Note: The reaction for K_b is the reaction of the conjugate base with water, **not** the reverse of K_a
- Equilibrium Constant: Products of K_a and K_b

$$K_a K_b = \frac{[H^+][A^-]}{[HA]} \times \frac{[OH^-][HA]}{[A^-]} = [H^+][OH^-] = K_w$$

$$K_a K_b = K_w$$

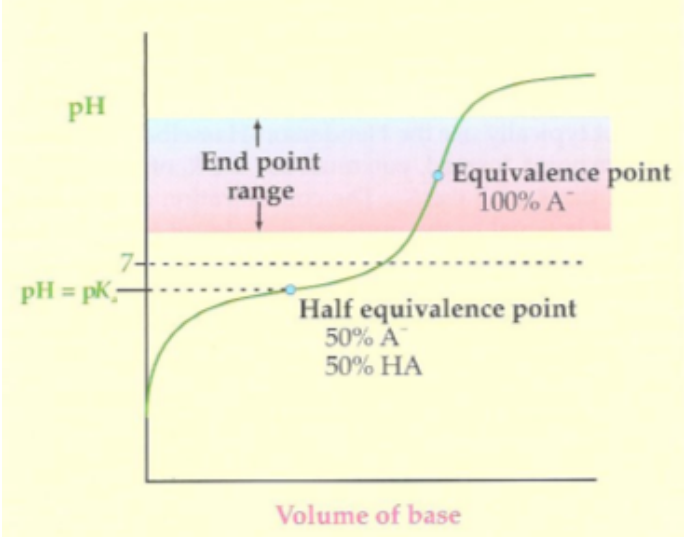
    - A.
    - B. Products of Equilibrium Constants:
        - 1. $K_a * K_b = K_w$
    - C. Products of Equilibrium Constants with log rule:
        - 1. $pK_a + pK_b = pK_w$
    - D. Products of Equilibrium Constants with log rule, at 25°C:
        - 1. $pK_a + pK_b = 14$
- Percent Dissociation
    - 1. [pH] / [(Original concentration) – (pH)]
- Finding the pH: Strong acids and bases
    - A. Strong acids and bases: Dissociate virtually 100%, unless the concentration is extremely high
        - 1. [HA] or [BOH] = virtually 0
        - 2. K_a and K_b = don't exist
        - 3. $[H^+]$ = initial [HA]
            - 1. 0.01M HCL = 0.01M H^+ ions
            - 2. $0.01 = 10^{-2}$
            - 3. $-\log(10^{-2}) = 2$
            - 4. pH = 2
        - 3. $[OH^-]$ = initial [BOH]
            - 1. 0.01M NaOH = 0.01M OH^- ions
            - 2. $0.01 = 10^{-2}$
            - 3. $-\log(10^{-2}) = 2$
            - 4. pOH = 2
            - 5. 14 – 2 = pH = 12
- Finding the pH: Weak Acids Example
    - A. pH of 0.01M HCN
        - 1. Set up equilibrium: $K_a = [H^+][CN]/[HCN] = 6.2 \times 10^{-10}$
        - 2. Add 0.01M HCN to pure water
        - 3. x amount of HCN dissociates :
            - a. x mol/L of H^+ ions
            - b. x mol/L of CN^- ions
        - 4. Undissociated HCN = 0.01 – x
        - 5. Plug all this into equation from step 1

        - a. $[x][x]/[0.01 - x] = 6.2 \times 10^{-10}$
    - 6. Solving for x requires a quadratic formula! We make the assumption that x < 5% of 0.01
    - 7. After throwing out x
        - a. $[x][x]/[0.01] = 6.2 \times 10^{-10}$
    - 8. $x = 2.5 \times 10^{-6} = [H^+] = 5 < pH < 6$
- Finding the pH: Weak Base Example
    - A. Same exact steps, just find pOH and subtract that from 14
- Salts
    - A. **Salts:** Ionic compounds that dissociate in water
        - 1. The higher the charges between the two ions, the harder it is to dissolve them in water
    - B. Composed of (both):
        - 1. Metal
        - 2. Nonmetal
    - C. Upon dissociation: create acidic or basic conditions
    - D. pH: predicted by comparing the conjugates of the respective ions
- Salts: Example
    - A. Na^+ and Cl^- are the conjugates of NaOH and HCl, respectively
    - B. Thus, NaCl dissociates = neutral solution
- Salts: Example 2
    - A. NH_4NO_3 composed of conjugate acid of the base NH_3 and the (weak) conjugate base of the strong acid NO_3, respectively
    - B. NH_4^+ = acidic
    - C. NO_3^- = neutral (super weak base)
    - D. Thus, NH_4NO = weakly acidic
- Salts: Weak Lewis Acids
    - A. **Remember:** All cations act as weak Lewis acids in aqueous solutions, except:
        - a. Alkali metal cations
        - b. Heavier Alkaline Earth metal cations (Ca^{2+}, Sr^{2+}, Ba^{2+})
- Titrations
    - A. **Titration:** drop-by-drop mixing of an acid and a base
    - B. Purpose: find [unknown] by comparing to [titrant]
    - C. ΔpH of the unknown as acid or base added: sigmoidal curve
- Titrations: Strong Acid and Strong Base
    - A. 

