

1 Chemistry

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Lecture 1

Elements

- Protons and neutrons have the same mass
- Mass Number - A - protons & neutrons (top)
 - Good approximation of mass of an atom
- Atomic Number - Z - protons (bottom)
- Atomic Weight/Molar Mass - 1 amu = 1 g/mol , 6.022×10^{23} amu = 1 gram

Empirical Formula - whole number ratio of elements to each other

Molecular Formula - exact number of elemental atoms in a molecule

★ Energy is always required to break a bond. Energy is NOT released during bond breaking.

Periodic Table

- Period - Horizontal row
- Group/Family - vertical column, elements in the same family have similar chemical properties such as same number of bonds or similarly charged ions
- Alkali Metals, Alkaline Earth Metals, Halogens, Noble Gases
- Representative/main-group elements and transition metals

Metals - large atoms that tend to lose electrons to form cations or positive oxidation states

- Ductility, malleability, thermal and electrical conductivity, luster
- All metals except mercury exist as solids at room temperature

Non-metals - form anions

- Lower melting points than metals

Group 1A (Alkali Metals)

- Low densities, low melting points
- Highly reactive, especially with nonmetals to form ionic ions

Group 2A (Alkali Earth Metals)

- Harder/denser, melt at higher temps than Group 1A(Alkali metals)

Group 5A

- Can form 3 covalent bonds
- Except for nitrogen all other group 5A can form 5 covalent bonds using d orbitals
- Nitrogen forms strong pi bonds to make double and triple bonds

Group 6A (Chalcogens)

- Oxygen is the 2nd most electronegative element
- Oxygen is divalent and can form strong pi bonds

Group 7A (halogens)

- Highly reactive
- Fluorine always has an oxidation state of -1 meaning it can't make more than one bond

Halogens	Room Temperature State
Fluorine, Chlorine	Diatomic gases
Bromine	Diatomic liquid
Iodine	Diatomic solid

- Small atoms have less room to stabilize charge by spreading it out making them bond more strongly to water resulting in greater heats of hydration
- The p orbitals on atoms that are too big don't overlap well so they don't bond (2nd row is fine, 3rd is not)

Transition Metals

- Lose electrons from their s subshell first and then from their d subshell
- Try to even out their d orbitals so they each have the same number of electrons

Atomic Size

- Cations are smaller than neutral counterparts because the loss of an electron decreases shielding
- Anions are larger than neutral counterparts
- Elements with the same number of electrons tend to get smaller as there are more protons
- Z-Effective Nuclear Charge

- Nuclear charge Z minus the average number of electrons between the nucleus and the electron in question
- Increases left to right and top to bottom

- Atomic radius decreases left to right, increases top to bottom

Ionization Energy

- Increases left to right and bottom to top
- Second ionization energy $>$ first ionization energy (not a contradiction of previous statement)

Electronegativity

- Tendency of an atom to attract an electron in a bond with another atom
- Increases left to right and bottom to top
- Undefined for noble gases (same with electron affinity)

Electron Affinity

- Willingness of an atom to accept an additional electron
- Increases from left to right and bottom to top

Metallic Character

- Increases from right to left and top to bottom

Types of Reactions

- Combination: $A + B \rightarrow C$
- Decomposition: $C \rightarrow A + B$
- Single Displacement: $A + BC \rightarrow AB + C$
- Double Displacement: $AB + CD \rightarrow AC + B$

Crystals

- Ionic Crystals - consist of oppositely charged ions held together by electrostatic forces
- Molecular Crystals - composed of individual molecules held together by intermolecular bonds

1 Nomenclature

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Ionic Compounds

- Add -ic to end of cation with greater positive charge and -ous to ion with less positive charge
- Monoatomic anions and simple polyatomic anions are given the suffix -ide
- Polyatomic anions with multiple oxygens end with the suffix -ite (less oxygens) or -ate (more oxygens)
- To name an ionic compound put the cation name in front of the anion name

Acids

- If the name of the anion ends in -ide the acid starts with hydro- and ends with -ic
- If the acid is an oxyacid the ending -ic is used for the species with more oxygens and -ous for the species with less oxygens

Binary Molecular Compounds

- The name begins with the name of the element that is farthest to the left and lowest in the periodic table

1 Fake Quantum

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Principle Quantum Number (n)

- *Transition metals* - lag one shell behind the period
- *Representative elements* - given by the period in the periodic table

Azimuthal Quantum Number (L)

- s, p, d, and f
- $L = n - 1$

Magnetic Quantum Number (m)

- From -L to L
- Gives the precise orbital of the subshell

Spin Quantum Number

- $-1/2$ to $1/2$

- $\lambda = h / mv$

- Aufbau Principle - each new proton added a new electron is added
- Hund's Rule - electrons will not fill any orbital in the same subshell until all orbitals in that subshell contain at least one electron

	s	p	d	f
1	1s			
2	2s	2p		
3	3s	3p	3d	
4	4s	4p	4d	4f
5	5s	5p	5d	5f

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2 Gases, Kinetics

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- STP Conditions - 0°C and 1atm, 22.4L/mol
- Mean Free Path - distance travelled by a gas between collisions
- Kinetics deals with rate of reaction as it moves towards equilibrium, thermodynamics deals with balance of reactants and products after they have achieved equilibrium

