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Gases

1. Pressure Formula: $Pressure(P) = \frac{force(F)}{area(A)}$
2. Celsius to Kelvin: $Kelvin = Celsius + 273.15$
3. Celsius to Fahrenheit: $Fahrenheit = (\frac{9}{5} Celsius) + 32$
4. Fahrenheit to Celsius: $\frac{5}{9}(Fahrenheit - 32)$
5. Pressure units:
 1. 1 atm = 101.325 kPa = 101325 Pa = 760 mmHg = 760 torr
 2. 1 pascal = 1 $\frac{kg}{ms^2}$
6. Compression factor: $Z = \frac{V_{m,actual}}{V_{m,ideal}}$
 - $V_{m,actual}$ = Measured molar volume
 - $V_{m,ideal}$ = Calculated molar volume from ideal gas law
7. Boyle's Law: $P_1V_1 = P_2V_2$
 - **P** = Pressure, **V** = Volume
8. Charles's Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
 - **T** = Temperature
9. Gay-Lussac's Law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
10. Combined Ideal Gas Law: $PV = nRT$
 - **R** = $0.08206 \frac{L \cdot atm}{K \cdot mol}$, **n** = moles (6.02×10^{23} molecules or atoms)
 - Variation 1: $PV = \frac{mass}{molar\ mass} RT$
 - Variation 2: $density = \frac{molar\ mass \cdot P}{RT}$
11. Universal Gas Constant (**R**) = $8.314 \frac{J}{K \cdot mol} = 0.08206 \frac{L \cdot atm}{K \cdot mol}$
12. Root mean squared velocity (V_{rms}) = $\sqrt{\frac{3RT}{molar\ mass}}$
 - **R** = $8.314 \frac{J}{K \cdot mol}$, **T** = temperature in Kelvin, molar mass in kilograms
13. Graham's Law: $\frac{time\ B}{time\ A} = \sqrt{\frac{MW_B}{MW_A}}$ Or $\frac{rate\ A}{rate\ B} = \sqrt{\frac{MW_B}{MW_A}}$
 - **MW** = molar mass
14. Dalton's Law: $P_{tot} = P_1 + P_2 + \dots + P_n$
15. Pressure of an individual gas within a mixture of gases: $P_1 = X_1 \cdot P_{tot}$
 - $X_1 = \frac{n_1}{total\ mol}$ where **X** = molar fraction, **n₁** = moles of individual gas, **total mol** = total number of moles of gas in mixture
16. Internal energy: $U = KE + PE$ or $\Delta U = Q + W$
 - **KE** = Kinetic Energy, **PE** = Potential Energy, **Q** = Heat, **W** = Work

17. Change in internal energy for a monatomic gas: $\Delta U = \left(\frac{3}{2}\right)n * R * \Delta T$

- $R = 8.314 \frac{J}{K * mol}$, ΔT = Change in Temperature

18. Work done by gas in an isobaric process: $W = P(V_f - V_i)$

- V_f = Final Volume, V_i = Initial volume

Thermodynamics

1. Enthalpy: $\Delta H = q = nC_m \Delta T = mC_s \Delta T$

- m = mass, C_s = Specific heat capacity ($\frac{J}{g * ^\circ C}$ or $\frac{J}{g * ^\circ K}$), C_m = Molar Heat Capacity ($\frac{J}{mol * ^\circ C}$ or $\frac{J}{mol * ^\circ K}$)

2. ΔH reaction equation: $\Delta H_{rxn} = \sum n H_f^o \text{ products} - \sum n H_f^o \text{ reactants}$

- H_f^o = Enthalpy of formation

3. Bond Enthalpy equation: $\Delta H_{rxn} = \sum (H \text{ bonds broken} - H \text{ bonds formed})$

4. Entropy units: J/K

5. Standard Molar Entropy (S_m^o) units: $\frac{J}{K * mol}$

6. Standard reaction entropy: $S_{rxn}^o = \sum n S_m^o \text{ products} - \sum n S_m^o \text{ reactants}$

7. Gibbs free energy equation: $\Delta G = \Delta H_{rxn}^o - T \Delta S_{rxn}^o$

- T must be in units of kelvin

8. Gibbs free energy of reaction: (ΔG_{rxn}^o) = $\sum n G_f^o \text{ products} - \sum n G_f^o \text{ reactants}$

- ΔG_f^o = standard Gibbs free energy of the reaction forming 1 mole of a substance from its elements in their standard state.

Equilibrium

1. Law of Mass action: $K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$

- a = activity, K = equilibrium constant

2. Relationship between Gibbs free energy and the equilibrium constant: $\Delta G = -RT \ln K_T$

- $R = 8.314 \frac{J}{mol * K}$ and K_T = Equilibrium constant at the given temperature T

3. Gibbs to equilibrium equation: $\Delta G_{toeq} = -RT \ln \left(\frac{Q}{K}\right)$

- Q = reaction quotient, $R = 8.314 \frac{J}{mol * K}$

4. Quantitative changes in K with T : $\ln \frac{K_2}{K_1} = \frac{\Delta H_{rxn}^o}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

- $R = 8.314 \frac{J}{mol * K}$, Temperatures in units of kelvin.

Solutions

- Percent by mass: $\%mass = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$
- Molarity: $M = \frac{\text{moles of solute}}{\text{volume of solution (liters)}}$
- Molality: $m = \frac{\text{moles solute}}{\text{mass of solvent (kilograms)}}$
- Mole Fraction: $X_A = \frac{\text{moles of A}}{\text{moles of A + moles of B + moles of C + ...}}$
- Henry's law: $S = k_H P$
 - K_H = Henry's constant, P = partial pressure of gas, S = solubility
- Enthalpy of solution equation: $\Delta H_{\text{sol}} = \Delta H_L + \Delta h_{\text{hyd}}$
 - ΔH_L = lattice enthalpy, Δh_{hyd} = enthalpy of hydration
- Vapor pressure: $K = P_{H_2O}$ in the reaction $H_2O_{(l)} \leftrightarrow H_2O_{(g)}$
- Raoult's Law: $P_{\text{solution}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$
- Boiling point elevation equation: $\Delta T_B = i K_B m$
 - i = van't hoff factor ($i = \frac{\text{mol particles}}{\text{mol solute}}$)
- Freezing point depression equation: $\Delta T_f = i K_f m$
- Osmotic pressure equation: $\Pi = i R T c$
 - c = concentration in mol/L (molarity), $R = 0.08206 \frac{L \cdot atm}{K \cdot mol}$
- Clausius-claperyon equation: $\ln \frac{P_{2,vap}}{P_{1,vap}} = \frac{\Delta H_{vap,m}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
 - $R = 8.314 \frac{J}{mol \cdot K}$

Acids and Bases

- pH: $pH = -\log[H_3O^+]$
- pOH: $pOH = -\log[OH^-]$
- pH/pOH relationship: $pH + pOH = 14$
- DAT math formulas to estimate logs:
 - $-\log(m \cdot 10^{-n}) \approx n - 1.10 - m$
 - $\log(m \cdot 10^{-n}) \approx (-n) + 1.10 - m$
 - $\ln(x) \approx 2.3(\log(x))$
 - $\log(m \cdot 10^n) \approx n + 1 + m$
- pKa = $pKa = -\log(K_a)$
 - K_a = equilibrium constant for a weak acid donating a proton in water to form its conjugate base
- pKb = $pKb = -\log(K_b)$
 - K_b = equilibrium constant for a weak base accepting a proton from water to form its conjugate acid
- $K_w/K_a/K_b$ relationship = $K_w = K_a \cdot K_b$ and at $25^\circ C$, $1 \cdot 10^{-14} = K_a \cdot K_b$
- Henderson-hasselbach equation: $pH = pKa + \log\left[\frac{H^-}{HA}\right]$ or $pOH = pKb + \log\left[\frac{HB^+}{B}\right]$
 - $[A^-]$ or $[HB^+]$ and $[HA]$ or $[B]$ must be within a factor of 10 of one another (ratio must be less than 10).

9. Titration equation: $M_1V_1 = M_2V_2$

Electrochemistry

- Full Cell Potential: $\Delta E^\circ = \Delta E^\circ_{\text{red}} + \Delta E^\circ_{\text{ox}}$
 - $\Delta E^\circ_{\text{red}}$ = Oxidizing half cell potential, $\Delta E^\circ_{\text{ox}}$ = Reducing half cell potential
- Relationship between Gibbs free energy and Full cell potential: $\Delta G^\circ = -nF\Delta E^\circ$
 - n = moles of electrons transferred, F = Faraday's constant (96485 coulombs/mol e⁻)
- Relationship between Full cell potential and the equilibrium constant: $\Delta E^\circ = \frac{RT}{nF} \ln K_{298}$ or

$$\Delta E^\circ = \frac{0.0592}{n} \log K_{298}$$
 - $R = 8.314 \frac{J}{K \cdot mol}$, n = moles of electrons
- Nernst equation: $\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q$
 - $R = 8.314 \frac{J}{K \cdot mol}$, n = moles of electrons
- Current: $I = \frac{Q}{t} = \frac{nF}{t}$
 - Q = charge (in Coloumbs), t = time in seconds, n = moles of electrons

Nuclear Chemistry

- First-order half life equation: $t_{1/2} = \frac{\ln[2]}{k}$ or $t_{1/2} = \frac{0.693}{k}$
 - k = rate constant
- Second-order half life equation: $t_{1/2} = \frac{1}{k[A]}$
- Zero-order half life equation: $t_{1/2} = \frac{[A]}{2k}$
- Nuclear binding energy: $E_{\text{bind}} = |\Delta m| c^2$
 - Δm = change in mass in kilograms, c = speed of light (3×10^8 m/s)
 - A proton is $\sim 1 m_u$ ($1.00728 m_u = 1.673 \times 10^{-27}$ kg)
 - A neutron is $\sim 1 m_u$ ($1.00866 m_u = 1.675 \times 10^{-27}$ kg)
 - An electron is $\sim 0 m_u$ ($0.00055 m_u = 9.11 \times 10^{-31}$ kg)
- The wave equation: $c = f\lambda$
 - c = speed of the wave (meters/second)
 - f = frequency in hertz (Hz)
 - λ = wavelength in meters

Kinetics

- Arrhenius Law: $k = Ae^{\frac{-E_A}{RT}}$
 - E_A = activation energy, $R = 8.314 \frac{J}{K \cdot mol}$, A = pre-exponential factor, k = rate constant

- Average rate of a reaction: $\frac{\Delta [C]}{\Delta T} = \frac{[C]_{final} - [C]_{initial}}{t_{final} - t_{initial}}$
- Rate law: $rate = k[A]^x[B]^y$
 - x** and **y** = usually integers that may or may not equal the stoichiometric coefficient
- General formula for finding unit of rate constant: $\frac{1}{M^{n-1} \cdot s}$
 - n** = the order of the reaction

Bonding

- Bond order: $Bond\ order = \frac{total\ number\ of\ bonds}{number\ of\ individual\ atoms} = \frac{pi\ bonds + sigma\ bonds}{number\ of\ individual\ atoms}$
- Formal Charge: $Formal\ Charge = VE - NE - \frac{BE}{2}$
 - VE** = valence electrons, **NE** = nonbonding electrons, **BE** = bonding electrons

Lab Techniques

- Percent change of heating a hydrated salt:
 $\%change = \frac{mass\ of\ salt\ after\ heating - mass\ of\ salt\ before\ heating}{mass\ of\ salt\ before\ heating} * 100$
 - % change can be a negative value
- Percent error: $\frac{|observed\ measurement - actual\ measurement|}{actual\ measurement} * 100$
- Beer's law: $Absorbance = \epsilon L c$
 - L** = path length of cell holder, **c** = concentration of solution (molarity), ϵ = molar extinction coefficient

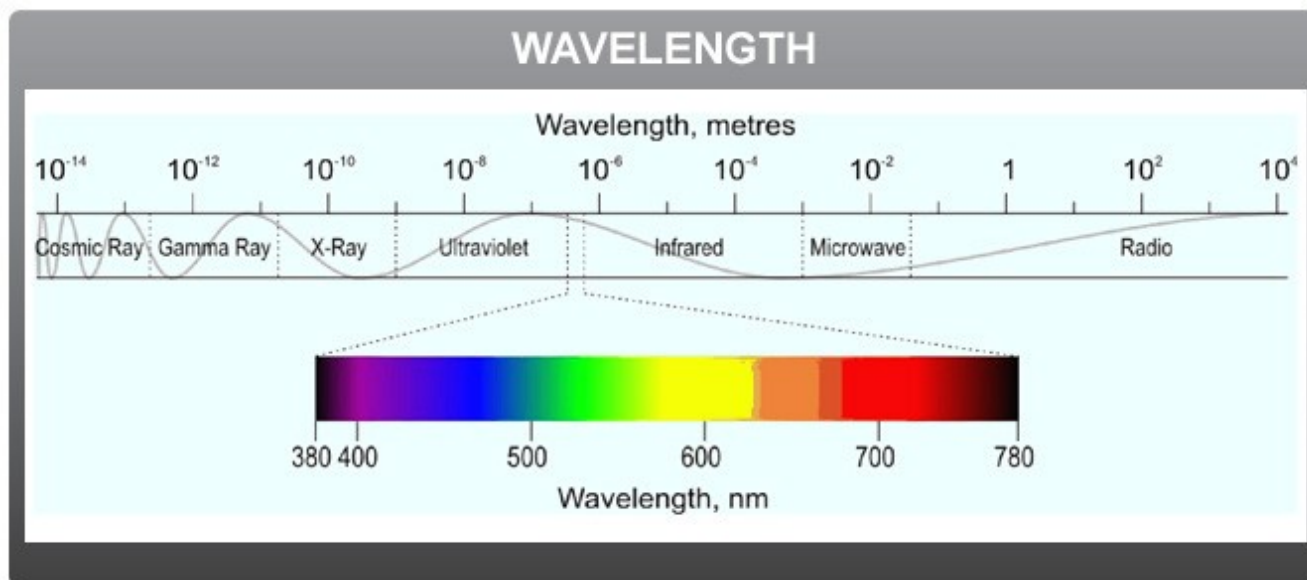
Before using my notes, please watch chad's videos for general chemistry (www.chadsvideos.com). My notes assume that you remember things from general chemistry in college. The main criticism of chad's videos is that it does not cover the last 7% of general chemistry that separates most students from a 20 to a 30. My notes cover everything chad covers and the 7%. Use these notes to bolster your knowledge. Memorize everything on my notes because they can and may be tested on your DAT.

I also included an equation sheet. It contains all formulas that are needed to my knowledge. Some may be missing. Please message me on student doctor network if you find any missing formulas so I can fix it. Thanks!

Advice for general chemistry: they ask the same questions time and time again, just in different formats. The calculation type questions are just variations with different numbers. And the conceptual questions can be learned as you continue to enhance your knowledge. The key is practice and learning everything you can.

- Important Note
 - These 3 links are fantastic. The author does a better job of explaining these chapters than I ever well. I identified the relevant sections you should focus on for the DAT. Only look at these sections. All section headers are in capital letters and bolded within the links.
- Atoms, Molecules and Ions
 - <https://apchemistrynmsi.wikispaces.com/file/view/02%20Atoms%20Molecules%20Ions.pdf/522332238/02%20Atoms%20Molecules%20Ions.pdf>
 - Relevant sections: Fundamental chemical laws, the modern view of atomic structure: an introduction, isotopes, molecules and ions, an introduction to the periodic table, naming simple compounds
- Stoichiometry
 - <https://apchemistrynmsi.wikispaces.com/file/view/03%20Stoichiometry%20with%20answers.pdf/522332384/03%20Stoichiometry%20with%20answers.pdf>
 - Relevant sections: All
- Types of Chemical Reactions & Solution Stoichiometry
 - <https://apchemistrynmsi.wikispaces.com/file/view/04%20Types%20of%20Chemical%20Reactions%20%26%20Solution%20Stoich%20with%20answers.pdf/522332588/04%20Types%20of%20Chemical%20Reactions%20%26%20Solution%20Stoich%20with%20answers.pdf>
 - Relevant sections: The nature of aqueous solutions: strong and weak electrolytes, types of chemical reactions, describing reactions in aqueous solution, chemical analysis of mixtures by precipitation reactions (ends half way down page 11)

- Light and the atom
 - An atom/molecule usually exists as the lowest possible energy state, which is called the ground state.
 - An atom/molecule that has more energy than in the ground state is said to be in the excited state.
 - When an atom loses energy in going from an excited state to a ground state, it loses energy.
- Electromagnetic spectrum
 - Mnemonic: Raging Martians Invaded ROY G BIV Using X-ray Guns



- Remember, as wavelength increases, frequency decreases (they are both inversely proportional). Therefore, gamma rays have the highest frequencies whereas radio waves have the lowest frequencies.
- Quantum Numbers
 - Governing principles:
 - Electrons are described as being in a state of rapid motion within spaces around nucleus called **orbitals**.
 - **Heisenberg uncertainty principle** – you cannot determine the precise location and momentum of an electron at once.
 - **Pauli exclusion principle** – no 2 electrons can occupy the same set of 4 quantum numbers.
 - **Hund's rule** – fill in all empty orbitals with 1 electron first, before completely filling up an orbital.
 - Quantum numbers:
 - **Principle quantum number (n)**– tells you about size. n = row on table. The larger n is, the higher the radius of the electron's orbit.
 - **Azimuthal quantum number (l)** – tells you about shape of orbitals. $L = 0, 1, 2$ or 3 . $0 = s$, $1 = p$, $2 = d$, $3 = f$.
 - **Magnetic quantum number (m)** – tells you about orientation of particle in space. Ranges from $-l$ to $+l$ including 0 . Tells you the number of orbitals possible.
 - **Spin quantum number** – tells you about spin of the electron. 2 electrons in the same orbital must have oppositely paired spins of $+1/2$ and $-1/2$.
 - Parallel spins are electrons with same direction spin (they are not in the same orbital).

- Electron Configuration
 - Use this link
http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Electronic_Structure_of_Atoms_and_Molecules/Electronic_Configurations to learn general information about electron configuration.
 - Special exceptions in electron configurations:
 - s^2d^4 switches to s^1d^5
 - s^2d^9 switches to s^1d^{10}
 - Finding configuration for cations:
 - (1) write the ground state electron configuration
 - (2) remove ions from the highest level (n value) first.
 - Finding configuration for anions:
 - (1) write the ground state electron configuration
 - (2) add ions to the outermost level that is occupied, then add more electrons to the next higher orbital.

- Network Solids

Type	Interaction between atoms	Properties
Ionic	Ionic bonding	High melting point, brittle, hard, non-conducting of electricity
Metallic	Metallic bonding	Variable hardness, malleable, conducting of electricity
Network	Covalent bonding	High melting point, hard, non-conducting of electricity
Molecular	Hydrogen bonding, dipole-dipole, van der waals	Low melting point, non-conducting of electricity, flexible

- Metalloids and Allotropes

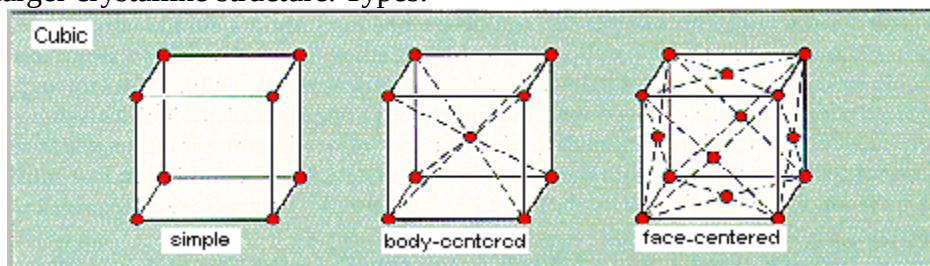
- **Metalloids** are elements bordering the metal and nonmetal line on the periodic table. They exhibit properties of metals and nonmetals.
- **Allotropes** are elements that have 2+ distinct sets of chemical and physical properties. Oxygen (O₂) and Ozone (O₃) are examples.

- Solid vs. liquid vs. gas

- gas:
 - conforms to the volume and shape of the container
 - particles are in continual motion
 - low density
 - compressible
- liquid:
 - conforms to the shape of the container but has definite volume
 - particles are in sliding motion past one another
 - moderate density
 - incompressible
- solid:
 - defined volume and shape
 - particles are in a fixed position
 - high density
 - incompressible

- Solids

- In solids, the kinetic energy of motion is predominantly vibrational energy. Therefore solids have definite shapes and volumes.
- A **crystalline solid** possesses an ordered structure; its atoms exist in a specific 3D lattice.
 - Crystals are defined by their **unit cells**, which represent the smallest repeating unit that composes the larger crystalline structure. Types:



- An **amorphous solid** (glass) has no ordered 3D arrangement although the molecules are fixed in place.

- Chemistry of the groups
 - **Hydrogen** – does not resemble alkali metals due to a single “s” valence electron. Rather, it resembles the halogens most closely since it only needs one electron for a full octet.
 - **Alkali metals** – possess most properties of metals except have lower densities. High reactivities due to low ionization energy. Low melting points.
 - **Alkaline** earth metals possess many metallic properties.
 - **Carbon group** – wide range of characteristics (metals, metalloids, nonmetals). Forms most stable molecules covalently with 4 bonds.
 - Pnictogens (Nitrogen....) exhibits a wide array of properties
 - **Chalcogens**—Oxygen....
 - **Halogens** are highly reactive nonmetals (form -1 anions). Highly variable physical properties. Low boiling points. Gases at room temperature.
 - **Transition elements** – very hard, very high melting and boiling points. Very malleable and conducts electricity since d electrons are loose. Low ionization energies; have various oxidation states since they can lose d and s electrons. Can form complex ions with water called **hydration complexes** or with nonmetals. They can also absorb frequencies of light. The frequencies not absorbed, their **subtraction frequencies**, gives complexes their characteristic colors.

Periodic Trends

- Electron Affinity
 - Electron Affinity** is defined as the energy released when an electron is added to an atom in the gas phase.

INCREASING ELECTRON AFFINITY

1 H Hydrogen 1.00794																	2 He Helium 4.003				
3 Li Lithium 6.941	4 Be Beryllium 9.012182															5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050															13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80				
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29				
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	58 Ce Cerium 140.12	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.50087	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93032	70 Yb Ytterbium 173.05468	71 Lu Lutetium 174.967	72 Hf Hafnium 178.49				
73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98039	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)								
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (288)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)				

INCREASING ELECTRON AFFINITY

- Exceptions:
 - Among nonmetals, elements in the first row have electron affinities below the atoms right beneath it. (i.e. Cl > F)
 - Elements with Xs^2 , Xp^3 , or Xp^6 shells have electron affinities less than 0 because they are unusually stable. Instead of energy being given off, these elements require an input of energy in order to gain electrons. (i.e. Be, N, Ne)
- Ionization Energy
 - Ionization Energy** is the minimum energy needed to remove an electron from an atom in the gas phase.