    - B. Portion of the graph that most closely represents a vertical line; the midpoint of this line is called the **equivalence point** or the **stoichiometric point**
- Titrations: Equivalence Point/Stoichiometric Point

- **A. Definition:** Midpoint of the line that is most closely vertical
- **B. For a monoprotic acid:** it is the point in the titration when there are equal **equivalents** of acid and base in solution
- **C. Example of Equally strong acid-base titrations: HCl and NaOH (Graph above)**
  - **1.** One-to-one correspondence
  - **2.** Equivalence point: same number of moles of each exist in solution
  - **3. Note:** this does **not** mean equal volumes; the concentrations may differ and thus volumes will too
  - **4. Note:** the graph above is slowly adding base to acid; the opposite graph would simply be inverted

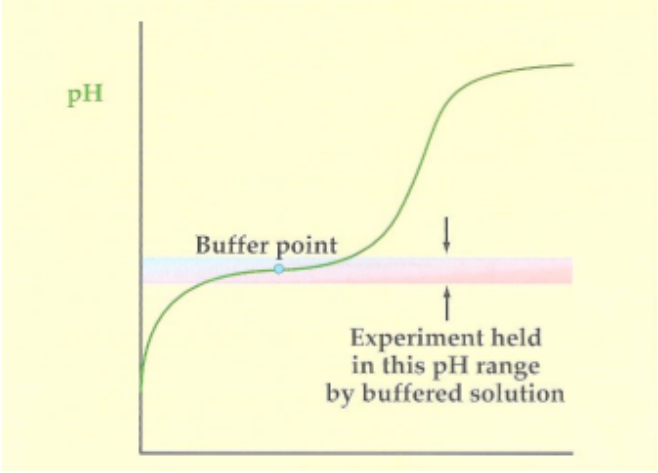
- **Titrations: Weak Acid and Strong Base**



- **A. Graph:**
- **B. Equivalence point:** not as predictable
  - **1.** Above 7: base strength > acid strength
  - **2.** Below 7: acid strength > base strength
- **C. Half equivalence point:** Midpoint of the line that is most closely horizontal

- **Titrations: Half equivalence point**
  - **A. Definition:** Midpoint of the line that is most closely horizontal
  - **B. Description:** the point where the *largest* amount of acid or base could be added with the *smallest* change in pH, i.e. a **buffer**
    - **1.** (0.5)[Acid] neutralized by base
    - **2.** Thus: [Acid] = [Base]
  - **C. Half equivalence point pH:** solution pH = pK_a of acid, predicted by the **Henderson-Hasselbalch equation**
- **What can be determined from a Titration Curve?**
  - **1.** The initial concentration of the acid
  - **2.** The pKa of the acid
  - **3. Not** the molecular weight of the acid
- **Titrations: Henderson-Hasselbalch Equation**
  - **A. Equation:** pH = pK_a + log($[A^-]/[HA]$)
  - **B. Review:**
    - **1.** log(1) = 0
    - **2.** When $[A^-]$ = [HA], pH = pK_a
  - **C.** Does **not** consider **ion-pairing**
  - **D. Thus:** Adding H_2O in *large* quantities will change the pH, but probably not in *small* quantities
    - **1. Acidic buffers:** H_2O acts a base
    - **2. Basic Buffers**: H_2O acts as an acid
- **To measure the pKa of a weak acid, you can:**

    - 1. Measure the pH of a given concentration of the acid
    - 2. Measure the pH halfway to the equivalence point of a titration
    - 3. Find the pKb of the conjugate base
    - 4. Cannot measure the amount of base needed to neutralize the acid
- Titrations: Henderson-Hasselbalch How to Find pH at *Half Equivalence Point*
    - A. Henderson-Hasselbalch is simply a form of the equilibrium expression K_a:
        - 1. $K_a = ([H^+][A^-]/[HA])$
        - 2. $K_a = [H^+]([A^-]/[HA])$
        - 3. Log rule: $-\log(K_a) = -\log[H^+] - \log([A^-]/[HA])$
        - 4. $pK_a = pH - \log([A^-]/[HA])$
        - 5. $pH = pK_a + \log([A^-]/[HA])$
- Titrations: Henderson-Hasselbalch How to Find pH at Equivalence Point
    - A. Cannot use H.H. to find the pH at the equivalence point
    - B. Must use K_b of conjugate base:
        - 1. Find K_b from K_a and K_w
        - 2. At equivalence point: [Conjugate base] = (# moles acid/volume acid) + (volume of base used to titrate)
        - 3. *Unless* the base has no volume, then the volume of the base: [Conjugate base at equivalence point] will not be equal to [original acid]
- Titrations: Henderson-Hasselbalch: Finding the pH at Equivalence Point vs. Half Equivalence Point
    - A. Half equivalence point
        - 1. $K_a = ([H^+][A^-]/[HA])$
        - 2. $K_a = [H^+]([A^-]/[HA])$
        - 3. Log rule: $-\log(K_a) = -\log[H^+] - \log([A^-]/[HA])$
        - 4. $pK_a = pH - \log([A^-]/[HA])$
        - 5. $pH = pK_a + \log([A^-]/[HA])$
    - B. Equivalence point
        - 1. $K_b = K_w/K_a$
        - 2. Equilibrium expression: $K_b = [OH^-][HA]/[A^-]$
        - 3. $[OH^-] = (K_b)[A^-]/[HA]$
        - 4. $-\log[OH^-] = pOH$
        - 5. $14 - pOH = pH$
- Titrations: Buffers
    - A. Buffer: the spot in a titration (specifically the half equivalence point) where the *most* amount of acid or base can be added with the *smallest* change in pH
    - B. To make a buffer:
        - 1. Choose an acid with a pK_a closest to desired pH of buffer solution
        - 2. Mix equal amounts of that acid and its' conjugate base
        - 3. Goal: [buffer] >>> [outside base] or [outside acid]
    - C. NOTE: the buffer depends on the ratio of the acid to base; diluting it with water won't do anything
    - D. Summary: tons of a weak acid and its conjugate base