Kinetic Molecular Theory

- Gas molecules exert no forces other than repulsive forces due to collisions
- Gas molecules make completely elastic collisions
- Average kinetic energy of gas molecules is directly proportional to temperature of gas
- $PV = nRT$ is a state equation. When gases do work by expanding the pressure drops to compensate for the volume increase but it also drops to compensate for the kinetic energy loss since the nRT side drops as well
- $K.E. = (3/2)RT$
- $v_1/v_2 = \sqrt{m_2/m_1}$. Find K.E. from temperature, plug into this formula to find relative velocities from relative mass
- Effusion - spreading of a gas from very high pressure to very low pressure through a "pinhole"
 - Effusion Rate 1 / Effusion Rate 2 = $\sqrt{M_2/M_1}$
- Diffusion - is the spreading of one gas into another gas or into empty space
 - Also approximated by above law
- $PV=nRT$ Adjustments
 - Real gases deviate from ideal behavior when their molecules are close together
 - High pressure pushes gas molecules together
 - Low temperature causes gas molecules to settle near each other
 - ? - $[P + a(n/V)^2](V-nb) = nRT$
 - b is a measure of volume actually occupied
 - a is strength of intermolecular attractions
 - A and B generally increase with molecular mass and complexity of gas
 - $V_{\text{real}} > V_{\text{ideal}}$ because gases have volume
 - $P_{\text{real}} < P_{\text{ideal}}$ because gases attract each other

2 Reaction Rates

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- $k = Zpe^{E_a/RT}$
 - P = steric factor
 - Z = fraction of collisions having the effective spatial orientation p
- Increasing the rate is NOT a statement about the equilibrium
- $\text{Rate}_{\text{forward}} = k_f[A]^a[B]^b$
 - overall order = a + b
- If looking at a table...when concentration is doubled reaction rate quadruples making the order = 2
- $-\text{[Reactants]}/x_t = \text{[Products]}/y_t$ where x and y are constants
- Elementary reactions - if the MCAT tells you a reaction is elementary then you can use the coefficients as the order...otherwise? No.

Order	Equation of graph necessary to make a straight line
[A] ⁰	[A], slope = -k _f
[A] ¹	ln[A], slope = -k _f
[A] ²	1/[A], slope = k _f
[A] ³	1/2[A] ² , slope = k _f

- Two Step Reactions
 - If second reaction is rate limiting then [reactants] for the second step depends on the rate constant of the first step

1.) NO + Br ₂ -> NOBr ₂	Fast Step
2.) NOBr ₂ + NO -> 2NOBr	Slow Step

- $k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$
 - $\therefore k_1/k_{-1}[\text{NO}][\text{Br}_2] = [\text{NOBr}_2]$
 - Since the rate is set by the slow step $k_2[\text{NOBr}_2][\text{NO}] = [\text{NOBr}]$
 - Making $k_2k_1/k_{-1}[\text{NO}]^2[\text{Br}_2]$
- Catalysts
 - A catalyst may lower the activation energy or increase the steric factor 'p'
 - Heterogeneous Catalyst - in a different phase than the reactants and products
 - The binding of a catalyst is almost always exothermic and the rate of catalysis depends upon the strength of the bond between the reactant and the catalyst
 - Too weak and not enough adsorption
 - Too strong and too much energy is required to remove the reactant
- Effects of Solvent on Rate -
 - the solvent bonds may stabilize an intermediate
 - Degree of solvation affects k
 - Rate constant is a function of solvent and temperature
 - Solvent bonds must be broken before

2 Equilibrium

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- Equilibrium -
 - The point where the forward rate is equal to the reverse rate
 - Equilibrium is the point of greatest entropy
 - Equilibrium is a dynamic process
- Law of Mass Action
 - ★ • The law of mass action is good for all chemical equations, including non-elementary equations
 - This means use the coefficients as the exponents regardless of molecularity(? pp39)
 - The equilibrium constant $K = \frac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}}$
 - If you look closely this means $K = k_f/k_r$ BUT only for elementary equations
 - K depends only upon temperature
 - Equilibrium constant for a series of reactions is equal to the product of the equilibrium constants for each step
 - Do NOT confuse equilibrium constant with equilibrium
 - ? ▪ Don't include solids or pure liquids
- Partial Pressure Equilibrium Constant (pp 39)
 - $K_p = K(RT)^{\Delta n}$
 - K is concentration equilibrium constant
 - K_p is partial pressure equilibrium constant, for gas reactions you can use this equation to find K
 - n is the sum of the coefficients of the products minus the sum of the coefficients of the reactants
 - Any two or more single reactions or series of reactions resulting in the same products from identical reactants must have the same equilibrium constant for a given temperature
 - MUST be able to work with partial pressure equilibrium constants for the MCAT so learn it...I know you don't understand it yet
- Reaction Quotient
 - $Q = \frac{\text{Products}^{\text{coefficients}}}{\text{Reactants}^{\text{coefficients}}}$
 - Since products always move towards equilibrium Q will always move towards K
 - If $Q=K$ reaction is at equilibrium
 - If $Q>K$ then the [products] is greater than it should be and the reaction will shift leftward
 - If $Q<K$ then the [products] is less than it should be and the reaction will shift rightward
- Le Chatelier's Principle
 - When a system **at equilibrium** is stressed the system will shift in a direction to reduce that stress
 - Three types of stress
 - i. Addition or removal of product or reactant
 - ii. Changing pressure
 - iii. Heating or cooling the system
 - If a product of a reaction is heat adding heat will shift the equilibrium to more reactants...not counterintuitive once you realize that heat is produced when bonds are made...and bonds are broken by adding heat
 - Molarity Effect
 - If you concentrate a solution the equilibrium will shift to the side with less moles...

