Measurement and Units

- SI – similar to (but not exactly the same as) the metric system

Measurement and Units

Physical Quantity	Name of unit	Symbol of Unit
Length	Meter	m
Mass	Kilogram	kg
Time	Second	s
Temperature	Kelvin	K
Amount of substance	Mole	mol
Electric current	Ampere	A
Luminous intensity	Candela	cd

Prefix	Multiple
Tera (T)	10^{12}
Giga (G)	10^{9}
Mega (M)	10^{6}
Kilo (k)	10^{3}
Centi (c)	10^{-2}
Milli (m)	10^{-3}
Micro (u or μ)	10^{-6}
Nano (n)	10^{-9}
Pico (p)	10^{-12}
Femto (f)	10^{-15}

More on measurement

- *Precision* – how “close” experimental values are to each other (consistency)
- *Accuracy* – how “close” experimental values are to a “true” or “accepted” value
- “closeness” can be measured by a variety of statistical techniques – mean, median, mode, standard deviation, etc.

Significant figures

- We live in the real world, not in theory!
- Aid in reporting experimentally measured quantities
  - Any instrument used for measurement will have a specified precision (+/-)
  - We are allowed to report <u>all</u> *known* digits and <u>one</u> *unknown* digit

Significant figures

- Any non-zero digit is significant (Ex. 1234)
- Zeros sandwiched between digits are significant (Ex. 1023)
- Zeros to the left of a decimal are NOT significant (Ex. 0.123)
- Zeros to the left of the first non-zero digit are NOT significant (Ex. 0.0000123)
- Zeros to the right of the last non-zero digit are significant (Ex. 0.123000)
- If there is no decimal point, zeros are NOT significant (Ex. 100 vs 100.)

Calculations involving significant figures

- "A chain is only as strong as its weakest link"
- Addition and Subtraction – use the number with the least number of significant figures AFTER the decimal (or least number if there is no decimal)
- Multiplication and Division – use the number with the least number of TOTAL significant figures
- Propagation of error – round only at the last step of a multi-step calculation (but keep track of how many sig figs there should be at each point)

Dimensional Analysis and Unit Conversion

- Can be used as a problem-solving tool
- It is always a good idea to include units, not just numbers!
- Ex. How many seconds are in one year?

$$1\,year\left(\frac{365\,days}{1\,year}\right)\left(\frac{24\,hours}{1\,day}\right)\left(\frac{60\,minutes}{1\,hour}\right)\left(\frac{60\,seconds}{1\,minute}\right)$$

Chemical Reactions (Equations)

- Note: In this course the phases for each chemical reaction are omitted
- Example
  - $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$ will be written as
  - $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Neutralizations

- Reaction of an acid with a base
  - Acid + Base → Salt + Water
- Overall/Complete formula/Molecular reaction:
  - $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
- However, we should really show this reaction as it would "look" in solution

Neutralizations

- Ionic equation:
  - $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

  (water only dissociates about every 1 in 10^7 molecules)
- Net ionic equation:
  - $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
  - *Spectator ions* – identity is irrelevant, however they are necessary for charge neutrality

Naming compounds

- Usually put metal first, then nonmetal (go from left to right from the periodic table)
- Exceptions – N, H, O
- Name = firstelement secondelement(-ide)
- Prefixes
  - Ionic substances generally have no prefixes
  - Covalent substances – prefixes are always used for the 2nd element (even if it only has one of them) but are only used for the 1st element if >1

Number	Prefix
1	Mono
2	Di
3	Tri
4	Tetra
5	Penta
6	Hexa
7	Hepta
8	Octa
9	Nona
10	Deca

Ionic Compounds

- Ions – atoms that have gained or lost electrons (have + or – charge)
  - Can have very different properties than their corresponding elements
- Cations - + charge (lost electrons)
  - Usually originate from metals
- Anions - - charge (gained electrons)
  - Usually originate from nonmetals
- Ions can also be *polyatomic* (composed of more than one atom)

Determining the charge for an ion

- For Groups IA-VIIIA the “usual” charge of an ion is based on its position
  - +1, +2, +3, +/-4, -3, -2, -1, 0
- For Group B (transition metals), use the Stock system
  - Roman numerals represent charges
  - Ex. Fe(II) ion = Fe^{2+}

Periodic Table of the Elements

6 12.011
C
Carbon

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** Hydrogen																	2 4.0026 **He** Helium
2	3 6.941 **Li** Lithium	4 9.0122 **Be** Beryllium											5 10.811 **B** Boron	6 12.011 **C** Carbon	7 14.007 **N** Nitrogen	8 15.999 **O** Oxygen	9 18.998 **F** Fluorine	10 20.18 **Ne** Neon
3	11 22.99 **Na** Sodium	12 24.305 **Mg** Magnesium											13 26.982 **Al** Aluminium	14 28.086 **Si** Silicon	15 30.974 **P** Phosphorus	16 32.065 **S** Sulfur	17 35.453 **Cl** Chlorine	18 39.948 **Ar** Argon
4	19 39.098 **K** Potassium	20 40.078 **Ca** Calcium	21 44.956 **Sc** Scandium	22 47.867 **Ti** Titanium	23 50.942 **V** Vanadium	24 51.996 **Cr** Chromium	25 54.938 **Mn** Manganese	26 55.845 **Fe** Iron	27 58.933 **Co** Cobalt	28 58.693 **Ni** Nickel	29 63.546 **Cu** Copper	30 65.38 **Zn** Zinc	31 69.723 **Ga** Gallium	32 72.64 **Ge** Germanium	33 74.922 **As** Arsenic	34 78.96 **Se** Selenium	35 79.904 **Br** Bromine	36 83.798 **Kr** Krypton
5	37 85.468 **Rb** Rubidium	38 87.62 **Sr** Strontium	39 88.906 **Y** Yttrium	40 91.224 **Zr** Zirconium	41 92.906 **Nb** Niobium	42 95.96 **Mo** Molybdenum	43 98 **Tc** Technetium	44 101.07 **Ru** Ruthenium	45 102.91 **Rh** Rhodium	46 106.42 **Pd** Palladium	47 107.87 **Ag** Silver	48 112.41 **Cd** Cadmium	49 114.82 **In** Indium	50 118.71 **Sn** Tin	51 121.76 **Sb** Antimony	52 127.60 **Te** Tellurium	53 126.90 **I** Iodine	54 131.29 **Xe** Xenon
6	55 132.91 **Cs** Caesium	56 137.33 **Ba** Barium	57-71	72 178.49 **Hf** Hafnium	73 180.95 **Ta** Tantalum	74 183.84 **W** Tungsten	75 186.21 **Re** Rhenium	76 190.23 **Os** Osmium	77 192.22 **Ir** Iridium	78 195.08 **Pt** Platinum	79 196.97 **Au** Gold	80 200.59 **Hg** Mercury	81 204.38 **Tl** Thallium	82 207.2 **Pb** Lead	83 208.98 **Bi** Bismuth	84 (209) **Po** Polonium	85 (210) **At** Astatine	86 (222) **Rn** Radon
7	87 (223) **Fr** Francium	88 (226) **Ra** Radium	89-103	104 (267) **Rf** Rutherfordium	105 (268) **Db** Dubnium	106 (271) **Sg** Seaborgium	107 (272) **Bh** Bohrium	108 (277) **Hs** Hassium	109 (276) **Mt** Meitnerium	110 (281) **Ds** Darmstadium	111 (280) **Rg** Roentgenium	112 (285) **Cn** Copernicium	113 (284) **Uut** Nihonium	114 (289) **Fl** Flerovium	115 (288) **Uup** Moscovium	116 (293) **Lv** Livermorium	117 (294) **Uus** Tennessine	118 (294) **Uuo** Oganesson

57 138.91 **La** Lanthanum	58 140.12 **Ce** Cerium	59 140.91 **Pr** Praseodymium	60 144.24 **Nd** Neodymium	61 (145) **Pm** Promethium	62 150.36 **Sm** Samarium	63 151.96 **Eu** Europium	64 157.25 **Gd** Gadolinium	65 158.93 **Tb** Terbium	66 162.50 **Gy** Dysprosium	67 164.93 **Ho** Holmium	68 167.26 **Er** Erbium	69 168.90 **Tm** Phulium	70 173.05 **Yb** Ytterbium	71 174.97 **Lu** Lutetium
89 (227) **Ac** Actinium	90 232.04 **Th** Thorium	91 231.04 **Pa** Protactinium	92 238.03 **U** Uranium	93 (237) **Np** Neptunium	94 (244) **Pu** Plutonium	95 (243) **Am** Americium	96 (247) **Cm** Curium	97 (247) **Bk** Berkelium	98 (251) **Cf** Californium	99 (252) **Es** Einsteinium	100 (257) **Fm** Fermium	101 (258) **Md** Mendelevium	102 (259) **No** Nobelium	103 (262) **Lr** Lawrencium

Table E
Selected Polyatomic Ions

H_3O^+	hydronium	CrO_4^{2-}	chromate
Hg_2^{2+}	dimercury (I)	$Cr_2O_7^{2-}$	dichromate
NH_4^+	ammonium	MnO_4^-	permanganate
$C_2H_3O_2^-$ / CH_3COO^-	acetate	NO_2^-	nitrite
		NO_3^-	nitrate
CN^-	cyanide	O_2^{2-}	peroxide
CO_3^{2-}	carbonate	OH^-	hydroxide
HCO_3^-	hydrogen carbonate	PO_4^{3-}	phosphate
$C_2O_4^{2-}$	oxalate	SCN^-	thiocyanate
ClO^-	hypochlorite	SO_3^{2-}	sulfite
ClO_2^-	chlorite	SO_4^{2-}	sulfate
ClO_3^-	chlorate	HSO_4^-	hydrogen sulfate
ClO_4^-	perchlorate	$S_2O_3^{2-}$	thiosulfate

Oxyanions

- Contain a varying number of oxygen atoms as part of a polyatomic ion

Oxyanion	Name
ClO^-	Hypochlorite
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate

Formula Unit

- Strictly speaking, this term should be used to describe ionic compounds
- It represents the smallest collection of ions that combine to form something neutral
- Ex. NaCl, Al_2O_3
- In naming formula units, prefixes are NOT used.

Hydrates

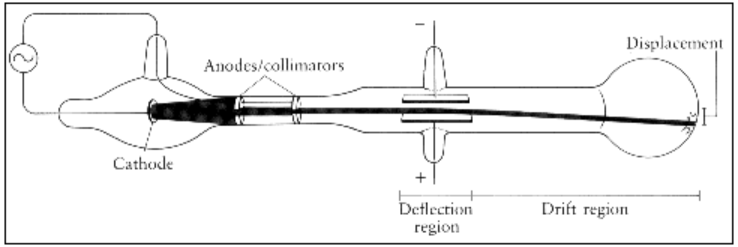
- Chemicals that contain H_2O in their formula
- The water molecules are actually associated with the cations/anions in a well-defined way
- A prefix must be used to indicate the number of H_2O molecules
- Anhydrous (dry) – no H_2O present
- Ex. $CuSO_4$ vs. $CuSO_4 \cdot 5H_2O$

What's an atom made out of?

- All atoms are comprised of subatomic particles, which are fundamental.
- All subatomic particles are created equal
  - They are exactly the same, even if they are present in different atoms
- Three are important for chemistry
  - Proton
  - Neutron
  - Electron

J. J. Thomson (1897)

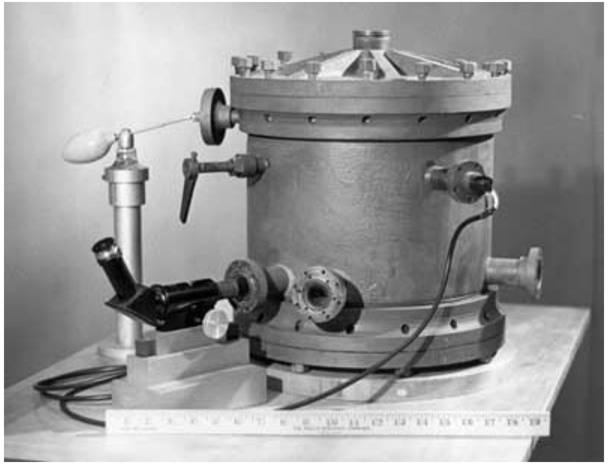
- Discovery of the electron
- (-) charged particles were produced, and they behaved exactly the same, regardless of the metal that was used.
- Was able to calculate the m/z ratio, $-5.69X10^{-12}$ kg/C, but wasn't able to get individual values for the mass or charge.

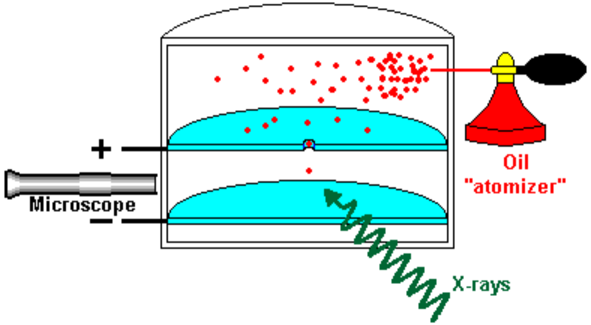


http://www.makingthemodernworld.org.uk/icons_of_invention/science/1880-1939/IC.026/
http://dbhs.wvusd.k12.ca.us/webdocs/AtomicStructure/Disc-of-Electron-Images.html

Robert Millikan (1909)

- Measured the velocity of a falling oil droplet in the presence/absence of a magnetic field
- Determined the charge on an electron (-1.602×10^{-19} C)
  - Mass of electron = 9.11×10^{-31} kg

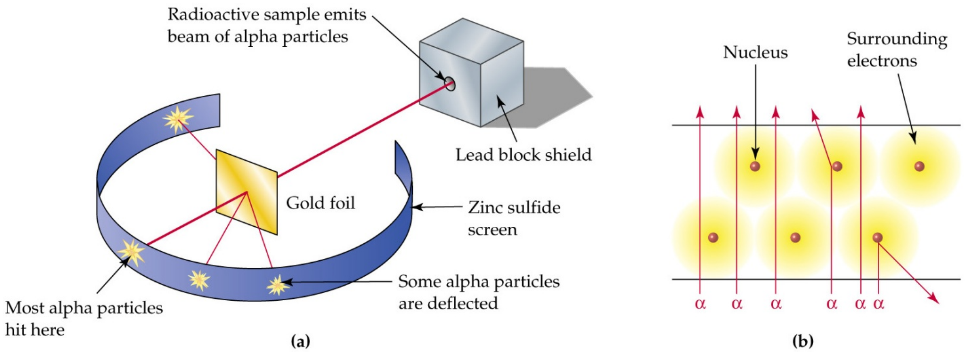




http://www.juliantrubin.com/bigten/millikanoildrop.html

Ernest Rutherford (1911)

- α particle = $^{4}_{2}He^{2+}$
- Most particle went straight through, but some were deflected
- Most of the atom is empty space, but all the (+) charge is concentrated in the center (nucleus)



http://wps.prenhall.com/wps/media/objects/602/616516/Media_Assets/Chapter02/Text_Images/FG02_05.JPG

Some definitions

- Isotope – same # of protons, but different # of neutrons
- Atomic Number (Z) – # of protons
- Mass Number (A, M) - # of nucleons (protons and neutrons)
- Atomic Mass – weighted average of all mass numbers (weighted by fractional abundance)

$$A.M. = \sum_{i} f_i M_i$$

The atomic mass unit (amu)

- One amu = 1/12 the mass of one atom of C-12 (by definition)
- This is the basic unit of mass for chemists, though it isn't an SI unit

Example

- Calculate the atomic weight of carbon.