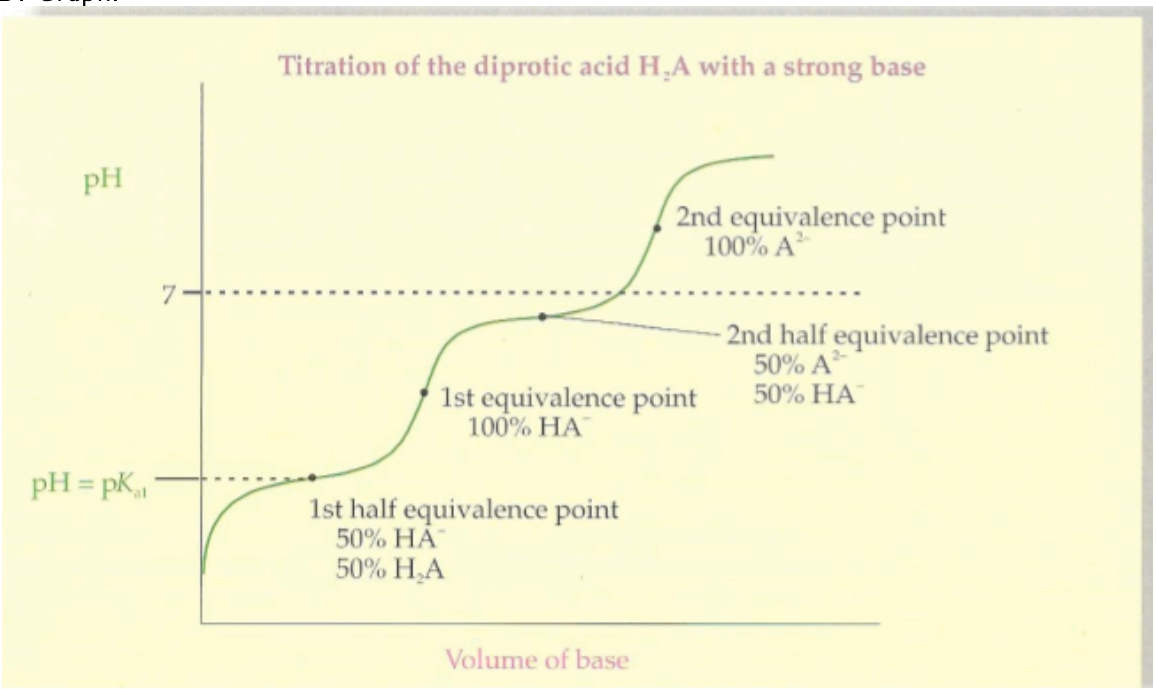


- D. Diagram:

- Indicators
  - A. Chemical used to find the equivalence point
  - B. (Usually) a weak acid (HIn) whose conjugate base is a different color (In-)
  - C. Human eye detection: [In-] ≥ (1/10)[initial HIn]
  - D. Titrate acid with base:
    - 1. Low pH = HIn form predominates
    - 2. pH rises = In- form arises
    - 3. Higher pH = In- becomes visible
  - E. Titrate base with acid:
    - 1. Reverse process
  - F. Summary: pH of color change depends upon *direction* of titration
- Indicators: Range
  - A. Range: pH values of the two points of color range, HH predicts:
    - 1. pH = pK_a + log[In-]/[HIn]
  - B. Lower range of color change
    - 1. pH = pK_a + log[1]/[10] → pH = pK_a – 1
  - C. Upper range of color change
    - 1. pH = pK_a + log[10]/[1] → pH = pK_a + 1
- Indicators: Endpoint
  - A. Point where the indicator changes color
  - B. Endpoint is **not** the equivalence point
  - C. Indicators (usually) have a range that covers the whole equivalence point
- Indicators: Endpoint and Henderson Hasselbalch
  - A. Question: If HH **cannot** be used to find the pH at the equivalence point…why can it be used to find the indicator range that will include the equivalence point?
  - B. Answers:
    - 1. In HH, we use [indicator]…
    - 2. … and the indicator never reaches the equivalence point in the titration
    - 3. That is, the indicator ions do **not** approach zero concentration near the color change range
- Polyprotic Titrations
  - `
    - 2. Half equivalence point
  - B. Volume of Titrant (Triprotic acid example)
    - 1. The ratio of base added to proton removed in a titration is one-to-one
    - 2. Therefore, each successive equivalence point will require the same volume of base to be added as the previous one
  - C. Assume:
    - 1. First proton: *completely* dissociates before the **second** proton *begins* to dissociate
    - 2. Only assume this if:

- 1. Second proton is *much* weaker acid than first
- 2. That is: (second proton acid strength) <<< (first proton acid strength)

- D. Graph:



CHAPTER 7
Electrochemistry

Equation Review

- Free Energy and Chemical Energy: Equation Review
  - A. Cell Potential Free energy
    - 1. $\Delta G = -nFE_{max}$
  - B. Standard State Equation
    - 1. $\Delta G° = -nFE°_{max}$
  - C. Nonstandard State Equation:
    - 1. $\Delta G = \Delta G° + RT\ln(Q)$
    - 2. $\Delta G = \Delta G° + 2.3RT\log(Q)$
  - D. Equilibrium, $\Delta G = 0$:
    - 1. $\Delta G° = -RT\log(Q)$ **or** $\Delta G° = -RT\ln(K)$
      - a. Varies with temperature:
        - 1. K (equilibrium constant)
        - 2. $\Delta G°$ (gibbs)
    - 3. Relationship: K and $\Delta G°$
      - 1. If: $K = 1$, then: $\Delta G° = 0$
      - 2. If: $K > 1$, then: $\Delta G° < 0$
      - 3. If: $K < 1$, then: $\Delta G° > 0$
    - 4. Warning:
      - 1. If: $K > 1$, does NOT mean the reaction is always spontaneous
      - 2. If: $K > 1$, DOES mean the reaction is spontaneous at standard state conditions and the specified temperature
  - E. Nernst Equation
    - Remember: "Q" not "K" because Nernst is used to find the potential when the concentrations are changing
    - 1. $E = E° - (RT/nF)\ln(Q)$
    - 2. $E = E° - (0.06/n)\log(Q)$