3 Thermodynamics

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System	Δ Energy	Δ Mass
Open	Yes	Yes
Closed	Yes	No
Isolated	No	No

Extensive Properties - change with amount

Intensive Properties - do not change with amount

State Functions - state properties describe the state of a system. The change in a state property going from one state to another is the same regardless of the process via which the system changed

Path functions - opposite of state functions

- i.e. work, heat

Work

- $w = P\Delta V$ under constant pressure
 - If force is constant pressure is constant by $P = F/A$
 - Work can be different going from one state to another...if pressure changes too then there is a different amount of work done
- If we have a piston on its side and add heat so that it expands (but keep the gas the same temperature) it does work on the surroundings
 - The temperature of the gas stays the same meaning pressure decreases as volume expands. This means that the pressure is decreasing so the force is not constant
 - Force can't be constant if temperature is constant
- Second Law of Thermodynamics
 - Heat can not be completely changed into work in a cyclical process
 - Efficiency = $1 - T_c/T_h$

$$K.E._{avg} = (3/2)kT$$

Enthalpy - $\Delta H = \Delta U + P\Delta V$

- Two systems may have the same amount of internal energy but if they are at different pressures they have a different capacity to perform work...hence enthalpy was invented
- Is a state function
- An ideal gas enthalpy depends only on temperature
- Is an extensive property
- At constant pressure change in enthalpy is equal to heat
- An element at 25C and 1atm is arbitrarily assigned an enthalpy value of 0J/mol
- Standard enthalpy of formation - ΔH°_f
 - Change in enthalpy that creates one mole of that product from its raw elements
- For a reaction involving no change in pressure $\Delta H = q$
- $\Delta H^\circ_{reaction} = \Delta H^\circ_{f, products} - \Delta H^\circ_{f, reactants}$
 - $\Delta H^\circ_{reaction} > 0$ the reaction is endothermic (counterintuitive?)
 - $\Delta H^\circ_{reaction} < 0$ the reaction is exothermic
- Hess' law says when you add reactions you can add their enthalpies

Entropy (Joules/Kelvin)

- is a state function
- is an extensive property (increases with number, volume, and temperature)

- a reaction can be unfavorable in enthalpy and proceed...but it can't be unfavorable with entropy and succeed
- reactions at equilibrium have achieved maximum universal entropy
- if a reaction increases the number of gaseous molecules then the reaction has positive entropy (nature likes more molecules)
- $\Delta S = dq_{rev}/T$ (defined by change in heat per kelvin in a reversible process)

Gibbs Free Energy(G)

- $\Delta G = \Delta H - T\Delta S$
 - Must minimize ΔG to achieve equilibrium
 - A negative delta G value ($-\Delta G$) corresponds to a spontaneous process
- This equation is only good for constant temperature reactions
- Is an extensive property
- Is a state function
- Represents the maximum Non- PV work available from a reaction
- An isolated system can change its gibbs free energy

3 Heat

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- There are two ways to transfer energy in a system: Heat(q) and Work
- Heat - movement of energy from hot to cold
 - 1.) Conduction - thermal energy transfer via molecular collisions
 - $Q/t = kA(T_h - T_c)/L$
 - k is thermal conductivity
 - ★- The rate of heat flow(Q/t) would be the same in all slabs even if they each had different lengths, thicknesses, and different thermal conductivities(this leads to the 5th bullet)
 - The order of the slabs wouldn't matter either
 - A higher conductivity results in a lower temperature difference across any slab of a given length
 - 2.) Convection - thermal energy transfer via fluid movements
 - Differences in pressure or density drive warm fluid in the direction of cooler fluid
 - 3.) Radiation
 - Rate at which an object radiates is its Power P
 - $P = \sigma \epsilon (T_e^4 - T_o^4)$
 - ϵ = emissivity of surface(between 0 and 1)

3 Solutions, Vapor Pressure

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Solution - homogeneous mixture of two or more compounds in a single phase

- Solvent - compound which there is more of
- Solute - compound there is less of
- Types of solutions
 - Ideal solutions - made from compounds with similar properties; compound can be interchanged within the solution without changing the spatial arrangement of the molecules or the intermolecular attractions
 - Ideally dilute solution - solute molecules are separated so that they have no interaction with each other; mole fraction of solvent is 1
 - Nonideal solutions -

Colloid - a colloid is like a solution except the solute forms into larger particles