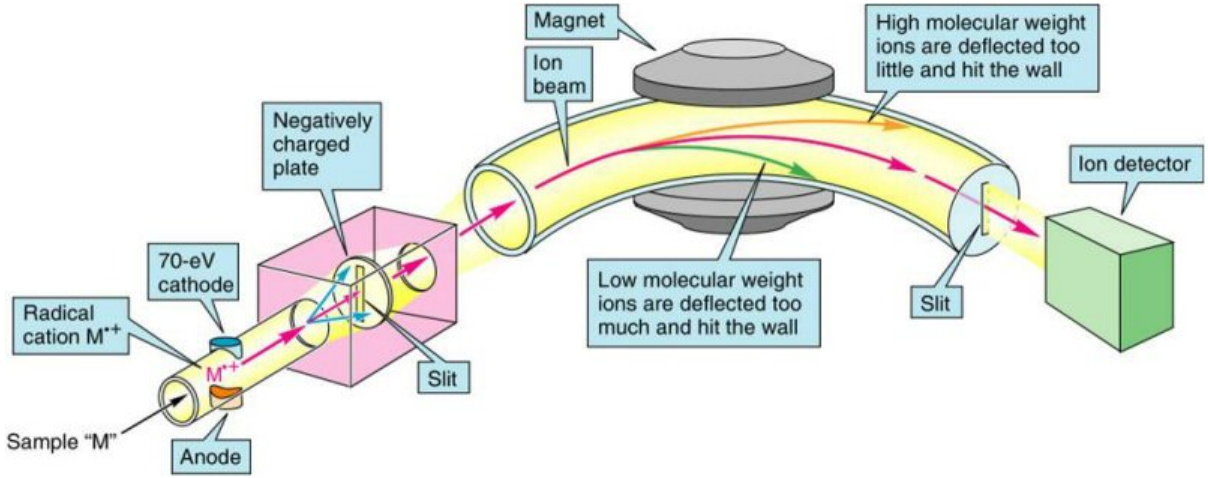
Solution

- Carbon exists in three isotopic forms: ^{12}C, ^{13}C and ^{14}C.
- The relative abundances of these isotopes are approximately 98.8%, 1.1% and 0.1%, respectively (this can be determined by mass spectrometry)
- Therefore the atomic weight would be = 12(0.988) + 13(0.011) + 14(.001) = 12.011 amu

Gas chromatography – Mass spectrometry (GC-MS)

- Usually requires ionization
- Form charged species with an unpaired electron (radical)
- Fragmentation pattern
  - Based on broken chemical bonds
  - Each piece (fragment) has a characteristic m/z ratio
- Molecular jigsaw puzzle

Diagram of a mass spectrometer



http://chemistry.umeche.maine.edu/CHY251/Ch13-Overhead4.html

GC-MS instruments

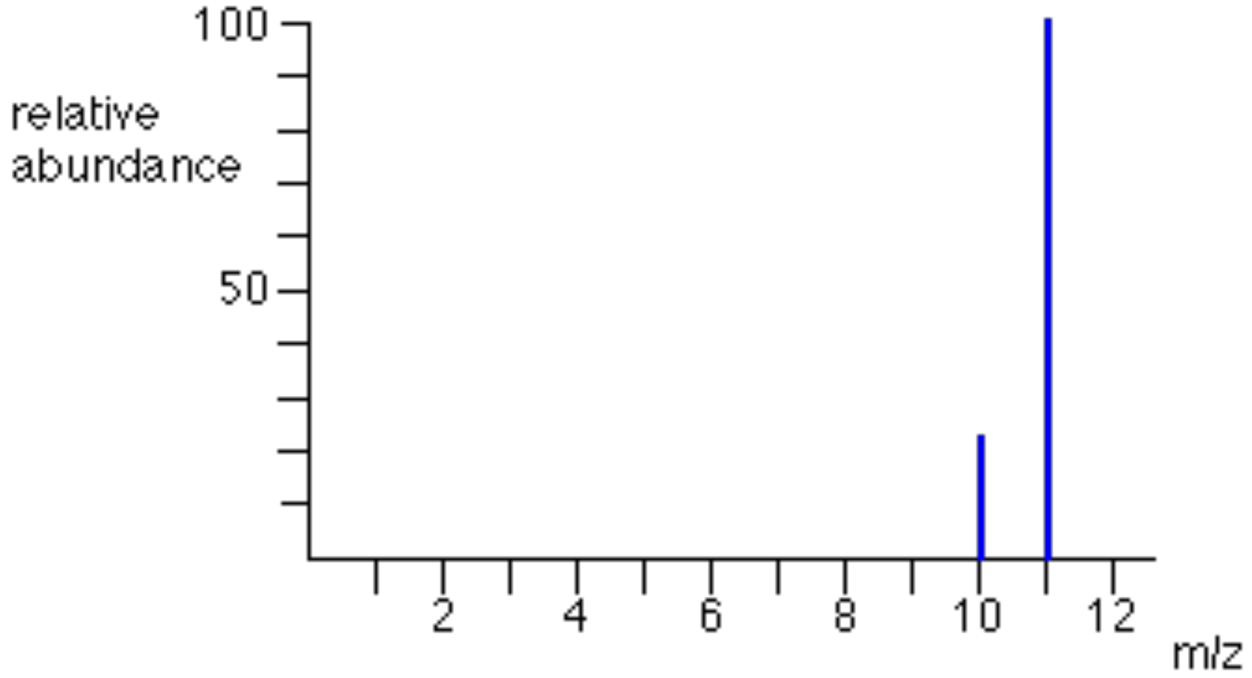
http://www.cooper.edu/~newmark/CH251/gcms.html

Common isotopic ratios

Element	Isotopes	Abundance (%)
Hydrogen	^{1}H, ^{2}H, ^{3}H	99.985, 0.015, (0)
Carbon	^{12}C, ^{13}C, ^{14}C	98.90, 1.10, (0)
Nitrogen	^{14}N, ^{15}N	99.63, 0.37
Oxygen	^{16}O, ^{17}O, ^{18}O	99.762, 0.038, 0.200
Chlorine	^{35}Cl, ^{37}Cl	75.77, 24.23
Bromine	^{79}Br, ^{81}Br	50.69, 49.31

- Ratios can tell you which atoms you have present (by comparing relative intensities)

Example: Boron

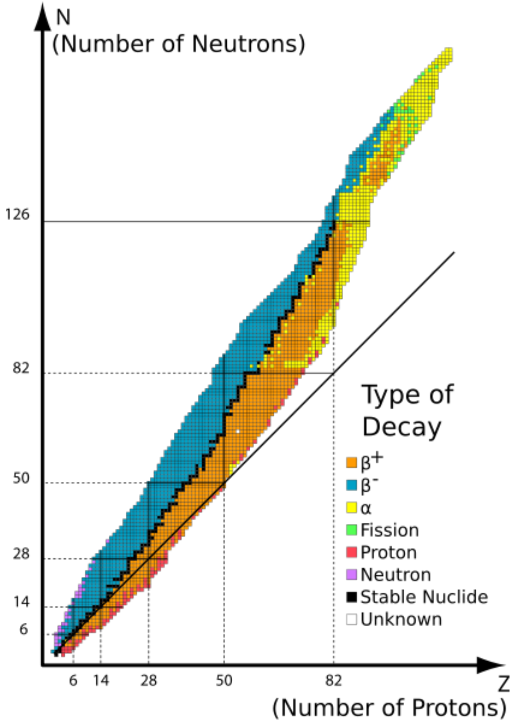


http://www.chemguide.co.uk/analysis/masspec/elements.html

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

Nuclear Stability

- Nuclei can be predicted to be stable or unstable "radioactive" based on the number of nucleons (protons and neutrons).
- Generally if Z>84 (Po) the nuclide will undergo radioactive decay. All elements where Z>92 are "artificial" in the sense that they are not naturally occurring.
- For "small" nuclei, stable configurations are achieved when (A-Z)/Z is 1.
- For "large" nuclei, (A-Z)/Z is >1 (1.2-1.4)
- "Magic numbers" exist where nuclei are exceptionally stable: 2, 8, 20, 28, 50, 82, 126.



http://www.kentchemistry.com/links/Nuclear/BandStability.htm

Radioactive Decay

- In order to achieve stability, radioactive nuclei will typically try to change their (A-Z)/Z ratio so they can fall in the band of stability. (α and β decays)
- It is also possible to become more stable yet keep the mass of the nucleus the same (γ decay)
- Other possibilities are *fission* (splitting of a heavy nuclide into smaller nuclides) and *fusion* (joining lighter nuclides into a heavier nuclide)

α decay

- Loss of a helium nucleus $^{4}_{2}He$
  - Results in ejection of positive particles
- Typically occurs with heavier nuclei
- Example $^{238}_{92}U \rightarrow ^{4}_{2}He + ^{234}_{90}Th$

β decay

- Common for medium-sized nuclides
- β⁻ decay – loss of an electron $_{-1}^{0}e$
  - Example $_{6}^{14}C \rightarrow {}_{-1}^{0}e + {}_{7}^{14}N$
  - Net conversion of a neutron into a proton [(A-Z)/Z too high] $_{0}^{1}n \rightarrow {}_{-1}^{0}e + {}_{1}^{1}H$
- β⁺ decay (positron emission) – loss of an positron $_{1}^{0}e$
  - Example $_{11}^{22}Na \rightarrow {}_{1}^{0}e + {}_{10}^{22}Ne$
  - A positron is the *antiparticle* of an electron $_{1}^{0}e + {}_{-1}^{0}e \rightarrow 2\,{}_{0}^{0}\gamma$
- Electron capture – gain of an electron
  - Example $_{33}^{73}As + {}_{-1}^{0}e \rightarrow {}_{32}^{73}Ge$
  - Net conversion of a proton into a neutron [(A-Z)/Z too low]

γ decay

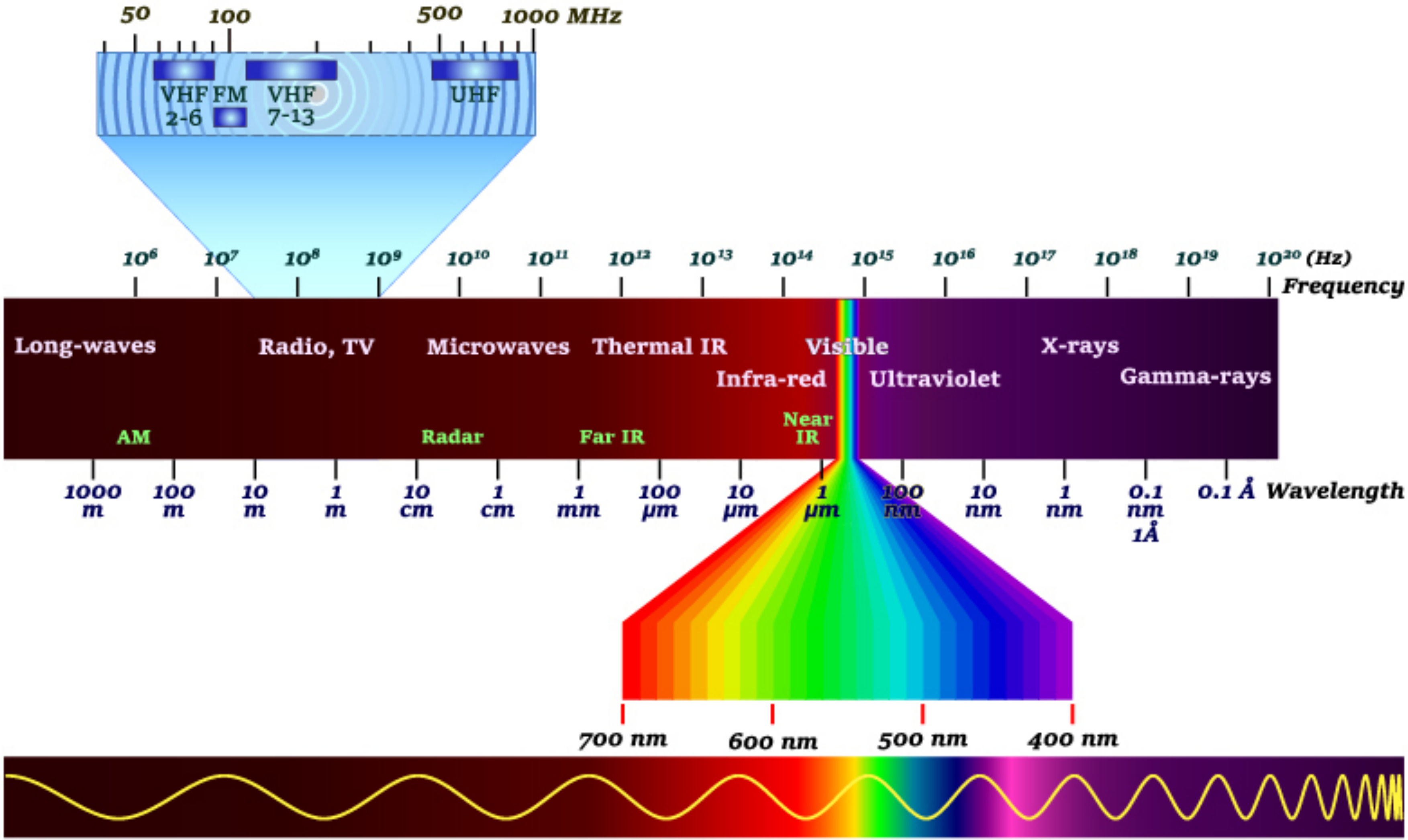
- Loss of a high energy photon $\,^{0}_{0}\gamma$
- No change in atomic or mass number
  - Example $\,^{99,m}_{43}Tc \rightarrow \,^{0}_{0}\gamma + \,^{99}_{43}Tc$
- We can think of the nucleons as being found in various energy levels, just like electrons

Nuclear fission

- Artificial transmutation process that releases a tremendous amount of energy $^{1}_{0}n + ^{235}_{92}U \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3^{1}_{0}n$
- Typically initiated by a “magic bullet”, commonly a neutron:
- Notice that for every one neutron that is used, three neutrons are produced. Each of these neutrons can then be used for another fission reaction, and so the reaction leads to an unstable (supercritical) situation since the number of particles grows exponentially. This is known as a *chain reaction*.

Light and spectroscopy

- EM Spectrum has waves of varying frequencies and wavelengths
- $E = h\nu = hc/\lambda$
- Spectroscopy deals with the interaction of matter with light

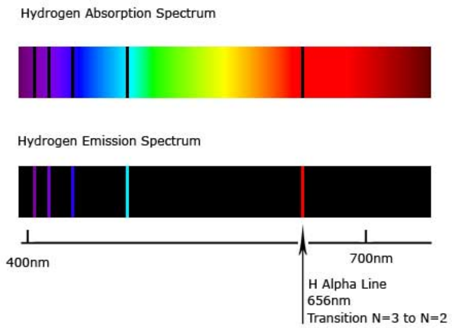


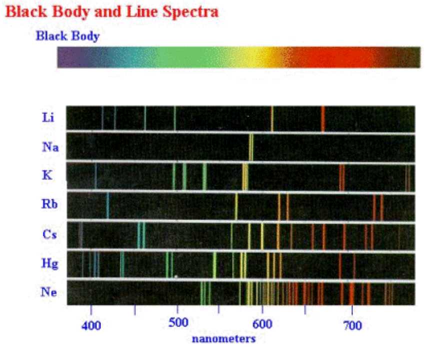
50
100
500
1000 MHz
VHF 2-6
FM
VHF 7-13
UHF
10⁶ 10⁷ 10⁸ 10⁹ 10¹⁰ 10¹¹ 10¹² 10¹³ 10¹⁴ 10¹⁵ 10¹⁶ 10¹⁷ 10¹⁸ 10¹⁹ 10²⁰ (Hz)
Frequency
Long-waves
Radio, TV
Microwaves
Thermal IR
Visible
X-rays
Infra-red
Ultraviolet
Gamma-rays
AM
Radar
Far IR
Near IR
1000 m
100 m
10 m
1 m
10 cm
1 cm
1 mm
100 µm
10 µm
1 µm
100 nm
10 nm
1 nm
0.1 nm 1Å
0.1 Å
Wavelength
700 nm
600 nm
500 nm
400 nm

Atomic line spectra

- A cuvette filled with a sample is then exposed to a beam of light. Since light of all possible wavelengths are incident, it was believed that all possible wavelengths should be emitted, so the spectrum should be a rainbow (continuous emission)
- However, something else was observed…
- Balmer (1885) n = 3, 4, 5…

$$\frac{1}{\lambda} = 1.097 * 10^7 m^{-1} \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$





http://www.faculty.virginia.edu/consciousness/new_page_6.htm
http://www.astronomyknowhow.com/hydrogen-alpha.htm

A simple, yet revolutionary idea

- Planck proposed that energy is quantized:

$$E=h\nu$$

h= Planck's constant = $6.626*10^{-34}$ J*s

“Old” Quantum Mechanics

- Niels Bohr (1913)
  - Assumed that the angular momentum (not the energy!) of the electron in a hydrogen atom is quantized
  - Used a combination of classical physics and this new interpretation for energy to derive “orbits”, or energy levels (very similar to a planetary model)

$$E_n = -\frac{me^4}{8\varepsilon_o h^2}\frac{1}{n^2} = -\frac{B}{n^2}$$

  - This was based on well-understood fundamental constants in physics (and Planck’s constant)

A theoretical explanation of atomic line spectra

- Photons of light are emitted when electrons go from a higher to lower energy level (opposite is true for absorption)
- Because the energy levels are fixed, only certain wavelengths of light will be observed

The good, the bad and the ugly

- The good
  - Bohr was able to come up with a theoretical model for the energy levels in the hydrogen atom which accounted for the experimentally observed line spectra (Balmer series)
- The bad
  - It only worked for hydrogen!!! (and other one-electron systems)
- The ugly
  - The necessary mathematics get very difficult very quickly
  - Multi-electron systems often don’t have closed form solutions

Quantum numbers

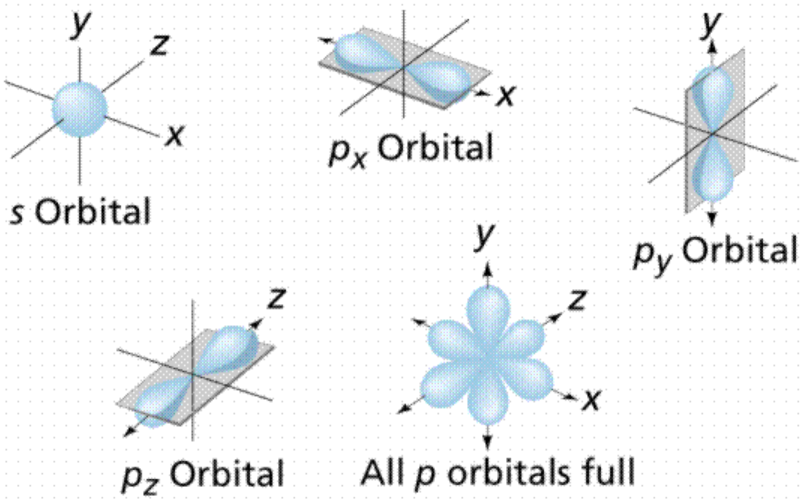
- Principal quantum number (n)
  - n = 1, 2, 3…
  - Same as Bohr's energy levels
  - Indicates what "shell" the electron is in
- Angular momentum quantum number (l)
  - $l \leq n-1$
  - Ex. l=0 → s orbital, l=1 → p orbital, l=2 → d orbital, l=3 → f orbital
  - Determines the *shape* of the orbital, or "subshell"

Quantum numbers

- Magnetic quantum number (m_l)
  - $|m_l| \leq l$
  - Determines the spatial *orientation* and degeneracy of the orbital
  - Ex. if l=1 (p orbital) then m_l = -1, 0, 1. These are usually called p_x, p_y, and p_z (directions do not directly correspond to these numbers). We can also see why there are three p orbitals, since there are three allowed values for m_l.