Increasing Ionization Energy →

IA

1	H
2	Li
3	Na
4	K
5	Rb
6	Cs
7	Fr

IIA

	Be
	Mg
	Ca
	Sr
	Ba
	Rd

III B	IV B	V B	VI B	VII B	VIII B			IX B	X B
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

IIIA

B
Al
Ga
In
Tl

IVA

C
Si
Ge
Sn
Pb

VA

N
P
As
Sb
Bi

VIA

O
S
Se
Te
Po

VIIA

F
Cl
Br
I
At

VIIIA

He
Ne
Ar
Kr
Xe
Rn

Low Energy

Increasing Ionization Energy ↑

- Why is the trend is as seen above?
 - As you move down a group, ionization energy decreases. There are two reasons: (1) Electrons are further from the nucleus and thus easier to remove the outermost one. (2) Adding more electron shells increases **shielding** (when electrons at lower energy levels essentially block the proton's force of attraction toward the nucleus) therefore making it easier to remove the outer electron.
 - As you move across a period, ionization energy increases. This is because the atomic radius also decreases, meaning the atom is smaller. The outer electrons are closer to the nucleus and are more strongly attracted to the center. Therefore, it becomes more difficult to remove the outermost electron.
- Exceptions:
 - $Xs^2 > Xp^1$ (i.e. Be > B)
 - $Xp^3 > Xp^4$ (i.e. N > O)
- Practice question: "The successive ionization energies for an unknown element are listed below. To which family in the periodic table does the unknown element likely belong. Explain your reasoning please. I1 = 896 kJ/mol I2 = 1752 kJ/mol I3 = 14807 kJ/mol I4 = 17948 kJ/mol"
 - To solve this, look for the spike in ionization energies. Notice the jump from I2 to I3 is massive compared to the rest (I2 = 1752 kJ/mol and I3 = 14807 kJ/mol). This means that it is easy for the atom to lose 2 electrons since I1 and I2 are so low compared to the rest, and when these 2 electrons are removed, the atom is stable. Therefore, you know the atom is in group 2 because group 2 elements are most stable at 2+ ions.

Atomic Radius

- Atomic radius** is the radius as measured from the center of the nucleus to the outermost shell of an atom.

INCREASING ATOMIC RADIUS

INCREASING ATOMIC RADIUS

1																	2				
H																	He				
Hydrogen																	Helium				
1.00794																	4.00260				
3	4															5	6	7	8	9	10
Li	Be															B	C	N	O	F	Ne
Lithium	Beryllium															Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
6.941	9.012182															10.811	12.0107	14.00644	15.9994	18.9984032	20.1797
11	12															13	14	15	16	17	18
Na	Mg															Al	Si	P	S	Cl	Ar
Sodium	Magnesium															Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon
22.989770	24.3050															26.981538	28.0855	30.973761	32.066	35.4527	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton				
39.0983	40.078	44.955910	47.867	50.9415	51.9961	54.938049	55.845	58.933200	58.6934	63.546	65.39	69.723	72.61	74.92160	78.96	79.904	83.80				
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon				
85.4678	87.62	88.90585	91.224	92.90638	95.94	(98)	101.07	102.90550	106.42	107.8682	112.411	114.818	118.710	121.760	127.60	126.90447	131.29				
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Cesium	Barium	Lanthanum	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon				
132.90545	137.327	138.9055	178.49	180.9479	183.84	186.207	190.23	192.223	195.078	196.96655	200.59	204.3833	207.2	208.98038	(209)	(210)	(222)				
87	88	89	104	105	106	107	108	109	110	111	112	113	114								
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt													
Francium	Radium	Actinium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium													
(223)	(226)	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(277)										

- Why is the trend is as seen above?
 - As you move down a group, atomic radius increases. This is because the number of energy levels increase as you move down a group. Each subsequent energy level is further from the nucleus than the last.
 - As you move across a period, atomic radius decreases. As you go across a period, electrons are added to the same energy level whereas protons are being added to the nucleus. The higher concentration of protons creates a higher effective nuclear charge. In other words, there is a stronger force of attraction pulling the electrons closer resulting in a smaller atomic radius.
- Anions are larger than its neutral atom counterpart. **Why?** Electron-electron repulsion forces forces the ion to spread further apart. Electrons also outnumber protons; the protons cannot pull the extra

electrons as tightly toward the nucleus.

- **Cations** are smaller than its neutral atom counterpart. **Why?** There is less electron-electron repulsion, so the ion can come closer together. Protons outnumber electrons; the protons can pull fewer electrons toward the nucleus more tightly. If the electron that is lost is the only valence electron so that the electron configuration of the cation is like that of a noble gas, then an entire energy level is lost. In this case, the radius of the cation is much smaller than its respective atom.
- To rank the order of radii in an **isoelectronic series** (all the ions have the same number of electrons):
 - (1) calculate the $\frac{\text{proton}}{\text{electron}}$ ratio for each atom.
 - (2) the smallest ratio has the largest radius, and so on.

- **Electronegativity**

- **Electronegativity** is defined as the ability for an atom to attract electrons.

INCREASING ELECTRONEGATIVITY

										INCREASING ELECTRONEGATIVITY																									
1 H Hydrogen 1.00794																		2 He Helium 4.003																	
3 Li Lithium 6.941		4 Be Beryllium 9.012182																5 B Boron 10.811		6 C Carbon 12.0107		7 N Nitrogen 14.00674		8 O Oxygen 15.9994		9 F Fluorine 18.9984032		10 Ne Neon 20.1797							
11 Na Sodium 22.989770		12 Mg Magnesium 24.3050																13 Al Aluminum 26.981538		14 Si Silicon 28.0855		15 P Phosphorus 30.973761		16 S Sulfur 32.066		17 Cl Chlorine 35.4527		18 Ar Argon 39.948							
19 K Potassium 39.0983		20 Ca Calcium 40.078		21 Sc Scandium 44.955910		22 Ti Titanium 47.867		23 V Vanadium 50.9415		24 Cr Chromium 51.9961		25 Mn Manganese 54.938049		26 Fe Iron 55.845		27 Co Cobalt 58.933200		28 Ni Nickel 58.6934		29 Cu Copper 63.546		30 Zn Zinc 65.39		31 Ga Gallium 69.723		32 Ge Germanium 72.61		33 As Arsenic 74.92160		34 Se Selenium 78.96		35 Br Bromine 79.904		36 Kr Krypton 83.80	
37 Rb Rubidium 85.4678		38 Sr Strontium 87.62		39 Y Yttrium 88.90585		40 Zr Zirconium 91.224		41 Nb Niobium 92.90638		42 Mo Molybdenum 95.94		43 Tc Technetium (98)		44 Ru Ruthenium 101.07		45 Rh Rhodium 102.90550		46 Pd Palladium 106.42		47 Ag Silver 107.8682		48 Cd Cadmium 112.411		49 In Indium 114.818		50 Sn Tin 118.710		51 Sb Antimony 121.760		52 Te Tellurium 127.60		53 I Iodine 126.90447		54 Xe Xenon 131.29	
55 Cs Cesium 132.90545		56 Ba Barium 137.327		57 La Lanthanum 138.9055		72 Hf Hafnium 178.49		73 Ta Tantalum 180.9479		74 W Tungsten 183.84		75 Re Rhenium 186.207		76 Os Osmium 190.23		77 Ir Iridium 192.217		78 Pt Platinum 195.078		79 Au Gold 196.96655		80 Hg Mercury 200.59		81 Tl Thallium 204.3833		82 Pb Lead 207.2		83 Bi Bismuth 208.98038		84 Po Polonium (209)		85 At Astatine (210)		86 Rn Radon (222)	
87 Fr Francium (223)		88 Ra Radium (226)		89 Ac Actinium (227)		104 Rf Rutherfordium (261)		105 Db Dubnium (262)		106 Sg Seaborgium (263)		107 Bh Bohrium (264)		108 Hs Hassium (265)		109 Mt Meitnerium (266)		110 (269)		111 (272)		112 (277)		113 (280)		114 (285)									

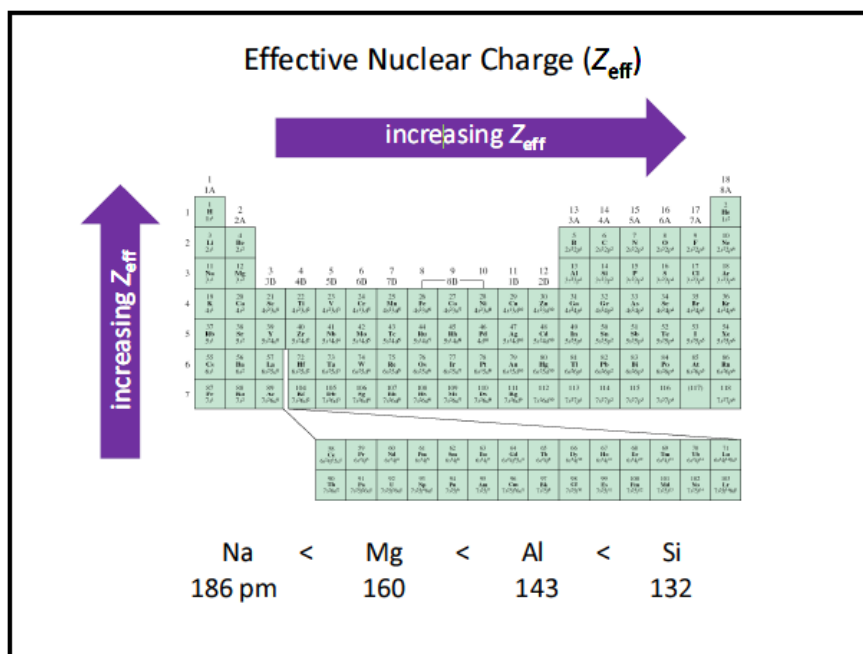
- Why is the trend seen as above?
 - From left to right across a period of elements, electronegativity increases. If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.
 - From top to bottom down a group, electronegativity decreases. This is because atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.

- **Electron Shielding**

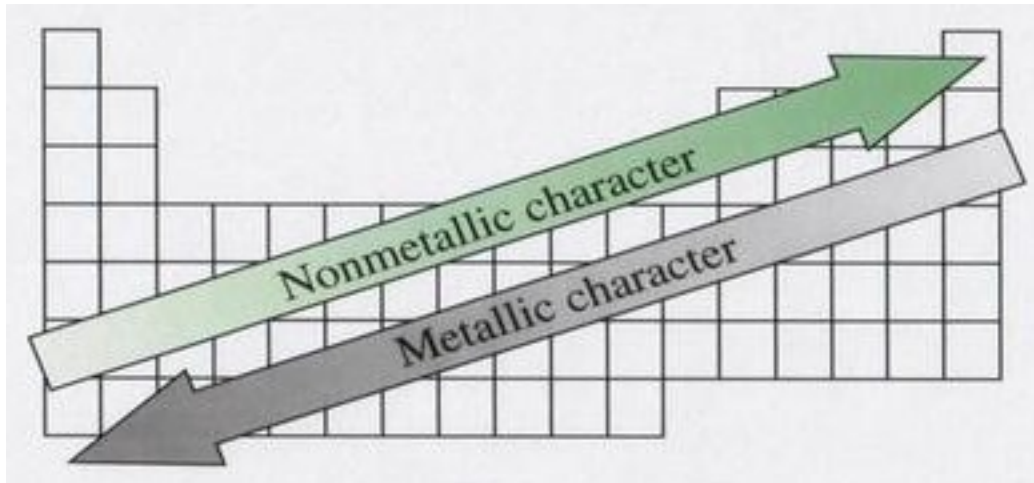
- **Electron shielding** is when electrons at lower energy levels essentially block the proton's force of attraction toward the nucleus.
- Electron shielding increases from left to right across a period of elements.
- Electron shielding increases from top to bottom down a group.

- **Effective Nuclear Charge**

- **Effective nuclear charge** (Z_{eff}) is the attractive positive charge of nuclear protons acting on valence electrons. It is always less than the total number of protons present in a nucleus due to shielding effect.
- Effective nuclear charge increases across a period due to increasing nuclear charge with no accompanying increase in shielding effect.
- Effective nuclear charge decreases down a group. Although nuclear charge increases down a group, shielding effect more than counters its effect.

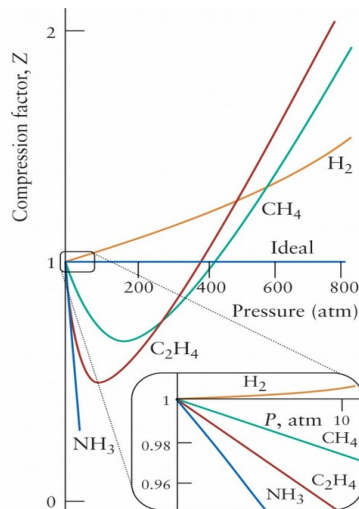


- Metallic and non-metallic character

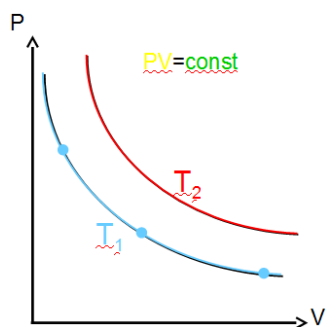


Gases

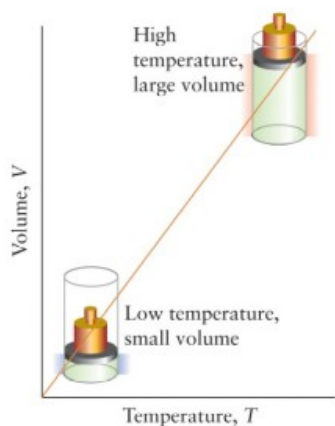
- Temperature Conversions
 - **Temperature** is a measure of the average kinetic energy of an object.
 - Kelvin = Celsius + 273.15
 - $Celsius = \frac{5}{9}(Fahrenheit - 32)$
 - $Fahrenheit = (\frac{9}{5}Celsius) + 32$
 - Unique Properties of Gases
 - Relatively low viscosity and density.
 - Relatively great expansion and contraction with temperature and pressure changes.
 - Ability to diffuse and effuse readily.
 - Spontaneously becomes uniform throughout any container.
 - Pressure
 - **Pressure** is defined as force divided by area. $Pressure(P) = \frac{force(F)}{area(A)}$
 - 1 atm = 101.325 kPa = 760 mmHg = 760 torr
 - 1 pascal = 1 $\frac{kg}{ms^2}$
 - What causes an increase in pressure?
 - Smaller volume (V)
 - More moles of gas (n)
 - Faster moving gas particles (higher temperature) (T)
 - Problem solving tip: If the pressure of gas is collected over water, use $P_{gas} = P_{tot} - P_{H_2O}$
 - Ideal Gas
 - Assumptions:
 - (1) Gases are comprised of a large number of round particles moving constantly and randomly.
 - (2) Gas particles move in a straight line until they collide with another particle or the walls of the container.
 - (3) No intermolecular attractions between gas molecules. “a”
 - (4) Collisions do not cause change in the energy of particles.
 - (5) Most of the volume of a gas is empty space; gas molecules are infinitesimally small points. “b”
 - Compression factor:
 - **Compression factor** is the ratio of the measured molar volume to the calculated molar volume.
- $$Z = \frac{V_{m,actual}}{V_{m,ideal}} \quad \text{It tells us whether the gas is acting ideally or not. For ideal gases, } Z = 1.$$



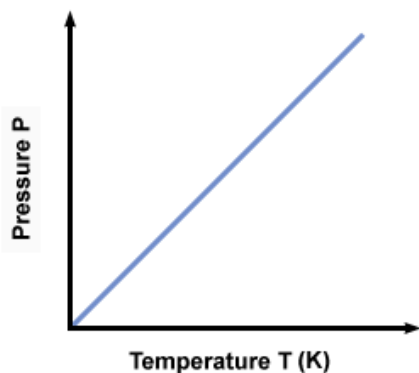
- At lower pressures, $Z < 1$. $V_{m, \text{actual}}$ is smaller than $V_{m, \text{ideal}}$. Attractive forces (“a”) between the gas particles reduce volume.
- At higher pressures, $Z > 1$. $V_{m, \text{actual}}$ is larger than $V_{m, \text{ideal}}$. Volume of the gas particles (“b”) fills the container. To keep from condensing, molecules expand.
- When are gases ideal?
 - At high temperatures, gases act more ideally because they are further away from condensation point and experience less intermolecular forces (IMFs)
 - At low temperatures, gases act less ideally since they move closer together and experience more IMFs.
 - At low pressure, gases behave more ideally since they experience less IMFs as the molecules are further spread apart.
 - At high pressure, gases behave less ideally since they are packed closer together and experience more IMFs.
- Ideal gas equations:
 - Boyle's Law = $P_1 V_1 = P_2 V_2$



- Charles's Law = $\frac{V_1}{T_1} = \frac{V_2}{T_2}$



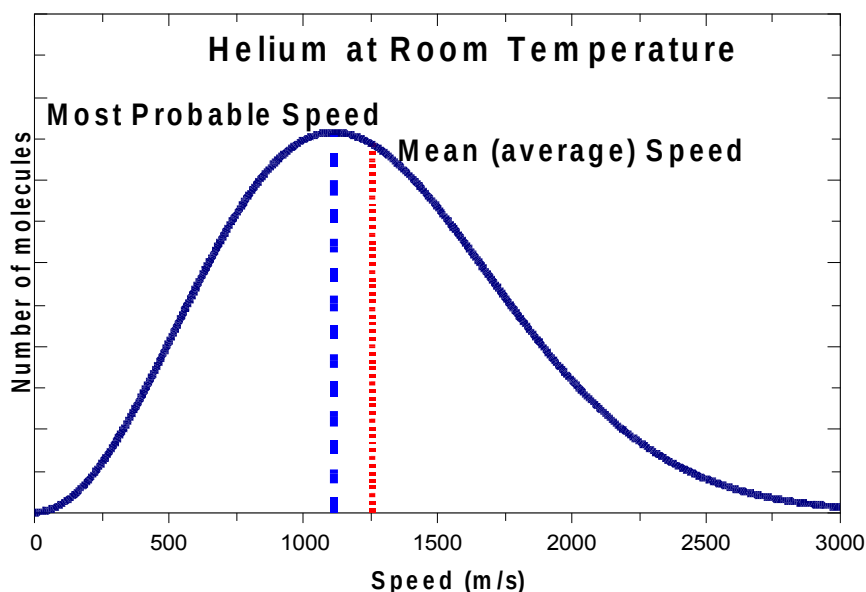
- Gay-Lussac's Law = $\frac{P_1}{T_1} = \frac{P_2}{T_2}$



- Combined gas law: $PV = nRT$
- Problem solving tip: important variations of the combined gas law
 - $n = \frac{\text{mass}}{\text{molar mass}}$, so $PV = \frac{\text{mass}}{\text{molar mass}} RT$
 - $\text{density} = \frac{\text{mass}}{\text{volume}}$, so $\text{density} = \frac{\text{molar mass} * P}{RT}$
- Key relationship: 1 mol of any gas @ STP (0°C, 1 bar) = 22.4 Liters
- Variables defined:
 - P = pressure
 - V = Volume
 - n = moles
 - R = the **universal gas constant** = $8.314 \frac{J}{K * mol} = 0.08206 \frac{L * atm}{K * mol}$

- Speed of Gases

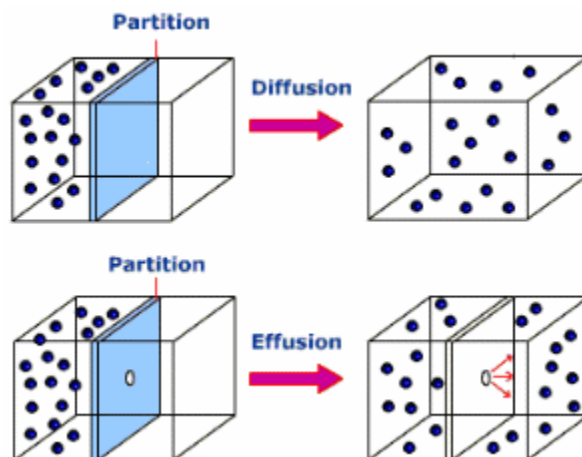
- **Maxwell distribution of speeds** graph the frequency of speeds exhibited by gas molecules at a given temperature.



- Average speed = V_{rms} average speed > most probable speed
- Increasing the temperature causes a broader maxwell distribution and a higher V_{rms} .
- When comparing the maxwell distribution of gases at the same temperature, gases with higher molecular weight have narrower distributions and a lower V_{rms} than gases with lower molecular weight.
- Root mean squared velocity
 - **Root mean squared velocity** (V_{rms}) = $\sqrt{\left(\frac{3RT}{\text{molar mass}}\right)}$
 - $R = 8.314 \frac{J}{K * mol}$, T = temperature in Kelvin, molar mass in kilograms

- Diffusion and Effusion

- **Diffusion** is the gradual dispersal of one substance through another substance.
- **Effusion** is the process of gas particles escaping a container through a small, molecular-sized vacuum.
- It takes a long time for a gas to diffuse because gas molecules randomly collide with each other and switch directions constantly.



- **Graham's law:** At constant temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of their molar masses.

$$\frac{\text{time } B}{\text{time } A} = \sqrt{\frac{MW_B}{MW_A}} \quad \text{Or} \quad \frac{\text{rate } A}{\text{rate } B} = \sqrt{\frac{MW_B}{MW_A}}$$

- MW = molar mass. As MW goes up, the time to diffuse/effuse goes up, and the rate of diffusion/effusion goes down.

- Gas mixtures

- **Dalton's law:** the total pressure of a mixture of gases is the sum of pressure of the individual components.

$$P_{tot} = P_1 + P_2 + \dots + P_n$$

- In a mixture of gases, V and P are constant, so pressure of an individual gas within the mixture depends on its mole fraction (X):

$$X_1 = \frac{n_1}{\text{total mol}} \quad P_1 = X_1 * P_{tot}$$

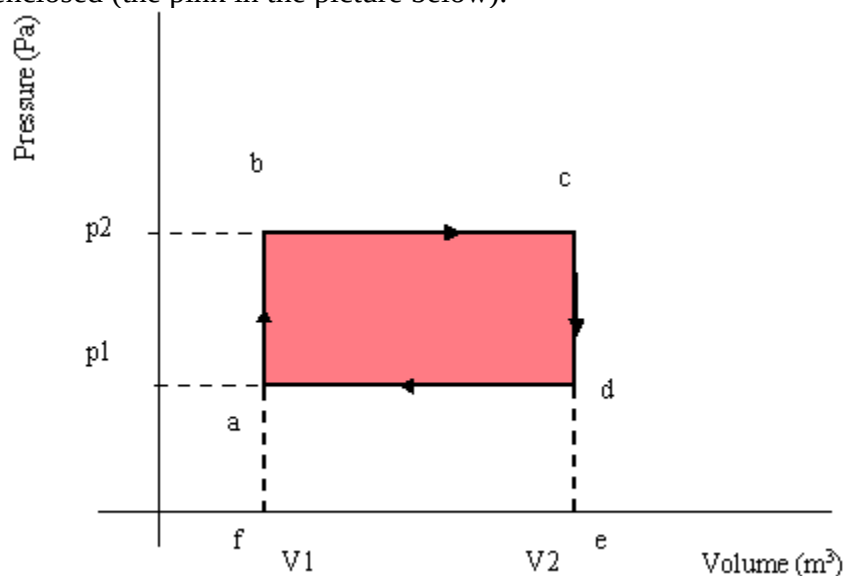
- Gas stoichiometry

- General road map to approach the problem:
 - (1) Convert volume to moles using $PV = nRT$ using the initial set of T and P
 - (2) Use a ratio and proportion to determine moles of other substance involved in the problem
 - (3) Use $PV = nRT$ with new T and P as well as moles of substances from step 2. You will calculate a new volume.
- Remember, at STP, 22.4 L of any gas = 1 mol of gas!
- **Key point:** Look for are the conditions of temperature and pressure. If they remain constant, you may treat the volumes in the same manner you treat moles. This is because, under conditions of constant T and P, the volumes are directly proportional to the moles.
- Fantastic link to solving these types of problems: <http://www.chemteam.info/Stoichiometry/vol-vol-stoichiometry.html>

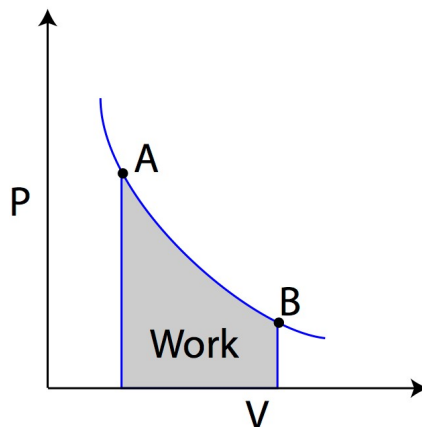
- Internal energy, heat, and work

- The **internal energy** of a gas (U) is equal to the sum of its potential and kinetic energies.
 - For a mono-atomic gas, $\Delta U = \left(\frac{3}{2}\right)n * R * \Delta T$ note: $R = 8.314 \frac{J}{K * mol}$
 - Also seen as $U = Q - W$
- Q = heat
 - When $Q > 0$, heat is being added to the system.
 - When $Q < 0$, heat is being removed from the system.
- W = work

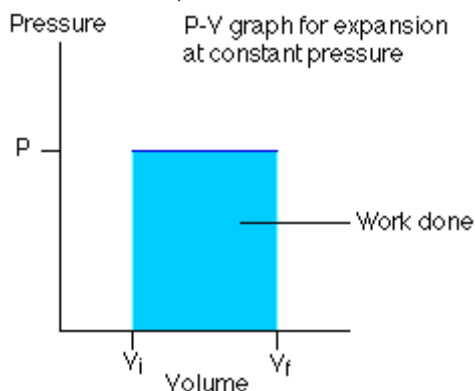
- When $W > 0$, work is done by the gas and it expands.
- When $W < 0$, work is done on the gas by the surroundings and it contracts.
- P-V curves
 - A **P-V curve** shows the work done by a sample of gas during any thermodynamic process. To calculate work, find the area enclosed by the curve.
 - Volume is on the x-axis and pressure is on the y-axis
 - When the volume of a gas decreases, $W < 0$ as work is being done on the gas by the surroundings.
 - When the process is **cyclic**, meaning initial state = final state, the total work done by the gas is equal to the area enclosed (the pink in the picture below).