- i.e. aerosol, foam, emulsion
- Can be separated with a semipermeable membrane using dialysis

London Dispersion Forces - Nonpolar molecules are held together by weak bonds caused by instantaneous dipole moments

- The bonds of a nonpolar solute are too strong to be broken by the weak forces of a nonpolar solvent

Electrolyte - a compound which forms ions in aqueous solution

- Strong electrolytes create solutions which conduct electricity well and contain many ions

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-}

Molarity - (mol/L) moles of the compound divided by the volume of the solution

Molality - (mol/kg) moles of solute divided by kilograms of solvent

Normality - measures the "number of equivalents" per liter of solution

- Depends on the type of reaction taking place in the solution
- An acid-base reaction with H_2SO_4 would be a 2 normal solution because two equivalents of protons

Solution Formation

- 3 steps to making a solution
 - 1.) break bonds between solute molecules
 - 2.) break bonds between solvent molecules
 - 3.) formation of bonds between solvent and solute
- At constant pressure the enthalpy change of a reaction equals the heat
- For condensed phases not at high pressure (most MCAT solutions) the enthalpy change approximately equals the internal energy change ($\Delta H \approx \Delta U$)

- ★- Heat of Hydration - the combined enthalpy of steps 2 and 3
- A solution with negative enthalpy will give off heat when it forms creating a stronger bond
- A solution with positive enthalpy will take in heat when it forms
- Positional entropy always increases in the formation of a solution so solution formation ALWAYS has positive entropy

Vapor Pressure

- Clausius-Clapeyron equation
 - $\ln(P_v) = -(\Delta H_{\text{vap}}/R) * (1/T) + C$
 - ΔH_{vap} is the heat of hydration
 - P_v is vapor pressure
 - ? - WHAT IS R?
 - Vapor pressure increases with temperature
- Vaporization is an endothermic process
- When vapor pressure equals local atmospheric pressure a compound boils
- Melting point - temperature at which the vapor pressures of the solid is equal to the vapor pressure of the liquid
 - Above the melting point the liquid vapor pressure is greater than that of the solid
 - Below the melting point the liquid vapor pressure is less than that of the solid
- Nonvolatile solute - when a solute with no vapor pressure is added to a solution it reduces that solutions vapor pressure by taking up room at the surface of the liquid reducing the area in which the liquid interacts with the vapor

Raoult's Law - $P_v = \chi_a P_a$

- For nonvolatile solutes - if 97% of the solution is solvent, the vapor pressure will be 97% of the vapor pressure of the pure solvent
- For volatile solutes - if 97% of the solution is solvent, then the vapor pressure will be 97% of the pure solvent PLUS 3% of the vapor pressure of the pure solute
- Vapor pressure if a nonideal solution will deviate from Raoult's law
 - Negative heats of solution form stronger bonds so less molecules can break free so there is lower vapor pressure and there will be a negative deviation
 - Positive heats of solution form weaker bonds so more molecules can break free so there is increased vapor pressure and there will be a positive deviation
 - ∴ a positive heat of solution leads to an increase in vapor pressure while a negative heat of solution leads to a decrease in vapor pressure

4 Solubility

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- Saturated - when the rate of dissolution and precipitation are equal
- Solubility - number of moles of solute per liter of a solution that can be dissolved in a given solvent
 - Depends on the common ions in the solution
 - Solubility is found from the solubility product
 - Solubility Product is not the same thing as Solubility, you look up the SP in a table and it is independent of common ions(duh)
- For most salts, crystallization is exothermic (random much? Think about it.)

Solubility Product (K_{sp})

- Equilibrium of a solvation reaction has its own equilibrium constant called the K_{sp}
- Solids and pure liquids have a mole fraction of approximately 1 and are excluded
- *Set K_{sp} equal to products over reactants raised to the power of their coefficients!!!*
- ★ - Changes ONLY with temperature, solubility depends on temperature and common ions in solution
 - Example:
 - $\text{BaF}_2(\text{s}) \leftrightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$
 - Then $K_{sp} = [\text{Ba}^{2+}][\text{F}^{-}]^2$
 - If 'x' moles per liter of BaF_2 dissolve then there will be x mol/L of Ba^{2+} and twice as many(2x) mol/L of F^{-} . If K_{sp} is 2.4×10^{-5} then...
 $2.4 \times 10^{-5} = (x)(2x)^2$
 - Solve for 'x' and that is the solubility of BaF_2 in mol/L
 - What if we had added 1 mol of NaF to the solution?
 - It would completely dissociate forming 1 mole of F^{-} and 1 mole of Na^{+}
 - Remember, the order in which you mix doesn't make a difference so choose the most convenient
 - $2.4 \times 10^{-5} = (x)(2x+1)^2$
 - Since we have more F^{-} the solution is going to shift to the left and 'x' will be smaller
 - ◆ Therefore, we can approximate "2x+1" as "1"
 - ◇ $2.4 \times 10^{-5} = (x)(1)^2$
 - ◇ $x \approx 2.4 \times 10^{-5}$. We can check our assumption by comparing with the original equation. Since $2x = 4.8 \times 10^{-5}$ and this is $\ll 1$ assumption = valid