Subshell (orbital) shapes

- Orbitals



- Nodes are possible – regions of zero probability of finding the electron

http://www.emc.maricopa.edu/faculty/farabee/biobk/biobookchem

Quantum numbers

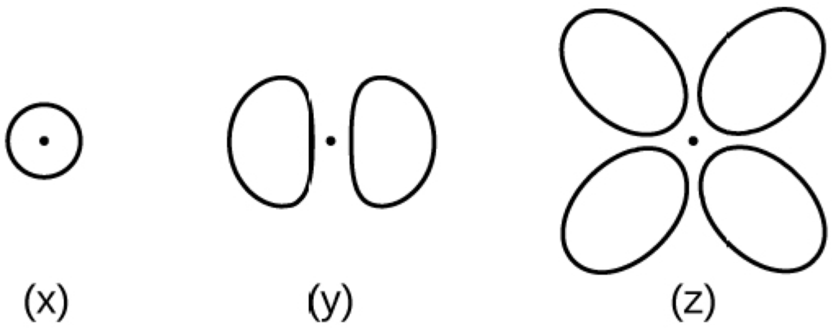
- Spin quantum number (m_s)
  - Unrelated to the other three quantum numbers
  - Unrelated to spatial coordinates
  - Each electron has an "intrinsic" spin coordinate
    - There is no classical analog, but it behaves similar to angular momentum
  - m_s = +/- ½ (half-integer)

- “All electronic wave functions must be antisymmetric under the interchange of any two electrons”

- It is impossible for two electrons in the same orbital to have the same spin

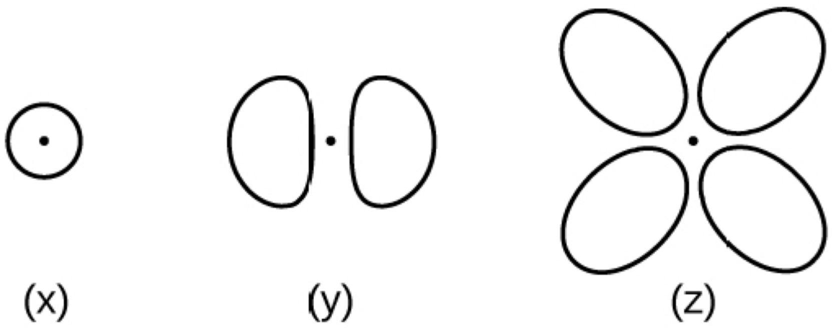
- No two electrons can have identical quantum numbers (in the same atom)

Consider the orbitals shown here in outline.



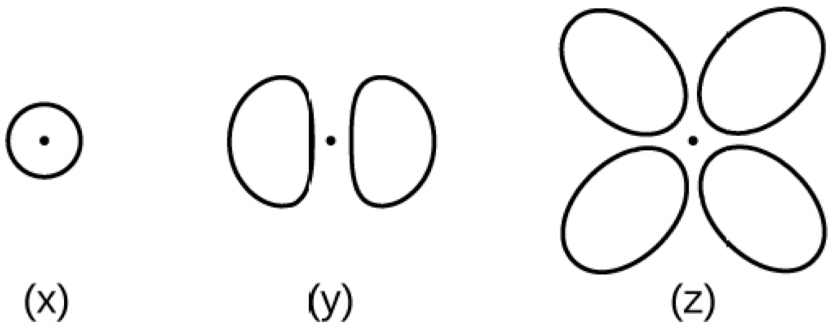
(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?

Consider the orbitals shown here in outline.



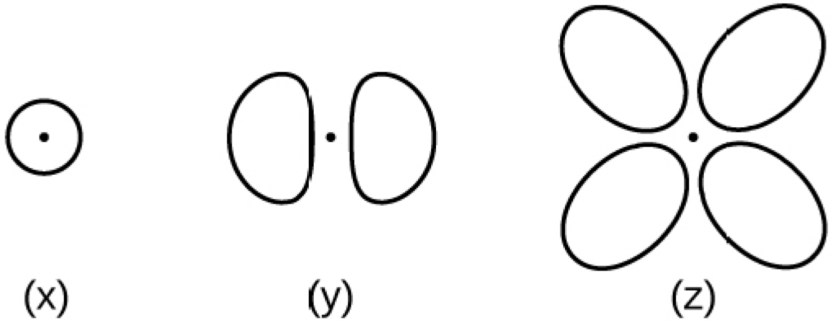
(b) How many orbitals of type (x) are found in a shell with *n* = 2? How many of type (y)? How many of type (z)?

Consider the orbitals shown here in outline.



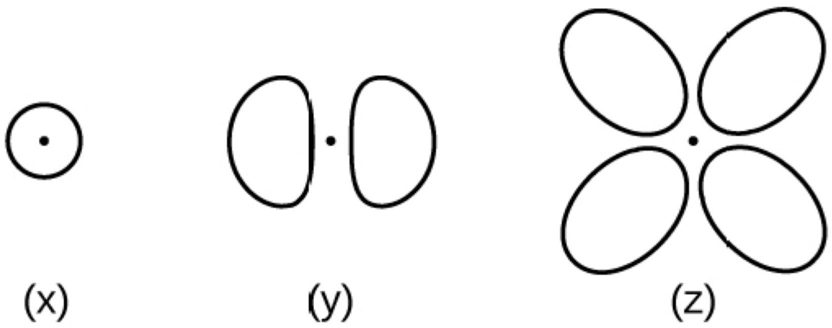
(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.

Consider the orbitals shown here in outline.



(d) What is the smallest possible *n* value for an orbital of typ

Consider the orbitals shown here in outline.



(e) What are the possible *l* and *ml* values for an orbital of type (x)? Of type (y)? Of type (z)?

The periodic table

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)

Main-group elements (“the A-list”)

- The valence (outer shell) consists only of s and p orbital electrons
- Group number = # of electrons in the valence shell (using the older Roman numeral system)
- Period number = principal quantum number (n)
- s block – alkali metals and alkali earth metals
- p block – metals, metalloids and nonmetals (including halogens and noble gases)

Transition metals (“the B-team”)

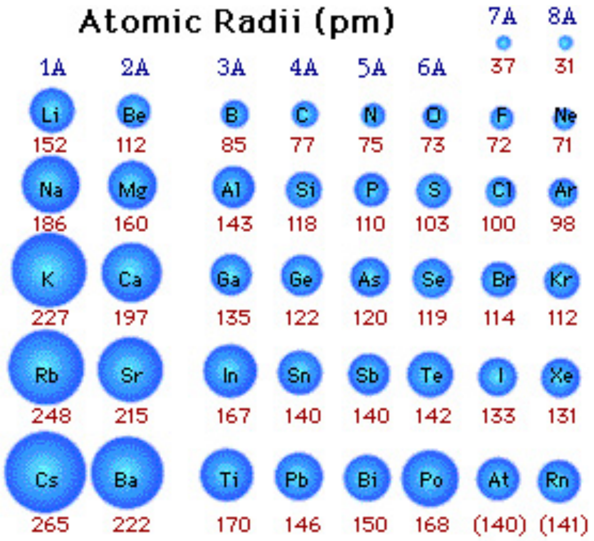
- Contain d and f orbitals
- d block - transition metals
- f block – rare earth (lanthanide/actinide)
- These are considered “inner shell” electrons
- The highest energy electrons are actually in a shell with a smaller value of n that that of the outermost shell (valence shell)
  - d block – (n-1)
  - f block – (n-2)

Periodic Trends

- Patterns that emerge in chemical and physical properties when elements are arranged in the periodic table
- Can usually be explained by the number of valence electrons, the number of core electrons, and the number of protons (nuclear charge)

Atomic Radius

- Generally atomic radius decreases across a period and increases down a group
  - The trend only works for main group elements



http://edtech2.boisestate.edu/kilnerr/502/jigsaw.html

Atomic Radius

- Group – increase in the number of principal energy levels (greater average distance that the electron is from the nucleus)
- Period – increase in effective nuclear charge (the net charge the valence electrons "feel")

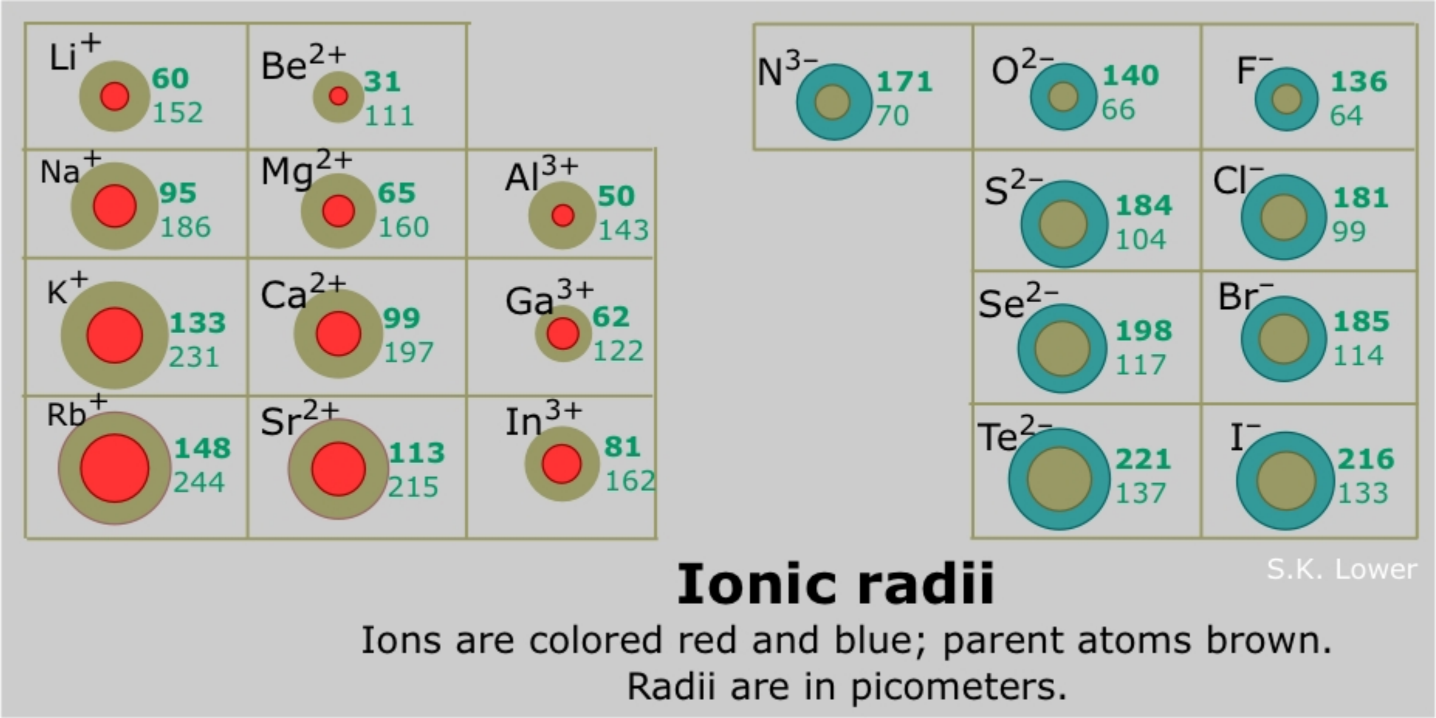
Effective Nuclear Charge (Z_{eff})

- Z_{eff} is meant to incorporate the shielding effect of core (inner) electrons
  - Valence electrons can penetrate inner shells (ex 3d and 4s)
  - Core electrons are not all equally effective in shielding valence electrons
  - Valence electrons can shield each other, though the effect is weak
- Transition metals in the same period have almost the same radius since Z_{eff} is the same

Ionic Radius

- Defined in a similar fashion to atomic radius (distance between two ions in a formula unit)
- Metals tend to lose valence electrons, so their highest occupied principal energy level decrease by one
  - Ionic radii for metals are smaller than those of the corresponding atomic radii
- Nonmetals tend to gain valence electrons, so their highest occupied principal energy level remains the same, but there is increased repulsion among the electrons in that level
  - Ionic radii for nonmetals are larger than those of the corresponding atomic radii

In pictures



http://chemwiki.ucdavis.edu/Wikitexts/UC_Davis/UCD_Chem_124A%3A_Kauzlarich/ChemWiki_Module_Topics/Periodic_Trends_in_Ionic_Radii

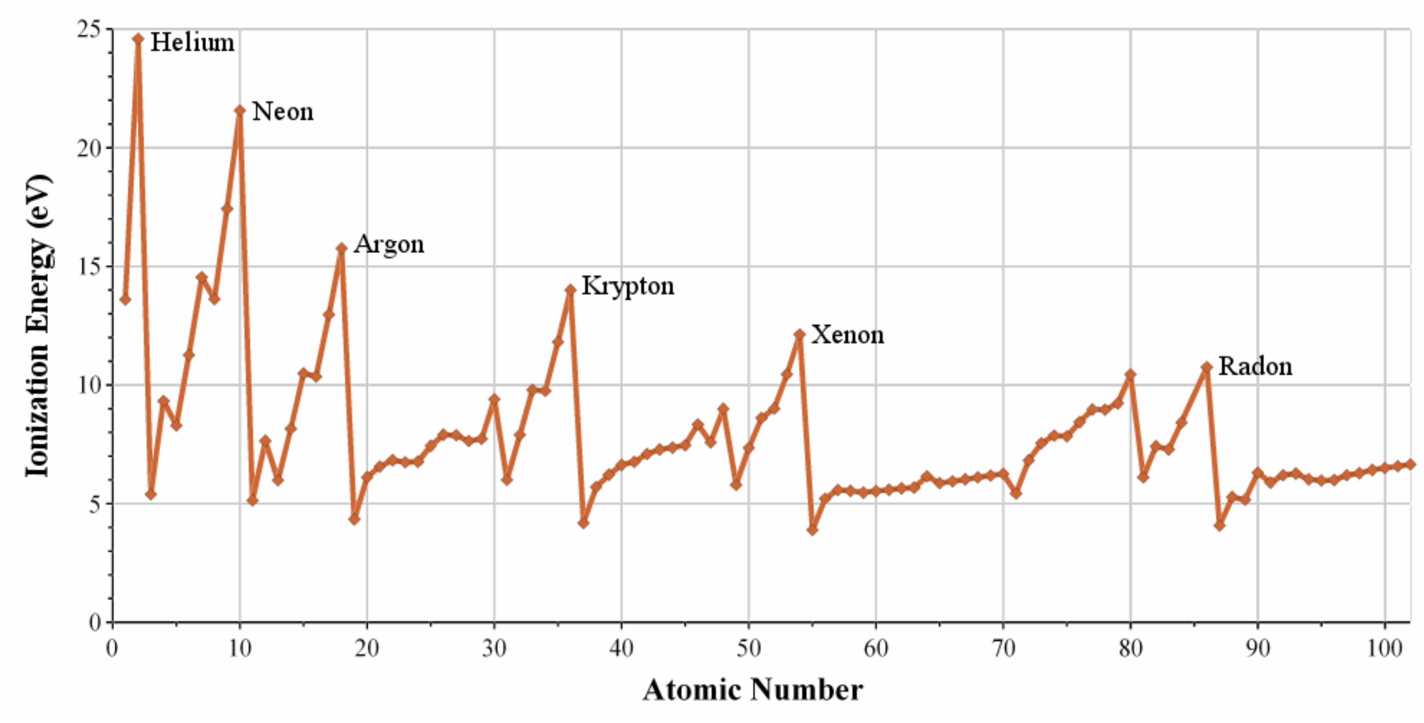
Ionization Energy

- Defined as the energy required to *remove* an electron from the ground state, in the gas phase
  - $A(g) \rightarrow A^{+}(g) + e^{-}$
- This can be repeated successively (1st, 2nd, 3rd, etc.)
  - It gets progressively harder to remove electrons since the species is already charged
  - Large jumps occur for a given element as you break up an octet (going from valence electrons to core electrons)

Ionization Energy

- Generally decreases as you go down a group
  - Outermost electrons are (on average) further away from the nucleus, so there is a greater shielding effect
- Generally increases as you go across a period
  - Elements have a greater tendency to gain electrons (rather than lose)
- Minor effects can be due to
  - what subshell the electron is in (s>p>d>f because of energy)
  - Paired vs. unpaired electrons (unpaired>paired because of repulsions)