- Oxidation-Reduction: Terms
  - A. **Oxidation reduction reactions** are also called **redox reactions**
  - B. Electrons are transferred from atom to another
    - 1. **Oxidized:** atoms that lose electrons are oxidized
    - 2. **Reduced:** atoms that gain electrons are reduced
  - C. Reducing Agent/Reductant
    - 1. Gives electrons to and thus **reduces** another atom
    - 2. Loses electrons and is thus itself **oxidized**
    - 3. Reducing agents are compounds **not** atoms; the atom is oxidized, the compound is the reducing agent
  - D. Oxidizing Agent/Oxidant
    - 1. Accepts electrons from and thus **oxidizes** another atom
    - 2. Gains electrons and is thus itself **reduced**
    - 3. Reducing agents are compounds **not** atoms; the atom is reduced, the compound is the oxidizing agent
  - E. Example: $CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$
    - 1. **Reducing agent**: methane; carbon goes from -4 → + 4
    - 2. **Oxidizing agent:** dioxygen; oxygen goes from 0 → -2
- Oxidation States
  - A. **Oxidation states:** possible charge values that any atom may hold within a molecule
  - B. Must add up to the charge on the molecule or ion, i.e. a neutral molecule = 0
  - C. When tables conflict, use table 1
  - D. Memorize 1:

Oxidation State	Atom
0	Atoms in their elemental form
–1	Fluorine
+1	Hydrogen (except when bonded to a metal: then –1.)
–2	Oxygen (except when it is in a peroxide like H_2O_2)

  - E. Memorize 2:

Oxidation State	Group on Periodic Table
+1	Group 1 elements (alkali metals)
+2	Group 2 elements (alkaline earth metals)
–3	Group 15 elements (nitrogen family)
–2	Group 16 elements (oxygen family)
–1	Group 17 elements (halogens)

  - F. **Transition metals**: change their oxidations state according to the atoms they are bonded to
- Oxidation Reduction
  - A. Example Reaction: $2H_2 + O_2 \rightarrow 2H_2O$
    - 1. Hydrogen is oxidized: loses electrons, goes from 0 → +1
    - 2. Oxygen is reduced: gains electrons, goes from 0 → -2
  - B. **Note:** wherever there is oxidation there **must** be reduction
- Oxidation-Reduction Titrations
  - A. **Find the molarity of a reducing agent**: titrate it with a strong oxidizing agent
  - B. **Example:** Find molarity of Sn^{2+} ions
    - 1. Titrate: with known concentration of strong oxidizing agent, Ce^{4+}
    - 2. Sn^{2+} ions oxidize to Sn^{4+} ions; Ce^{4+} reduces to Ce^{3+}
    - 3. Analyze: 1 electron to reduce Ce^{4+} but 2 electrons to oxidize Sn^{2+}

        - **4.** Summary: # moles Ce^{4+} to reach equivalent point = 2x # moles Sn^{2+} in solution
- Potentials
    - **A. Electric potential, E:** electric potentials are associated with redox reactions because electrons are transferred, and electrons have charge
- Potentials: SHE
    - **A. Standard Hydrogen Electrode (SHE):** used to separate the potentials of a reaction into oxidation and reduction components, called **half reactions**
- Potentials: Half reaction
    - **A.** Half a component of a redox reaction
    - **B.** Every half reaction must be accompanied by another
    - **C.** Half reactions are usually listed as **reduction potentials**, with **oxidation potentials** just being the opposite
    - **D. Half reactions at 25°C to memorize:**
        - **1. Strongest oxidizing agent:** top left
        - **2. Strongest reducing agent:** bottom right
        - **3.**

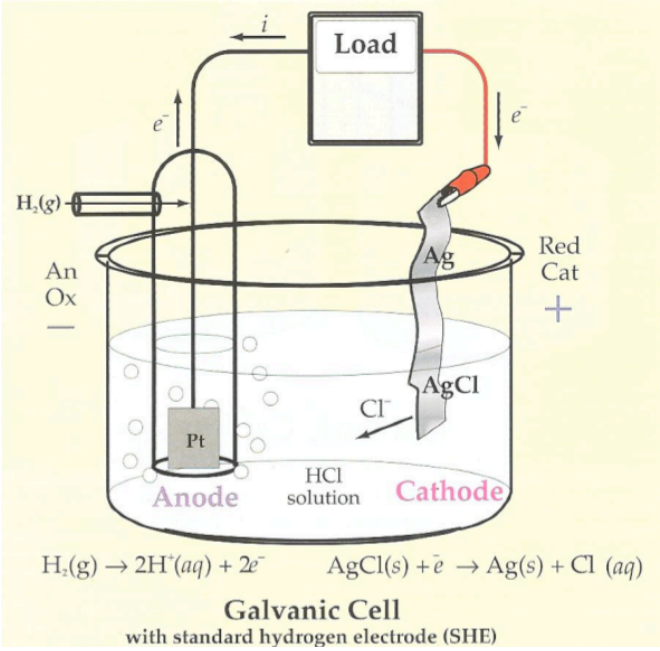
Standard Reduction Potentials at 25°C	
Half reaction	**Potential $E°$**
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	1.50
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow H_2O(l)$	1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	1.2
$Ag^{2+}(aq) + 2e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.80
$Cu^{+}(aq) + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.036
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.23
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83

            - **a.** Second half of bottom reaction: final reaction of aerobic respiration
- Potentials: Electric Potential
    - **A. Electric potential**: has no absolute value, but rather arbitrary assignments based on the zero value of the half reaction at SHE:
        - **1.** $2H^+ + 2e^- \rightarrow H_2$
        - **2.** $E° = 0.00V$
- Potentials: Electric Potential Example
    - **A. Find the potential:** $2Au^{3+} + 3Cu \rightarrow 3Cu^{2+} + 2Au$
    - **B. Separate into two half reactions**
        - **1.** $2(Au^{3+} + 3e^- \rightarrow Au)$……$E° = 1.50$ V
        - **2.** $3(Cu \rightarrow Cu^{2+} + 2e^-)$…..$E° = -0.34V$