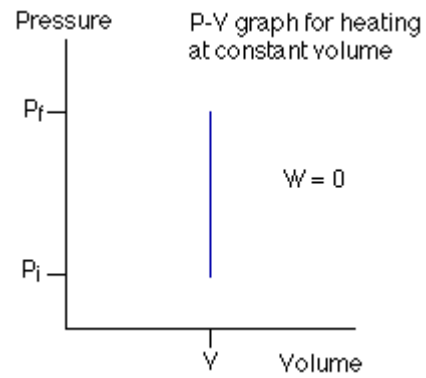
- An **isothermal process** is when the temperature is held constant. The P-V graph will show a curve rather than a line. In this situation $U = 0$, so $Q = W$.



- An **isobaric process** is where the pressure is held constant. It shows up as a horizontal line on the P-V graph. To find work done, $W = P(V_f - V_i)$



- An **isovolumetric process** is when the volume stays constant. It shows up as a vertical line on the P-V graph. $W = 0$, so $U = Q$.



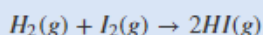
- An **adiabatic process** is when there is no heat transfer into or out of the system. $Q = 0$, so $U = -W$.

- Enthalpy
 - **Enthalpy** (H), at constant pressure is equal to heat (Q). Units = J. $\Delta H = q = nC_m \Delta T = mC_s \Delta T$
 - C can refer to specific heat or molar heat capacity
 - **Specific heat capacity** (C_s) = $\frac{J}{g \cdot ^\circ C}$ or $\frac{J}{g \cdot ^\circ K}$ (per GRAM)
 - **Molar heat capacity** (C_m) = $\frac{J}{mol \cdot ^\circ C}$ or $\frac{J}{mol \cdot ^\circ K}$ (per MOLE)
 - Note that heat capacity changes based on the phase you are in. For example, the specific heat for water in solid, liquid, and gas forms are all different!
 - **Phase changes** cause change in enthalpy.
 - Note: endothermic = +Q and exothermic = -Q
 - Melting = $n \Delta H_{fus}$ = endothermic
 - Freezing = $-n \Delta H_{fus}$ = exothermic
 - Vaporization = $n \Delta H_{vap}$ = endothermic
 - Condensing = $-n \Delta H_{vap}$ = exothermic
 - Heat problem types:
 - (1) A steel rod (mass 10 g) is heated to 75°C. The rod is set on a 20 g block of concrete that is at 25°C. When the two materials come to thermal equilibrium, what is their temperature?
 - For thermal equilibrium problems, $q_{material1} = -q_{material2}$. The hotter material is material 1 (it will be giving off heat so +Q). The colder material is material 2 (it will be gaining heat so -Q). For this problem, $q_{steel} = -q_{concrete}$. Replace q for $q = mC(T_f - T_i)$, fill in what you know, and then solve for what you don't know.
 - (2) A calorimeter containing 739 grams of water as its only heat source/sink is used to measure the heat of combustion of 0.303 g of sucrose ($C_{12}H_{22}O_{11}$ MW = 342 g/mol). The temperature increase was found to be 1.62°C. Calculate the heat of the reaction.
 - For calorimetry problems decide whether the reaction is exothermic or endothermic. If the temperature increases, the reaction is exothermic and if the temperature decreases, the reaction is endothermic. If the reaction is exothermic, $q_{reaction} = -q_{calorimeter}$. If the reaction is endothermic, $q_{calorimeter} = -q_{reaction}$ replace q for $q = mC(T_f - T_i)$, fill in what you know, and then solve for what you don't know.
 - (3) How much heat energy is needed to raise the temperature of 50.0 grams of ice at -10.0°C to form steam at 120.0°C?
 - For this type of problem, first determine if phase changes will occur. Here, the ice is heated to water, and then eventually to vapor since it moves from -10.0°C to 120.0°C. As a result, you need to include the heat of melting and the heat of vaporization. In addition, you will need to include $q = nC_m \Delta T$ for each phase since the specific heats are different. As a result, the equation will be $q = n_{ice} C_{ice} \Delta T + n \Delta H_{fus} + n_{water} C_{water} \Delta T + n \Delta H_{vap} + n_{vapor} C_{vapor} \Delta T$.
 - **ΔH formation** (ΔH°_f) is the enthalpy when one mole of substance is formed at SATP (298K, 1 bar) from reactants at SATP in their standard states.
 - The **standard state** of a substance is a reference point used to calculate its properties under different conditions.
 - ΔH°_f may be positive or negative.
 - **ΔH reaction** (ΔH_{rxn}) = $\sum n H^\circ_f \text{ products} - \sum n H^\circ_f \text{ reactants}$
 - Use ΔH formation values to calculate ΔH_{rxn} .
 - Remember, $\Delta H^\circ_f = 0$ for elements and diatomic molecules in their standard states!
 - The standard state of carbon is graphite (solid) phase.
 - If $\Delta H < 0$, the reaction is exothermic and if $\Delta H > 0$, the reaction is endothermic.

- **ΔH combustion** is ΔH for the combustion reaction (remember combustion is when you burn a molecule in the presence of oxygen).
 - ΔH_{comb} is always less than 0!
- **Hess's law** allows you to combine ΔH s of individual reactions to find a combined ΔH for the overall reaction. Rules:
- **Bond enthalpy** can be used to calculate ΔH_{rxn} as well. It is defined as the average energy needed to break bonds into atoms of the gas phase.
 - $\Delta H_{\text{rxn}} = \sum (\text{bonds broken} - \text{bonds formed})$
 - Note that ΔH is positive when bonds are broken (energy is released) and ΔH is negative when bonds are made (energy is required).
 - Look at picture below to understand how to solve a bond enthalpy problem:

Example 2

What is the enthalpy change for this reaction and is it endothermic or exothermic?



SOLUTION

First look at the equation and determine what bonds exist.

- one H-H bond,
- one I-I bond, and
- two H-I bonds

Then examine the bond breakage which is located in the reactant side:

- 1 mol H-H bonds: 436 kJ/mol
- 1 mol I-I bonds: 151 kJ/mol

The sum of enthalpies on the reaction side is: **436 kJ/mole + 151 kJ/mole = 587 kJ/mol**. This is how much energy is needed to break the bonds on the reactant side.

Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is **2 x 297 kJ/mol = 594 kJ/mol**. This is how much energy is needed to break the bonds on the product side.

- The net change of the reaction is therefore **594-587= +7 kJ/mol**. Since this is positive ($\Delta H > 0$), the reaction is **endothermic**

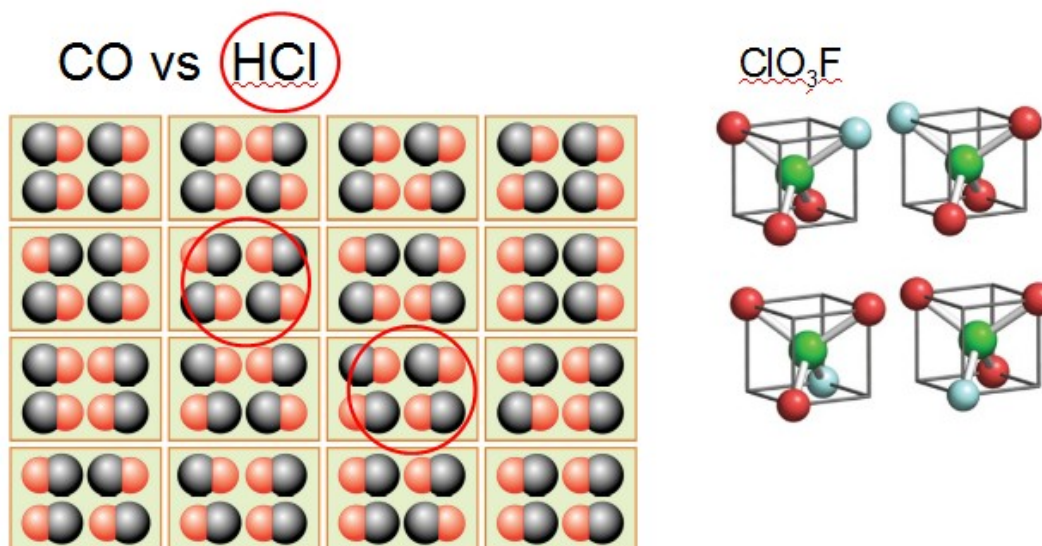
Hess's Law relates to this equation as it depicts how the energy of the overall reaction is equal to the sum of the individual steps involving energy change.

- Entropy
 - **Entropy** is defined as the measure of degree of spreading of thermal energy in a system. It measures disorder. Units = J/K.
 - Factors that affect entropy:
 - Increasing temperature increases entropy. ΔS is greater at lower temperatures than at higher ones.
 - Melting and vaporizing causes an increase in entropy ($\Delta S > 0$).
 - Freezing and condensing cause a decrease in entropy ($\Delta S < 0$).
 - Entropy increases with mixing ($\Delta S > 0$).
 - The more matter there is in a system, the higher the entropy.
 - Increasing volume increases entropy.
 - Increasing molar mass increases entropy.
 - **Standard molar entropy** (S°_{m}) is the total entropy per one mole of substance. Units = $\frac{\text{J}}{\text{K} \cdot \text{mol}}$
 - solid < liquid <<< gas ($\text{H}_2\text{O}_{(\text{l})} < \text{H}_2\text{O}_{(\text{g})}$)
 - lighter substance < heavier substance ($\text{Al}_{(\text{s})} > \text{B}_{(\text{s})}$)
 - less complex < more complex ($\text{D}_2\text{O}_{(\text{g})} > \text{HF}_{(\text{g})}$)

Note:

This may seem confusing, that ΔS is greater at lower temperatures than at higher ones. It's because at low temperatures, the change in entropy per unit change of heat energy is greater, as $\Delta S = \Delta q/T$, where q equals heat change.

- Standard reaction entropy ($S^\circ_{\text{rxn}} = \sum n S^\circ_m \text{ products} - \sum n S^\circ_m \text{ reactants}$)
 - Unlike ΔH°_f , S°_m is not equal to zero for elements in the standard state!
- Hess's law can be used to find standard reaction entropy. The rules are the same as Hess's law for ΔH .
- Entropy at 0 K approaches zero but is not zero. The entropy that exists at this temperature is called **residual entropy**.
 - Unsymmetrical molecules have higher residual entropy.
 - Molecules with stronger dipoles have higher residual entropy.



- Predicting the sign of ΔS_{rxn}

c) Identify the reaction/s from the list A-H written below that you can confidently state that there is an increase in entropy. (*Write all letters in this box.*)

4

- A) $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$
 B) $\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$
 C) $\text{H}_{(g)} + \text{Cl}_{(g)} \rightarrow \text{HCl}_{(g)}$
 D) $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2 \text{HCl}_{(g)}$
 E) $\frac{1}{2} \text{H}_{2(g)} + \frac{1}{2} \text{Cl}_{2(g)} \rightarrow \text{HCl}_{(g)}$
 F) $\text{Na}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Na}^+_{(aq)} + \frac{1}{2} \text{H}_{2(g)} + \text{OH}^-_{(aq)}$
 G) $\text{Na}_{(s)} + \frac{1}{2} \text{O}_{2(g)} + \frac{1}{2} \text{H}_{2(g)} \rightarrow \text{NaOH}_{(s)}$
 H) $\text{NaOH}_{(s)} \rightarrow \text{NaOH}_{(l)}$
- Identify the phases of the products and the reactants. Remember that solid < liquid <<< gas. If you generate more liquid or gas, then entropy increases. Concentrate on change in moles of gas because gas has a much higher entropy than liquids or solids.
 - In (A), you go from liquid to gas, so entropy increases. In (B) you go from solid to aqueous ions (like liquid), so entropy increases. In (C) you go from 2 mol gas in reactants to 1 mol gas in products. Since the mol of gas decreases, entropy decreases. In (D) you go from 2 mol of gas in reactants to 2 mol of gas in products. Since there is no net change in mol of gas, you can't confidently state if there is an entropy increase or decrease just by looking at it. In (E) you from 1 mol of gas in reactants to 1 mol of gas in products. Since there is no net change in mol of gas, you can't confidently state if there is an entropy increase or decrease just by looking at it. In (F) you go from 0 mol of gas to 1 mol of gas, so entropy increases. In (G) you go from 1 mol of gas to 0 mol of gas, so entropy decreases. In (H) you go from solid to liquid so entropy increases.

- Gibbs Free Energy

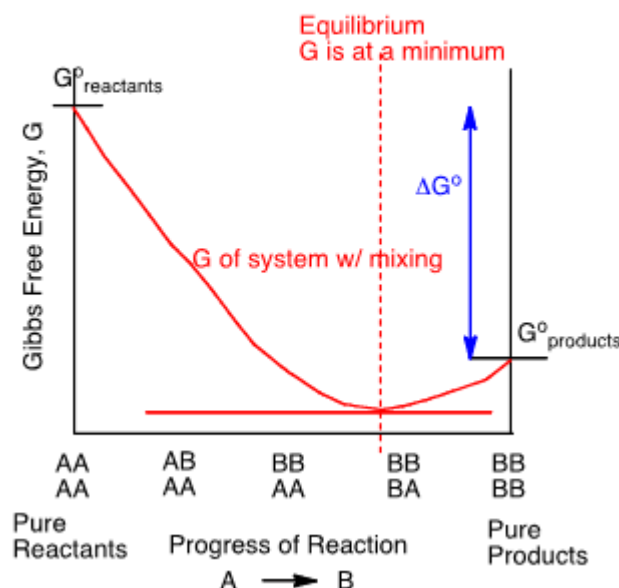
- **Gibbs free energy** is measured at constant temperature and pressure. It tells us if a process is spontaneous and if temperature change will change spontaneity. Units = J/mol

$$\Delta G = \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ} \quad \text{Note: } T \text{ must be in kelvin}$$

- When $\Delta G < 0$, the reaction is spontaneous. When $\Delta G = 0$, the reaction is at equilibrium. When $\Delta G > 0$, the reaction is not spontaneous.
 - Random Note: All spontaneous reactions result in an increase in entropy for the universe.
- 4 different scenarios:
 - $\Delta H < 0, \Delta S > 0$ = spontaneous at all temperatures
 - $\Delta H > 0, \Delta S < 0$ = never spontaneous
 - $\Delta H > 0, \Delta S > 0$ = spontaneous only at high temperatures
 - $\Delta H < 0, \Delta S < 0$ = spontaneous only at low temperatures
- **Gibbs free energy of reaction** (ΔG_{rxn}°) = $\sum n G_f^{\circ} \text{ products} - \sum n G_f^{\circ} \text{ reactants}$
 - ΔG_f° standard Gibbs free energy of the reaction forming 1 mole of a substance from its elements in their standard state.
 - $\Delta G_f^{\circ} = 0$ for an element in its standard state.
- Gibbs free energy tells you nothing about the reaction rate.
- Hess's law can be used to find Gibbs free energy of reaction. The rules are the same as Hess's law for ΔH .

- Mixing
 - Entropy increases with mixing.
 - Mixing results in a lowering of G . The system will spontaneously act to minimize G . The very minimum G is **equilibrium**.

Gibbs free energy as the reaction takes place if mixing is considered.



- Gibbs free energy and product to reactant ratios
 - A reaction with $\Delta G^\circ < 0$ does not go to completion but makes more products than reactants; the more negative ΔG° , the more products that are made.
 - A reaction with $\Delta G^\circ > 0$ will form some product; the more positive ΔG° , the smaller the quantity of products made. More reactants are left over than product made.
- Law of mass action
 - **The law of mass action** states that at equilibrium (the minimum Gibbs free energy of a reaction), the composition of the reaction mixture can be expressed in terms of an equilibrium constant (K).
 - Given the equation: $a A_{(g)} + b B_{(g)} \rightleftharpoons c C_{(g)} + d D_{(g)}$
 - The equilibrium constant $K = \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$ where "a" is an activity.
 - **Activities** are unitless. They account for deviations from ideality and for intermolecular forces.
 - A simplified form can be used for ideal gases and for solutes in dilute solutions.
 - For ideal gases, activity = pressure in atm. The equilibrium constant for gases is called K_p .
 - For solutes in dilute solutions, activity = concentration in molarity. The equilibrium constant for solutes in solutions is called K_c .
 - Solids and pure liquids are never factored into these calculations. Only take gases or aqueous solutes into account.

- Gibbs free energy and equilibrium
 - Gibbs free energy and the equilibrium constant relates as follows: $\Delta G = -RT \ln K_{298K}$
 where $R = 8.314 \frac{J}{mol \cdot K}$ and $T = 298 K$.
 - Note that it is K_{eq} at 298K and not K_c or K_p .
 - This equation tells us, the more negative ΔG is, the greater the value of K is and the more positive ΔG is, the smaller the value of K is.
 - ΔG varies with temperature in a linear fashion. K_{eq} varies with temperature in a curve fashion.

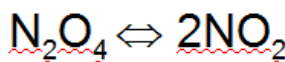
ΔG_T and K change with T

@each T :

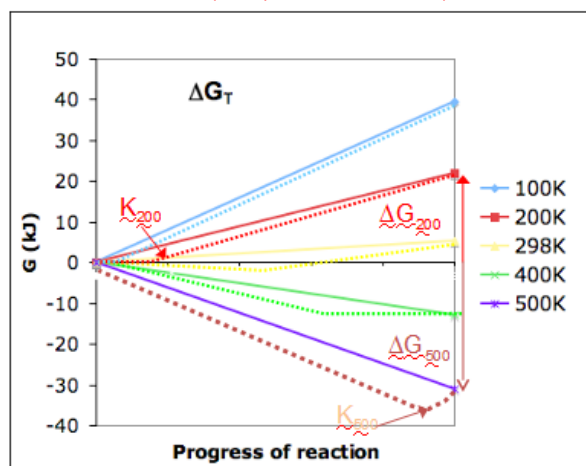
1) a straight line (ΔG_T)

2) a curve (K)

$$\Delta G_T = -RT \ln K_T$$



T (K)	ΔG (kJ)	K
100	39.6	2.06×10^{-21}
200	22.0	1.75×10^{-6}
298	5.3	0.13
400	-12.9	47.9
500	-30.9	1.69×10^3



- K and temperature
 - The equilibrium constant (K) is constant at constant temperature.
 - Varying temperature is the only way to change K for a given reaction!
- Great summary slide regarding Gibbs and Equilibrium:

ΔG° is the difference in Gibbs free energy of the products and reactants @298K

It tells you if a reaction is thermodynamically favored (spontaneous) @298K AND how reactant or product favored the reaction is @298K

$$\Delta G^\circ = -RT \ln K_{298} \quad T = 298K$$

ΔG_T is the difference in Gibbs free energy of the products and reactants @ T

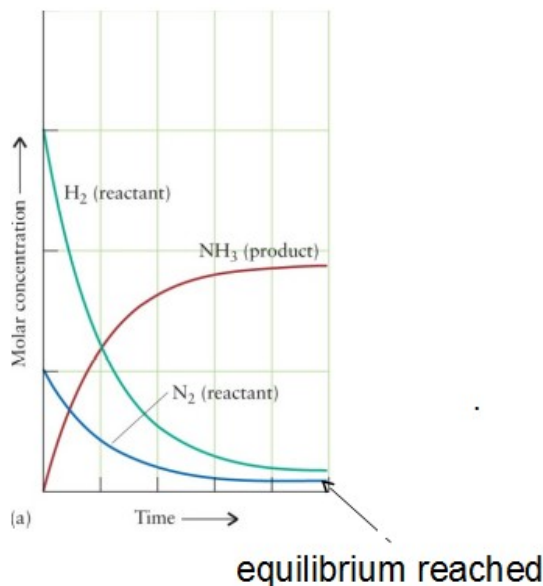
It tells you if a reaction is thermodynamically favored (spontaneous) @ T AND how reactant or product favored the reaction is @ T

$$\Delta G_T = -RT \ln K_T$$

The more negative the ΔG_T , the greater the K .

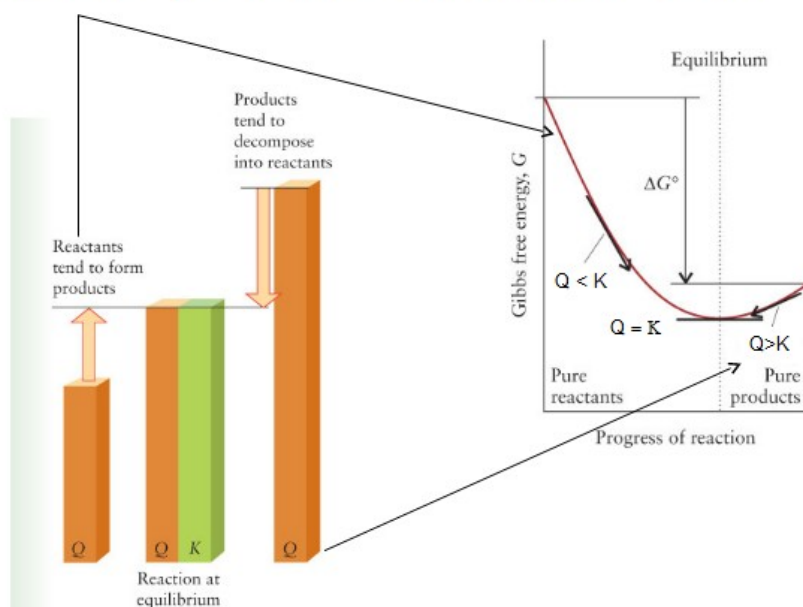
The more positive the ΔG_T , the smaller the K .