In pictures

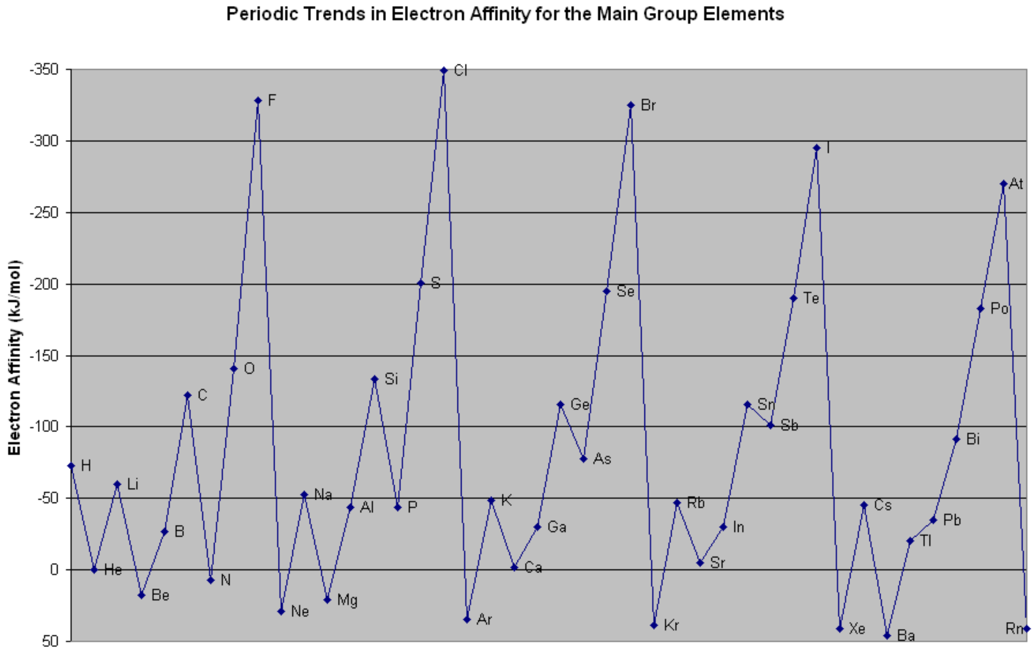


http://websites.pdesas.org/jvogus/2010/5/18/44324/page.aspx

Electron Affinity

- Defined as the energy required to *add* an electron to the ground state, in the gas phase
  - $A(g) + e^- \rightarrow A^-(g)$
- This has the same general trend as ionization energy, although it is less clear-cut
  - Complications due to repulsions between the incoming electron and the atomic electrons

In pictures



http://www.angelo.edu/faculty/kboudrea/periodic/trends_electron_affinity.htm

Electronegativity

- "Tendency" of an element to gain electrons

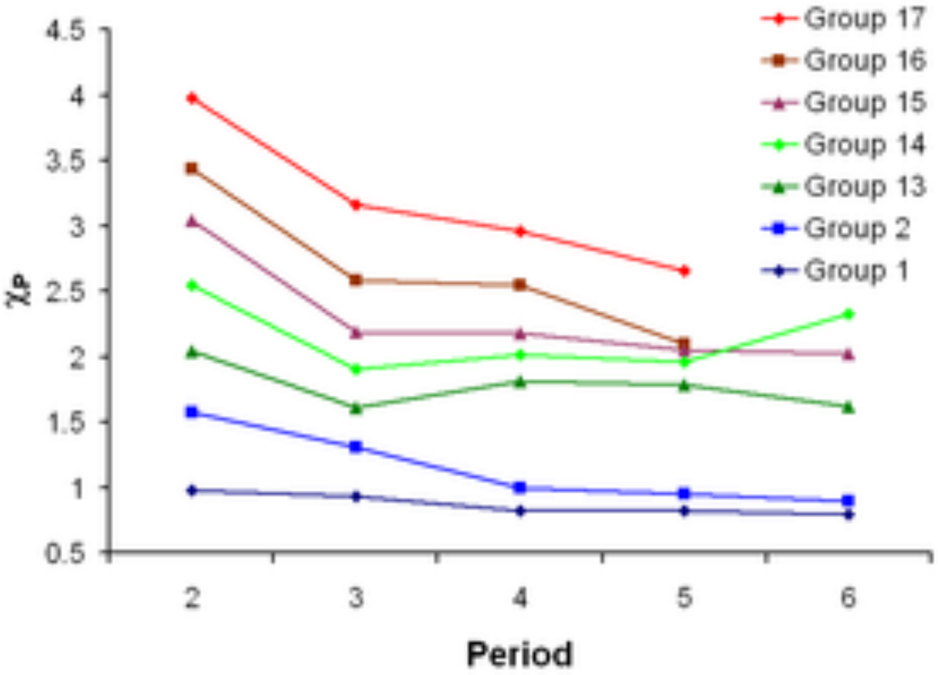
$$\chi = \frac{I.E. - E.A.}{2}$$

- Pauling scale:

$$\chi_B = \chi_A + 0.102\{(A-B) - [(A-A)(B-B)]^{1/2}\}^{1/2}$$

  - (i-j) = bond-dissociation energy between i and j
  - F is arbitrarily given the maximum value of 4.0
- Also follows the same general trend as ionization energy and electron affinity

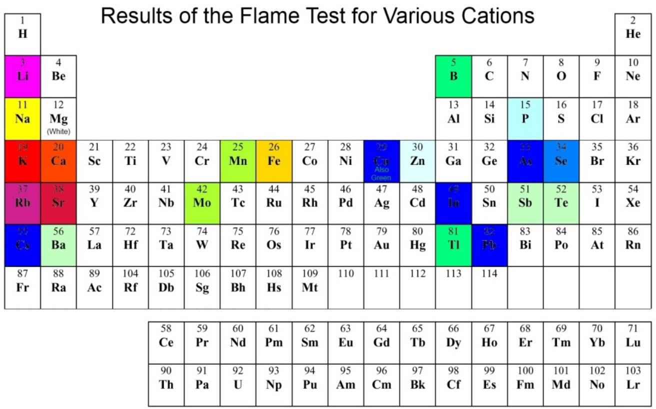
In pictures



http://en.wikipedia.org/wiki/Electronegativity

Chemical Properties of Elements

- Flame test
  - Based on characteristic absorbance of light energy
  - Wavelength emitted will be related to the energy gap between electronic levels
  - Used to identify various metals



http://wesleydowler.com/?p=242

http://alchemist.edublogs.org/2008/11/17/which-ion-causes-the-color/

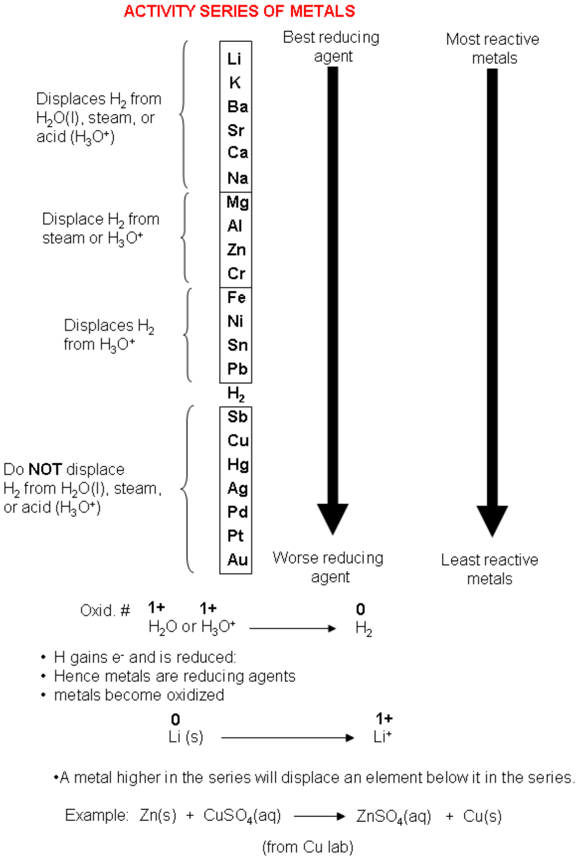
Redox reactions (an introduction)

- Redox reactions involve a simultaneous *red*uction and *ox*idation.
- Reduction – gain of electrons
  - oxidation number is decreased
- Oxidation – loss of electrons
  - Oxidation number is increased
- Disproportionation – redox reaction where the same species is both oxidized and reduced.
  - Ex. $2H_2O_2 \rightarrow 2H_2O + O_2$

Agents

- Reducing agent – causes a reduction
  - Gets oxidized
  - Usually metal
- Oxidizing agent – causes an oxidation
  - Gets reduced
  - Usually nonmetal

Activity series



- "Noble" metals (Cu, Ag, Hg, Au) – can't produce H_2

http://employees.csbsju.edu/hjakubowski/classes/ch123/summer_chem/ch123OLSGMM0405.htm

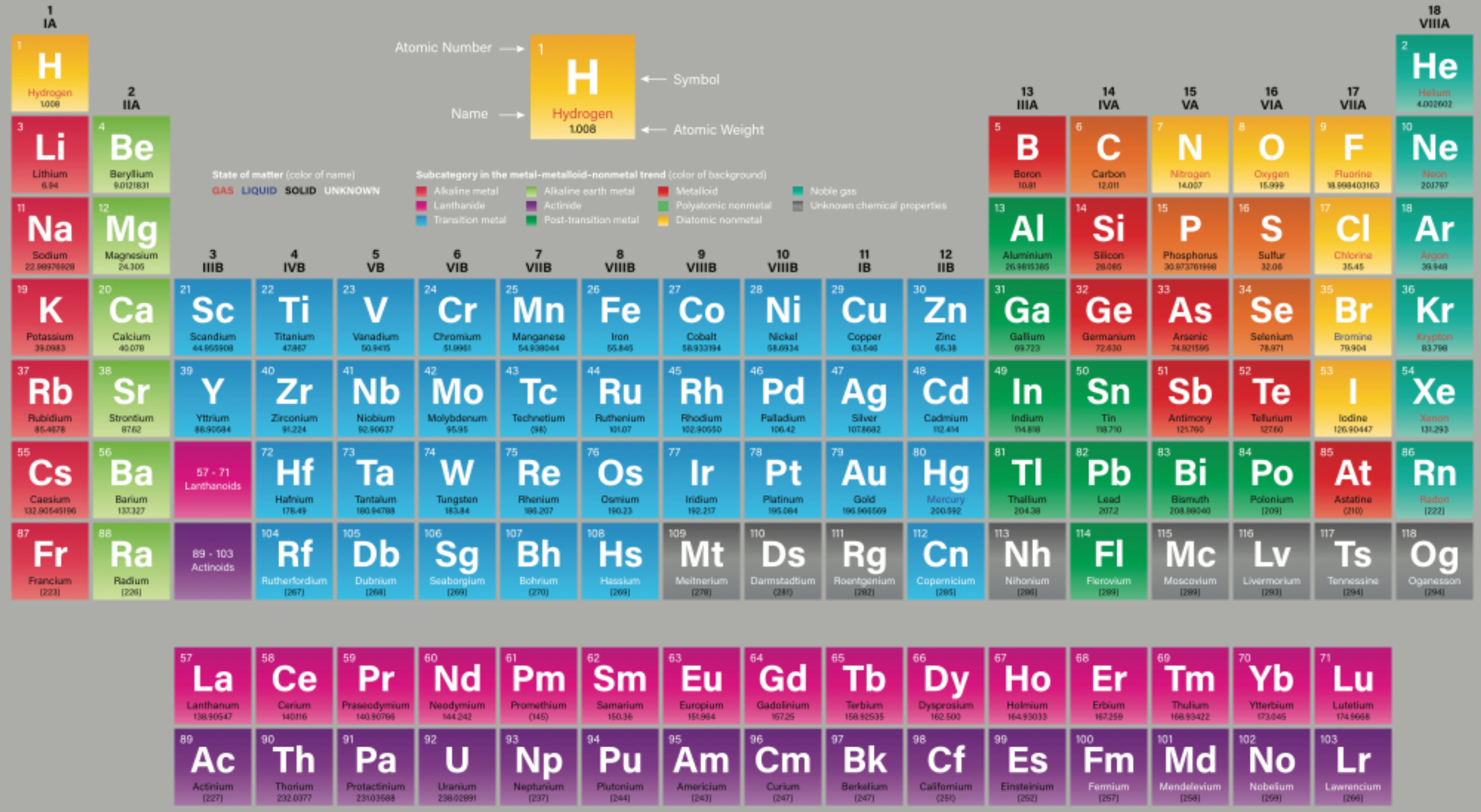
Chemical Properties of Elements

- Reduction
  - Reducing agents have a tendency to lose electrons
  - This property can be correlated with ionization energy, electronegativity and electron affinity
- Metals can react with sources of H^+ (acids, or even water if they are active enough) to generate ions and hydrogen gas
- $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$
- $Ca + 2H_2O \rightarrow Ca^{2+} + 2OH^- + H_2$

Chemical Properties of Elements

- Oxidation
  - Oxidizing agents have a tendency to gain electrons
  - This property can be correlated with ionization energy, electronegativity, and electron affinity
- $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ will occur since Cl atoms have a higher (more negative) electron affinity than I atoms (-349 kJ/mol vs. -295 kJ/mol)
- $I_2 + Cl^- \rightarrow 2I^- + Cl_2$ will NOT occur

List the following ions in order of increasing radius: Li^{+}, Mg^{2+}, Br^{-}, Te^{2-}.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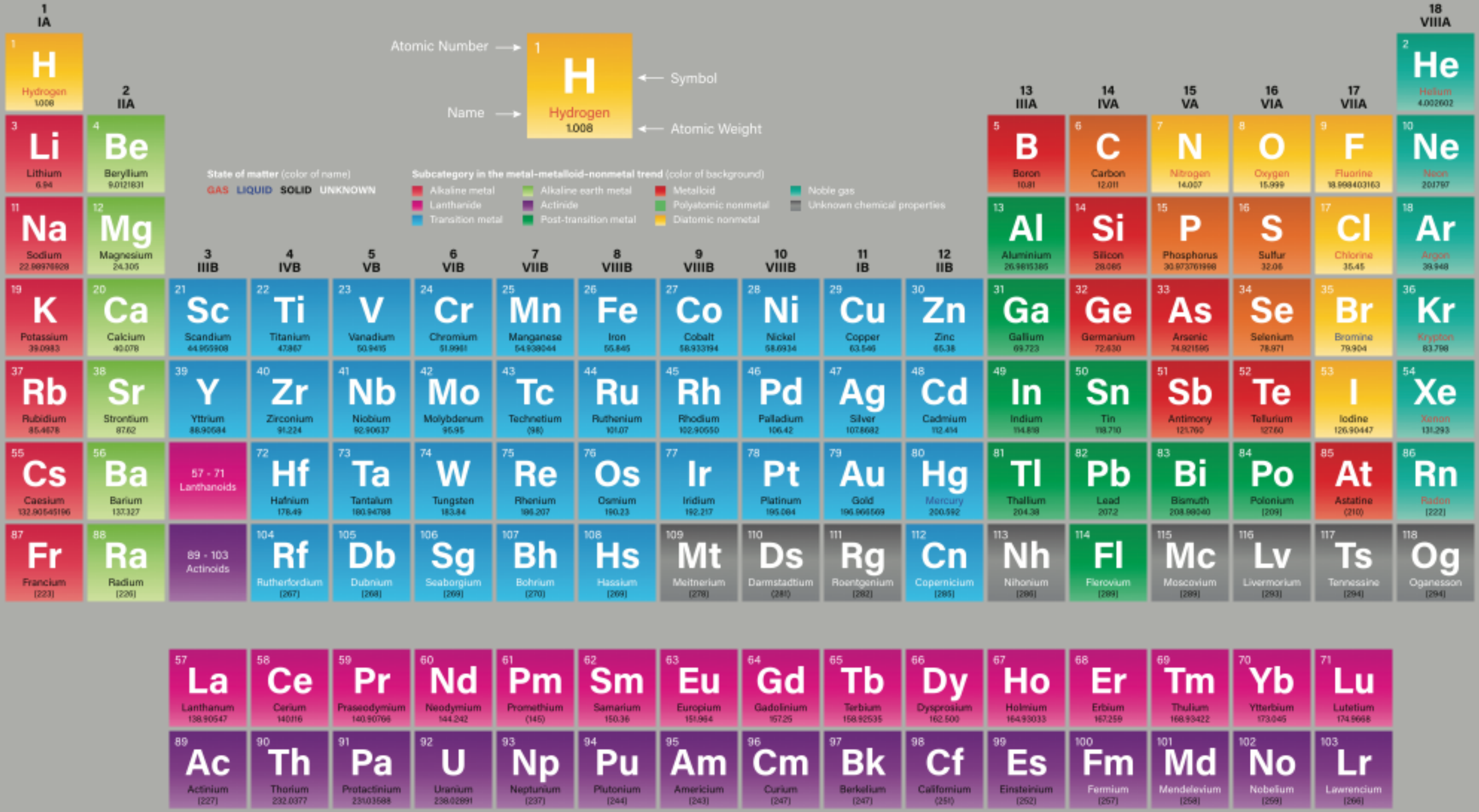
Write the Lewis structure for $SeCl_3^+$.