        - 3. ……. $E° = 1.16V$
    - C. Note:
        - 1. Reduction potentials are intensive properties
        - 2. Thus do **not** multiply the (half reaction potential) by (# of times it occurs)
- Balancing Redox Reactions
    - 1. Divide the reaction into its corresponding half reactions
    - 2. Balance the elements other than H and O
    - 3. Add H_2O to one side until the O atoms are balanced
    - 4. Add H^+ to one side until the H atoms are balanced
    - 5. Add e^- to one side until the charge is balanced
    - 6. Multiply each half reaction by an integer so that an equal number of electrons are transferred in each reaction
    - 7. Add the two half reactions and simplify (canceling substances that show up on both sides of the equations)
    - 7B. **Basic solutions:** Add OH^- to any H^+ to form water, adjust H_2O as needed
- Balancing Redox Reactions: Acidic Example
    - 1. $I_2 + OCl^- \rightarrow IO_3^- + Cl^-$
    - 2. $6H_2O + I_2 \rightarrow 2IO_3^- + 12H^+ + 10e^-$
        - a. Balance iodine first; 2
        - b. Balance oxygen second; 6
        - c. Balance hydrogen third; 12
        - d. Count charges:
            - 1. Left side: 0 charge
            - 2. Right side: +10 charge (-2 + 12)
        - e. Balance charges: 10 electrons right side makes both sides = 0 charge
    - 3. $2e^- + 2H^+ + OCl^- \rightarrow Cl^- + H_2O$
        - a. Balance oxygen first; 1
        - b. Balance hydrogen second; 2
        - c. Count charges:
            - 1. Left side: +1 charge (2 + -1)
            - 2. Right side: -1 charge (-1 + 0)
        - d. Balance charges: 2 electrons left side makes both sides = -1 charge
    - 4. Balance the electrons for both equations
        - a. **Electrons must be on opposite sides:** Equation 1 has 10 electrons on the **right side**, whereas Equation 2 has 2 electrons on the **left side**
        - b. **Balance electrons:** Multiply entire Equation 2 by 5:
            - 1. $(2e^- + 2H^+ + OCl^- \rightarrow Cl^- + H_2O) \times 5 =$
            - 2. $10e^- + 10H^+ + 5OCl^- \rightarrow 5Cl^- + 5H_2O$
    - 5. Cancel extras
        - a. Compare the equations
            - 1. $6H_2O + I_2 \rightarrow 2IO_3^- + 12H^+ + 10e^-$
            - 2. $10e^- + 10H^+ + 5OCl^- \rightarrow 5Cl^- + 5H_2O$
        - b. **N ow** electrons
            - 1. $6H_2O + I_2 \rightarrow 2IO_3^- + 12H^+$
            - 2. $10H^+ + 5OCl^- \rightarrow 5Cl^- + 5H_2O$
        - a. Fight to the death, Hydrogen ions
            - 1. $6H_2O + I_2 \rightarrow 2IO_3^- + 2H^+$
            - 2. $5OCl^- \rightarrow 5Cl^- + 5H_2O$
        - a. You too, water molecules
            - 1. $H_2O + I_2 \rightarrow 2IO_3^- + 2H^+$
            - 2. $5OCl^- \rightarrow 5Cl^-$
    - 6. Check this out:
        - a. $H_2O + I_2 + 5OCl^- \rightarrow 2IO_3^- + 2H^+ + 5Cl^-$
- Balancing Redox Reactions: Basic Example
    - 1. $MnO_4^- + Br^- \rightarrow MnO_2 + BrO_3^-$
    - 2. $3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$

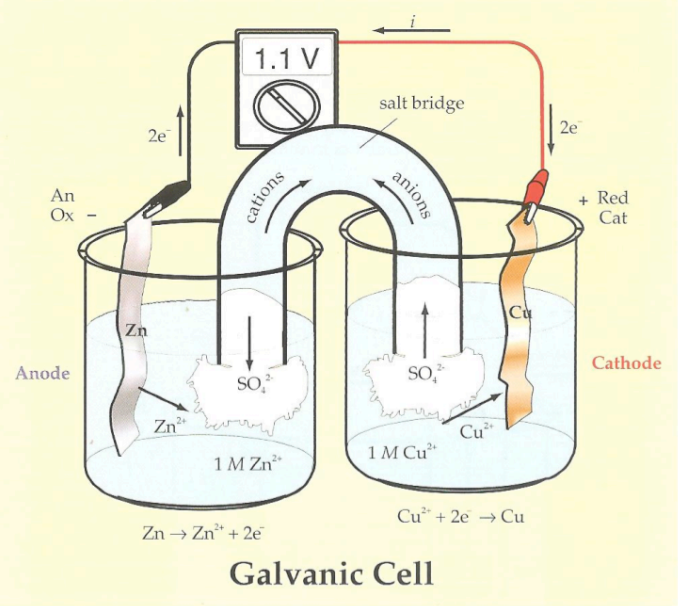
        - a. Balance Manganese atoms: N/A
        - b. Balance Oxygen atoms: 2
        - c. Balance Hydrogen atoms: 4
        - d. Count charges:
            - 1. Left side: +3 charge (4 + -1)
            - 2. Right side: 0 charge (0 + 0)
        - e. Balance charges: 3 electrons left side makes both sides = 0 charge
    - 3. $3H_2O + Br^- \rightarrow BrO_3^- + 6H^+ + 6e^-$
        - a. Balance bromine atoms: N/A
        - b. Balance Oxygen atoms: 3
        - c. Balance Hydrogen atoms: 6
        - d. Count charges:
            - 1. Left side: -1 charge (-1)
            - 2. Right side: +5 charge (-1 + 6)
        - e. Balance charges: 6 electrons right side makes both sides = -1 charge
    - 4. Balance the electrons for both equations
        - a. **Electrons must be on opposite sides:** Equation 1 has 3 electrons on the **left side**, whereas Equation 2 has 6 electrons on the **right side**
        - b. **Balance electrons:** Multiply entire Equation 1 by 2:
            - 1. $(3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O) \times 2 =$
            - 2. $6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$
    - 5. Add the equations together
        - a. $6e^- + 8H^+ + 2MnO_4^- + 3H_2O + Br^- \rightarrow 2MnO_2 + 4H_2O + BrO_3^- + 6H^+ + 6e^-$
    - 6. Cancel extras
        - a. Examine the equation
            - 1. $6e^- + 8H^+ + 2MnO_4^- + 3H_2O + Br^- \rightarrow 2MnO_2 + 4H_2O + BrO_3^- + 6H^+ + 6e^-$
        - b. **No w electrons**
            - 1. $8H^+ + 2MnO_4^- + 3H_2O + Br^- \rightarrow 2MnO_2 + 4H_2O + BrO_3^- + 6H^+$
        - a. **Fight to the death, Hydrogen ions**
            - 1. $2H^+ + 2MnO_4^- + 3H_2O + Br^- \rightarrow 2MnO_2 + 4H_2O + BrO_3^-$
        - a. **You too, water molecules**
            - 1. $2H^+ + 2MnO_4^- + Br^- \rightarrow 2MnO_2 + H_2O + BrO_3^-$
    - 7. Basic Solution: Neutralize Hydrogen ions with Hydroxides
        - a. $2OH^- + 2H^+ + 2MnO_4^- + Br^- \rightarrow 2MnO_2 + H_2O + BrO_3^- + 2OH^-$
            - 1. Left side: 2 hydrogen ions get whacked by 2 hydroxide ions
            - 2. Whatever goes on one side must go on the other: 2 hydroxide ions to the right side
            - 3. These combine to form water molecules…
    - 8. Balance the Water Molecules
        - a. Examine the equation
            - 1. $2H_2O + 2MnO_4^- + Br^- \rightarrow 2MnO_2 + H_2O + BrO_3^- + 2OH^-$
        - b. **Water molecules, FIGHT!**
            - 1. $H_2O + 2MnO_4^- + Br^- \rightarrow 2MnO_2 + 2OH^- + BrO_3^-$
    - 9. Check this out
        - a. $H_2O + 2MnO_4^- + Br^- \rightarrow 2MnO_2 + 2OH^- + BrO_3^-$
- Galvanic/Voltaic Cell
    - A. Preface:
        - 1. Two electrically conducting chemical phases are placed in contact
        - 2. One charged species from one phase cannot freely flow to the other phase
        - 3. Result: charge difference between the phases → creates electric potential (1 – 2V)
    - B. Galvanic/Voltaic cell:
        - 1. Provides an alternative path for electron flow
        - 2. Thus uses electric potential between two phases to generate a current of electrons from one phase to another