- Meaning of equilibrium
 - When equilibrium is reached, the rates of the forward and reverse reactions are equal (not necessarily zero).
 - This means that the concentrations of the products and reactants stay constant. This does NOT necessarily mean $[\text{reactants}] = [\text{products}]$ at equilibrium.
 - K tells you the ratio of products to reactants!



- Reaction Quotient (Q)
 - **The reaction quotient**, Q , is the law of mass action applied to a reaction at some given point in time. This means that Q may or may not be equal to K as you may be finding Q when the reaction is not yet at equilibrium.
 - If $Q = K$, then the system is at equilibrium.
 - If $Q > K$, there are too many products and the reverse reaction will be **favored** (meaning that it is spontaneous) whereas the forward reaction **will not be favored** (meaning that it is nonspontaneous). $\Delta G < 0$ for reverse reaction, and $\Delta G > 0$ for forward reaction.
 - If $Q < K$, there are not enough products and the forward reaction will be favored whereas the reverse reaction will not be favored. $\Delta G < 0$ for forward reaction, and $\Delta G > 0$ for reverse reaction.

Q tells you the direction to K



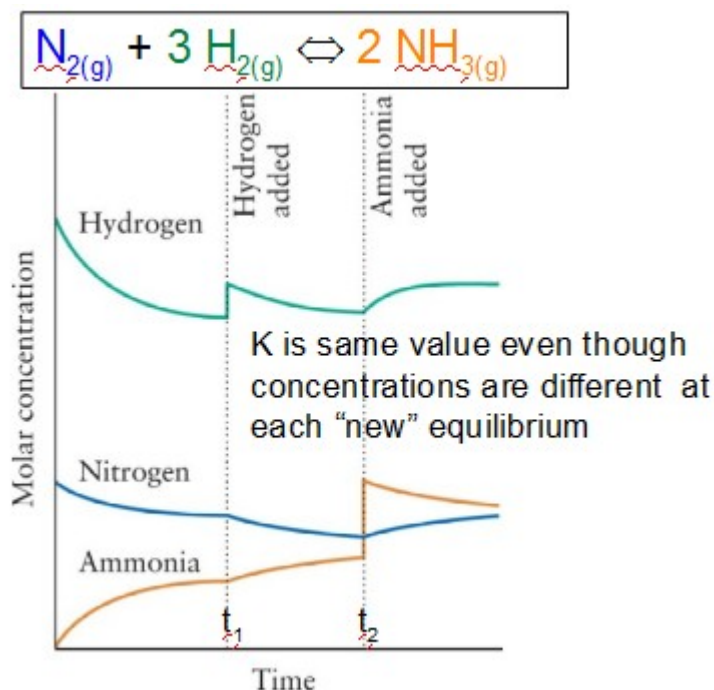
- Gibbs to equilibrium
 - Gibbs to equilibrium** (ΔG_{toeq}) is the difference in Gibbs energy between where the reaction is and gibbs at equilibrium (the minimum gibbs of the system).
 - $\Delta G_{\text{toeq}} = -RT \ln\left(\frac{Q}{K}\right)$
 - $R = 8.314 \frac{J}{mol \cdot K}$
 - $\Delta G_{\text{toeq}} > 0$ is same as $Q > K$.
 - $\Delta G_{\text{toeq}} < 0$ is same as $Q < K$.
 - $\Delta G_{\text{toeq}} = 0$ is at equilibrium.
- Hess's law and Keq
 - Hess's law also applies to K_{eq} , but the **rules are different**:
 - When you reverse an equation, you invert its equilibrium constant.
 - When you multiply an equation by a coefficient, raise the K value to the power of the coefficient.
 - When you combine equations, multiply the equilibrium constants.

Chemical equation	Equilibrium constant
$a A + b B \rightleftharpoons c C + d D$	K_1
$c C + d D \rightleftharpoons a A + b B$	$K_2 = 1/K_1$ $= K_1^{-1}$
$na A + nb B \rightleftharpoons nc C + nd D$	$K_3 = K_1^n$

*For a reaction that can be expressed as the sum of other reactions, the equilibrium constant is the product of the equilibrium constants of the component reactions

- Le Chatelier's principles
 - NOTE: only by changing temperature you can change the value of K_{eq} .
 - Temperature and K:
 - Endothermic reaction ($\Delta H > 0$): “add heat to reactants”
 - Temperature increase favors products.
 - Temperature decrease favors reactants
 - Exothermic reaction ($\Delta H < 0$): “add heat to products”
 - Temperature increase favors reactants.
 - Temperature decrease favors products
 - Enthalpically neutral reaction ($\Delta H = 0$), temperature has no effect.
 - Quantitative changes in K with T: $\ln \frac{K_2}{K_1} = \frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

- $R = 8.314 \frac{J}{mol \cdot K}$ and Temperatures in kelvin.
- Adding/removing reactant or product to the system:
 - Remove reactant or product = shift in the direction of the removed reactant/product.
 - Add reactant or product = shift in opposite direction of the added reactant/product.
 - Adding/taking away solids or pure liquids have no effect on shift unless its H₂O or completely removed.

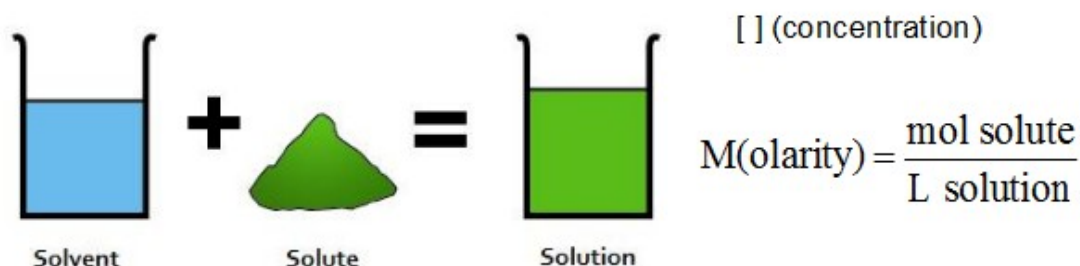


- Change in volume/pressure
 - Increase in pressure, decrease in volume; side with the fewer moles of gas is favored to minimize pressure increase.
 - Decrease in pressure, increase in volume; side with more moles of gas is favored to minimize pressure decrease.
 - For aqueous ions, H₂O is like volume!!!!
- Inert gases
 - Inert gases only affects the reaction if it causes change in the volume meaning the reaction must be in a flexible container.
- Adding a catalyst changes how reacts form products (the rate) but does not effect K!
- ICE boxes
 - An **ICE (Initial, Change, Equilibrium) table** is simple matrix formalism that used to simplify the calculations in reversible equilibrium reactions (e.g., weak acids and weak bases or complex ion formation).
 - ICE is an acronym for the titles of the first column of the table:
 - **I** stands for initial concentration. This row contains the initial concentrations of products and reactants.
 - **C** stands for the change in concentration. This is the concentration change required for the reaction to reach equilibrium. It is the difference between the equilibrium and initial rows. The concentrations in this row are, unlike the other rows, expressed with either an appropriate positive (+) or negative (-) sign and a variable; this is because this row

represents an increase or decrease (or no change) in concentration.

- **E** is for the concentration when the reaction is at equilibrium. This is the summation of the initial and change rows. Once this row is completed, its contents can be plugged into the equilibrium constant equation to solve for K_c .
- Use this link to learn how to solve ice problems (learn how to do each type of problem):
<http://www.chem.purdue.edu/gchelp/howtosolveit/Equilibrium/ICEchart.htm>

- Terminology
 - Solute** is a dissolved substance.
 - Solvent** is the most abundant part of the solution; the compound of a solution in which the other components are considered to be dissolved in.
 - Solution** is a homogenous mixture.
 - Concentration (use both links and learn from them they are great):
 - Concentration calculations: use this link <http://www.chem.purdue.edu/gchelp/howtosolveit/Solutions/concentrations.html> to learn all the different types!
 - Various examples to calculation problems and solutions: <http://www.chemteam.info/Solutions/Dilution.html>

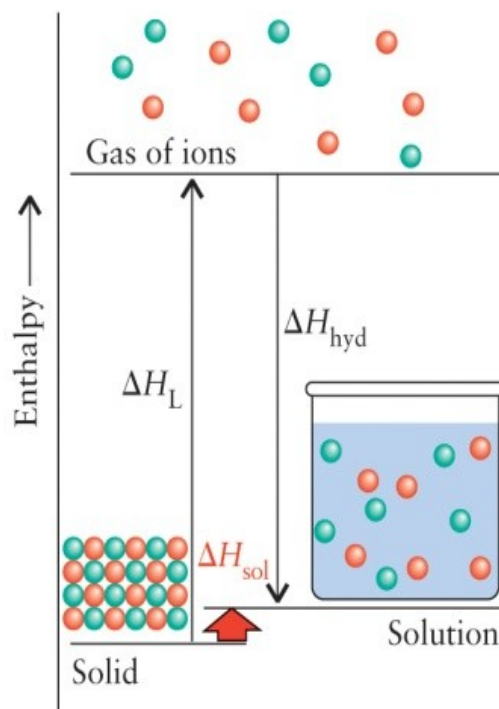


- Solubility rules (memorize):

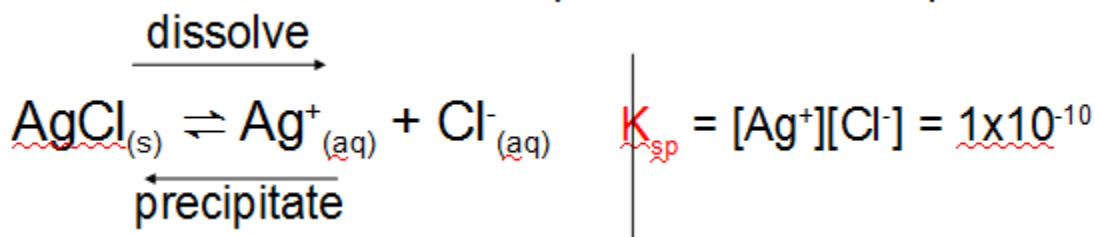
Ion	General Solubility Rule
NO_3^-	All nitrates are soluble
$\text{C}_2\text{H}_3\text{O}_2^-$	All acetates are soluble ($\text{AgC}_2\text{H}_3\text{O}_2$ only moderately)
Cl^- , Br^- , I^-	All chlorides, bromides and iodides are soluble except Ag^+ , Pb^+ and Hg_2^{2+} . (PbCl_2 is slightly soluble in cold water and moderatel soluble in hot water.)
SO_4^{2-}	All sulfates are soluble except those of Ba^{2+} , Pb^{2+} , Ca^{2+} and Sr^{2+}
CO_3^{2-} and PO_4^{3-}	All carbonates and phosphates are insoluble except those of Na^+ , K^+ and NH_4^+ . (Many acid phosphates are soluble).
OH^-	All hydroxides are insoluble except those of Na^+ and K^+ . Hydroxides of Ba^{2+} and Ca^{2+} are slightly soluble.
S^{2-}	All sulfides are insoluble except those of Na^+ , K^+ , NH_4^+ and those of the alkaline earths: Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . (Sulfides of Al^{3+} and Cr^{3+} hydrolyze and precipitate as the corresponding hydroxides.
Na^+ , K^+ and NH_4^+	All salts of sodium ion, potassium ion and ammonium ion are soluble except several uncommon ones.

- Henry's law and gas solubility
 - Henry's law** states that the solubility of a gas is directly proportional to its partial pressure.
 - $S = k_H P$
 - k_H = Henry's constant (temperature dependent)
 - P = partial pressure of gas
 - Gases are most soluble at low temperatures and high pressures.
- Energetics and dissolving
 - 2 major steps of dissolving: solid \rightarrow gaseous ions \rightarrow dissolved aqueous ions

- (1) is **lattice enthalpy**. This is the for ΔH_{rxn} for solid \rightarrow gas ions. $\Delta H_L > 0$ (*endothermic*)
- (2) is **enthalpy of hydration**. This is the ΔH_{rxn} for gas ions \rightarrow dissolved aqueous ions. $\Delta H_{\text{hyd}} < 0$ (*exothermic*)
- **Enthalpy of solution** $\Delta H_{\text{sol}} = \Delta H_L + \Delta h_{\text{hyd}}$. This is the change in molar enthalpy when a substance dissolves at a constant pressure.
 - If $\Delta H_{\text{sol}} < 0$, the solution temperature increases since the reaction is exothermic and will release heat to the surroundings.
 - If $\Delta H_{\text{sol}} > 0$, the solution temperature decreases since the reaction is endothermic and will absorb heat from the surroundings.



- Solubility product constant
 - soluble vs. insoluble
 - Soluble solutes dissociate completely (“one way rxn”)
 - Insoluble solutes are in equilibrium (“two way rxn”)
 - K_{sp} is the equilibrium constant for a salt dissolving in water reaction:



- K_{sp} describes the saturation point of the solute; that is, it tells you the amount of products formed when the maximum amount of solid has dissolved.
- Looking at the K_{sp} value above, we can say that the solubility (s) of AgCl is 1×10^{-5} M.
 - The molar **solubility** of a salt (s) is the number of moles that can dissolve per L of water.
- Q and K_{sp}
 - When $Q = K_{\text{sp}}$, you are at saturation point.
 - When $Q > K_{\text{sp}}$, there is precipitation as the reverse reaction is favored.
 - When $Q < K_{\text{sp}}$, there is dissolving as the forward reaction is favored.
- **Common ion effect**: decrease in the solubility of an ionic salt because there is a “common” ion present in solution already. This causes a shift to the left (precipitation).

- Example problem: K_{sp} of $\text{Fe}(\text{OH})_2$ is 1.6×10^{-15} . What is the solubility of $\text{Fe}(\text{OH})_2$ in 0.025 M FeCl_2 ?

- (1) Draw an ICE box and fill in the chart:

	$\text{Fe}(\text{OH})_2 \rightarrow$	$\text{Fe}^{2+} +$	2OH^-
I	XXXXXXXXXX	0.025 M	0 M
C	XXXXXXXXXX	+ x	+ 2x
E	XXXXXXXXXX	0.025 + x M	2x M

- Why is the initial concentration of Fe^{2+} 0.025 M and not 0 M? Because you are adding the salt to a dissolved FeCl_2 solution. Since FeCl_2 will have completely dissolved, there are Fe and Cl ions in the solution and you need to account them in the ICE box.
- (2) Write out the K_{sp} equation and solve for "x." To help make the calculation easy on the DAT, ignore the "+x" value to the common ion. X = solubility

$$1.6 \times 10^{-16} = (0.025 + x)(2x)^2$$

$$1.6 \times 10^{-16} = (0.025)(4x^2)$$

$$1.6 \times 10^{-16} = 0.1 x^2$$

$$(1.6 \times 10^{-16})(1.0 \times 10^{-1}) = x^2$$

$$16 \times 10^{-16} = x^2$$

$$4 \times 10^{-8} \text{ M} = x$$

- The "saturated solution problem"

- Example: What will happen if 0.05 moles of $\text{NaCl}_{(s)}$ are added to 1 L of a saturated solution of AgCl ($K_{sp} = 1 \times 10^{-10}$)?
 - (1) draw out the dissolving reaction that occurs and the corresponding K_{sp}
 - (2) since you are given the K_{sp} value, solve for solubility. This gives you the concentration of the Ag and Cl ions at saturation (equilibrium).
 - (3) Add 0.05 M to the Cl- concentration and calculate Q. Since $Q > K$, AgCl will precipitate as the reverse reaction is favored.

Concept Question

What will happen if 0.05 moles of $\text{NaCl}_{(s)}$ are added to 1 L of a saturated solution of AgCl ($K_{sp} = 1 \times 10^{-10}$)?

A. No change

B. AgCl will dissolve

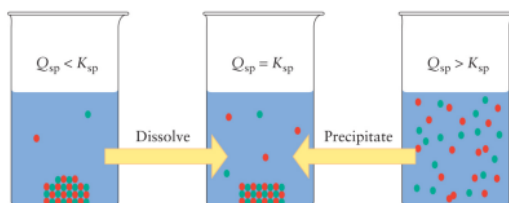
C. AgCl will precipitate



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1 \times 10^{-10}$$

$$s = 1 \times 10^{-5}$$

$$Q = [1 \times 10^{-5}][1 \times 10^{-5} + 0.05] > K$$

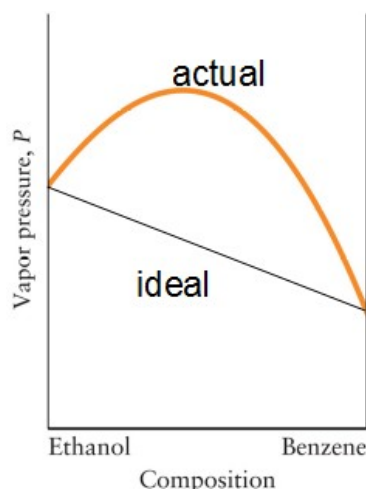


- pH change** can also affect solubility. This can only occur if an acid-base reaction can occur. Anions of weak acids will significantly be affected. This is because anions of weak acids increases pH. $\text{A}^- + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{HA}$. Lowering pH adds more H^+ . H^+ will react with OH^- , and lower the $[\text{OH}^-]$. This pushes the reaction to the right and lowers the $[\text{A}^-]$. $\text{AB} \leftrightarrow \text{A}^- + \text{B}^+$. As $[\text{A}^-]$ goes down, this reaction is pushed to the right and solubility increases.

- **Colligative properties** are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent particles in a solution, and not on the type of chemical species present. There are 4 colligative properties that we focus on: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.
- Vapor pressure and vapor pressure lowering
 - **Vapor pressure** is the equilibrium constant for the liquid \leftrightarrow gas reaction.

$$H_2O_{(l)} \leftrightarrow H_2O_{(g)} \quad \text{where} \quad K = P_{H_2O}$$
 - In general, liquids boil when their vapor pressure equals the atmospheric pressure. A liquid with a higher vapor pressure boils at a lower temperature and a liquid with a lower vapor pressure boils at a higher temperature.
 - If you go to a higher altitude, atmospheric pressure decreases. Since the liquid needs to achieve a lower P_{vap} to equal $P_{\text{atmosphere}}$, boiling point decreases.
 - If you increase atmospheric pressure (i.e. go to a lower altitude), you increase the boiling point.
 - Unrelated but important: increasing altitude increases melting point if solid is less dense than liquid and decreases melting point if the liquid is more dense than the solid.
 - The **normal boiling point** is defined as the temperature at which the vapor pressure of the liquid is 1 atm.
 - What affects vapor pressure?
 - Vapor pressure decreases with increasing IMF.
 - Vapor pressure increases with increasing boiling point.
 - Vapor pressure decreases with increasing molar mass.
 - Note: vapor pressure does not depend on the surface area of a liquid.
 - **Vapor pressure lowering** says that the vapor pressure of a solvent in solution is always lower than the vapor pressure of the pure solvent. This lowering is quantitatively described in Raoult's Law.
 - **Raoult's Law** states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present. $P_{\text{solution}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$
 - In a liquid:liquid mixture, the total vapor pressure is equal to the sum of the individual pressures:

$$P_{\text{vap, tot}} = P_{\text{vap, A}} + P_{\text{vap, B}}$$
 - Raoult's Law accurately describes vapor pressure lowering only in ideal solutions. Solutions are most ideal at low solute concentrations:
 - $x < 0.1$ M for **non-electrolyte** (molecular) solutions.
 - $x < 0.01$ M for **electrolyte** (ionic) solutions.
 - **Azeotropes** are real liquid:liquid mixtures and deviates from Raoult's law. Two different types:
 - When the 2 liquids have dissimilar IMFs (i.e. polar + non-polar liquid):
 - $\Delta H_{\text{mix}} > 0$ so the mixing process is endothermic.
 - The mixture's boiling point decreases.
 - The total vapor pressure is higher than what Raoult's law would predict.

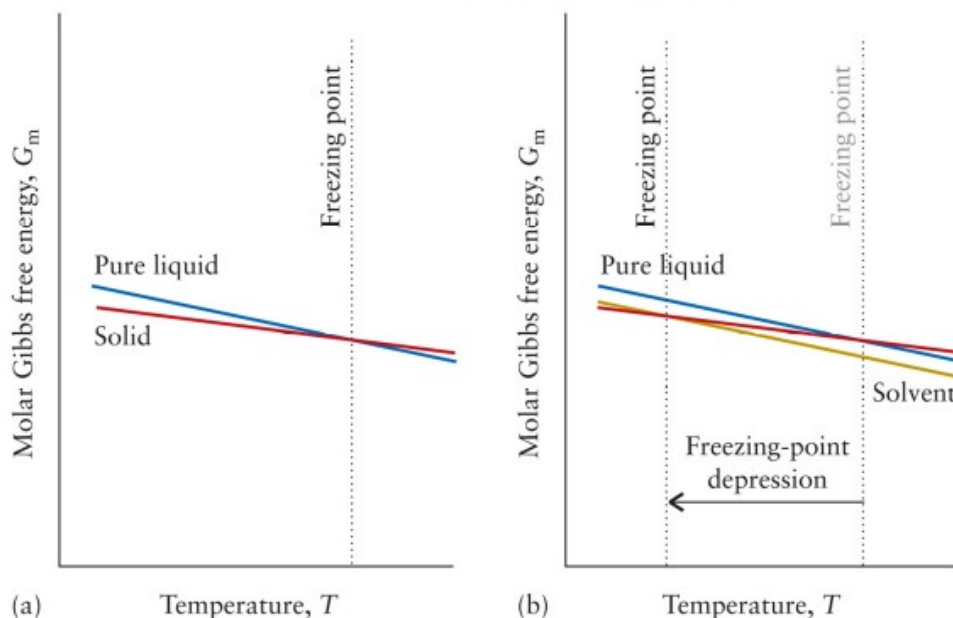


- When the 2 liquids have similar IMFs (i.e. 2 polar liquids):
 - $\Delta H_{mix} < 0$ so the mixing process is exothermic.
 - The mixture's boiling point increases.
 - The total vapor pressure is lower than what Raoult's law would predict.
- Boiling point elevation and freezing point depression
 - When a solute is added to a liquid, the boiling point of the resulting solution increases. **This is boiling point elevation.** In addition, the freezing point of the resulting solution decreases; this is called **freezing point depression**.
 - Quantitatively, we can describe the changes in the boiling point and the freezing point as follows:

$$\Delta T_f = iK_f m \text{ (freezing point depression)} \quad \Delta T_b = iK_b m \text{ (boiling point elevation)}$$
 - m = molality
 - K_f and K_b are constants – depends on the solvent
 - i = van't hoff factor
 - The van't hoff factor (i) expresses how many ions and particles are formed (on average) in a solution from one formula unit of solute.
 - For ionic compounds: the total number of ions that make up the compound is equal to the van't hoff factor. For example, $i = 4$ for K_3PO_4 since 3 potassium ions and 1 phosphate ion make up the compound ($3+1 = 4$).
 - For molecular compounds, $i = 1$ because they don't dissociate. For example, $i = 1$ for $C_6H_{12}O_6$.
 - Treat strong acids/bases like ionic compounds because they dissociate completely! For example, $i = 2$ for HBr ($1 H + 1 Br = 2$).
 - Weak acids/bases partially dissociate. To find i , use the equation: $i = \frac{\text{mol particles}}{\text{mol solute}}$.
 - Gibbs vs. temperature graphs for liquid and solutions
 - Remember: $G^\circ = -TS^\circ + H^\circ$. We can treat this like $y = mx + b$ and graph it. Temperature is on the x-axis and gibbs free energy is on the y-axis.
 - **Freezing point depression:** The temperature at which the solid and the pure-liquid intersects (equilibrium since their gibbs values are equal) is the freezing-point. Compared to the pure liquid, the solvent has the same slope but a lower y-intercept. Therefore, the intersection between the solvent and the solid is farther to the left. This shows freezing-point depression.