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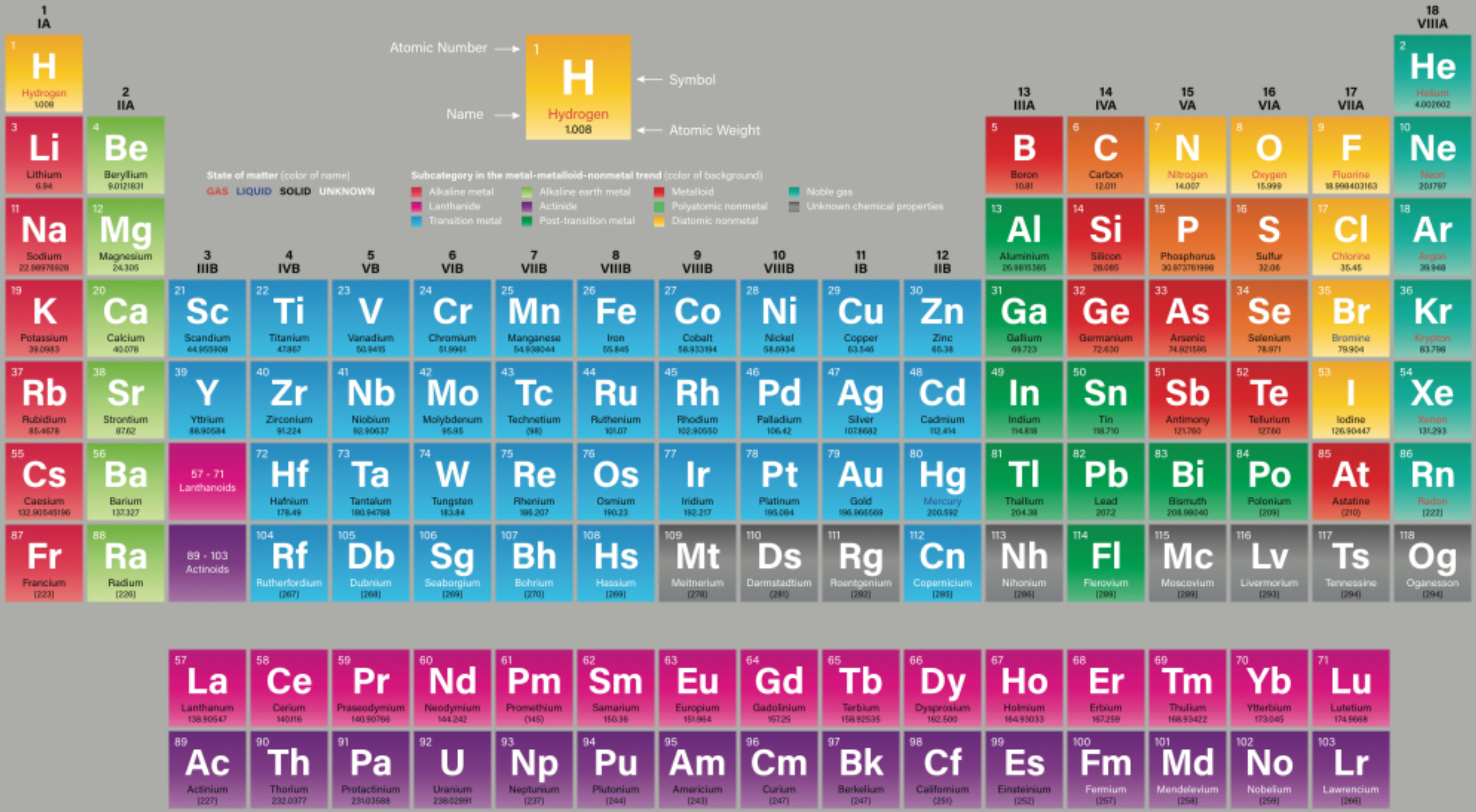
Explain why the H_2O molecule is bent, whereas the BeH_2 molecule is linear.



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110 Ds Darmstadtium [281]
111 Rg Roentgenium [282]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
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118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
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61 Pm Promethium (145)
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102 No Nobelium [259]
103 Lr Lawrencium [266]

Reactions of alkali metals

- With halogens (F_2, Cl_2, Br_2, I_2):
  - $M + X_2 \rightarrow MX$
- With hydrogen:
  - $M + H_2 \rightarrow MH$
- With (excess) oxygen:
  - $Li + O_2 \rightarrow Li_2O$ (plus some Li_2O_2)
  - $Na + O_2 \rightarrow Na_2O_2$ (plus some Na_2O)
  - $M + O_2 \rightarrow MO_2$ (M = K, Rb, Cs)
- With water:
  - $M + H_2O \rightarrow MOH + H_2$

Reactions of alkaline earth metals

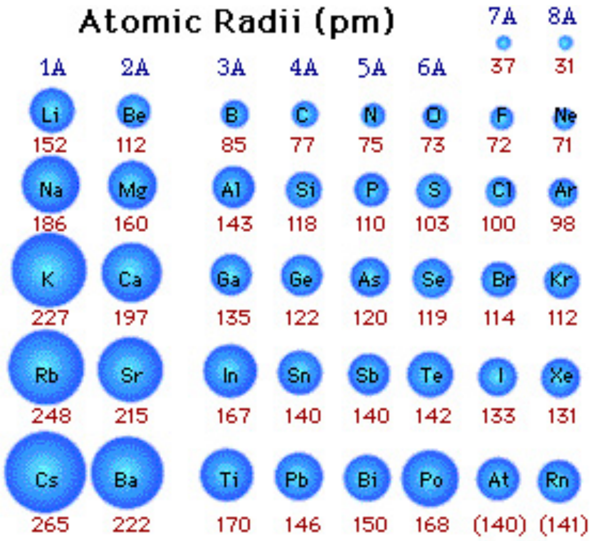
- With halogens (F_2, Cl_2, Br_2, I_2):
  - $M + X_2 \rightarrow MX_2$
- With nitrogen:
  - $M + N_2 \rightarrow M_3N_2$
- With oxygen:
  - $M + O_2 \rightarrow MO$
- With water:
  - $Mg + H_2O(g) \rightarrow MgO + H_2$
  - $M + H_2O \rightarrow M(OH)_2 + H_2$ ($M \neq Mg$)

Periodic Trends

- Patterns that emerge in chemical and physical properties when elements are arranged in the periodic table
- Can usually be explained by the number of valence electrons, the number of core electrons, and the number of protons (nuclear charge)

Atomic Radius

- Generally atomic radius decreases across a period and increases down a group
  - The trend only works for main group elements



http://edtech2.boisestate.edu/kilnerr/502/jigsaw.html

Ionization Energy

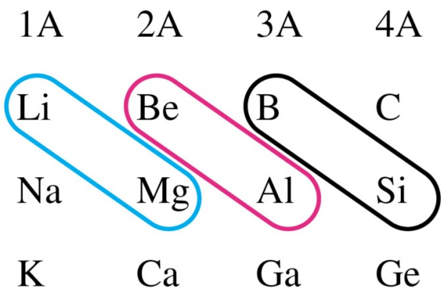
- Generally decreases as you go down a group
  - Outermost electrons are (on average) further away from the nucleus, so there is a greater shielding effect
- Generally increases as you go across a period
  - Elements have a greater tendency to gain electrons (rather than lose)
- Minor effects can be due to
  - what subshell the electron is in (s>p>d>f because of energy)
  - Paired vs. unpaired electrons (unpaired>paired because of repulsions)

Overview - Periodic Trends in Group 13

- B is a nonmetal/metalloid – forms covalent bonds but displays electrical properties of semiconductors (diagonal relationship with Si)
- Al is a metal/metalloid –forms covalent bonds but can also lose valence electrons to form ions (Al^{3+})
- Ga – forms Ga^{3+} ions to achieve stable configuration ($[Ar]3d^{10}$)
- In and Tl tend to form +1 ions because they lose the valence p electron but NOT the valence s electrons (inert pair)

Diagonal relationships

- Often the 1st member of a group has properties that are different from the other members of the group, but are similar to those of the 2nd member of the adjacent group
  - Relatively high charge density



- Example: Li
- Li_2CO_3, LiF, LiOH and Li_3PO_4 are much less soluble than the corresponding salts of the other alkali metals
  - Li_2CO_3 and LiOH form Li_2O
- $Li + N_2 \rightarrow Li_3N$ (other alkali metals don't react)
- $Li + O_2 \rightarrow Li_2O$ (other alkali metals form peroxides or superoxides)

What is stoichiometry?

- (Probably) the most important topic in chemistry!
- This is the basis for **many** subsequent chapters
- Related to the *amount* of a species or substance
- Sometimes referred to as the mathematics of chemistry

Some definitions

- Molar mass (aka molecular weight) – sum of atomic masses (weights) for all the atoms in a given molecule.
  - Use the periodic table and the molecular formula to determine this
- Formula mass (formula weight) – sum of the masses for all the ions in a given formula unit

The periodic table

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)

An Important Interpretation

- The stoichiometric coefficients that are present in a balanced chemical reaction are related to the *ratios* of reactants and products in a chemical reaction
- This ratio is only in terms of moles (or molecules), BUT NOT mass!

Example

- The final step in the production of nitric acid involves the reaction of nitrogen dioxide with water; nitrogen monoxide is also produced. How many grams of nitric acid are produced for every 100.0 g of nitrogen dioxide that reacts?

Solution

- Step 1: Write down the chemical reaction
  - $NO_2 + H_2O \rightarrow HNO_3 + NO$
- Step 2: Balance the chemical reaction
  - $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
- Step 3: Determine the moles of NO_2 that will react
  - 100 g NO_2 / 46.006 g/mol = 2.174 mol NO_2

Solution (continued)

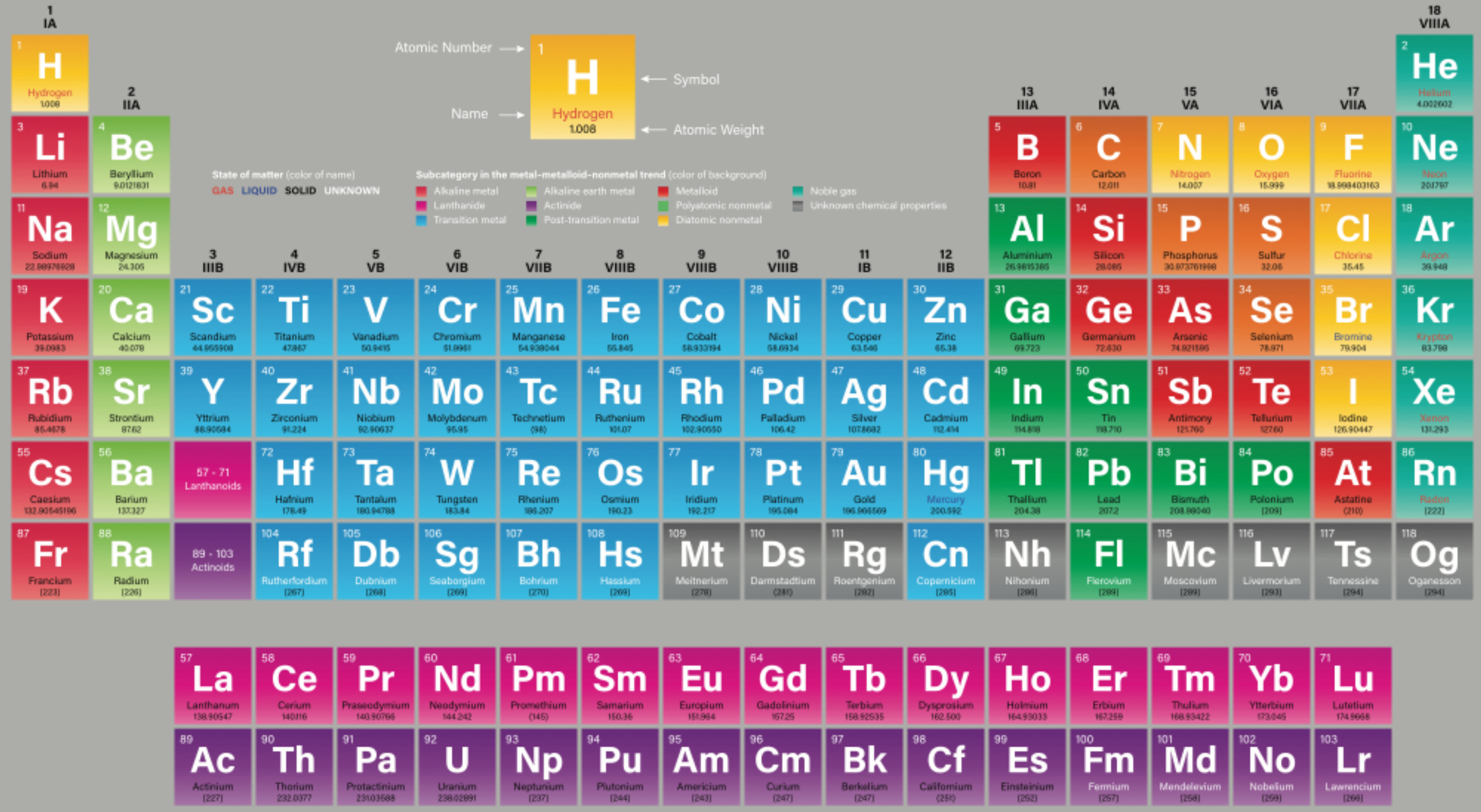
- Step 4: Use stoichiometry to determine the moles of HNO_3 that will be produced

$$\frac{NO_2}{HNO_3} = \frac{3}{2} = \frac{2.174\ mol}{x}$$

  Solving for x, x = 1.449 mol HNO_3

- Step 5: Convert to grams of nitric acid
  - 1.449 mol HNO_3 * 63.013 g/mol = 91.31 g HNO_3

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$,PCl_5, and CCl_4.



1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Alkaline earth metal
Metalloid
Noble gas
Lanthanide
Actinide
Polyatomic nonmetal
Unknown chemical properties
Transition metal
Post-transition metal
Diatomic nonmetal
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
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79 Au Gold 196.966569
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85 At Astatine (210)
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
89 - 103 Actinoids
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Limiting and Excess Reagents (Reactants)

- Equivalent – a mathematically equal amount of a chemical substance (in terms of moles)
- Sometimes you don't have the "stoichiometrically correct" number of equivalents
  - Cost
  - Availability
  - Reaction conditions
- Limiting – gets used up entirely
- Excess – remaining (left over)

More on limiting reagents

- This is based on the # of moles in a **balanced** chemical reaction
  - You *cannot* simply look at # of moles directly, or the mass (grams) that are given.
- The limiting reagent *always* determines the outcome of a chemical reaction
  - # of moles (or grams) of product that can be formed

Example

- Magnesium nitride can be formed by the reaction of magnesium metal with nitrogen gas.
- A) How many grams of magnesium nitride can be made in the reaction of 35.00 g of magnesium and 15.00 g of nitrogen?
- B) How many grams of the excess reactant remain after the reaction?

Solution (part a)

- Step 1: Write down (and balance) the chemical reaction
  - $3Mg + N_2 \rightarrow Mg_3N_2$
- Step 2: Find the # of moles of each reactant. This represents the moles you HAVE.
  - mol Mg = 35.00 g / 24.305 g/mol = 1.440 mol Mg
  - mol N_2 = 15.00 g / 28.013 g/mol = 0.5355 mol N_2

Solution (part a)

- Step 3: Pick *one* reactant, and find the number of moles of the *other* using stoichiometry. This represents the moles you NEED.

$$\frac{Mg}{N_2} = \frac{3}{1} = \frac{1.440\ mol}{x}$$

Solving for x, x = 0.4800 mol N_2

Solution (part a)

- Step 4: Compare the moles you HAVE with the moles you NEED. If HAVE > NEED, this is in *excess*. If you HAVE < NEED, this is *limiting*.
  - We have 0.5355 mol N_2 and need 0.4800 mol of N_2, so N_2 must be in excess. Therefore Mg is limiting.

Solution (part a)

- Step 5: Using the limiting reactant and stoichiometry, determine the number of moles of product.

$$\frac{Mg}{Mg_3N_2} = \frac{3}{1} = \frac{1.440\,mol}{x}$$

  Solving for x, x = 0.4800 mol Mg_3N_2.
- Step 6: Find the mass of the product
  - 0.4800 mol Mg_3N_2* 100.93 g/mol = 48.45 g Mg_3N_2

Solution (part b)

- Step 1: Determine how much N_2 (the excess reagent) is actually used.
  - 0.4800 mol N_2 * 28.013 g/mol = 13.45 g N_2
- Step 2: Determine the amount of excess.
  - 15.00 g – 13.45 g = 1.55 g N_2

An alternate solution to part b

- Conservation of mass
  - The total mass *before* the chemical reaction must be the same as the total mass *after* the chemical reaction
  - mass Mg + mass N_2 = 35.00 g + 15.00 g = 50.00 g
  - Mass of Mg_3N_2 = 48.45 g
  - Therefore mass of excess N_2 must be 50.00 – 48.45 g = 1.55 g

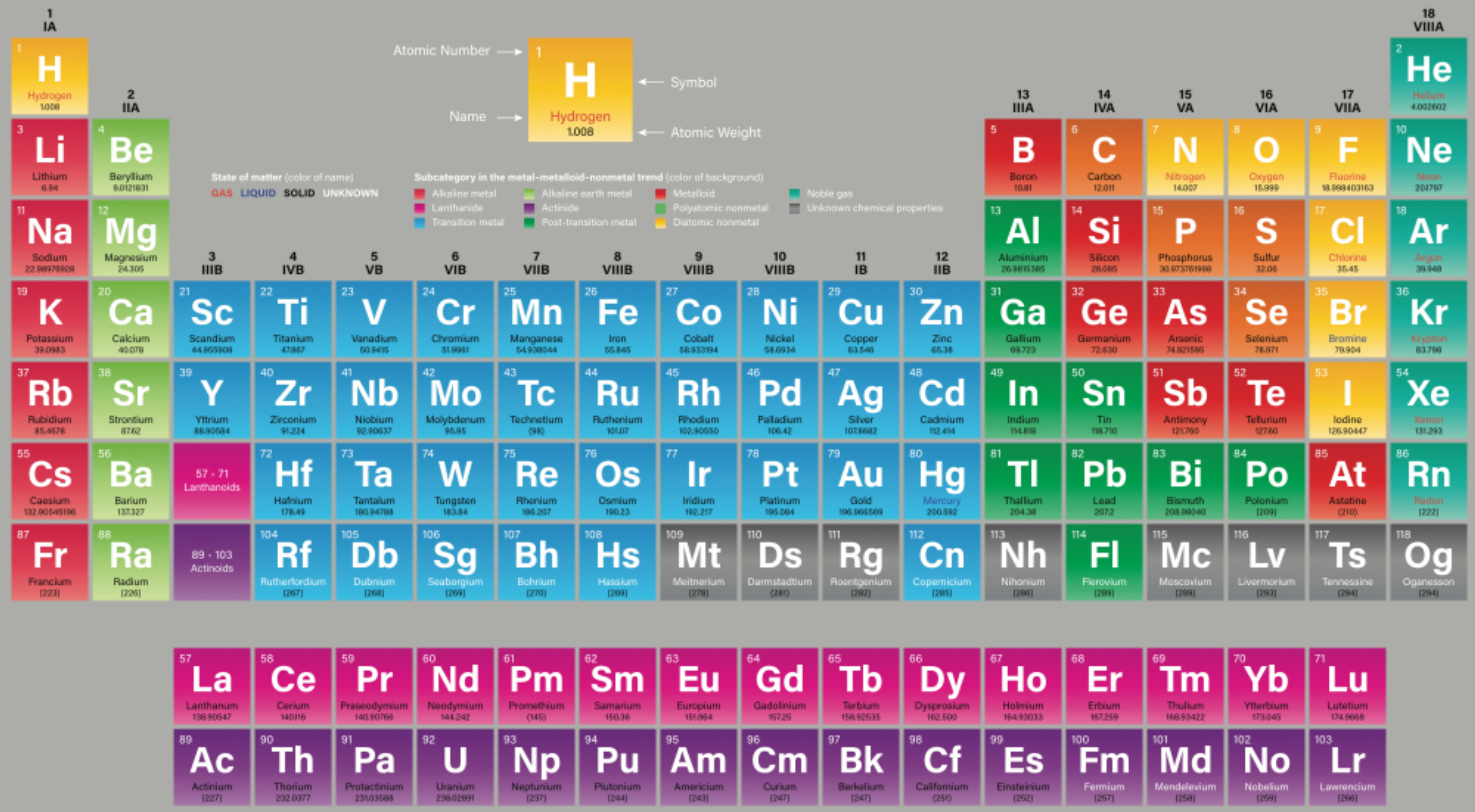
Yield

- This is related to the efficiency of a chemical reaction (how well it worked)

$$\% \, Yield = \frac{actual}{theoretical} \, X \, 100\%$$

- Actual refers to an experimental quantity
- Theoretical refers to the amount calculated using stoichiometry
- The amounts used can be mass or moles, as long as you are consistent (and both #'s refer to the product)
- Engineers usually also are concerned with *selectivity* and *conversion*.