        - 3. This converts *chemical energy* to *electrical energy*
- Galvanic/Voltaic Cell: Components
    - A. Multiphase series of components; no component is in more than one phase
    - B. All phases **must** conduct electricity
    - C. **One** must be **impermeable** to electrons (if not: electrons would come to equilibrium quickly due to free movement)
        - 1. **Impermeable phase**: ionic conductor that carries current in the form of ions
        - 2. **Impermeable phase**: an electrolyte solution called a **salt bridge**
    - D. **Symbolization:** T-E-I-E'-T'
        - 1. **T** = terminals (conductors: metal wires)
        - 2. **E** = electrodes (conductors)
        - 3. **I** = ionic conductor (**salt bridge**)
    - E. **Voltage ("Electromotive force")** = potential difference between T and T'
- Galvanic/Voltaic Cell: Electrodes
    - A. **Anodes:**
        - 1. Negative sign
        - 2. Oxidation half reaction occurs here
    - B. **Cathodes**
        - 1. Positive sign
        - 2. Reduction half reaction occurs here
    - C. **Electrode** may refer to
        - 1. Strip of metal only, **or**
        - 2. Strip of metal + electrolyte solution it's submerged in = **half cell**
    - D. **Both terminals**: must be made of the same material
- Galvanic/Voltaic Cell: Cell Potential *E*
    - A. **Cell Potential *E*/Electromotive force (emf)**
        - 1. Potential difference between the two terminals when **not** connected
        - 2. Always positive: always has chemical energy than can be converted to work
        - 3. Affected by:
            - a. Concentrations of the solutions in the half cells
            - b. Reactions of the solutions in the half cells
            - c. Temperature of the solutions in the half cells
            - d. **NOT** the length of the wire connecting the half cells (doesn't make sense; think resistivity of a wire: pl/a)
    - B. **Connecting terminal:**
        - 1. Reduces the potential difference due to internal resistance
        - 2. Potential difference decreases as current increases
    - C. **Current**:
        - 1. Flow of positive charge, through the **load**, in opposite direction of electrons
        - 2. Pathway of electrons and thus the opposite of current:
            - **a**. Anode (-): electrons are repelled from here
            - **b**. Through the load
            - **c**. Cathode (+): electrons are attracted to here
            - **d**. Thus current flows from the cathode to the anode
    - D. **Load:** the resistance
- SHE Galvanic/Voltaic Cell: Diagram Explanation
    - A. **Process Below:**
        - 1. H_2 gas bubbles off platinum (catalyst) plate = H^+ ions produced
        - 2. Platinum (Pt) plate carries electrons through wire to silver (Ag) strip
        - 3. Ag^+ accepts electron, converts it to solid silver, and allows a Cl^- to solvate in the solution



- B. Diagram:
- C. Note:
  - 1. Oxidation potential of hydrogen is zero…
  - 2. …the oxidation potential of any electrode used in conjunction with SHE = reduction potential of the half reaction occurring at the other electrode
  - 3. Thus: *some* half reaction reduction potentials can be measured using SHE
- D. Note: No **salt bridge** in the above cell
  - 1. Why? Both electrodes are in contact with the same solution…salt bridge not necessary
- E. Liquid Junction:
  - 1. Required when a cell contains: two different solutions
  - 2. Ions can move across the liquid junction; thus creates an additional potential difference that affects the potential of the galvanic cell
  - 3. A **salt bridge** minimizes this potential difference