Solubility Guidelines

- Nearly all ionic compounds containing nitrate(NO_3^{-}), ammonium(NH_4^{+}), and alkali metals(Li^{+} , Na^{+} , K^{+} ...) are **soluble**.
- Ionic compounds containing halogens(Cl^{-} , Br^{-} , I^{-}) are **soluble**, EXCEPT for silver, mercury, and lead compounds(Ag^{+} , Hg_2^{2+} , Pb^{2+})
- Sulfate compounds(SO_4^{2-}) are **soluble**, EXCEPT for mercury, lead, and the heavier alkaline metals(Hg_2^{2+} , Pb^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+})
- Compounds containing the heavier alkaline metals(Ca^{2+} , Sr^{2+} , Ba^{2+}) are **soluble** when paired with sulfides(S^{2-}) and hydroxides(OH^{-}).
- Carbonates, phosphates, sulfides, and hydroxides(CO_3^{2-} , PO_4^{3-} , S^{2-} , OH^{-}) are generally insoluble other than in the cases mentioned above.

Solubility Factors

- Pressure and temperature affect solubilities. Pressure on liquids and solids has little effect, but pressure on a gas increases its solubility. For an ideally dilute solution, the increase in pressure of a gas over a solution is directly proportional to the solubility of a gas, if the

gas does not react with, or dissociate in, the solvent. This relationship is given by Henry's Law:

Henry's Law: $C = k_{a1}P_v$

- C is the solubility of the gas a (in mol/L)
- k_{a1} is Henry's law constant which varies with each solute-solvent pair
- P_v is the vapor partial pressure of the gas a above the solution
- DOES NOT agree with Raoult's Law because both are approximations

When to Use Raoult's or Henry's

- The partial vapor pressure of a solution component is always proportional to its mole fraction. If the component predominates as the solvent the P_v is proportional to the pure vapor pressure. If the component represents a tiny amount of solution Henry's law says that the vapor partial pressure is proportional to a Henry's law constant.
- Raoult's law is more accurate when looking at the vapor partial pressure of a solvent with high concentration
- Henry's law is more accurate when looking at the vapor partial pressure of a volatile solute where the solute has a low concentration
- In an ideally dilute solution, the solvent obeys Raoult's Law and the solute obeys Henry's Law

Tidbits

- As temperature increases the solubility of salts generally increases. This is NOT true for gases. The solubility of gases in liquid decreases with increased temperature.
 - Can remember this by remembering why hot waste water is hazardous to aquatic life. It contains less oxygen and also tends to float on cold water limiting its gas exchange with the air.
- Heavier, larger gases tend to be more soluble.
- Gases that react with a solvent have greater solubility.

5 Heat Capacity, Phase Change

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Heat Capacity (C , in units of J/K) - measure of the energy change needed to change the temperature of a substance

- $C = q/\Delta T$
- There is a constant volume and constant pressure heat capacity
 - When pressure is held constant some energy escapes as PV work so at constant pressure a substance can absorb energy with less change in temperature by expelling some of the energy to the surroundings as work
 - Thus, $C_p > C_v$
- Specific heat capacity (usually c , $J/kg \cdot K$) - heat capacity divided by unit mass (not molality!)
 - You might get a question with specific heat capacity per volume, per mole, etc.
 - Each phase of a substance has its own specific heat

Coffee Cup Calorimeter

- An example of a constant pressure calorimeter because it measures energy change at atmospheric pressure
- Used to measure heats of reaction
- Specific heat capacity 'c' of water is $1 \text{ cal/g} \cdot \text{C}^\circ$
- You measure the change in temperature because at constant pressure $q = \Delta H$

Bomb Calorimeter

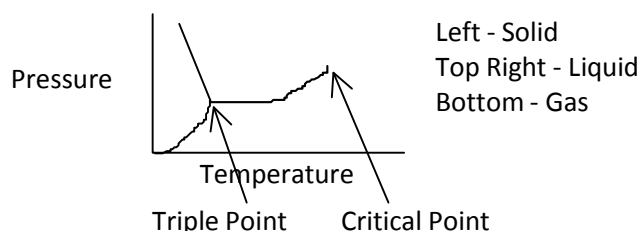
- An example of a constant volume calorimeter because it measures energy change in a confined volume
- A small blast chamber is inside of a larger chamber with the inner chamber surrounded by water
- Heat is transferred to water outside the blast chamber and the change in temperature is recorded so the heat of the reaction can be figured out using the equation $q = C\Delta T$

Phase Change

- Heat of fusion - enthalpy change associated with melting
- Heat of vaporization - enthalpy change associated with boiling
- Each phase of a substance has its own specific heat
 - The slope of the heating curve (heat(x-axis) v. temperature(y-axis)) is the reciprocal of specific heat
- Enthalpy and entropy are positive for melting and vaporizing
- Melting and boiling are endothermic
- Enthalpy and entropy are negative for condensing and freezing
- Condensing and freezing are exothermic