In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?



Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Lanthanide
Transition metal
Alkaline earth metal
Actinide
Post-transition metal
Metalloid
Polyatomic nonmetal
Diatomic nonmetal
Noble gas
Unknown chemical properties
1 IA
2 IIA
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4 IVB
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Balancing Chemical Reactions

- The # of each type of atom must balance (conservation of mass)
  - Can use coefficients in front to make things work.
- Good rule of thumb – try to balance the atoms that show up in the least # of spots (# of compounds) 1^{st}
- It’s OK to use fractions
  - If whole #’s are wanted/needed just multiply by LCD

Example: Combustion of Ethane

- Step 1: Write down the reaction
  - $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$
- Step 2: Balance the C's
  - $C_2H_6 + O_2 \rightarrow 2CO_2 + H_2O$
- Step 3: Balance the H's
  - $C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$
- Step 4: Balance the O's
  - $C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O$
- Step 5: Use whole number coefficients (optional)
  - $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Balancing redox reactions

- Key: The number of electrons "lost" (in an oxidation) must be the same as the number of electrons "gained" (in a reduction)

1) Determine oxidation numbers and write down the half-reactions.
2) Balance the atoms in each half-reaction (except O and H)
3) Balance the charge in each half-reaction by adding electrons.
4) Balance the total number of electrons for both half-reactions and add the two reactions.
5) Add H_2O to balance the O's (and H's).
6) If acidic, add H^+ to balance the H's.
7) If basic, add H^+ to balance the H's, then add an equal number of OH^- to both sides ($H^+ + OH^- \rightarrow H_2O$), and simplify.

Check: The total charge on the left side must be equal to the total charge on the right side of the overall reaction.

Example

- In basic solution, Br_2 disproportionates to bromide ions and bromate ions. Use the half-reaction method to balance the equation for this reaction:

$Br_2(l) \rightarrow Br^{-}(aq) + BrO_3^{-}$

Solution

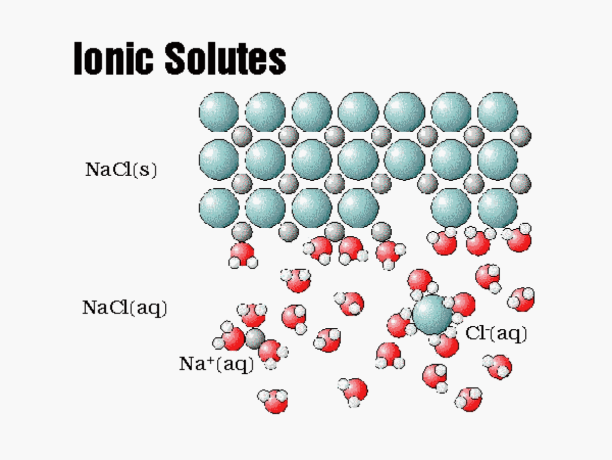
- First assign oxidation numbers to the Br's: Br_2 = 0, Br^- = -1, Br in BrO_3^- = +5 (since O has an oxidation number of -2)
- So the half-reactions are $Br_2 + 2e^- \rightarrow 2Br^-$ and $Br_2 \rightarrow 2BrO_3^- + 10e^-$
- Balance the number of electrons by multiplying the reduction reaction by 5, and add the two reactions: $6Br_2 + 10e^- \rightarrow 10Br^- + 2BrO_3^- + 10e^-$
- Simplify: $3Br_2 \rightarrow 5Br^- + BrO_3^-$
- Add H_2O to balance the O's: $3Br_2 + 3H_2O \rightarrow 5Br^- + BrO_3^-$
- Add H^+ and OH^- (since the solution is basic) to balance the H's: $3Br_2 + 3H_2O + 6OH^- \rightarrow 5Br^- + BrO_3^- + 6H^+ + 6OH^-$
- Simplify: $3Br_2 + 6OH^- \rightarrow 5Br^- + BrO_3^- + 3H_2O$
- Check: Total charge on the left = 3(0) + 6(-1) = -6, and the total charge on the right is 5(-1) + -1 +3(0) = -6

Balance the following equation according to the half-reaction method:

$Zn(s) + NO_3^-(aq) \longrightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)

Arrhenius Theory of Dissociation

- Dissociation happens spontaneously when ionic (soluble) compounds dissolve in H_2O.
- The more ions are present (i.e. the better it dissociates), the more electricity is conducted.



http://antoine.frostburg.edu/chem/senese/101/reactions/slides/sld006.htm

Classification of electrolytes

- Strong – soluble ionic substances (salts), mineral acids, bases
  - Acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$
  - Bases: LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
- Weak – carboxylic acids, amines
- Non-electrolytes – most organic compounds
- The words "strong" and "weak" refer *only* to how well something dissociates and forms ions, NOT if it is dangerous, reactive, etc.

Determining concentrations of ionic solutions

- For the [ ] of ions, we need to consider **both** the formula and whether or not it dissociates completely (strong electrolyte)

Solubility and Precipitates

- Everything dissolves in everything else, but to what extent?
- *Rule of thumb*: If solubility limit < 0.01 M, it is considered insoluble

Solubility rules (guidelines)

- **All** NO_3^-, $C_2H_3O_2^-$, ClO_4^-, Group IA metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and NH_4^+ salts are **soluble**.
- **Most** Cl^-, Br^-, and I^- salts are **soluble**.
  - *Exceptions*: Pb^{2+}, Ag^+, and Hg_2^{2+}
- **Most** SO_4^{2-} salts are **soluble**.
  - *Exceptions*: Sr^{2+}, Ba^{2+}, $Pb^{2+}$and Hg_2^{2+} (Ca^{2+} is slightly soluble)
- **Most** CO_3^{2-}, OH^-, PO_4^{3-}, and S^{2-} salts are **insoluble**.
  - *Exceptions*: Group IA metal ions (Ca^{2+}, Ba^{2+} and Sr^{2+} are slightly soluble)

If you're not part of the solution…

- You're part of the precipitate!
- In net ionic equations, the precipitate does not dissociate (stays as one entity)
- Example: $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ (overall)
- $Ag^+ + NO_3^- + Na^+ + Cl^- \rightarrow AgCl + Na^+ + NO_3^-$ (ionic)
- $Ag^+ + Cl^- \rightarrow AgCl$ (net ionic)

Empirical Gas Laws

- Early experiments conducted to understand the relationship between P, V and T (and number of moles n)
- Results were based purely on observation
  - No theoretical understanding of what was taking place
- Systematic variation of one variable while measuring another, keeping the remaining variables fixed

Boyle's Law (1662)

- For a closed system (i.e. no gas can enter or leave) undergoing an isothermal process (constant T), there is an inverse relationship between the pressure and volume of a gas (regardless of the identity of the gas)

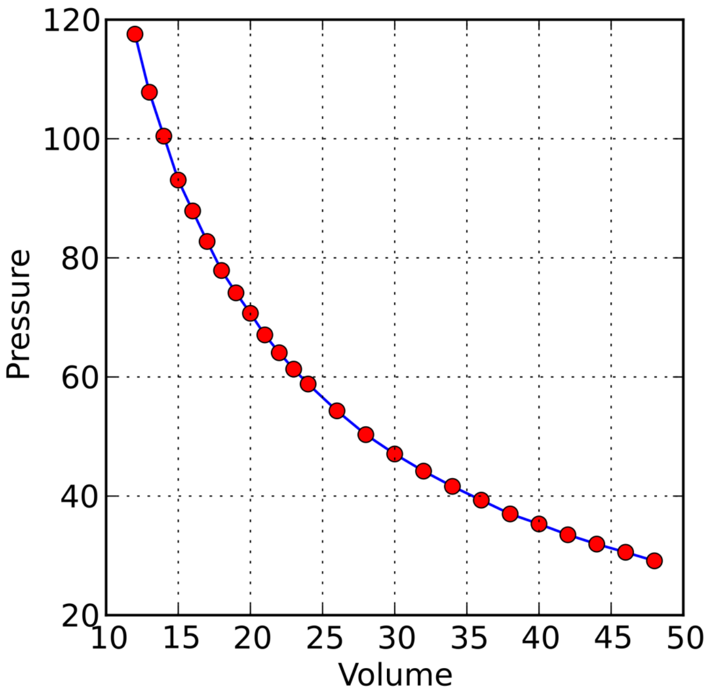
$$V \propto 1/P$$

- To turn this into an equality, introduce a constant of proportionality (a) → $V = a/P$, or $PV = a$
- Since the product of PV is equal to a constant, it must UNIVERSALLY (for all values of P and V) be equal to the same constant

$$P_1V_1 = P_2V_2$$

Boyle's Law

- There is an *inverse* relationship between P and V (isothermal, closed system)



https://en.wikipedia.org/wiki/Boyle%27s_law

Charles' Law (1787)

- For a closed system undergoing an isobaric process (constant P), there is a direct relationship between the volume and temperature of a gas.

$$V \alpha T$$

- Proceeding in a similar fashion as before, we can say that V = bT (the constant need not the same as that of Boyle's Law!) and therefore V/T = b

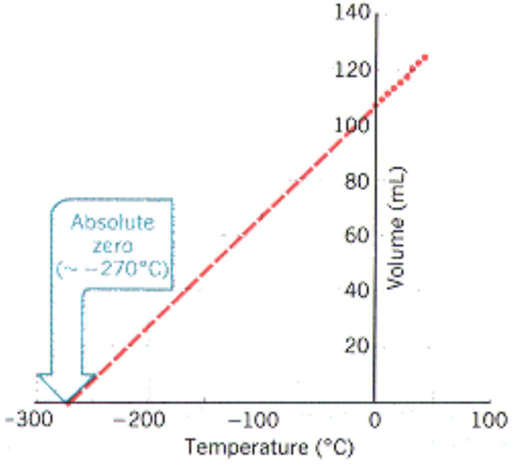
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles' Law (continued)

- This equation presumes a plot of V vs T would give a straight line with a slope of b and a y-intercept of 0 (i.e. equation goes through the origin).
- However the experimental data did have an intercept!
- Lord Kelvin (1848) decided to extrapolate the data to see where it would cross the x-axis (T)
  - Regardless of the nature of the gas, the data always would yield the same value: $-273.15^{o}C$
  - Therefore to make it go through zero, just add 273.15 to each point!
- This established the Kelvin (absolute) scale

Absolute temperature (Kelvin)

- The establishment of an absolute temperature scale was based on experiments



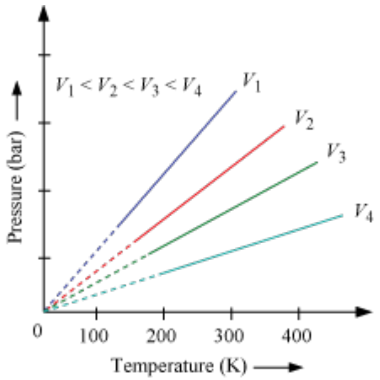
http://chemed.chem.purdue.edu/genchem/history/charleslaw.html

Gay-Lussac's Law (1809)

- For a closed system undergoing an isochoric process (constant V), there is a direct relationship between the pressure and temperature of a gas
- P α T
- Or proceeding as for Charles' Law, P/T = c

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

- In this relation, we also must use absolute temperature



http://www.meritnation.com/ask-answer/question/what-is-gay-lussacs-law-need-help/science/1780970

Avogadro's Law (1811)

- For an open system (mass is allowed to be transferred in or out), the volume of gas is directly proportional to the amount of gas present (given isothermal and isobaric conditions)

$$V \alpha n$$

- Mathematically this can be written as V = dn (yet another constant)

Avogadro's Law (continued)

- Since the T and P must be constant, it would be useful to define a reference state (T and P) so that gases can be compared to each other
- STP (standard temperature and pressure)
  - T = 0 ^{o}C and P = 1 atm
- Standard state
  - T = 25 ^{o}C and P = 1 bar

Combined Gas Law (?)

- It would appear that all the relationships can be combined into one equation. For example, volume is seen to be inversely proportional to pressure, directly proportional to the temperature and directly proportional to the number of moles of gas. Therefore

$$V \alpha nT/P$$

- Or $$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$
- This will eventually lead to the ideal (perfect) gas law, PV=nRT, as well.

Kinetic Molecular Theory

- Provides a theoretical explanation for the behavior of gases
- KMT is simply a model – it is not a perfect description of reality
  - Good enough! (if not we will fix it later)

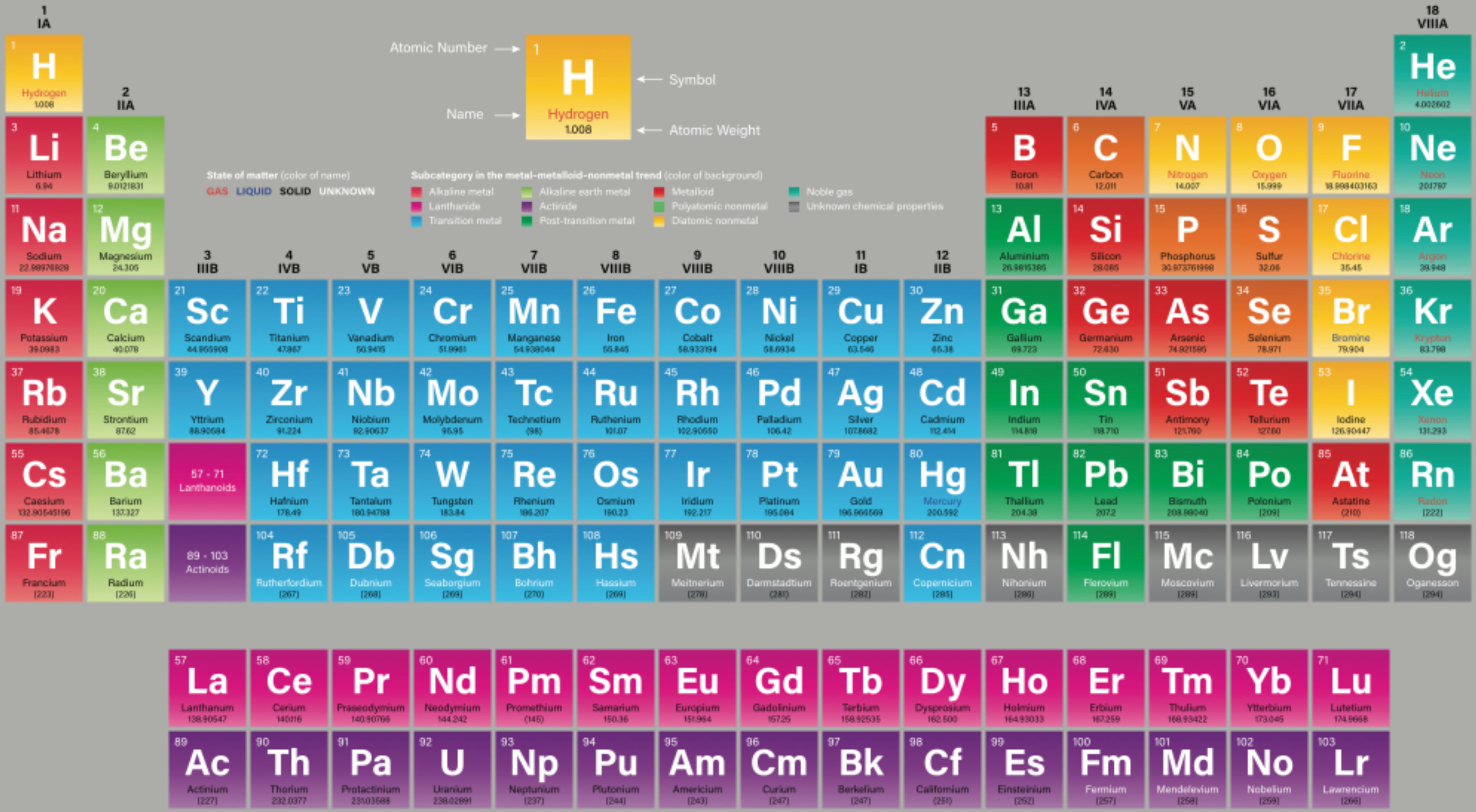
Postulates of the KMT

- A gas is composed of particles (molecules or atoms) that are perfect spheres
- Gas particles are in constant, random motion
- Gas particles move in straight lines (i.e. not accelerating)
- Gas particles are very far apart
  - $\mathbf{V_{gas}} \ll V_{container}$ (most of a gas is empty space)
- The **temperature** is proportional to the average kinetic energy of the motion

More postulates of the KMT

- Gas particles move **independently** of each other
  - The position and momentum of one particle are not affected by the position/momentum of another.
  - *There are no forces of attraction or repulsion between particles*
- Eventually gas particles will collide.
  - Collisions with other particles will be perfectly elastic
  - Collisions with the walls of the container will result in **pressure**.