Freezing Point Depression

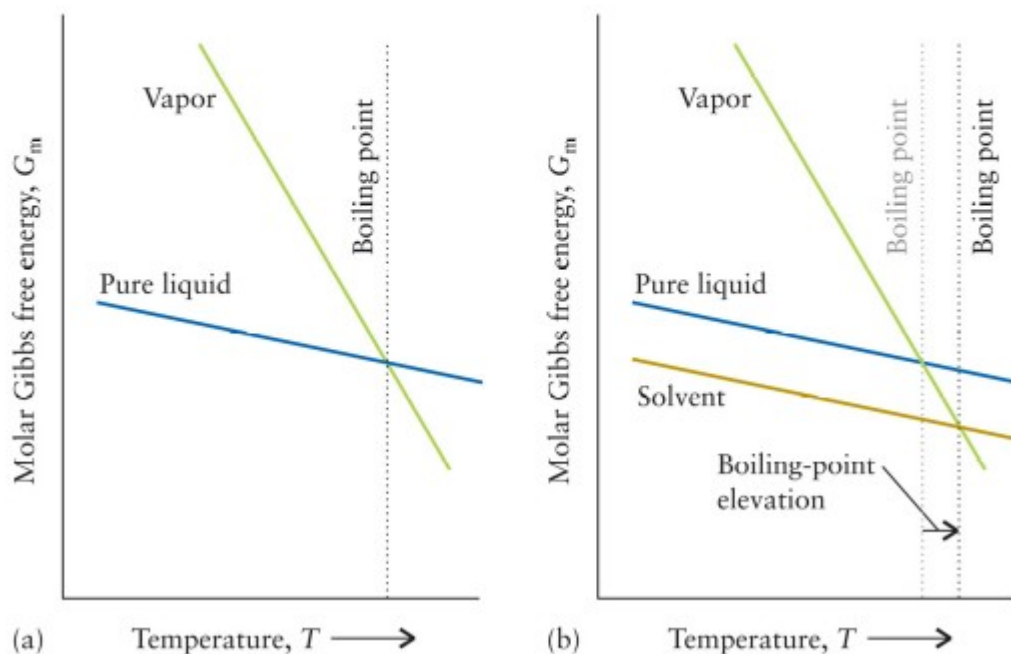
Lower T needed for solution/solid equilibrium



- Boiling point elevation: The temperature at which the vapor and the pure liquid intersect is the boiling point. Compared to the pure liquid, the solvent has the same slope but a lower y-intercept. Therefore, the intersection between the solvent and the vapor is farther to the right. This shows boiling point elevation.

Boiling Point Elevation

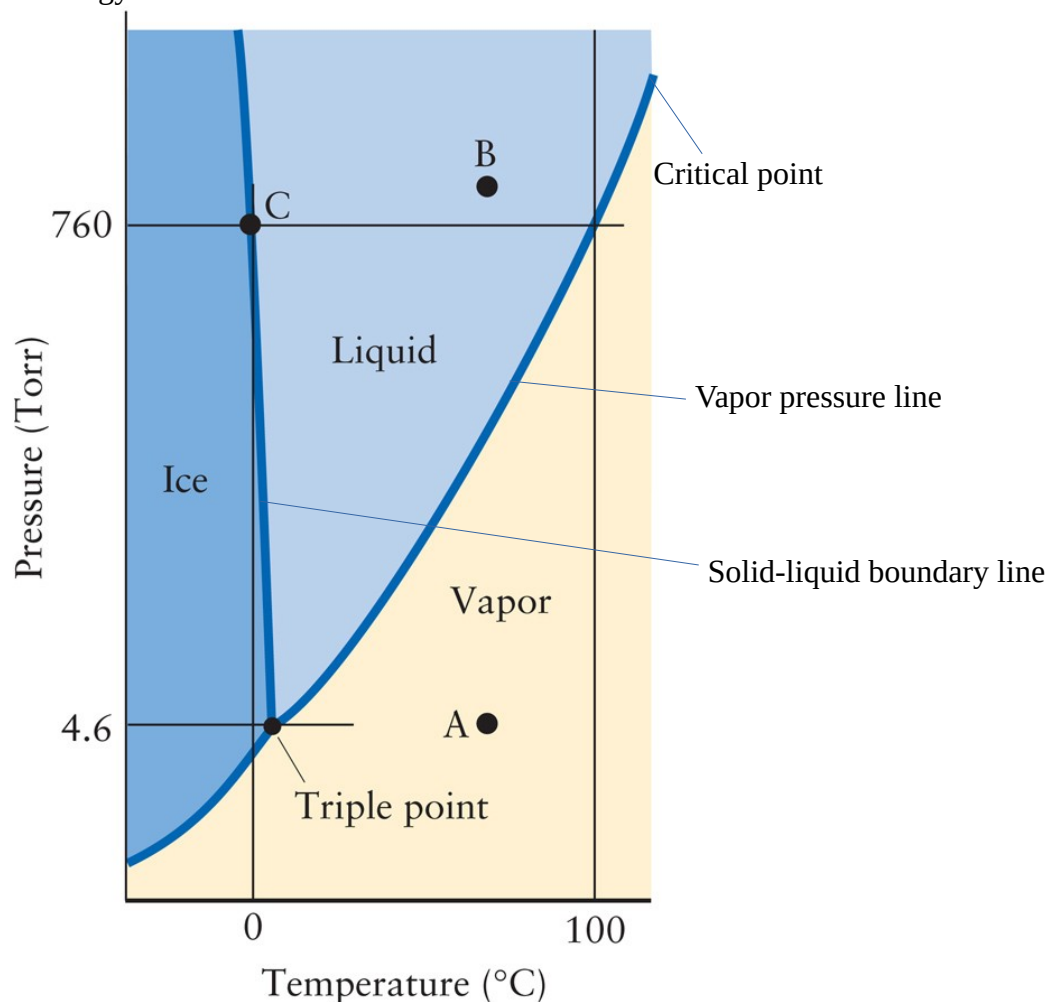
raise T to reach equilibrium between solution and gas



- Osmotic pressure
 - Osmosis** is the flow of a solvent through a semipermeable membrane into a more concentrated solution. Solvent will flow until **osmotic equilibrium** is reached (occurs when the free energies of the diffusible molecules are the same on the two sides of the membrane).
 - Osmotic pressure** (Π) is the pressure needed to stop the flow.
 - Hydrostatic pressure** is the pressure created by the difference in height of the columns after flow = Π .
 - Formula for osmotic pressure:

$$\Pi = iRTc$$
 - c = concentration in mol/L (molarity)
 - $R = 0.08206 \frac{L \cdot atm}{K \cdot mol}$
- Real ions in water and colligative properties
 - Assuming non-ideal behavior, ions have a smaller decrease in freezing point, boiling point elevation, etc.
 - small for +/- 1 ions, moderate for +/- 2 ions, and large for +/- 3 ions.

- Phase diagram terminology



- **Triple point:** 3 phase boundaries meet on a phase diagram. At this temperature and pressure, all 3 phases co-exist.
 - **Critical point:** The point at which the particles are thought to be vaporizing at such a fast rate that the density of liquid and vapor are equal, and thus form a **supercritical fluid**. The distinction between the liquid and the gas can no longer be made.
 - The **liquid-vapor boundary line** indicates the vapor pressure needed to achieve boiling. Given a phase diagram, you can find the vapor pressure at any given temperature on the graph.
 - The **solid-liquid boundary line** indicates the melting point and indicates which phase is denser.
 - When the solid is more dense than liquid, the solid-liquid boundary line will have a positive slope. Higher pressure favors with the more dense (solid) phase and as a result, T_m increases with increasing pressure.
 - When the liquid is more dense than solid, the solid-liquid boundary line will have a negative slope (as seen above). Higher pressure favors the more dense (liquid) phase and as a result, melting point decreases with increasing pressure.
- Random info
 - solid \rightarrow gas is **sublimation**
 - gas \rightarrow solid is **deposition**

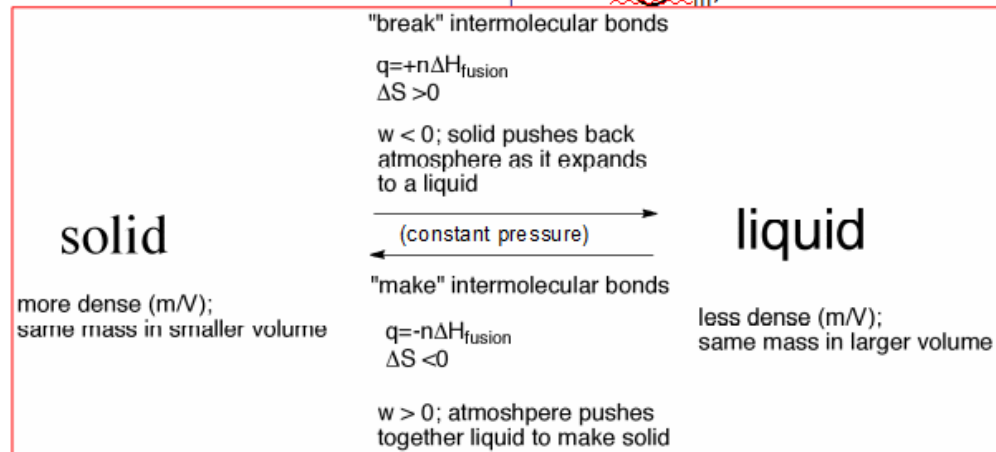
Thermodynamics of Melting and Freezing

*measured at T_m not 298K

ΔH_{fus} : enthalpy of fusion
latent heat of fusion
specific melting heat

$$\Delta S_{\text{fus}} = \Delta H_{\text{fus}} / T_m$$

$$\Delta G_{T_m} = \Delta H_{\text{fus}} - T_m \Delta S_{\text{fus}} = 0 @ T_m, K = 1$$



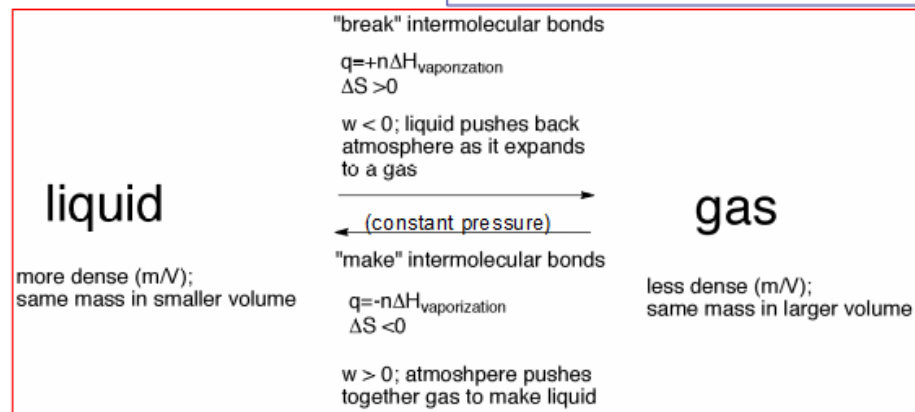
Thermodynamics of vaporizing/condensing

*measured at T_b not 298K

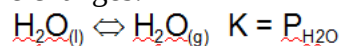
ΔH_{vap} : enthalpy (heat) of vaporization

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T_b$$

$$\Delta G_{T_b} = \Delta H_{\text{vap}} - T_b \Delta S_{\text{vap}} = 0, K = 1$$



- Clausius-claperyon equation
 - The **clausius-claperyon equation** describes the quantitative changes in vapor pressure when temperature changes.



Clausius-Clapeyron Equation

$$\ln \frac{P_{2,\text{vap}}}{P_{1,\text{vap}}} = \frac{\Delta H_{\text{vap},m}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Pressures in same units

ΔH in kJ/mol

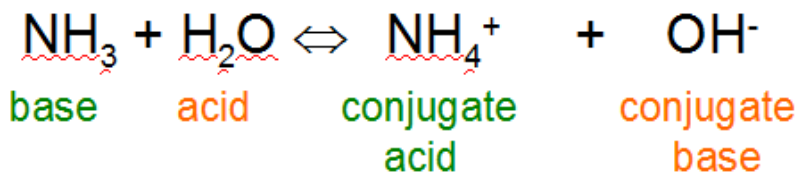
R in J/(K mol)

T in K

Convert to kJ or J

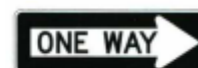
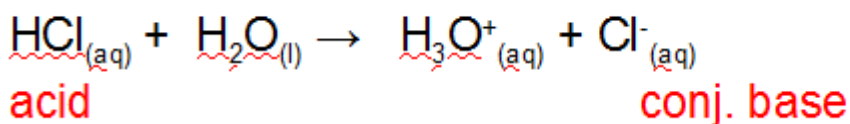
- Definitions

- **Bronsted-lowry acid** is a proton donor.
- **Bronsted-lowry base** is a proton acceptor.
- **Conjugate base** is the species left over when an acid donates a proton.
- **Conjugate acid** is the species left over when a base accepts a proton.

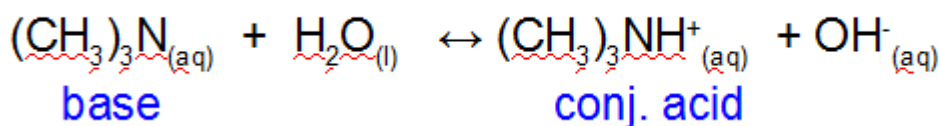


- Strong vs. weak

- **Strong acids and bases** completely dissociate in water. Its essentially a one-way reaction.

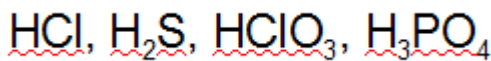


- Strong acids:
 - HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄
- Strong bases:
 - group I hydroxides
 - group II hydroxides
 - NH₂⁻, O₂⁻, H⁻, R₃C⁻
- **Weak acids and bases** do not dissociate completely. Instead, an equilibrium is established in water between an acid, its conjugate base, and hydronium (for an acid) or a base, its conjugate acid, and hydroxide (for a base)

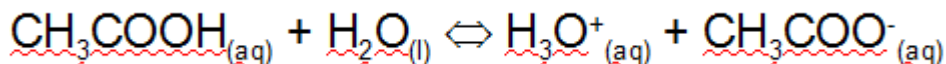


- Identifying acids and bases

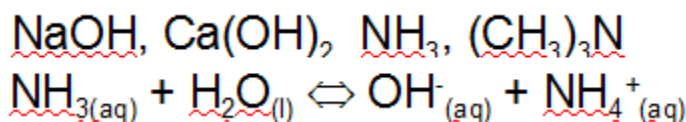
- **Molecular acids** = H⁺ + anion.



- **Carboxylic acids** have the functional group -COOH.



- **Bases** tend to be hydroxides and amines.



- **Metallic oxides** are basic (i.e. Mg₂O).
- **Molecular oxides** are acidic (i.e. CO₂).
- Identifying salts as acids or bases:
 - (1) break up the salt into its cation and anion
 - (2) add "OH" to cation and "H" to anion
 - (3) check to see if the resulting acid or base is strong. If it is strong, then the anion/cation is neutral. If it is not strong, then use this following table to determine if the anion/cation is acidic or basic:

- anions:
 - acidic = HSO_4^-
 - basic = all other weak acids
- cations:
 - neutral = group I and II cations and other +1 metal cations
 - acidic = NH_4^+ , first row d block or p block with at least +2 charge.

Identifying **Salts** as Acids or Bases: Look at Anion and Cation

Identifying Anions as Aqueous Acids & Bases

Neutral	
Conj. Base of strong acids	Cl^- , Br^- , I^- , NO_3^- , ClO_4^-
Acidic	HSO_4^-
Amphoteric	
conj. base of polyprotic acid	H_2PO_4^- , HS^- , HCO_3^-
$\text{HS}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{S}^{2-}_{(\text{aq})}$	$\text{HS}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{OH}^-_{(\text{aq})} + \text{H}_2\text{S}_{(\text{aq})}$
Basic	
O^{2-} , OH^- , NH_2^- strong bases	
Conj. Base of weak acids	F^- , S^{2-} , CN^- , CO_3^{2-} , PO_4^{3-} , NO_2^- , CH_3CO_2^-
$\text{F}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{HF}_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$	

Identifying Cations as Aqueous Acids & Bases

Basic	None
Neutral	
Gp 1 and 2 cations Other metal cations +1	Li^+ , Na^+ , K^+ , Mg^{+2} , Ca^{2+} , Ag^+ , Cu^+
Acidic	
"Ammonium" cations	NH_4^+ , CH_3NH_3^+ , $\text{C}_6\text{H}_5\text{NH}_3^+$
first row d block or p block +2 > charge <div style="border: 1px solid black; padding: 2px; display: inline-block;">K_as in Table 11.8</div>	Fe^{+3} as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ Cr^{+3} as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ Al^{+3} as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ Cu^{+2} as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ Ni^{+2} as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$
$\text{Fe}(\text{H}_2\text{O})_6^{3+}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}_{(\text{aq})}$	

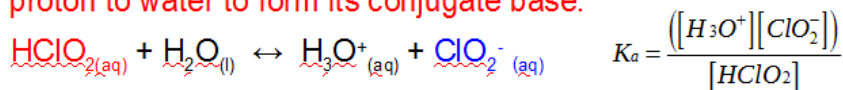
- For binary acids, the more polar the bond, the stronger the acid. However, the more polarizable the atom bound to H leads to the stronger acid.
- The more electronegative atom bound in the molecule but not directly to H, the stronger the acid.
- Resonance of the conjugate base increases acidity.
- For oxoacids, the more oxygens bound to the central atom, the more acidic it is.
- For carboxylic acids, the greater the electronegativity of the groups attached to COOH , the stronger the acid.

- pH/pOH
 - Formulas:
 - $pH = -\log[H_3O^+]$
 - $pOH = -\log[OH^-]$
 - $pH + pOH = 14$
 - A difference of 1 pH/pOH unit is a difference in concentration of a factor by 10!!!!
 - DAT math formulas to estimate logs:**
 - $-\log(m \cdot 10^{-n}) \approx n - 1.10 - m$
 - $\log(m \cdot 10^{-n}) \approx (-n) + 1.10 - m$
 - $\ln(x) \approx 2.3(\log(x))$
 - $\log(m \cdot 10^n) \approx n + 1 + m$
- K_a, K_b
 - K_a is the equilibrium constant for an acid dissociating in water to form its conjugate base.
 - K_b is the equilibrium constant for base dissociating in water to form its conjugate acid.
 - Stronger acids have higher K_a values and smaller K_b values.
 - Stronger bases have higher K_b values and smaller K_a values.

Weak Aqueous Acids/Conj. Bases



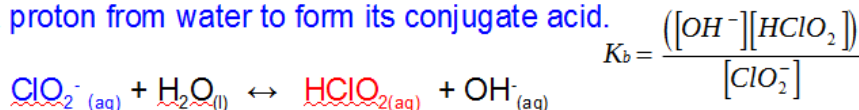
K_a is the equilibrium constant for a weak acid donating a proton to water to form its conjugate base.



Stronger weak acids have higher $[\text{H}_3\text{O}^+]$,
higher K_a , (and lower pK_a)

$$pK_a = -\log K_a$$

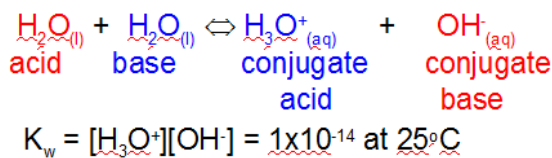
K_b is the equilibrium constant for a weak base accepting a proton from water to form its conjugate acid.



Stronger weak bases have higher $[\text{OH}^-]$,
higher K_b , (and lower pK_b)

$$pK_b = -\log K_b$$

- K_a and K_b can be converted using a logarithmic scale to pK_a and pK_b :
 - $pK_a = -\log(K_a)$ $pK_b = -\log(K_b)$
 - Stronger acids have lower pK_a and higher pK_b values.
 - Stronger bases have higher pK_a and lower pK_b values.
- The special case of water
 - Water is **amphiprotic**, meaning it can act as an acid or base.
 - At 25°C, there is $1 \cdot 10^{-7}$ M H_3O^+ and $1 \cdot 10^{-7}$ M OH^- .
 - The equilibrium constant that describes this association is K_w .

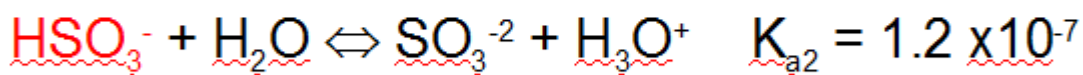
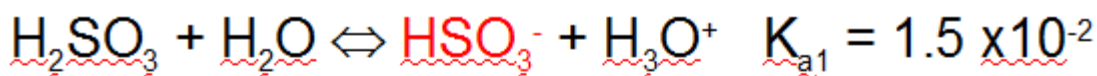


- The autoionization of water is an endothermic reaction. As the temperature increases, the pH and the pOH decreases. Why?
 - Increasing the temperature shifts the reaction to the right, meaning that there will be an increase in $[H^+]$ and $[OH^-]$. Therefore
- A special and important relationship arises from K_w :

$$K_w = K_a * K_b \quad \text{and at } 25^\circ\text{C: } 1 * 10^{-14} = K_a * K_b$$

- Polyprotic acids

- Some acids have multiple protons that can be removed from it. These acids are **polyprotic acids**.
- Polyprotic acids have multiple K_a values, one for each proton.
 - The easiest proton to remove from the polyprotic acid is the first proton. This proton has the highest K_a value and the lowest pK_a value.
 - After removing the first proton, every successive proton is harder to remove. As a result, the K_a value increases and the pK_a value increases of every successive proton.
- If an acid has already lost one proton but not all of them, then it tends to be amphoteric.



HSO_3^- is amphiprotic & amphoteric

- Problem solving: How to find pH of weak acids and bases
 - Example problem (note that the numbers will be easier to work with on the DAT):

Problem 1: Find the K_a of acetic acid if a 0.10 M $\text{CH}_3\text{COOH}_{(aq)}$ solution has a pH = 2.9.

$$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$

I	0.1 M		0	0
C	-x		+x	+x
E	0.1-x		x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$pH = -\log[H_3O^+] = 2.9$$

$$[H_3O^+] = 10^{-2.9} = 1.26 \times 10^{-3} = x$$

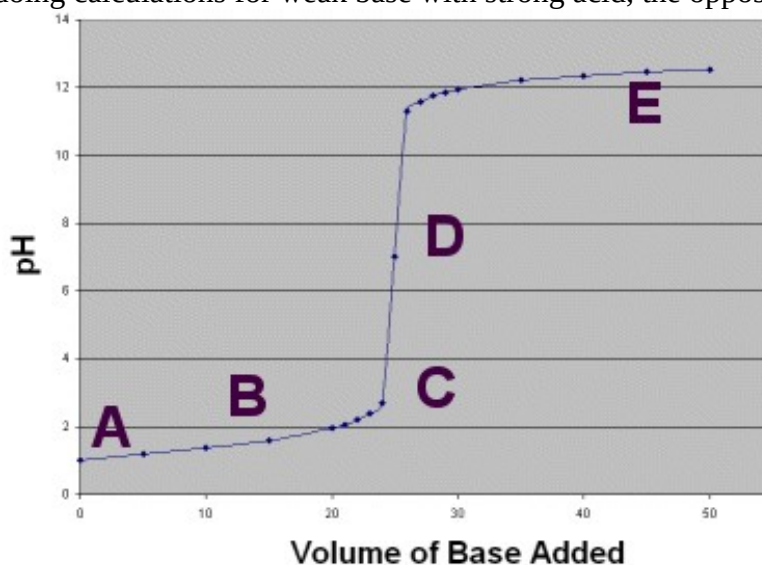
$$K_a = \frac{x * x}{0.1 - x} = \frac{(1.26 \times 10^{-3})^2}{0.1 - 1.26 \times 10^{-3}} = 1.61 \times 10^{-5}$$

- 1) Write out the equilibrium reaction for the constant given/what you are looking for. If you are given the K_b value, write out the reaction for K_b . In the problem above, they are asking for the K_a , so write out the reaction for K_a (an acid reacting with water).
- 2) Draw an ICE box and fill out the 3 rows.
- 3) Write out the equation for K_a or K_b , depending on the problem. Here, write out the equation for K_a because the problem asks you for the K_a value.