Phase Diagram

- Triple point - the one point where a substance can exist in equilibrium as a solid, liquid, and gas
- Critical temperature - the temperature above which a substance cannot be liquefied regardless of pressure applied
- Critical pressure - the pressure required to produce liquefaction while the substance is at the critical temperature
- Critical point - defined by the critical temperature and pressure
- Supercritical fluid - fluid beyond the critical point has characteristics of both gas and liquid



- During the phase change temperature goes towards breaking bonds not increasing temperature

5 Colligative Properties

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Colligative properties - depend only upon the number of molecules, not the type

- There are 4 colligative properties: vapor pressure, boiling point, freezing point, osmotic pressure

Vapor Pressure

- Adding a nonvolatile solute lowers the vapor pressure so the remaining surface area has to have more molecules vaporizing and condensing...this increases the boiling point

Boiling Point Elevation

- The equation for an ideally dilute solution due to the addition of a nonvolatile solute is:

- $\Delta T = k_b m i$
 - k_b is a substance dependent constant
 - m is the molality
 - i is the van't Hoff factor - the number of particles into which a single solute particle will dissociate when added to solution

★- You can't use this equation for volatile additions

- Making predictions: An endothermic heat of solution indicates weaker bonds, which leads to higher vapor pressure, so you can predict the boiling point will go down

Freezing Point Depression

- $\Delta T = k_f m i$
- If you add a liquid solute the impurities will initially lower the melting point but as the mole fraction of the "impurity" goes up the solvent becomes the impurity preventing the solute from freezing. Thus, the freezing point of the solution will rise as solute is added

Osmotic Pressure

- Measure of the tendency of water to move into a solution via osmosis
 - The pressure pulling a liquid into a solution
- $\Pi = iMRT$
 - M is molarity
 - i is number of dissociated particles
 - Let's say you have a semi-permeable membrane separating two sides of a U-shaped tube filled with water. If you have more salt on one side and the membrane is only permeable to water the water will flow more to the salt side. The pressure at the bottom of the solution on the salt side will be greater because more liquid is above it. The difference in pressure is the osmotic pressure.
 - "extra pressure" on solution side is osmotic pressure

Osmotic Potential

- Partial measure of a system's free energy
- When a solute is added osmotic potential becomes negative
- Water flows from higher osmotic potential to lower osmotic potential

6 Acids and Bases

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Arrhenius

- Acid - anything that produces hydrogen ions in aqueous solution
- Base - anything that produces hydroxide ions in aqueous solution

Bronsted and Lowry

- Acid - anything that donates a proton
- Base - anything that accepts a proton

Lewis

- Acid - anything that accepts an electron pair
 - All simple cations except alkali and heavier alkaline earth metal cations
 - Smaller the cation and the higher the charge, the stronger the acid strength
- Base - anything that donates an electron pair
- Most general, includes all B/L

Conjugate Acid/Base

- The reactants are referred to as the acid and base while the products are referred to as the conjugate acid and conjugate base
- Strong acids have weak conjugate bases
- However, weak acids may have strong or weak conjugate bases
 - Weak acid/weak conjugate is possible

Amphoteric - substances that can act as either acids or bases depending on their environment

Strong Acids		Strong Bases	
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 hydroxide	Na ₂ O
Sulfuric acid	H ₂ SO ₄	Calcium hydroxide	CaO

- The second proton donated by a polyprotic acid can usually be ignored if the K_a values differ by > 10³
- Percent dissociation of an acid decreases with the acidity of the solution...but more concentrated acids are more acidic

Three Factors that Determine Acidity

- Strength of the bond holding the hydrogen molecule
- The polarity of the bond (polar bonds are easier to separate)
- The stability of the conjugate base

H-F H-Cl H-Br H-I

← Increasing Polarity, Bond Strength
— Increasing Acidity

- Keeping conjugate stability in mind, the molecule with the most oxygens makes the strongest acid

Hydrides

- Acidity increases down (period 2 to 3) the periodic table and to the left (from groups 4A to 6A)

Equilibrium constants for Acid-Base Reactions

- Autoionization of Water

- $K_w = 10^{-14}$
- $pH + pOH = 14$
- Acid dissociation constant
 - $HA + H_2O \rightarrow H_3O^+ + A^-$
 - $K_a = \frac{[H^+][A^-]}{[HA]}$
- Base dissociation constant
 - The equilibrium constant for the reaction of the conjugate base with water
 - NOT the reverse of the reaction for K_a
 - $A^- + H_2O \rightarrow OH^- + HA$
- $K_a K_b = K_w$
- The larger the K_a and the smaller the pK_a the stronger the acid
 - A $K_a > 1$ or a $pK_a < 0$ indicates a strong acid. The same is true for a base.

Finding the pH

- Very strong acids and bases dissociate almost completely
 - Ex. If you have a 0.01M HCl solution it is completely dissociated so you will have 0.01M of H^+ ions. Since $0.01 = 10^{-2}$ the pH is 2
- Weak Acids and Bases are trickier
 - Ex. Suppose you have 0.01M HCN and $K_a = 6.2 \times 10^{-10}$
 - $K_a = \frac{[H^+][CN^-]}{[HCN]} = 6.2 \times 10^{-10}$
 - $6.2 \times 10^{-10} = \frac{[x][x]}{[0.01-x]}$ can be approximated to $\frac{x^2}{[0.01]}$
 - Thus $x \sim 2.5 \times 10^{-6}$. This is much smaller than 0.01 so the approximation stands
 - For a weak base the process is the same, except that you use K_b and your result is the pOH.
 - Subtract the pOH from 14 to get pH. Seriously. Don't forget this.