Determine the number of moles of compound and the number of moles of each type of atom in 3.06 × 10^{-3} g of the amino acid glycine, $C_2H_5NO_2$.


Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Lanthanide
Transition metal
Alkaline earth metal
Actinide
Post-transition metal
Metalloid
Polyatomic nonmetal
Diatomic nonmetal
Noble gas
Unknown chemical properties
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
41 Nb Niobium 92.90637
42 Mo Molybdenum 95.95
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 112.414
49 In Indium 114.818
50 Sn Tin 118.710
51 Sb Antimony 121.760
52 Te Tellurium 127.60
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54 Xe Xenon 131.293
55 Cs Caesium 132.90545196
56 Ba Barium 137.327
57 - 71 Lanthanoids
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 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium [209]
85 At Astatine [210]
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
89 - 103 Actinoids
104 Rf Rutherfordium [267]
105 Db Dubnium [268]
106 Sg Seaborgium [269]
107 Bh Bohrium [270]
108 Hs Hassium [269]
109 Mt Meitnerium [278]
110 Ds Darmstadtium [281]
111 Rg Roentgenium [282]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
114 Fl Flerovium [289]
115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
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 162.500
67 Ho Holmium 164.93033
68 Er Erbium 167.259
69 Tm Thulium 168.93422
70 Yb Ytterbium 173.045
71 Lu Lutetium 174.9668
89 Ac Actinium [227]
90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium [237]
94 Pu Plutonium [244]
95 Am Americium [243]
96 Cm Curium [247]
97 Bk Berkelium [247]
98 Cf Californium [251]
99 Es Einsteinium [252]
100 Fm Fermium [257]
101 Md Mendelevium [258]
102 No Nobelium [259]
103 Lr Lawrencium [266]

Applications of the Ideal Gas Law

- Determination of the molar mass of a gas
- Since PV=nRT we can say that n=PV/RT
- We can also say that the number of moles is given by n=m/M
- Setting these expressions equal to each other yields PV/RT = m/M, which can be rearranged to solve for the molar mass:

$$M = \frac{mRT}{PV}$$

Applications of the Ideal Gas Law

- Determination of the density of a gas
- Let's use the fact that $\rho = m/V$ and rearrange the ideal gas law to yield $V=nRT/P$
- Combining this with $n=m/M$ and doing some algebra gives

$$\rho = \frac{MP}{RT}$$

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

What is a mole?

- Small furry animal

- Facial blemish

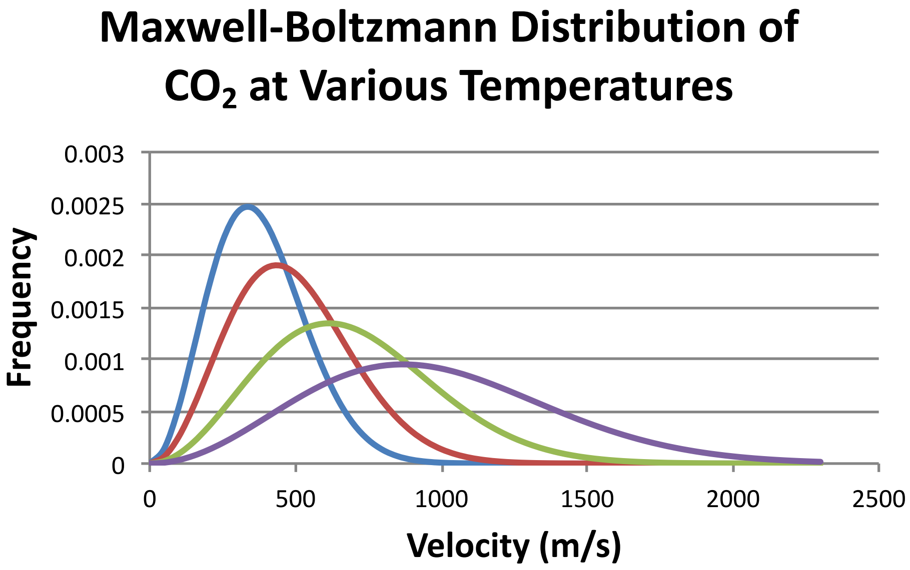
What is a mole?

- A mole represent the number of “particles” (elementary entities) present in a sample.
- Avogadro’s Number (N_A)
  - 6.022×10^{23} /mol
- The mole can also be related to mass
  - $n = m/M$
  - n = # of moles
  - m = mass
  - M = molar mass (or formula mass or atomic mass)

Molecular velocities

- The KMT can be used to calculate the root-mean-square velocity

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$



Graham's Law of Diffusion/Effusion (1831)

- Diffusion – movement due to a driving force (i.e. concentration gradient)
- Effusion – movement through a small hole
- Both are a "spreading out", and their behavior is based on KMT
- If two gases are at the same temperature, then they must have the same average kinetic energy $\frac{1}{2}M_1{u_1}^2 = \frac{1}{2}M_2{u_2}^2$
- Rearranging this, $\frac{u_2}{u_1} = \sqrt{\frac{M_1}{M_2}}$

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(a) The pressure of the gas is increased by reducing the volume at constant temperature.

(b) The pressure of the gas is increased by increasing the temperature at constant volume.

(c) The average velocity of the molecules is increased by a factor of 2.

Real gases

- There are a number of reasons why the ideal gas law might break down
  - Molecular forces
    - Attractive and repulsive forces do exist, and may be substantial (i.e. polar molecules)
  - Conditions
    - Under extreme cases of “high” pressure and/or “low” temperature gases start to behave more like condensed phases (liquids and solids) and intermolecular forces cannot be ignored

van der Waals equation

- First account for the finite volume that a gas molecule occupies
  - V → V-nb
- Since this will decrease the volume "available" for the molecules to collide, they should collide more often. This will mean that the pressure should *increase*.
- Mathematically a collision is defined as two particles in the same place at the same time. We can think of the "particle density" as being n/V. Thus the number of collision should be proportional to $(n/V)(n/V) = n^2/V^2$
  - $P \rightarrow P + an^2/V^2$

van der Waals equation

- Putting all of this together leads to

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where v = V/n. v is known as the specific volume, or molar volume.

It is important to note that the constants (a and b) are different for each substance.

van der Waals equation

- Typically corrections are “small” but can improve agreement
  - v=22.4 L/mol for ideal gas at STP so b/v is << 1
- Corrections tend to be larger for larger molecules, as well as for polar molecules

Substance	a (L^2atm/mol)	b (L/mol)
He	0.0341	0.02370
Ar	1.34	0.0322
H_2	0.244	0.0266
O_2	1.36	0.0318
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

- **(a) high pressure, small volume**
- **(b) high temperature, low pressure**
- **(c) low temperature, high pressure**

A comparison of the three main phases of matter

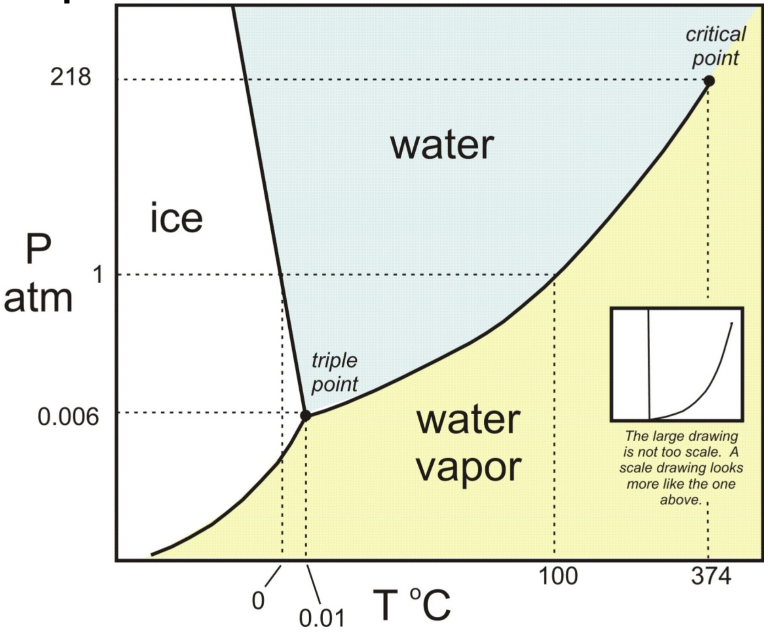
- Gases, liquids and solids differ from each other in the relative magnitudes of *inter*- and *intra*molecular forces

Phase	Volume	Shape	Compressibility	Fluidity
Gas	Indefinite	Indefinite	High	High
Liquid	Definite	Indefinite	Low	High
Solid	Definite	Definite	Low	Low

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Phase diagrams

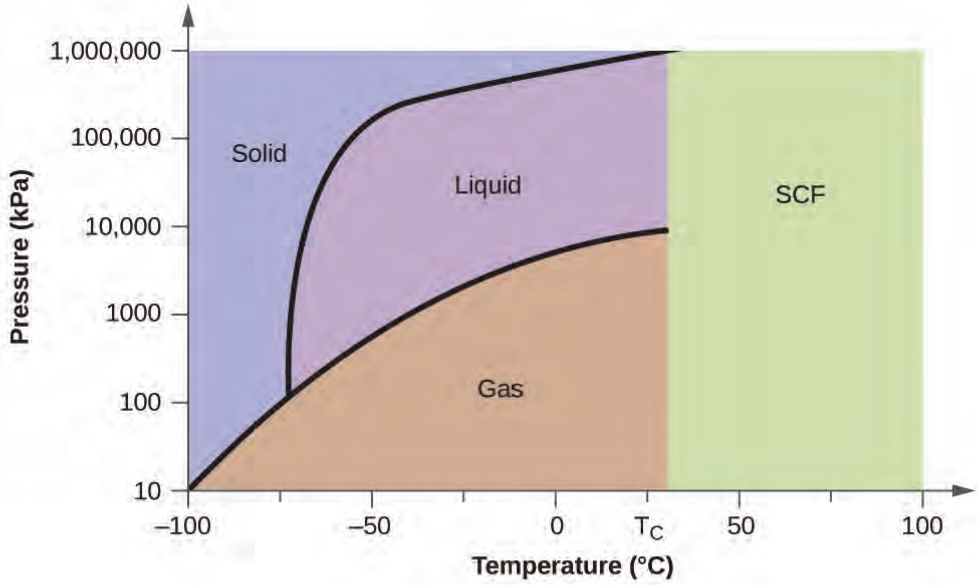
- Graphical representation of the states of matter as a function of temperature and pressure



http://serc.carleton.edu/research_education/equilibria/phaserule.html

From the phase diagram for carbon dioxide, determine the state of CO_2 at:

(a) 20 °C and 1000 kPa
(b) 10 °C and 2000 kPa
(c) 10 °C and 100 kPa
(d) −40 °C and 500 kPa
(e) −80 °C and 1500 kPa
(f) −80 °C and 10 kPa

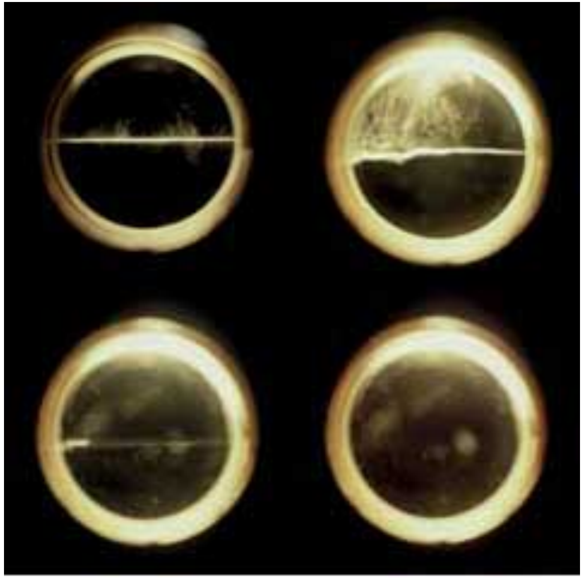


Critical Points

- Critical Temperature (T_c)– highest temperature that liquid and gas can exist as distinct phases
  - – A liquid can be produced by simply increasing the pressure of the gas
- Critical Pressure (P_c) – highest pressure that liquid and gas can exist as distinct phases
  - – A liquid can be produced by simply decreasing the temperature of the gas
- Beyond the critical point, supercritical fluid exists

Critical Point – in pictures

- Phase boundary disappears, so the two phases are indistinguishable



http://www.rsc.org/Education/EiC/issues/2008November/SupercriticalProcessing.asp

Triple Point

- For a one component system, there exists a **unique** temperature and pressure where *all three phases coexist at equilibrium*
- It is a physical property of the substance and can't be varied!
- Ex. H_2O T = 0.0098^oC and P = 4.58 mm Hg

http://www.maniacworld.com/water-at-triple-point.html

Solids

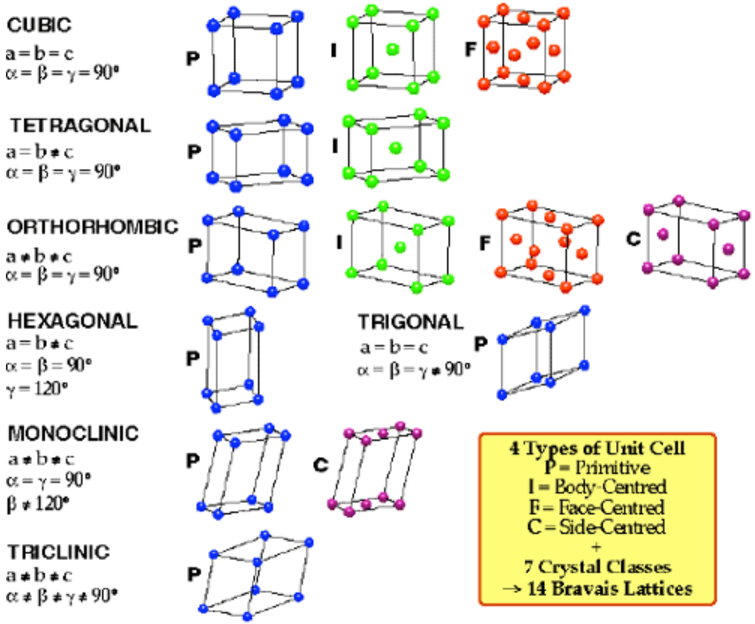
- Most difficult phase to model because particles (ions, atoms, molecules) are in very close contact
  - Strongest intermolecular forces
- *Amorphous* – disorganized clusters with no long-range order
- *Crystalline* – highly ordered lattice-like assemblies

Types of Crystalline Solids

- Molecular
  - Nonpolar
  - Polar
  - H-bonded
- Network covalent
- Ionic
- Metallic

Crystal lattices

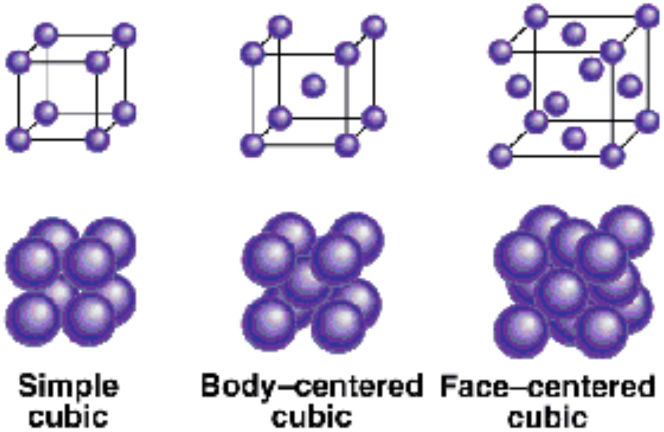
- 14 different types
- Lengths (a,b,c)
- Angles (α,β,γ)
- Different types of symmetry
- Cubic has the greatest degree of symmetry (a=b=c, $\alpha=\beta=\gamma=90^o$)



http://blogs.agu.org/georneys/2011/09/15/geology-word-of-the-week-p-is-for-pleochroism/