- 4) You will either have to solve for x or solve for the K_a or K_b value depending on what the problem is asking for. In this problem, you need to solve for K_a . But what is x equal to? You are given pH, meaning you can find the hydronium ion concentration at equilibrium. Solve for it, then replace x with the answer and then solve for K_a .
- What is a titration?
 - A **titration** is an analytical technique where an unknown concentration of a substance is determined via a chemical reaction by the addition of a known amount of a known concentration of a substance that reacts with the unknown.
 - A **burette**, a piece of graduated glassware, allows the volume of the known to be measured.
 - The **equivalence point/stoichiometric point** occurs when moles of added known substance have stoichiometrically reacted with the moles of the unknown substance (the reaction is complete.)
 - The $\frac{1}{2}$ **equivalence point** is when $[\text{acid}] = [\text{conjugate base}]$ or when $[\text{base}] = [\text{conjugate acid}]$ in the beaker. At this point the $\text{pK}_a = \text{pH}$ (more on this later).
- 3 different titration scenarios
 - Note that in each scenario, the “strong” must always be in the buret!
 - (1) strong acid with strong base. The equivalence point is always at $\text{pH} = 7$.
 - (2) Weak acid with strong base. Equivalence point is always greater than $\text{pH} = 7$.
 - (3) Weak base with strong acid. Equivalence point is always less than $\text{pH} = 7$.
- The henderson-hasselbach equation:
 - Useful equation for titration calculations:

$$\text{pH} = \text{pK}_a + \log\left[\frac{H^-}{HA}\right] \quad \text{or} \quad \text{pOH} = \text{pK}_b + \log\left[\frac{HB^+}{B}\right]$$

- **IMPORTANT LIMITATION:** $[A^-]$ or $[HB^+]$ and $[HA]$ or $[B]$ must be within a factor of 10 of one another (ratio must be less than 10).
- The titration curve and titration calculations (assuming weak acid titrated with strong base):
 - NOTE: when doing calculations for weak base with strong acid, the opposite applies.



- (A) = No base has been added to the beaker. Use a simple ICE box to determine the $[\text{H}_3\text{O}^+]$ of the acid, and then from there calculate pH.
- (Between A and B when 10 mL base has been added) = Base has been added. Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box (Put in, Use up, Get out). A **PUG box** is essentially the same as an ICE box, but everything is in terms of moles rather than pressures or concentrations. Note that this point, the moles of acid will be greater than the moles of base. Therefore, you will Get out with some moles of acid, 0 moles of original base, and some moles of the conjugate base.

	HA	+ OH ⁻	→ H ₂ O	+ A ⁻
Put in	Mol acid	Mol base	XXXX	0
Use up	- mol base	- mol base	XXXX	+ mol base
Get out	Mol acid – mol base	0	XXXX	Mol base

After completing the PUG table, reconvert the moles of the acid and the conjugate base back into their respective molarities. Because you added base to the beaker, the volume has changed!

New volume = volume of acid + volume of base added. Once you have re-converted back into molarity, use the henderson-hasselbach equation to find the pH of the solution.

- (B) = $\frac{1}{2}$ equivalence point. The amount of moles of HA = moles of A⁻. At this point, the pH = pKa of the weak acid.
- (D) = Equivalence point (Moles of OH⁻ = moles of HA). Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box. Because mol base = mol acid, there are no leftover moles of the acid or the base. All that remains is the conjugate base. Convert back the moles of conjugate base back into molarity. Because you added base to the beaker, the volume has changed! New volume = volume of acid + volume of base added.

	HA	+ OH ⁻	→ H ₂ O	+ A ⁻
Put in	Mol acid	Mol base	XXXX	0
Use up	- mol base	- mol base	XXXX	+ mol base
Get out	0	0	XXXX	Mol base

The conjugate base can react with water. Draw an ICE box.

	A ⁻	+ H ₂ O	→ HA	+ OH ⁻
Initial	$\frac{\text{mol conjugate acid}}{\text{new volume}}$	XXXX	0	0
Change	- x	XXXX	+ x	+ x
Equilibrium	$\frac{\text{mol conjugate acid}}{\text{new volume}} - x$	XXXX	x	x

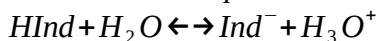
In order to solve for x, you will need the K_b value. In these problems, they will give you the K_a of the original acid. Use K_w = K_a*K_b to find K_b. Write out the Kb equation and solve for x. Once you solved for x, then find pOH and then convert that to pH.

- (E) = Past the equivalence point. Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box. From the PUG table, you will see that there will be some leftover moles of base and some moles of conjugate acid. You can ignore the moles of conjugate acid because that plays a negligible role in affecting the pH. Convert back the excess moles of OH back into molarity. Because you added base to the beaker, the volume has changed! New volume = volume of acid + volume of base added. Then find pOH and convert to pH.

• Indicators

- An **indicator** is used to tell when the equivalence point has been reached. The goal is to choose an indicator with a pK_{ind} value near the pH of the stoichiometric point. Why is this the case?

- Indicators are in equilibrium when in water with their deprotonated form:



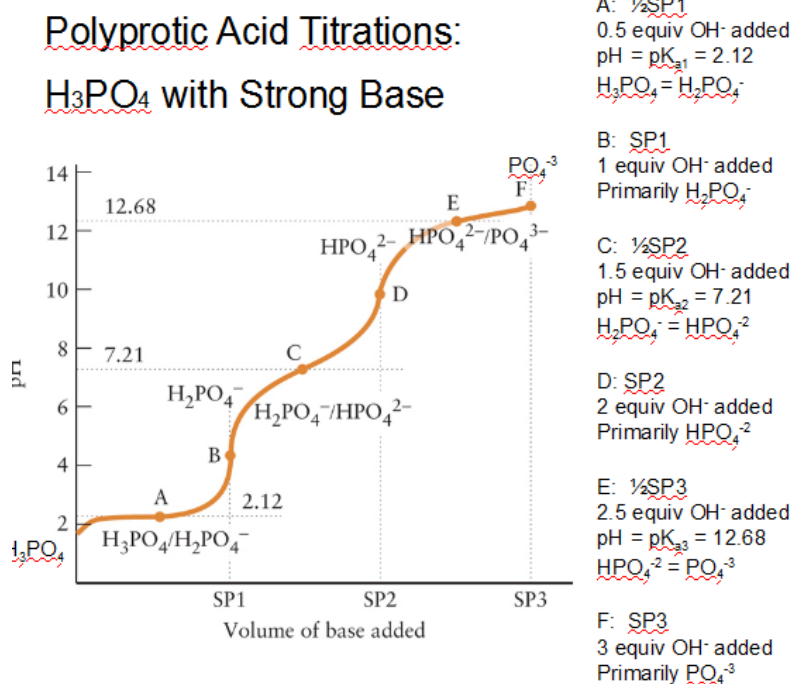
- HInd and Ind⁻ both have different colors and they are pH dependent:

- If you add OH⁻ ions (base), it will react with H₃O⁺, and lower [H₃O⁺]. Due to le chatelier's principle, the reaction will shift right and the overall color will be closer to that of Ind⁻.

- If you add H_3O^+ ions (acid), the reaction will shift left (as you are adding product) and the overall color will be closer to HInd.
- When $[\text{HInd}] = [\text{In}^-]$, the color will be in between. You will see a color change occur here.
- $K_{\text{ind}} = \frac{[\text{H}^+][\text{Ind}^-]}{[\text{HInd}]}$. When $[\text{HInd}] = [\text{In}^-]$, $K_{\text{ind}} = \text{H}^+$, so $\text{p}K_{\text{ind}} = \text{pH}$.

- Polyprotic acid titrations

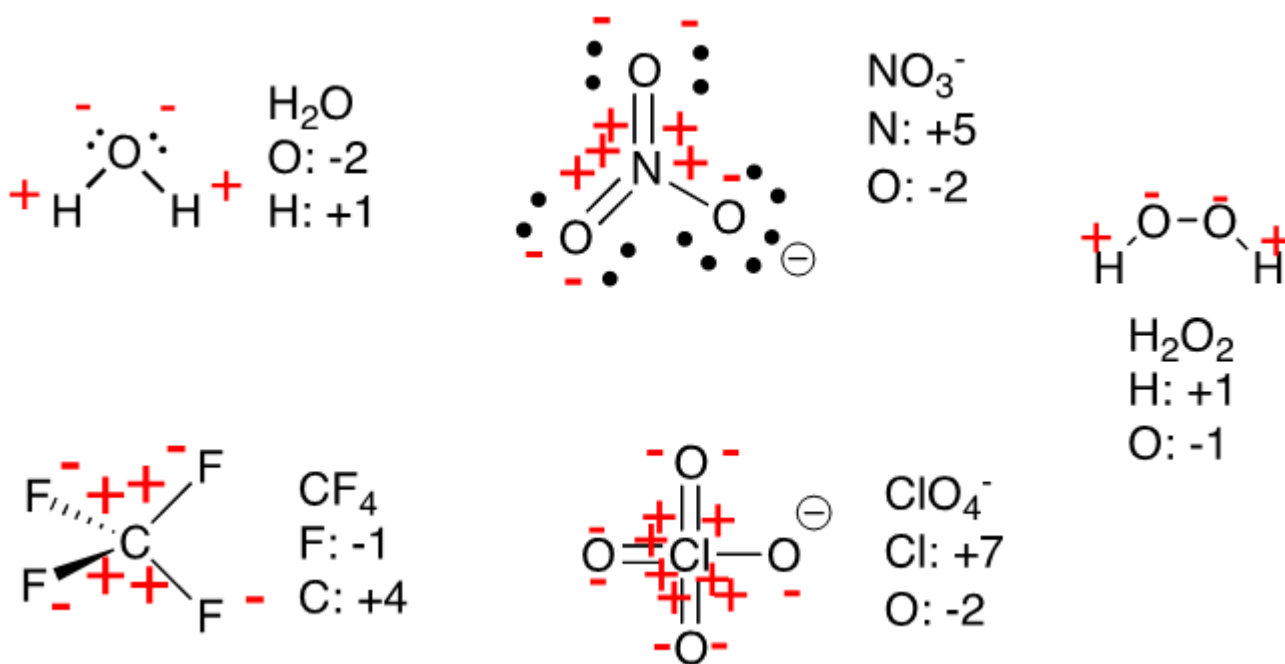
- Polyprotic acids have multiple equivalence points and $\frac{1}{2}$ equivalence points.
- The pH at each $\frac{1}{2}$ equivalence point corresponds to the $\text{p}K_a$ of the proton that is being ripped off.



- The $M_1V_1 = M_2V_2$ titration problem
 - From diluting solutions, you should remember the equation $M_1V_1 = M_2V_2$ where M = molarity and V = volume in liters.
 - DAT loves asking equations relating this formula to titrations. The formula is now:
 $(X)M_{\text{acid}}V_{\text{acid}} = (Y)M_{\text{base}}V_{\text{base}}$ You need to be careful in how you approach this:
 - (1) identify the amount of OH^- ions that are in each molecule of base and the amount of Hs that are in each molecule of acid.
 - (2) Replace “Y” with the number of OH^- ions you counted and “X” with the number of Hs you counted.
 - (3) Fill in the known variables and solve for the unknown variable.
 - **Example:** If it takes 50 mL of 0.5 M KOH solution to completely neutralize 125 mL of sulfuric acid (H_2SO_4) solution, what is the concentration of H_2SO_4 solution?
 - (1) For every molecule of base, there is 1 OH^- . For every molecule of acid, there are 2 Hs.
 - (2) $2 \cdot M_{\text{acid}} \cdot V_{\text{acid}} = 1 \cdot M_{\text{base}} \cdot V_{\text{base}}$
 - (3) $2 \cdot x \cdot 125 = 1 \cdot 0.5 \cdot 50 \rightarrow x = 0.1 \text{ M}$
- Buffers
 - A **buffer** is a solution in which pH resists change when small amounts of acids or bases are added because the system contains a weak acid and its conjugate base.
 - Buffers only exist when $[\text{A}^-]$ and $[\text{HA}]$ or $[\text{B}]$ and $[\text{HB}^+]$ are within a factor of 10 of each other. Another way of saying this is that the pH is within 1 unit of the $\text{p}K_a$.
 - The region described above is called the **buffering region**. Adding OH^- or H^+ does not significantly change the pH.
 - **Buffer capacity** is the maximum amount of acid or base that can be added to a buffer before the buffer loses its ability to resist large changes in pH.

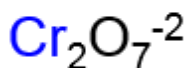
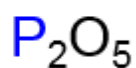
- A more concentrated buffer has a higher buffer capacity than a less concentrated buffer.
- 3 buffer recipes (the pairs must be within a concentration factor of 10):
 - mix weak acid + conjugate base pair
 - strong acid + weak base
 - weak base + strong acid

- Oxidation Numbers
 - **Oxidation state** (or oxidation number) system that allows tracking of movement of electrons in reactions.
 - Inorganic method for oxidation numbers:
 - An atom in its elemental form has a 0 oxidation state.
 - The oxidation number of a monoatomic ion equals the charge of the ion.
 - For specific elements:
 - The oxidation state for oxygen is almost always -2. The only major exception is peroxides (H-O-O-H), where oxygen has an oxidation state of -1.
 - The oxidation state of hydrogen is +1 when bonded to non-metals and -1 when bonded to metals.
 - The oxidation state of halogens is almost always -1.
 - The sum of the oxidation states of all atoms in a neutral compound must equal 0. The sum of the oxidation states of all atoms in a polyatomic ion equals the charge of the ion.
 - Organic method:
 - For each covalent bond, assign the more electronegative atom a “-” and the less electronegative atom a “+”; Sum up charges and add in formal charge)



- Practice question:

What are the oxidation numbers of the highlighted atom in each compound?

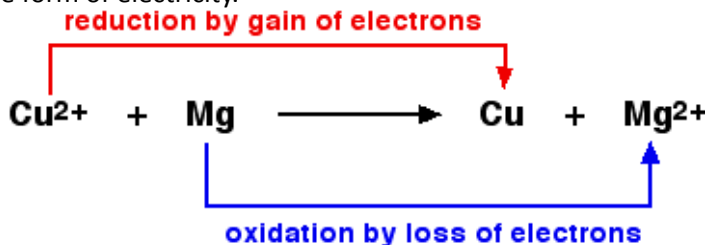


A	+5	+2	+4	+7
B	+5	+2	+4	+6
C	+5	+2	+2	+6
D	+10	+2	+4	+7

- (answer is B)

- Electrochemistry terminology

- An atom is **oxidized** when it loses an electron.
- An atom is **reduced** when it gains an electron.
- An **oxidizing agent** brings about oxidation (it gets reduced).
- A **reducing agent** brings about a reduction (it gets oxidized).
- **Redox reactions** involve the transfer of electrons from one reactant to another. The reaction energy can be harnessed in the form of electricity.



- Balancing Redox Reactions in **Base** (follow the step-by-step guide):

- (1) Divide the net ionic reaction into oxidation and reduction half reactions
- (2) For each half reaction:
 - (a) Balance all the elements other than oxygen and hydrogen.
 - (b) Balance the oxygen by adding water.
 - (c) Balance the hydrogens using H^+
 - (d) Balance the electrons
 - (e) Check charge and elemental balance
- (3) Combine the balanced half reactions. You will need to multiply one or both of the equations by some number (each half-reaction may be multiplied by a different number) so that the total number of electrons in both half-reactions will cancel out when combined.
- (4) When in base, add OH^- for every H^+ to both sides of the equation. OH^- and H^+ , when on the same side, will combine into H_2O .
- (5) Combine, cancel, and check.

- Balancing Redox Reactions in **Acid** (follow the step-by-step guide):

- **NOTE:** the steps in acid are the same as base except that you will not do step 4 (add OH^- for every H^+). Go immediately from step 3 to step 5.
- 1) Divide the net ionic reaction into oxidation and reduction half reactions
- (2) For each half reaction:
 - (a) Balance all the elements other than oxygen and hydrogen.
 - (b) Balance the oxygen by adding water.
 - (c) Balance the hydrogens using H^+
 - (d) Balance the electrons
 - (e) Check charge and elemental balance
- (3) Combine the balanced half reactions. You will need to multiply one or both of the equations by some number (each half-reaction may be multiplied by a different number) so that the total number of electrons in both half-reactions will cancel out when combined.
- (5) Combine, cancel, and check.

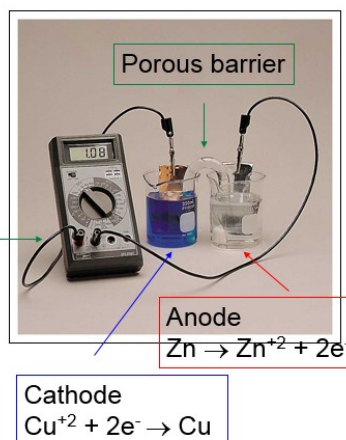
- http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Redox_Chemistry/Balancing_Redox_reactions is a great link for how to solve redox problems. Use this!

- Parts of electrochemical cells

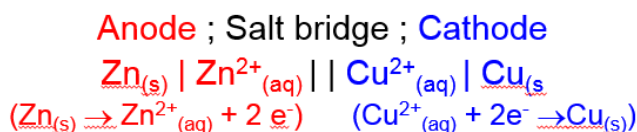
- **Anode** is the compartment where oxidation occurs.
- **Cathode** is the compartment where reduction occurs.
- There is an **external pathway** that allows the flow of electrons from one cell to the other (this can include a light bulb, voltmeter, motor, etc.)
- **Salt bridge** or porous barrier: allows ions to flow back and forth so that charge does not build up in individual cells.

Parts of Electrochemical Cells

1. The **anode**: the compartment where **oxidation** occurs.
2. The **cathode**: the compartment where **reduction** occurs.
3. External pathway to allow the **flow of electrons**. (This can include a light bulb, voltmeter, motor, etc.)
4. **Salt bridge** or **porous barrier**: allows ions to flow back and forth so that charge does not build up.



- Types of electrochemical cells and nomenclature
 - Electrolytic cell** is a cell where nonspontaneous electrochemical reactions are produced by applying electrical energy to the system.
 - Voltaic/Galvanic cell** is an electrochemical cell or group of cells in which a product favored redox reaction is used to replace an electrical current.
 - Cell line notation:
 - Write all half reaction components in the order that they appear.
 - Use | to show interface between phases.
 - Use , in between components in the same phase.
 - No need to include stoichiometric coefficients.
 - Pressure/concentration may be included after phase symbol.
 - Electrode is the outermost component. Use Pt electrode if needed.



- Half-cell potential and ΔE°
 - Cell potential** is a measure of an ability of a cell reaction to force electrons through a circuit. Measured in the unit Volt.
 - You usually find the cell potential values in a table of standard potentials. Note that in this table, all the reactions listed are reductions. If you want to find the cell potential for the oxidation reaction, flip the reduction reaction and the cell potential's sign.
 - Reactions in a reduction table are likely to get reduced if positive and high in magnitude. They are likely to get oxidized if negative and high in magnitude.

TABLE 14.1 Standard Potentials at 25 °C*

Species	Reduction half-reaction	E° (V)
Oxidized form is strongly oxidizing		
F_2/F^-	$\text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
Au^+/Au	$\text{Au}^+(\text{aq}) + e^- \rightarrow \text{Au}(\text{s})$	+1.69
$\text{Ce}^{4+}/\text{Ce}^{3+}$	$\text{Ce}^{4+}(\text{aq}) + e^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{MnO}_4^-/\text{H}^+/\text{Mn}^{2+}, \text{H}_2\text{O}$	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
Cl_2/Cl^-	$\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+/\text{Cr}^{3+}, \text{H}_2\text{O}$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{O}_2/\text{H}^+/\text{H}_2\text{O}$	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23; +0.82 at pH = 7
Br_2/Br^-	$\text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.09
$\text{NO}_3^-/\text{H}^+/\text{NO}, \text{H}_2\text{O}$	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96
Ag^+/Ag	$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}/\text{Fe}^{2+}$	$\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
I_2/I^-	$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-(\text{aq})$	+0.54
$\text{O}_2/\text{H}_2\text{O}/\text{OH}^-$	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4e^- \rightarrow 4\text{OH}^-(\text{aq})$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}/\text{Ag}, \text{Cl}^-$	$\text{AgCl}(\text{s}) + e^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
H^+/H_2	$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$	0, by definition
Fe^{3+}/Fe	$\text{Fe}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Fe}(\text{s})$	-0.04
$\text{O}_2/\text{H}_2\text{O}/\text{HO}_2^-, \text{OH}^-$	$\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2e^- \rightarrow \text{HO}_2^-(\text{aq}) + \text{OH}^-(\text{aq})$	-0.08
Pb^{2+}/Pb	$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb}(\text{s})$	-0.13
Sn^{2+}/Sn	$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sn}(\text{s})$	-0.14
Fe^{2+}/Fe	$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Fe}(\text{s})$	-0.44
Zn^{2+}/Zn	$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{H}_2\text{O}/\text{H}_2, \text{OH}^-$	$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83; -0.42 at pH = 7
Al^{3+}/Al	$\text{Al}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Al}(\text{s})$	-1.66
Mg^{2+}/Mg	$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg}(\text{s})$	-2.36
Na^+/Na	$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na}(\text{s})$	-2.71
K^+/K	$\text{K}^+(\text{aq}) + e^- \rightarrow \text{K}(\text{s})$	-2.93
Li^+/Li	$\text{Li}^+(\text{aq}) + e^- \rightarrow \text{Li}(\text{s})$	-3.05
Reduced form is strongly reducing		

Cell notation components

Likely to be reduced (gain electrons)

Likely to be oxidized (lose e⁻)

- ΔE° , **full cell potential**, is the sum of the cell potentials for the half reactions. IT describes the cell potential for the overall reaction.

$$\Delta E^\circ = \Delta E^\circ_{\text{red}} + \Delta E^\circ_{\text{ox}}$$

- When $\Delta E^\circ > 0$, the reaction is spontaneous.
- When $\Delta E^\circ = 0$, the reaction is at equilibrium.
- When $\Delta E^\circ < 0$, the reaction is nonspontaneous.
- Potential (E° or ΔE°) is an intensive property: it does not depend on the amount of oxidizing agent or reducing agent but rather what they are.