- Salt Bridge
  - A. A type of **liquid junction** used to minimize the potential difference in a SHE galvanic cell
  - B. Composed of: **aqueous electrolyte solution**, like KCl
  - C. Purpose:
    - 1. Allows ionic conduction between solutions **without** creating extra potential within the galvanic cell.
  - D. How?
    - 1. K+ ions move toward the cathode at the **same** rate that Cl- ions move toward the anode
  - E. And if we don't have one?
    - 1. Solutions mix →
    - 2. Low resistance path for electrons to move from Zn(s) to Cu^{2+} (aq) →
    - 3. Short circuits the cell →
    - 4. Cell potential = 0
  - F. Diagram, bitches



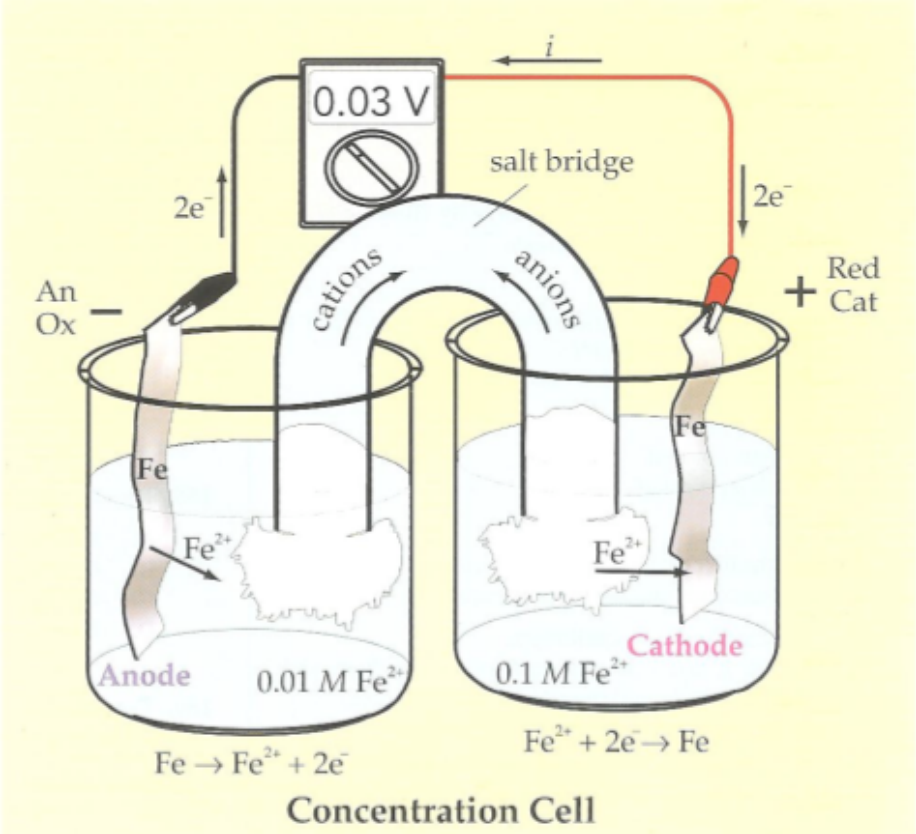
    - 1.
- IUPAC Conventions: Cell Diagram
    - A. **Cell diagram:** represents galvanic cells
    - B. **Phase:** listed from left to right
        - 1. **Left**: terminal attached to anode
        - 2. **Right**: terminal attached to cathode
    - C. **Terminals**: omitted because:
        - 1. They are the same material
        - 2. Do not participate in the reaction
    - D. **Vertical line**:
        - 1. Placed between two phases
    - E. **Double vertical line:**
        - 1. Salt bridge
    - F. **Dotted vertical line**:
        - 1. Boundary between two miscible liquids
    - G. **Comma**:
        - 1. Boundary between species in the same phase
- IUPAC Conventions: Cell Diagram Example

$$\mathrm{Pt'(s)\,|\,Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)\,|\,Pt(s)}$$

    - A.
    - B. Find Standard State Potential
        - 1. Subtract the potential of the reduction half reaction on the left (reaction at anode) from the potential of the reduction half reaction on the right (reaction at cathode)
- Free Energy and Chemical Energy
    - A. Positive cell potential
        - 1. Indicates a spontaneous reaction
        - 2. Indicates a negative ΔG
    - B. **Equation**: $\Delta G = -nFE_{max}$
        - 1. **n =** # of moles of electrons transferred in balanced redox reaction
        - 2. **F** = Faraday's constant = charge on one mole electrons = 96,500 C
        - 3. **Implications**: Free energy = (total charge, NF)(voltage, E)
    - C. **Standard State Equation:** $\Delta G° = -nFE°_{max}$
    - D. **Nonstandard State Equation:** $\Delta G = \Delta G° + RT\ln(Q)$ **or** $\Delta G = \Delta G° + 2.3RT\log(Q)$
        - 1. **Q** = reaction quotient