Titration

- A drop-by-drop mixing of an acid and base
- Performed to find the concentration of some unknown by comparing it with the concentration of the titrant
- The titration curve is sigmoidal when titrating a strong acid with a strong base
- The midpoint is called the equivalence point or the stoichiometric point
 - This is also the point where there are equal amounts of acid and base
 - Titrating a strong acid with a strong base means slowly adding base to an acid...obvious if you look at the x-axis of the graph to see the original pH of a graph
 - The point where the curve has the greatest slope
 - Thus if it's the other way around it would be an inverted sigmoidal graph
- Titrating a weak acid with a strong base the graph shoots up..then goes flat, then shoots up again and then goes flat again
 - If base is stronger than the acid the equivalence point > 7
 - If the acid is stronger than the base the equivalence point < 7
- Half equivalence point - point where exactly one half of the acid has been neutralized by the base
 - $pH = pK_a$
 - In other words, concentration where there is the same amount of acid as there is its conjugate base
 - Occurs where there is a flat part of the graph...point where you could add the largest amount of acid or base with the least change in pH
 - Is the point where the solution is most buffered

Henderson-Hasselbalch equation

- $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$
- To make a buffered solution
 - you would start with an acid whose pK_a is closest to the pH at which you would want to buffer your solution
 - Mix equal amounts of that acid with its conjugate base
 - Would want the concentration of the buffer solution to greatly exceed the

concentration of the acid or base that will be added to it

- A buffer solution is made from equal and copious amounts of a weak acid and its conjugate base

WARNING

- You can't use the Henderson-Hasselblach equation to find the pH at the equivalence point. You must use the K_b of the conjugate base. You can find the K_b from the K_a and K_w . The concentration of the conjugate base at the equivalence point is equal to the number of moles of acid divided by the volume of acid plus the volume of base used to titrate.
 - $K_b = K_w / K_a$
 - $K_b = [\text{OH}^-][\text{HA}]/[\text{A}^-]$. Solve for $[\text{OH}^-]$ to find the pOH.
 - DON'T forget to do $14 - \text{pOH} = \text{pH}$

Indicators

- To find the equivalence point use an indicator
- Usually a weak acid whose conjugate base is a different color
- Example: We have an indicator HIn where In^- represents the conjugate base and we add a small amount of indicator to the acid so as not to disturb the pH. At low pH the HIn form of the indicator predominates. As we titrate and the pH increases the In^- form also increases. When the In^- concentration reaches 1/10 of the HIn concentration a color change can be detected by the human eye. If we titrate a base with an acid the process works in reverse. Thus, the pH of the color change depends upon the direction of titration. The pH values give the range of the indicator.
- Range can be predicted by Henderson Hasselblach
 - Lower range: $\text{pH} = \text{pK}_a + \log(1/10) \rightarrow \text{pH} = \text{pK}_a - 1$
 - Upper range: $\text{pH} = \text{pK}_a + \log(10/1) \rightarrow \text{pH} = \text{pK}_a + 1$
- The point where the indicator changes color is called the endpoint

7 Electrochemistry

Wednesday, January 02, 2008
12:11 AM

Oxidation - loss of electron

Reduction - gain of electron

Oxidation States - possible charge values that an atom may hold within a molecule

Oxidation State	Atom
0	Atoms in their elemental form
-1	Fluorine
+1	Hydrogen (except when bound to a metal, then -1)
-2	Oxygen (except when it is in a peroxide like H ₂ O ₂)

General guidelines below, can't always be true otherwise would never have redox reactions

Oxidation State	Group on Periodic Table
+1	Alkali Group 1
+2	Alkaline Earth Metals Group 2
-3	Nitrogen Family
-2	Oxygen Family
-1	Halogens

- Oxidation states must add up to the total charge on the ion
- Losing electrons increases oxidation state
- Reducing Agent (reductant)
 - o Reducing agent gets oxidized because it is giving up electrons
- Oxidizing Agent (oxidant)
 - o Oxidizing agent gets reduced because it is taking electrons
- Reducing or oxidizing agents are compounds, NOT atoms
Example: $\text{Cd(s)} + \text{NiO}_2\text{(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2\text{(s)} + \text{Ni(OH)}_2\text{(s)}$
 - Ni is reduced, NiO₂ is the oxidizing agent

Oxidation-Reduction Titrations

- To find the molarity of a reducing agent you titrate with an oxidizing agent. You know what concentration you have by balancing the change of electrons. Instead of measuring pH you measure voltage. Trippy.
- There is an electric potential E associated with any redox reaction since in a redox reaction electrons are transferred.
- Since the reverse of a reduction half potential is an oxidation half potential you just switch the signs.
 - Reduction potential format: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, $E^\circ = 0.00 \text{ V}$ (memorize)
- **Do NOT** multiply the half reaction potential by the number of times it occurs because voltage is an intensive property!