- ΔG° , ΔE° , and K

- $\Delta G^\circ = -nF\Delta E^\circ$
 - n = moles of electrons transferred
 - F = Faraday's constant (96485 coulombs/mol e-)
- We know that $\Delta G = -RT \ln K$. Replace ΔG with the equation up above and you get a combined equation:

$$nF\Delta E^\circ = RT \ln K_{298}$$

- Solving for ΔE° , we end up with 2 equations:

$$\Delta E^\circ = \frac{RT}{nF} \ln K_{298} \quad \text{or} \quad \Delta E^\circ = \frac{0.0592}{n} \log K_{298}$$

- R = 8.314 J/mol*K
- F = 96495 coulombs/mol e-
- T = 298 K
- n = moles of electrons
- K = equilibrium constant

ΔG°	K_{298}	ΔE°	Reaction under standard conditions
< 0	> 1	> 0	Spontaneous/ product favored
0	1	0	Reactants/products equally favored
> 0	< 1	< 0	Nonspontaneous/ reactant favored

- The Nernst Equation

- You can find ΔE under non-standard conditions using the **nernst equation**.

$$\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q$$

- R = 8.314 J/mol*K
- F = 96495 coulombs/mol e-
- T = 298 K
- n = moles of electrons
- Q = reaction quotient
- When $\Delta E > 0$, the reaction is spontaneous.
- When $\Delta E = 0$, the reaction is at equilibrium.
- When $\Delta E < 0$, the reaction is nonspontaneous.

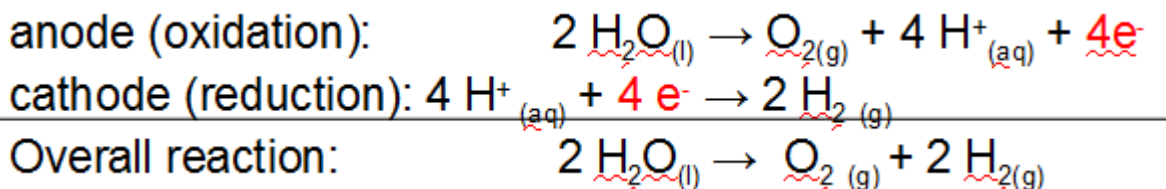
- Electrolysis, current, and electroplating

- **Current** is the rate of charge (electron) flow: how many electrons move between the electrodes per second. Measured in Amperes. 1 Ampere = 1 Coulomb/ second.

$$I = \frac{Q}{t} = \frac{nF}{t}$$

- Q = charge (coulomb), t = time in seconds, F = faraday's constant, n = moles of electrons

- "n" in electrochemistry refers to the number of moles of electrons in the overall equation.
- Electrolysis and electroplating problems:
 - (1) How many coulombs of charge is needed to electrolyze 1 mol H₂O?
 - First, draw out the half reactions, balance them, and write the overall reaction.



- You now know that the net amount of water consumed per every 4 electrons is 2 molecules of water, or 4 moles of electrons per 2 moles of water. Now convert the moles of water to coulombs.

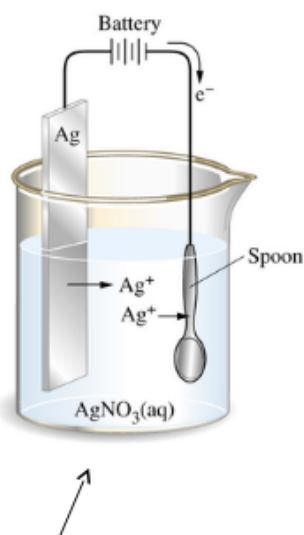
$$1 \cancel{\text{mol H}_2\text{O}} \left(\frac{4 \cancel{\text{mol e}^-}}{2 \cancel{\text{mol H}_2\text{O}}} \right) \left(\frac{96485 \text{ C}}{\cancel{\text{mol e}^-}} \right) = 192974 \text{ C}$$

- (2) A power supply unit puts out a maximum current of 10 amps. How long will it take to electrolyze 18g (1 mole) of water?
 - From the previous question, we know the amount of charge needed to electrolyze 1 mol of water. Remember that 1 amp = 1 coulomb / second. Use this relationship to convert coulombs into time:

$$192974 \text{ C} \left(\frac{\cancel{\text{sec}}}{10 \cancel{\text{ C}}} \right) \left(\frac{\text{hr}}{3600 \cancel{\text{ sec}}} \right) = 5.36 \text{ hours}$$

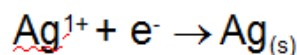
- (3) How long does it take to electroplate 0.3 mm of silver on an object with surface area of 36 cm² from an Ag⁺_(aq) solution with a 12 amp current? Density of silver is 10.5 g/cm³.
 - (1) convert 0.3 mm to grams using density. Then convert grams to moles.
 - (2) Write out the silver half-reaction and find how many electrons are associated with 1 mole of silver. Using this, convert the moles of silver from (1) to coulombs.
 - (3) divide coulombs by amps to find the time.

Electroplating (reducing a metal cation)



[Ag⁺]
does not
change

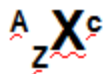
How long does it take to electroplate 0.3 mm of silver on an object with a surface area of 36 cm² from an Ag¹⁺_(aq) solution with a 12 A current? The density of silver is 10.5 g/cm³.



$$\begin{aligned} & \frac{0.3 \text{ mm}}{10 \text{ mm}} \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right) \left(\frac{36 \text{ cm}^2}{\text{cm}^2} \right) \left(\frac{10.5 \text{ g Ag}}{\text{cm}^3} \right) \left(\frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \right) = \\ & 0.105 \text{ mol Ag} \left(\frac{1 \text{ mole}^-}{1 \text{ mol Ag}^+} \right) \left(\frac{96487 \text{ C}}{\text{mole}^-} \right) \left(\frac{\text{s}}{12 \text{ C}} \right) \\ & = 845 \text{ s} = 14.1 \text{ min} \end{aligned}$$

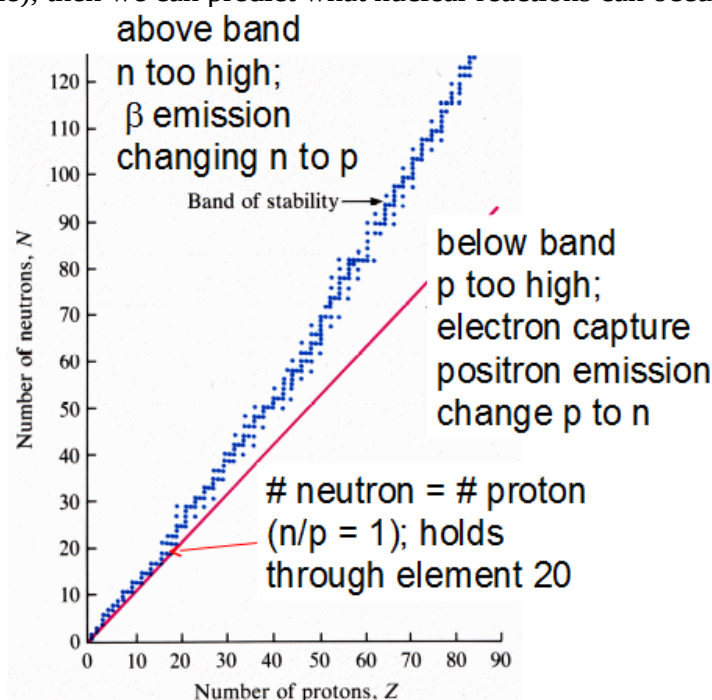
Not sure what the reaction is?
Consider forming element from ions

- Definitions
 - Isotopes** have the same atomic number but different mass number. They undergo the same chemical reactions but different nuclear reactions.
 - Nuclear decay** describes processes when the nucleus of an atom spontaneously emits particles/energy
 - Nuclear decay** describes processes when the nucleus of an atom spontaneously emits particles/energy.
 - The **emissions** (particles + energy) are called radioactivity.
 - Nucleons** are particles that make up the nucleus (protons and neutrons). The neutron has a slightly higher mass than the proton.
- Isotope nomenclature



A: mass (# of protons + # neutrons)
Z: atomic number (usu. # of protons)
c: overall charge of the atom/ion
 = # protons - # electrons

- Nuclear Stability
 - Small nuclei have proton to neutron ratio of 1:1 and is stable.
 - As the nuclei get larger, the proton to neutron ratio increases and the nucleus becomes less stable.
 - All elements with atomic number greater than 82 are radioactive.
 - If we know the position of an isotope on the graph below relative (above/below) to the band of stability (blue line), then we can predict what nuclear reactions can occur:



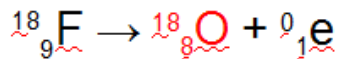
- Alpha, beta, gamma radiation
 - Alpha particles** are positively charged and are the weakest type of radiation (penetrate the least).
 - Beta particles** are negatively charged and are the 2nd strongest (penetrate 2nd most).
 - Gamma particles** are neutrally charged and are the strongest type of radiation (penetrates the most).
- Nuclear Reactions
 - Alpha decay** – mass number decreases by 4 and atomic number decreases by 2.



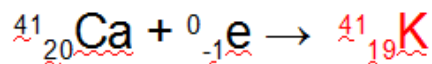
- Beta decay – no change in atomic mass, +1 to atomic number.



- Electron capture – no change in atomic mass, -1 to atomic number.



- Positron emission – no change in mass, -1 to atomic number.



- Half-life

- The **half-life** ($t_{1/2}$) of a reaction is the time it takes for a reactant to reach half of its original concentration. These equations depend on the order of the reaction:

- First-order: $t_{1/2} = \frac{\ln[2]}{k}$

- Second-order: $t_{1/2} = \frac{1}{k[A]}$

- Zero-order: $t_{1/2} = \frac{[A]}{2k}$

- Nuclear decay is always first order kinetics. Use the formula below:

$$t_{1/2} = \frac{0.693}{k}$$

- Note that half-life is given in seconds.

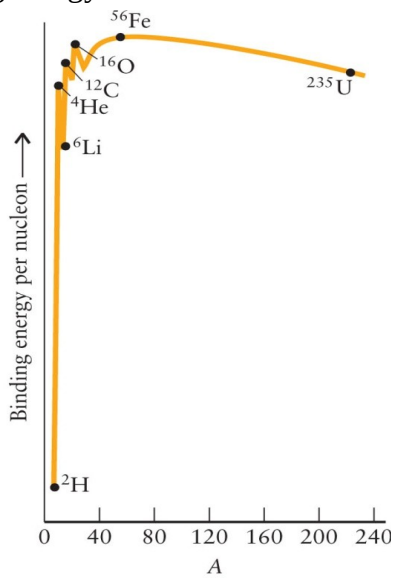
- Binding Energy

- **Nuclear binding energy** (E_{bind}) is the energy released when protons and neutrons come together to form the nucleus. Most likely won't need to do calculations on the DAT since these calculations require calculators.

$$\Delta m = \sum m_{(\text{products})} - \sum m_{(\text{reactants})}$$

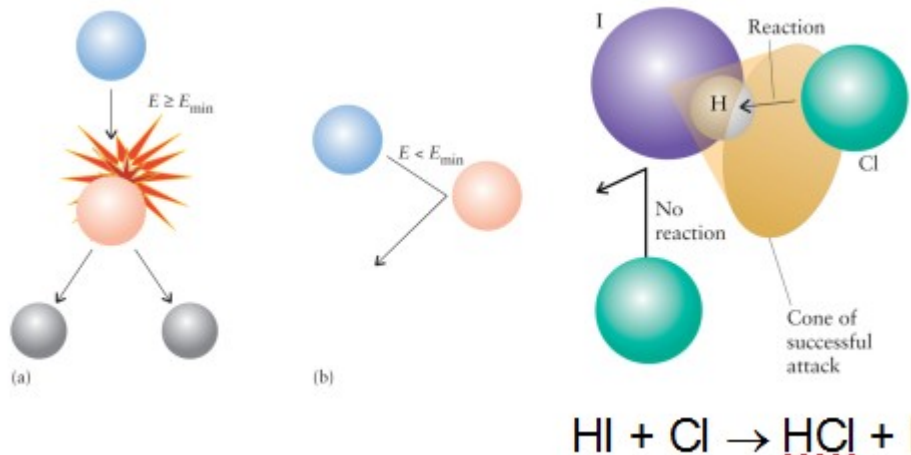
$$E_{\text{bind}} = |\Delta m| * c^2$$

- C = speed of light (3×10^8 m/s)
 - m = mass in kilograms
 - A proton is $\sim 1 m_u$ ($1.00728 m_u = 1.673 \times 10^{-27}$ kg)
 - A neutron is $\sim 1 m_u$ ($1.00866 m_u = 1.675 \times 10^{-27}$ kg)
 - An electron is $\sim 0 m_u$ ($0.00055 m_u = 9.11 \times 10^{-31}$ kg)
- The more energy released, the more stable the nucleus is.
- The greatest binding energy is found at 56-Iron. Follows this graph:

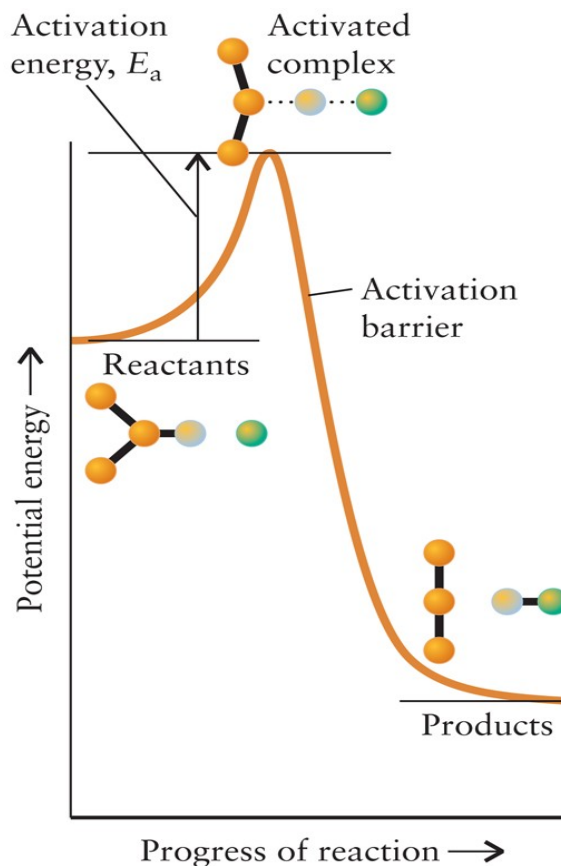


- Kinetics and Basic Theory

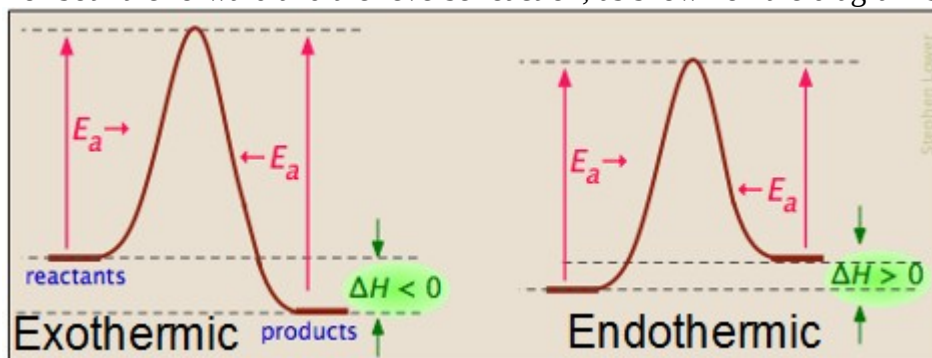
- Kinetics** studies rates of reactions.
 - This cannot be predicted from stoichiometry, ΔH° or ΔG° .
 - You must study each reaction's individual mechanisms to understand rate.
 - Collision theory states that molecules must collide to react. A reaction will only take place if:
 - There is enough energy (E_{\min} aka E_a)
 - The orientation is correct



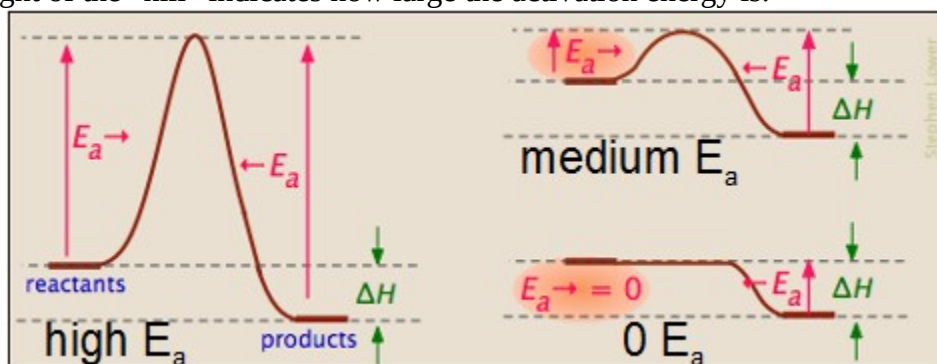
- How to make rate faster:
 - 1) Increase concentration
 - 2) Increase surface area
 - 3) Stir
 - 4) Increase temperature
 - 5) Add a catalyst
 - 6) Add light
 - E_{\min} is **Activation energy**, the minimum energy required in a given collision between molecules for a reaction to occur.
 - The **activated complex** (the transition state) is the transient, highest energy complex.



- Activation Energy plots
 - Exothermic** reactions have product energies that are lower than the reactants. **Endothermic** reactions have product energies that are higher than the reactants. Note that there are activation energies for both the forward and the reverse reaction, as shown on the diagram below:



- The height of the “hill” indicates how large the activation energy is.



- Arrhenius Law
 - The rate constant is exponentially related to the activation energy and Temperature.
 - The higher the temperature, the more collisions and the more molecules with enough activation energy.
 - Arrhenius Law states that:

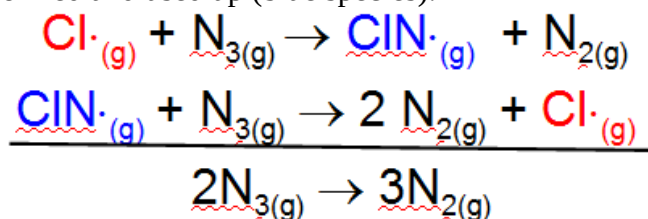
$$k = Ae^{\frac{-E_a}{RT}}$$

- k = rate constant
 - E_a = activation energy
 - $R = 8.314 \text{ J/K}\cdot\text{mol}$
 - A = pre-exponential factor
 - T = temperature
 - You can use a modified version of Arrhenius Law to find the rate constants for the same reaction at another temperature:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- Catalysts
 - Catalysts** are substances that speed up a reaction but which are not consumed by it and do not appear in the net reaction equation.
 - Catalysts affect the forward and reverse rates equally; this means that catalysts have no effect on the equilibrium constant and thus on the composition of the equilibrium state.
 - Catalysts function by allowing the reaction to take place through an alternative mechanism that requires a smaller activation energy. This change is brought about by a specific interaction between the catalyst and the reaction components.
 - Types of catalysts:

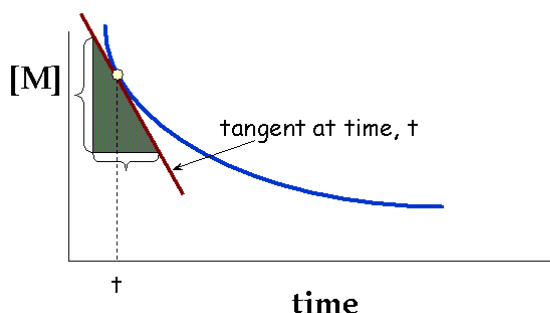
- Homogeneous = same phase
- Heterogeneous = different phase (interaction of reactions with solid particle surface)
- Enzymes
- Catalysts vs. Intermediates in Chemical Reactions
 - A catalyst goes into the reaction and comes back out (red species).
 - An intermediate is formed and used up (blue species).



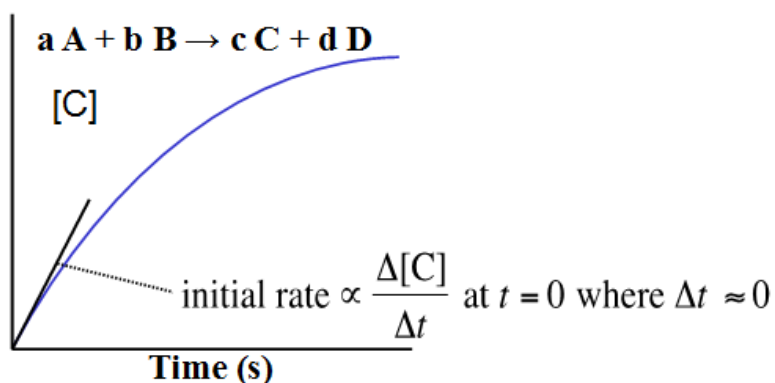
- Average Rate of a Reaction
 - As a reaction progresses, the rate decreases.
 - The average rate of a reaction can be found as follows:

$$\frac{\Delta[C]}{\Delta T} = \frac{[C]_{\text{final}} - [C]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$
 - The average rate depends on the starting point and the stopping point of measurements, so it is not a fixed quantity.
- Instantaneous Rate
 - The **instantaneous rate** is the rate at an exact point in time (the slope of tangent line drawn to the graph at that point).
 - The instantaneous rate depends on the time chosen.

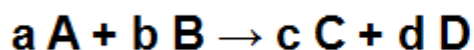
Instantaneous Rate_{time, t} = slope of the tangent at time = t



- Initial Rate
 - The Initial rate is the rate of the reaction under the starting conditions, before the decrease in [reactants] and increase in [products] significantly affects the rate.
 - Formally, the initial rate is the instantaneous rate when $t = 0$.



- Applying Rate with Stoichiometry
 - (1) Given the equation: $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$, if 10 moles of NH_3 are formed in 30 seconds, how many moles of H_2 were consumed?
 - If 10 moles of NH_3 are formed in 30 s, then 0.33 moles of NH_3 are formed in 1 s. Write out the balanced equation now with the coefficient of NH_3 is 0.33. It would look like: $(.33/2)\text{N}_{2(g)} + (.33*1.5)\text{H}_{2(g)} \rightarrow 0.33\text{NH}_{3(g)}$. This is the balanced equation for the number of moles that would be used up or formed in 1 second. Now multiply the new coefficient of H_2 that you just calculated by 30. $.33*1.5*30 = \text{about } 15 \text{ moles}$.
 - (2) Using all the information from question 1, if 50 moles of N_2 were reacted, how many were left after 24 seconds.
 - From question 1, we altered the coefficients to reflect the number of moles that would be used up or formed in 1 second $((.33/2)\text{N}_{2(g)} + (.33*1.5)\text{H}_{2(g)} \rightarrow 0.33\text{NH}_{3(g)})$. Take the coefficient of N_2 and multiply it by 24 to get the number of moles of N_2 used up. Then subtract that number from 50. Answer is 46 moles.
- Rate Law
 - The **rate law** is the relationship between the rate of a reaction and the concentrations of reactants.