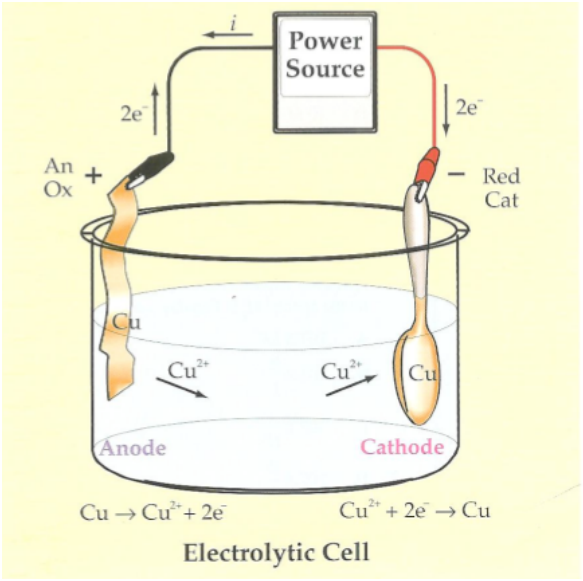
        - 2. **ln** = natural logarithm
- Free Energy and Chemical Energy: **ΔG vs. ΔG°**
    - A. **ΔG°** = standard conditions (**Note:** standard conditions can be at any temperature; just assumed to be at 298 K)
        - 1. **If**: we use only one molar concentrations for Q…
        - 2. **Then**: Q = 1
        - 3. **And:** RTln(Q) = 0
        - 4. **Thus:** ΔG = ΔG°
    - B. **ΔG**= nonstandard conditions
    - C. Equilibrium
        - 1. No available free energy to do work, so…
        - 2. ΔG = 0
        - 3. Plug in 0 for ΔG in ΔG = ΔG° + RTln(Q) =
        - 4. ΔG° = -RTln(Q)
        - 5. **Rewritten:** ΔG° = -RTln(K)
- Free Energy and Chemical Energy: Equilibrium Equation
    - A. ΔG° = -RTln(K) or
        - 1. **Varies with temperature**:
            - a. K
            - b. ΔG°
    - B. **Relationship:** K and ΔG°
        - 1. **If**: K = 1, **then**: ΔG° = 0
        - 2. **If**: K > 1, **then**: ΔG° < 0
        - 3. **If**: K < 1, **then**: ΔG° > 0
    - C. Warning:
        - 1. **If**: K > 1, does **NOT** mean the reaction is **always** spontaneous
        - 2. **If**: K > 1, **DOES** mean the reaction is spontaneous at **standard state conditions and the specified temperature**
- Free Energy and Chemical Energy: When Concentrations Change, How Do We Find the Potential? God Damn Nernst Equation
    - A. **Take the equation:** ΔG = ΔG° + RTln(Q)
    - B. **Substitute:** -nFE for ΔG
    - C. **And Substitute:** -nFE for ΔG°
    - D. **Divide by:** -nF
    - E. **Equals:** E = E° - (RT/nF)ln(Q) = **Nernst Equation**
- Free Energy and Chemical Energy: Nernst Equation
    - A. E = E° - (RT/nF)ln(Q)
    - B. **Base 10 logarithm:** E = E° - (0.06/n)log(Q)
    - C. Purpose:
        - 1. Plug in nonstandard concentrations to create Q…
        - 2. Allows us to find the cell potential
- Galvanic vs. Electrolytic
    - A. Potential/Spontaneity
        - 1. **Galvanic**: positive and thus spontaneous by $\Delta G = -nFE_{max}$
            - A. Note: If the reaction is to be spontaneous, ΔG must be negative; this doesn't necessarily mean ΔG° is negative
            - B. If the reaction is to be spontaneous, Q < K has to be true
        - 2. **Electrolytic**: negative and thus forced by an outside power source by $\Delta G = -nFE_{max}$
- Concentration Cells
    - A. Concentration Cell
        - 1. Limited form of a galvanic cell
        - 2. Contains a reduction half reaction taking place in one half cell
        - 3. Reverse half reaction taking place in the other half cell
        - 4. **Never**: at standard conditions, thus…

        - 5. **Always**: requires the Nernst equation to solve for the cell potential
    - B. Half Reactions
        - 1. Adding the two half reactions: E° = 0
        - 2. Must use the Nernst equation to find the potential
    - C. Entropy
        - 1. Nature wants greatest entropy
        - 2. Thus: the more concentrated side will try to become less concentrated; electrons flow accordingly
    - D. Potential
        - 1. **Concentration cells**: tend to have small potential
- Concentration Cell: Diagrams
    - A. Diagram:
        - 1.



    - B. Nernst Equation for potential at 25°C
        - 1. **Fe^{2+}:** both a product (left side) and reactant (right side)
        - 2. **Substitute:** for Q the Fe^{2+} ratios on either side
        - 3. **Result (for the case above):** E = E° - (0.06/2)log(0.01/0.1)
            - a. **n** = 2 because 2 electrons are used each time the reaction occurs
            - b. **E°** = 0
    - C. Entropy
        - 1. Nature wants greatest entropy
        - 2. Thus: the more concentrated side will try to become less concentrated; electrons flow accordingly
        - 3. Observe this above:
            - A. More ions on the right side than the left side, right? Right.
            - B. Left Side
                - 1. So, solid Fe on the left side is trying to increase the number of ions by undergoing oxidation reactions.

        - 2. It does this happily, with a positive (thus spontaneous) potential of +0.44
    - C. Right side
        - 1. Ions are trying to reduce their numbers by taking the electrons from the right side and reducing themselves to pure iron.
        - 2. Now, this goes against spontaneity, with a negative potential of -0.44. So why does this happen?
        - 3. Because entropy would rather see the sides balanced in terms of reactants, which overrides the electric potential factor.
        - 4. This can be seen in the equation: $E = E° - (0.06/n)\log([products]/[reactants])$
        - 5. That is, if E is positive, then the reaction is spontaneous.
        - 6. Well, in concentration cells, E° is zero, so whatever is being subtracted from it must be negative (zero minus a negative = positive)
        - 7. When the numerator (products from the right half of the equation in the left half-cell) is smaller than denominator (reactants from the left half of the equation in the right half-cell), log(products/reactants) = negative
        - 8. Zero minus a negative = positive E = spontaneous; makes sense, more concentrated side tries to become less concentrated
        - 9. Science, bitches.
- Electrolytic Cell
    - A. Electrolytic cell:
        - 1. Hook up a power source across the resistance of a galvanic cell and force the cell to run backwards
    - B. Potential: negative
    - C. Terminals
        - 1. Anode:
            - a. Marked *positive*
            - b. Oxidation still occurs here
        - 2. Cathode
            - a. Marked *negative*
            - b. Reduction still occurs here
        - 3. Why?
            - a. Galvanic cells: are used to provide energy to an external load
            - b. Thus: the electrodes are labeled so that the negative electrons will flow toward the positive electrode
    - D. Diagram



    - 1.
- "Electrochemical"
    - A. Electrochemical can refer to both types of batteries:
        - 1. Galvanic, or
        - 2. Electrolytic