Balancing Redox Reactions

- 1.) Divide the reaction into its corresponding half reactions.
- 2.) Balance the elements other than H and O.
- 3.) Add H₂O to one side until all O atoms are balanced.
- 4.) Add H⁺ to one side until all 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.

Galvanic(voltaic) Cell

- If two distinct electrically conducting chemical phases are placed in contact and one charged species from one phase can't freely flow to the other a tiny amount of charge difference occurs resulting in a potential. By offering an alternative pathway for the electrons to flow you can convert chemical into electrical energy.
- All phases must conduct electricity but one phase has to be impermeable to electrons.
- The phase that is impermeable to electrons is an ionic conductor carrying the current in the form of ions--usually an electrolyte solution in the form of a salt bridge. Salt bridges aren't necessary when both anode and cathode are in the same solution(0
- Anode - negative terminal, where ions are oxidized(where they lose electrons)
- Cathode - positive terminal, where ions are reduced(where they gain electrons)
- Strip of metal and solution can be referred to as a *half cell*
- Cell Potential E / electromotive force (emf)
 - The potential difference between the terminals when they are NOT connected
 - Once they are connected the potential difference is reduced due to internal resistance in the galvanic cell
 - The drop in the emf increases as the current increases

★- Current

- Flows in direction opposite electron flow

- ★- Electrons in the anode have *higher potential energy* than those in the cathode so electrons flow anode to cathode
- Cell potential for a galvanic cell is ALWAYS positive
- Real cell potential depends upon the half reactions, concentrations of reactants and products, and temperature
- When a cell has two different solutions a *liquid junction* has to be used to separate the solutions. Because ions can move across a liquid junction any liquid junction creates an additional small potential difference that affects the potential of the galvanic cell. A salt bridge is a type of liquid junction that minimizes this.
- A good salt bridge provides an ionic conductor between two solutions without creating a strong extra potential within the galvanic cell
 - As electrons leave one half of a galvanic cell and flow to the other, a difference in charge is established. If no salt bridge was used, this charge difference would prevent further flow of electrons. A salt bridge allows the flow of ions to maintain a balance in charge between the oxidation and reduction vessels while keeping the contents of each separate. With the charge difference balanced, electrons can flow once again, and the reduction and oxidation reactions can proceed.

Electrochemistry

- A positive cell potential indicates a spontaneous reaction: $\Delta G = -nFE_{\max}$
- When all the conditions are standard $\Delta G^{\circ} = -nFE^{\circ}$
- For non-standard state conditions: $\Delta G = \Delta G^{\circ} + RT\ln(Q)$
 - Q is the reaction quotient
- ΔG° is a specifically described ΔG with standard state conditions (1M products and reactants, 1atm pressure)
- At equilibrium $\Delta G = 0$ so $\Delta G^{\circ} = -RT\ln(K)$
 - K is the equilibrium makeup
 - If $K=1$ then $\Delta G^{\circ} = 0$
 - If $K>1$ then $\Delta G^{\circ} < 0$
 - If $K<1$ then $\Delta G^{\circ} > 0$
 - This DOES NOT mean that if a reaction has $K>1$ that then the reaction is spontaneous because the spontaneity of a reaction depends on the starting concentrations of products and reactants. It does say that the reaction is spontaneous at standard conditions though.

- How to find potentials when concentrations aren't 1M?
 - $E = E^\circ - (RT/nF)\ln(Q)$ Nernst equation

Concentration Cells

- A type of galvanic cell
- NEVER at standard conditions so you need the Nernst equation to solve for the potentials
- A limited form of a galvanic cell with a reduction half reaction taking place in one half cell and the reverse of that half reaction taking place in the other half cell
- The more concentrated side will become less concentrated and electrons will flow accordingly.
 - Example: 0.01M Fe^{2+} on one side and 0.1M Fe^{2+} at the other side.
 - Electrons will flow to 0.1M Fe^{2+} side to lower the amount of Fe^{2+} on that side.

Electrolytic Cells

- If we hook up a power source across the resistance of a galvanic cell and force it to run backwards we get an electrolytic cell
- ANY electrolytic cell has a negative emf
- The cathode is marked negative and the anode is marked positive. RED CAT AN OX still applies.
- Often used for metal plating and purifying metals
 - Example: Piece of copper at cathode end. Electrons flow to cathode where there is a metal spoon. The copper at the anode loses electrons causing Cu^{2+} ions to flow into the solution. These ions are attracted to the spoon that has an excess of electrons so they plate onto the spoon and form a Cu surface at the cathode.
- A reaction will not run in a aqueous solution if water has a less negative reduction potential than the element trying to be purified.
 - Example: Collecting pure sodium through electrolysis
 - $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ $E^\circ = -2.71 \text{ V}$
 - $2\text{Cl}^- \rightarrow 2\text{e}^- + \text{Cl}_2$ $E^\circ = -1.36 \text{ V}$
 - $\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ $E^\circ = -0.83 \text{ V}$
 - Sodium can't be reduced because water will take the electrons.