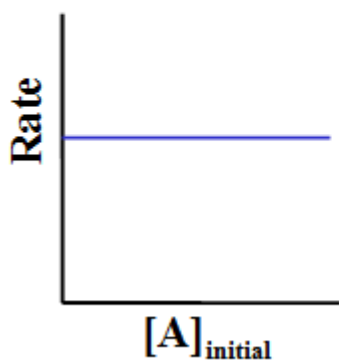


$$\text{rate} = k[A]^x[B]^y$$

- X and y = usually integers that may or may not equal the stoichiometric coefficient
- k is the rate constant, which is independent of initial concentration and dependent on temperature.
- K, x, and y are experimentally determined!
- The **order** of a reaction is the sum of the exponents in the rate law.
 - Zero-order reactions: $\text{Rate} = k$
 - First-order reactions: $\text{Rate} = k[A]$
 - Second-order reactions: $\text{Rate} = k[A][B]$ or $k[A]^2$ or $k[B]^2$
- The units of k, the rate law constant, will depend on the order of the reaction.
 - Zero-order: k in $\frac{M}{s}$
 - First-order: k in $\frac{1}{s}$
 - Second-order: k in $\frac{1}{M*s}$
 - n-order: k in $\frac{1}{M^{n-1}*s}$ where n = the order
- Rate vs. concentration graphs and the order of the reaction
 - The order of the reaction will change the line of the rate vs. concentration graph:

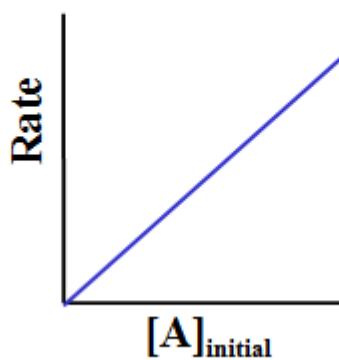
Zero-order reactions

$$\text{Rate} = k$$



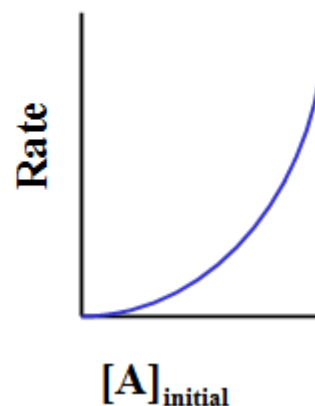
First-order reactions

$$\text{Rate} = k[A]$$

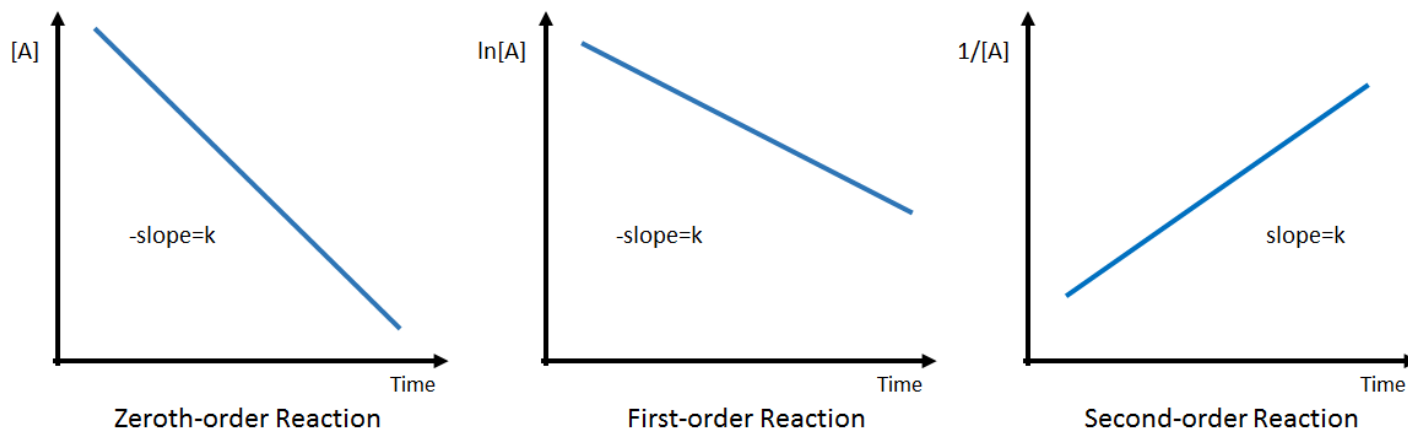


Second-order reactions

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

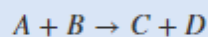


- Integrated rate law
 - Using rates and orders we can:
 - predict a concentration at a given time
 - determine when a reaction will be finished
 - predict impacts of changes on concentration and the rate
 - possibly disprove or support a mechanism
 - Integrating (yes calculus) the rate law allows us to do these more directly. For the DAT, you don't need to know the formulas, but you need to know what the graphs of the integrated rate laws look like for each “ordered” reaction. NOTE the units for the x and y axis and the slope of the lines!



- Experimental determination of rate law problem – only simple stuff on DAT – this is the standard problems and basically all of these problems are solved in this way:

Given the data below, find the rate law for the following reaction at 300 K and the corresponding rate constant.



Trial	[A] _{initial} (M)	[B] _{initial} (M)	r _{initial} (M/sec)
1	1	1	2
2	1	2	8.1
3	2	2	15.9

SOLUTION

First, look for two trials in which the concentrations of all but one of the substances are held constant.

- In trials 1 and 2, the concentration of A is kept constant while the concentration of B is doubled. The rate increases by a factor of approximately 4. Write down the rate expression of the two trials.

- Trial 1: $r_1 = k[A]^x[B]^y = k(1.00)^x(1.00)^y$
- Trial 2: $r_2 = k[A]^x[B]^y = k(1.00)^x(2.00)^y$

Divide the second equation by the first, which yields:

$$4 = (2.00)^y$$

$$y = 2$$

- In trials 2 and 3, the concentration of B is kept constant while the concentration of A is doubled; the rate is increased by a factor of approximately 2. The rate expressions of the two trials are as follows:

- Trial 2: $r_2 = k[A]^x[B]^y = k(1.00)^x(2.00)^y$
- Trial 3: $r_3 = k[A]^x[B]^y = k(2.00)^x(2.00)^y$

Divide the second equation by the third which yields:

$$2 = (2.00)^x$$

$$x = 1$$

Therefore, the rate law is

$$r = 2.0[A][B]^2$$

The order of the reaction with respect to A is 1 and with respect to B is 2; the overall reaction order is as follows:

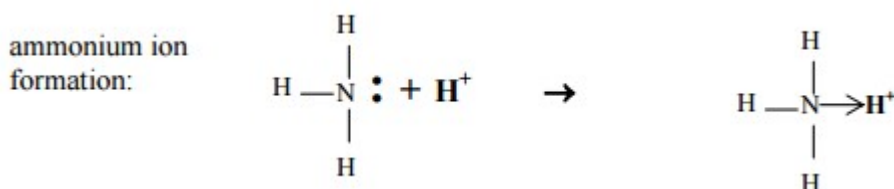
$$1 + 2 = 3$$

To calculate k, substitute the values from any one of the above trials into the rate law:

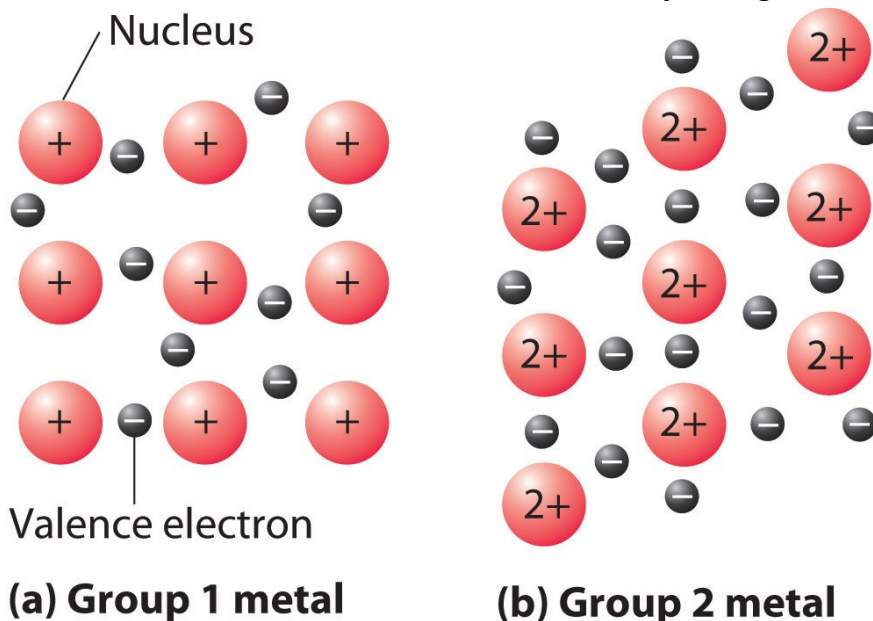
$$2.0 \text{ M/sec} = k(1.00 \text{ M})(1.00 \text{ M})^2$$

$$k = 2.0 \text{ M}^{-2} \text{ sec}^{-1}$$

- Important Note
 - Topics from this chapter also overlap with organic chemistry. Therefore, there are certain topics that are part of this chapter that are covered in my organic chemistry notes. They include:
 - Formal Charge
 - Resonance Structures
 - Bond Length (ranking)
 - Bond Strength
 - Molecular geometry (VESPR)
 - Look at my organic chemistry notes for information on these topics!
- Types of chemical bonds
 - **Ionic bonds** are electrostatic attractions between ions; usually produced by the reaction between a metal and nonmetal.
 - Causes very high melting points and usually a solid state since the attraction is so strong that the ions are very close together in a crystal formation.
 - **Covalent bonds** are valence electrons are shared by nuclei. Sharing is hardly ever 50-50 (due to electronegativity).
 - Electronegativity differences between two atoms helps tells you which type of bond they participate in.
 - Nonpolar bond has electronegativity differences less than 0.5.
 - Polar, covalent bonds have electronegativity differences between 0.5 and 2.
 - Ionic bonds generally have electronegativity differences greater than 2.
 - **Valence electrons** are the outermost electrons of an atom (they lie on the outermost shell).
 - Coordinate covalent bonding is the covalent bond usually formed in a molecule where the formal charge on the atom is not zero. In a coordinate covalent bond, both electrons come from a single atom. They are equivalent to ordinary covalent bonds. We show coordinate covalent bonds via arrows instead of dashes.

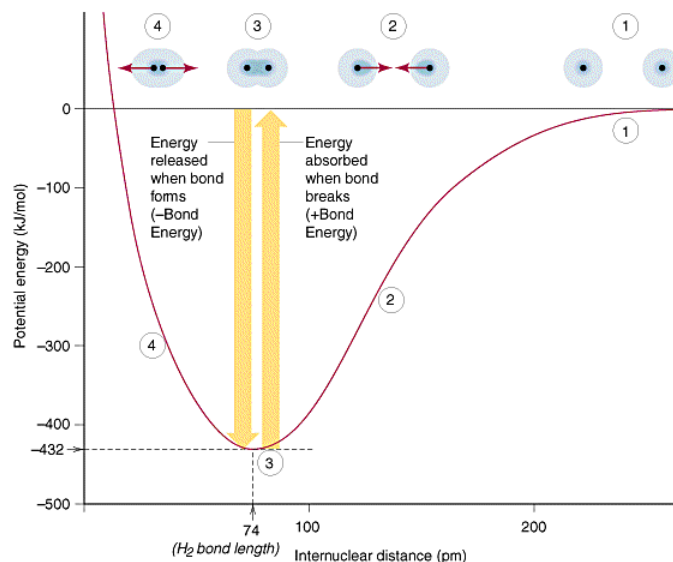


- **Metallic bonding** results in metallic crystals. Metals in a crystal will donate electrons to the “sea” so that it has a full octet. The valence electrons float in the sea and are not attached to one atom. The attraction between the valence electrons and the cations hold the crystal together.



- Chemical Bond Formation

- When two atoms approach each other, two “bad” energy things happen (will destabilize the system): electron/electron repulsion and proton/proton repulsion. One “good” energy thing happens (helps stabilize the system): proton/electron attraction. When the attractive forces offset the repulsive forces, the energy of the two atoms decreases and a bond is formed. Remember, nature is striving for a lower energy state!
- Note that all of these energy things are due to electrostatic forces (forces between charged atoms). Since the magnitude of an electrostatic force depends on the distance between the atoms, there will be only one distance where the magnitudes cancel and the system is at its lowest possible energy state (look at picture below). This distance is called the bond length.
- Bond length** is the distance between the 2 nuclei where the energy is minimum between the two nuclei.



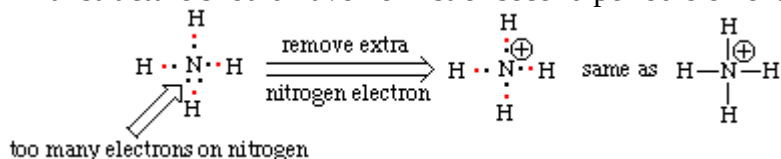
- Exceptions to the octet rule:

- Fewer than eight:
 - Hydrogen has at most 2 electrons (1 bond)
 - Beryllium has only 4 valence electrons (2 bonds)
 - Boron only has 6 valence electrons (3 bonds)
- Expanded Valence:
 - Can only happen if the central element has d-orbitals which means it is in the 3rd period or greater and thus can be surrounded by more than four valence pairs in certain compounds (i.e. S, Cl).

- Drawing Neutral Lewis Structures (not charged)

- 1) Decide how many valence (outer shell) electrons are possessed by each atom in the molecule.
- 2) If there is more than one atom type in the molecule, put the most metallic or least electronegative atom in the center. Recall that electronegativity decreases as atom moves further away from fluorine on the periodic chart.
- 3) Arrange the electrons so that each atom contributes one electron to a single bond between each atom.
- 4) Count the electrons around each atom: are the octets complete? If so, your Lewis dot structure is complete.
- 5) If the octets are incomplete, and more electrons remain to be shared, move one electron per bond per atom to make another bond. Note that in some structures there will be open octets (example: the B of BF₃), or atoms which have ten electrons (example: the S of SF₆).
- 6) Repeat steps 4 and 5 as needed until all octets are full.

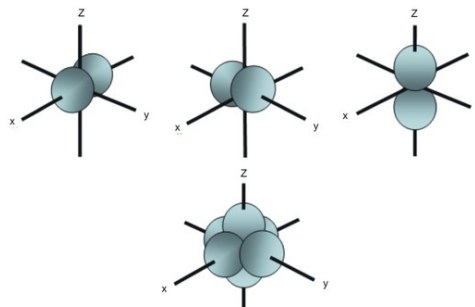
- 7) Redraw the dots so that electrons on any given atom are in pairs wherever possible.
- Drawing Positively Charged Lewis Structures
 - Use the same procedure as outlined above, then remove one electron per positive charge as needed to avoid expanded octets.
 - For each unit of positive charge on the ion remove one electron from these expanded octets. If done correctly, your final structure should have no first or second period elements with expanded octets.



- Drawing Negatively Charged Lewis Structures
 - Use the same procedure as outlined above, then as a last step add one electron per negative charge to fill octets.
- Molecular Polarity
 - Bonds can be polar while the entire molecule isn't and vice versa.
 - **Dipole moment** is the separation of charge in a molecule; product of the size of the charge and the distance of separation.
 - If the molecule has a net dipole moment, then it is polar.
 - If the molecule does not have a net dipole moment, it is non-polar.
 - How to identify the net dipole moment:
 - (1) identify the central atom
 - (2) for each bond the central atom makes (count any double or triple bonds as "1" bond), identify if the atom bonding to the central atom is more or less electronegative than the central atom.
 - (3) If the atom is MORE electronegative than the central atom, draw an arrow from the central atom pointing to the exterior atom it is bonded with. If the atom is LESS electronegative than the central atom, do not draw an arrow.
 - (4) Add up all the arrows you drew (vector addition). If 2 of the arrows are pointing in opposite directions, they cancel. If there is no "net" arrow after canceling, the molecule has no net dipole moment. If there is a "net" arrow after canceling, the molecule has a net dipole moment.
- Bond Order
 - **Bond order** describes the average number of bonds an atom makes to all other atoms. Count pi and sigma bonds!

$$\text{Bond order} = \frac{\text{total number of bonds}}{\text{number of individual atoms}} = \frac{\text{pi bonds} + \text{sigma bonds}}{\text{number of individual atoms}}$$

- Paramagnetic vs Diamagnetic
 - **Paramagnetic atoms** have unpaired electrons and will strongly be attracted to magnetic fields. Strength of attraction is directly proportional to the number of unpaired electrons.
 - **Diamagnetic atoms** have fully paired electrons and will not be attracted to magnetic fields.
- Molecular Orbital Theory (basic information):
 - A **sigma bond** occurs when orbitals of 2 different atoms overlap head-to-head.
 - **Pi bonds** occur when parallel orbitals of 2 different atoms interact.
 - A **bonding orbital** is when the signs of 2 orbitals are the same and they overlap.
 - An **antibonding orbital** is when the signs of 2 orbitals are different and they overlap.
 - There are 3 p orbitals: p_x , p_y , and p_z and they have dumbbell shapes.



Lab Glassware ([Search the specific glassware online for an image!](#))

- **Non-calibrated glassware** are used for containing, mixing, and reacting without specifically measuring the experimental materials.
 - **Test tubes** are relatively small and allow a larger number of samples to be analyzed in a rack for easy processing.
 - **Beakers** are wide-mouthed cylinders with lip to allow for pouring.
 - **Erlenmeyer flasks** are tapered and thus minimize accidental spills. Can be sealed easily with rubber, cork, or a stopper.
 - **Round bottom flasks** are good for heating.
 - A **retort** is a round vacuum flask that is used for distillation.
 - **Separatory funnels** are used for extractions.
 - **Transfer pipets** are made up of a plastic bulb at the top.
 - **Pasteur pipets** are made of glass require a second bulb.
- **Calibrated glassware** are used for any lab measurement that requires accuracy and precision. Measures volume.
 - **Graduated cylinders** are useful for measuring liquid to volumes within about 1%. Used for general purpose but not for quantitative measures.
 - **Burets** are used to deliver precisely-measured variable volumes. Used mostly for titrations and to make solutions.
 - **Graduated pipets** can deliver a variable amount of liquid precisely.
 - A **volumetric pipet** can deliver a single volume with great precision and accuracy.
 - **Volumetric flasks** are used to make solutions that require a specific volume of solution, such as molar solutions.

Precision vs Accuracy

- **Accuracy** is how close a measured value is to the actual (true) value.
- **Precision** is how close the measured values are to each other.
- Example problem:

An experiment was performed to find the number of moles of hydrochloric acid in a sample with the following results:

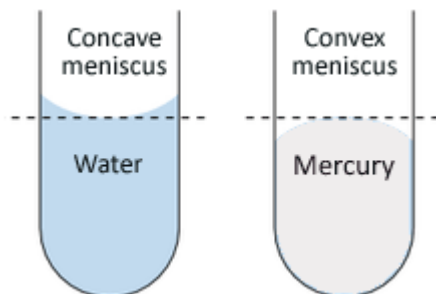
Trial	Moles
1	1.51
2	1.49
3	1.50

The actual number of moles was later determined to be 1.00. The above results are:

- both accurate and precise
 - accurate but imprecise
 - precise but inaccurate
 - both inaccurate and imprecise
- How to approach this type of problem and answer to example problem:
 - Look at the recorded results for each trial. Ask yourself if the value of each measurement close to each other. If yes, then the results are precise. If no, then the results are imprecise. In the example problem, they are all very close to each other as each value differs from the others by 0.01 to 0.02. Therefore, they are precise.
 - Now compare the recorded values for each trial to the actual value. If the recorded values are close to the actual value, then the values are accurate. If they are not, then they are inaccurate. In the example problem, they are all not close to the actual value (in these types of problems, it is usually obvious if the values are close to the actual value or not). Therefore, the values are inaccurate and the correct answer choice is C.

Meniscus

- A meniscus is the observed curved surface of a liquid at its interface with water. Two types:
 - A **concave meniscus** is observed if we placed water in a small-diameter tube. This type of meniscus results when the forces between the glass and the liquid molecules (**adhesion**) is greater than the forces between the liquid molecules themselves (**cohesion**).
 - A **convex meniscus** is observed if we placed mercury in a small-diameter tube. This type of meniscus results when the forces between the liquid molecules (**cohesion**) is greater than the force between the glass and the liquid molecule (**adhesion**).
 - <http://www.tutorvista.com/content/physics/physics-iii/solids-and-fluids/shape-meniscus.php> provides an in-depth physics style explanation as to why each meniscus forms. I think it does an excellent job of explaining this phenomenon. If you would like the full explanation, check this out!



- Parallax error** results when you view a meniscus from the incorrect line of sight (not head on). This will cause an incorrect measurement to be recorded.

Random vs. Systematic Error

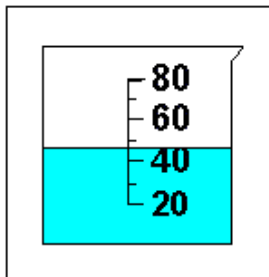
- Random errors** are caused by unknown and unpredictable changes in the experiment. These changes may occur in the measuring instruments or in the environmental conditions.
- Systematic errors** usually come from the measuring instruments. They may occur because: there is something wrong with the instrument or its data handling system, or because the instrument is wrongly used by the experimenter.

Heating a hydrated salt

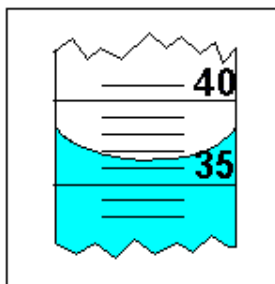
- % change = $\frac{\text{mass of salt after heating} - \text{mass of salt before heating}}{\text{mass of salt before heating}} * 100$
 - Note that this percent will always be negative!
- How to find the formula of the hydrate:
 - (mass before heating) – (mass after heating) = mass H₂O
 - convert mass H₂O → moles of H₂O
 - convert mass of anhydrous solid → moles of anhydrous solid
 - $n = \frac{\text{mol H}_2\text{O}}{\text{mol anhydrous solid}}$
 - http://ap-chem-resources.weebly.com/uploads/3/5/5/2/3552772/hydrates_practice.pdf is an excellent resource for practice problems (yes use a calculator to do these). Comes with answer key!
- Heating a hydrated salt must be controlled to prevent decomposition of the salt.
- If the % of the anhydrous salt was calculated to be lower than expected, a possible reason would be the loss of gas from an anhydrous salt.
- If salt binds tightly to water, it is possible for decomposition to occur.

Significant figures

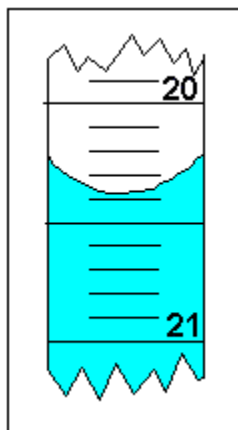
- Significant figure rules
 - Non-zero digits are always significant.
 - Any zeros between two significant digits are significant.
 - A final zero or trailing zeros in the decimal portion ONLY are significant. Any zero that come before the first significant digit is not significant!
 - HINT: change the number to scientific notation. It makes it easier to see how many significant figures there are.
 - <http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch1/sigfigs.html> is a great resource to learn significant figure rules. If you have time, also go into how to perform common math operations with significant figures and rounding!
- Beaker = 2 significant figures (round to the nearest 1). Note that there is no meniscus. An acceptable value for the beaker below would be 47 mL



- Graduated cylinder = 3 significant figures (round to the nearest 0.1). Because there is a meniscus, when we read the volume, we read it at the bottom of the meniscus. An acceptable value for the graduated cylinder below would be 36.4 mL.



- Buret = 4 significant figures (round to the nearest 0.01). Because there is a meniscus, when we read the volume, we read it at the bottom of the meniscus. An acceptable value for the buret below would be 20.37 mL.



Beer's law

- Go to the following website: http://www.chem.ucla.edu/~gchemlab/colorimetric_web.htm. This page does an excellent job on explaining how to find the concentration of a solution from using a spectrophotometer. Learn how to do all 3 types of these problems as they will show up on the DAT!