Cubic Arrangements

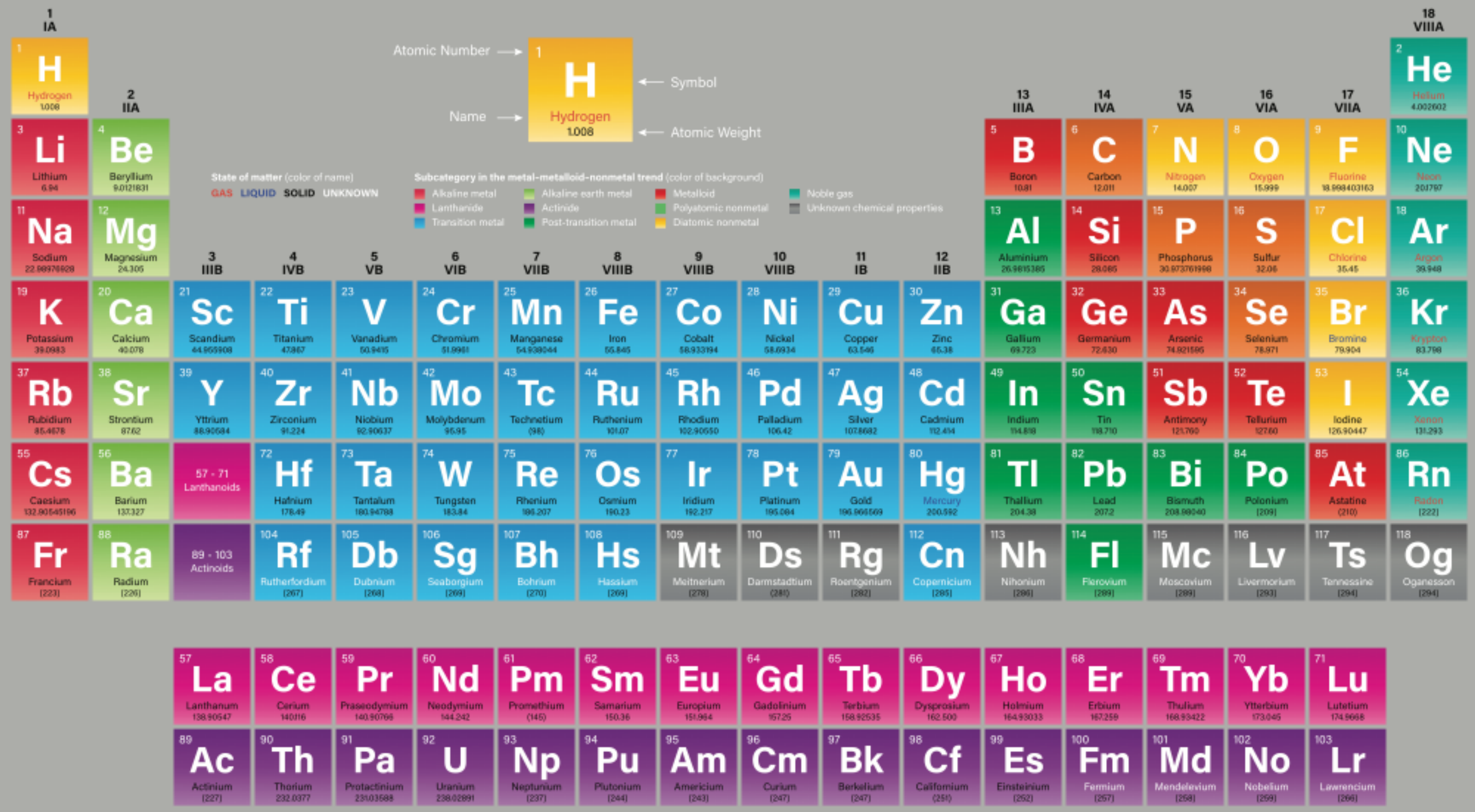
- Simple cubic cell
  - Has its constituents only at the edges (corners) of a cube
- Body-centered cubic (bcc)
  - Has an additional constituent at the center of the cube
- Face-centered cubic (fcc)
  - Has an additional constituent at the center of each face of the cube



http://martine.people.cofc.edu/111Lectweek14.htm

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) SiO_2
(b) KCl
(c) Cu
(d) CO_2
(e) NH_4F



1 IA
18 VIIIA
2 IIA
Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Alkaline earth metal
Metalloid
Noble gas
Lanthanide
Actinide
Polyatomic nonmetal
Unknown chemical properties
Transition metal
Post-transition metal
Diatomic nonmetal
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
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79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium [209]
85 At Astatine (210)
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
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105 Db Dubnium [268]
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108 Hs Hassium [269]
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115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
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 162.500
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90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium [237]
94 Pu Plutonium [244]
95 Am Americium [243]
96 Cm Curium [247]
97 Bk Berkelium [247]
98 Cf Californium (251)
99 Es Einsteinium [252]
100 Fm Fermium [257]
101 Md Mendelevium [258]
102 No Nobelium [259]
103 Lr Lawrencium [266]

Types of solutions

Solute	Solvent	Solution Phase	Examples
Gas	Gas	Gas	Air, natural gas
Gas	Liquid	Liquid	Club soda (CO_2 in H_2O), artificial blood (O_2 in perfluorodecalin)
Liquid	Liquid	Liquid	Vodka
Solid	Liquid	Liquid	Saline
Gas	Solid	Solid	H_2/Pd
Solid	Solid	Solid	14-karat gold (Ag in Au)

Energetics of solution formation

- 1) Pure solvent → separated solvent molecules
  - $\Delta H_1 > 0$ because intermolecular forces are being broken
- 2) Pure solvent → separated solute molecules
  - $\Delta H_2 > 0$ because intermolecular forces are being broken
- 3) Separated solvent and solute molecules → solution
  - $\Delta H_3 < 0$ because intermolecular forces are being formed

$\Delta H_{solution} = \Delta H_1 + \Delta H_2 + \Delta H_3$

What it means to be ideal

- For condensed phases, we know that there are intermolecular forces, which may be fairly significant. Considering the case of just two different types of molecules in a solution (A and B), there are really **three** types of interactions: A-A, A-B and B-B.
- If the solution is *ideal*, then the magnitudes of these interactions are all equal – i.e. it doesn’t really matter who your neighbor is!
- $\Delta H_{solution} = 0$, $\Delta V_{solution} = 0$

Ways to measure concentration

- Relative/qualitative terms
  - Dilute or concentrated
- Solubility – usually based on g of solute / 100 mL of water
  - Unsaturated – under solubility limit
  - Saturated – at solubility limit
  - Supersaturated – over solubility limit

Ways to measure concentration

- % by mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{total mass of solution}} X\ 100\%$$

  – Total mass = mass of solute + mass of solvent

- % by volume

$$\% \text{ by volume} = \frac{\text{volume of solute}}{\text{total volume of solution}} X\ 100\%$$

  – Total volume ≈ volume of solute + volume of solvent

Ways to measure concentration

- Molarity
  - Most common unit of concentration in chemistry

$$Molarity = \frac{moles\ of\ solute}{volume\ of\ solution\ (in\ L)}$$

  - M = n/V
- Molality

$$Molality = \frac{moles\ of\ solute}{mass\ of\ solvent\ (in\ kg)}$$

  - *m* = n/m
  - Better because with molarity you are unsure of the actual volume of liquid being added

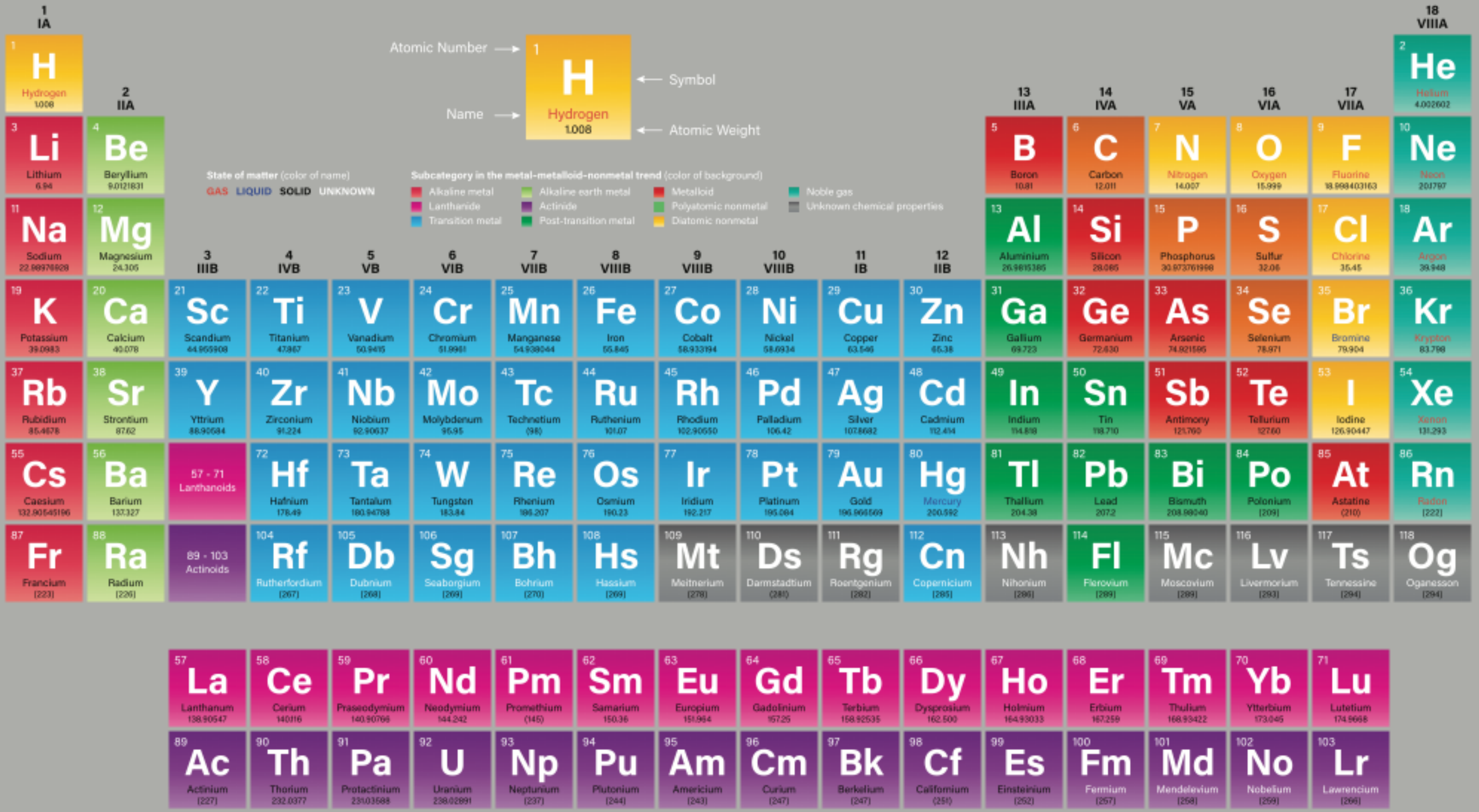
Ways to measure concentration

- Normality
  - Used almost exclusively for acids and bases
  - N = M*E, where M is the molarity and E is the # of equivalents (# of H^+ that will dissociate in an acid, or # of OH^- that will dissociate in a base)
  - Useful for titrations
- Mole fraction

$$X_A = \frac{n_A}{n_{tot}} = \frac{n_A}{\sum n_i}$$

  - Useful for colligative properties, chemical processes

Determine the molarity when 98.0 g of phosphoric acid, H_3PO4, is dissolved in 1.00 L of solution.


1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Alkaline earth metal
Metalloid
Noble gas
Lanthanide
Actinide
Polyatomic nonmetal
Unknown chemical properties
Transition metal
Post-transition metal
Diatomic nonmetal
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
41 Nb Niobium 92.90637
42 Mo Molybdenum 95.95
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 112.414
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 131.293
55 Cs Caesium 132.90545196
56 Ba Barium 137.327
57 - 71 Lanthanoids
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 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium [209]
85 At Astatine (210)
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
89 - 103 Actinoids
104 Rf Rutherfordium [267]
105 Db Dubnium [268]
106 Sg Seaborgium [269]
107 Bh Bohrium [270]
108 Hs Hassium [269]
109 Mt Meitnerium [278]
110 Ds Darmstadtium (281)
111 Rg Roentgenium [282]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
114 Fl Flerovium [289]
115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
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 162.500
67 Ho Holmium 164.93033
68 Er Erbium 167.259
69 Tm Thulium 168.93422
70 Yb Ytterbium 173.045
71 Lu Lutetium 174.9668
89 Ac Actinium [227]
90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
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98 Cf Californium (251)
99 Es Einsteinium [252]
100 Fm Fermium [257]
101 Md Mendelevium [258]
102 No Nobelium [259]
103 Lr Lawrencium [266]

Raoult's Law

- Consider a solution made up of solvent A (large purple spheres) and solute B (small green spheres).
- The rate at which A leaves the surface (vaporization) is proportional to how many you have on the surface, which is proportional to the mole fraction: $r=kx_A$
- The rate at which A comes back (condensation) is proportional to the concentration of the gas, which is proportional to the partial pressure: $r=k'P_A$
- Since these two rates must be the same:

$$P_A = \frac{k}{k'} x_A.$$

For a pure liquid $x_A=1$ so $k/k'=P_A^*$. This means that

$$P_A = x_A P_A^*$$

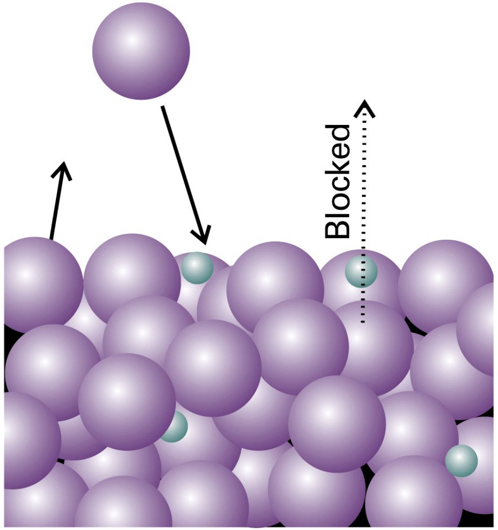


Figure 5-13
Atkins Physical Chemistry, Eighth Edition

Ideal solutions

- An ideal solution is one where Raoult's Law is obeyed.
- Since $P=P_A+P_B$, and the vapor pressure for a liquid is the same as that for a gas, for an ideal solution we can say that $P = P_A^* x_A + P_B^* x_B$
- Furthermore, since $x_A+x_B=1$,

$P = P_A^* x_A + P_B^*(1-x_A)$ or

$$P = (P_A^* - P_B^*)x_A + P_B^*$$

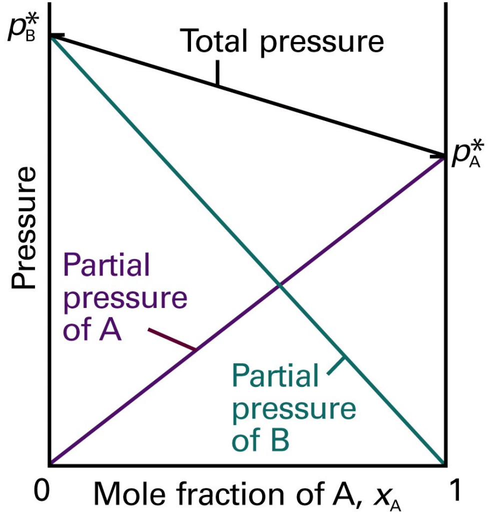


Figure 5-11
Atkins Physical Chemistry, Eighth Edition

Example of an ideal solution

- Solutions tend to behave ideally when the solvent (A) and solute (B) are "similar" to each other in terms of molecular structure, polarity, intermolecular forces, etc.
- Ex. Benzene and toluene (methylbenzene)

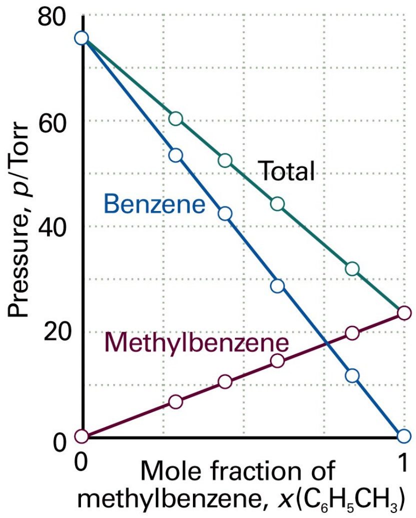
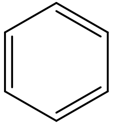
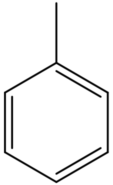


Figure 5-12
Atkins Physical Chemistry, Eighth Edition



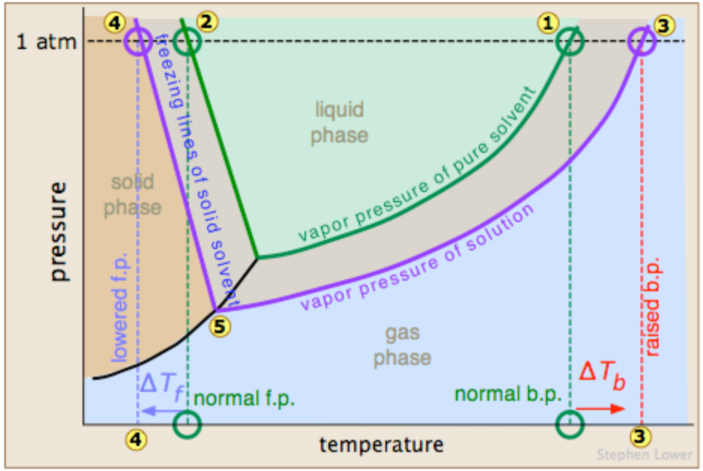


Colligative properties

- The presence of a solute can affect the properties of a solution
- This effect is (primarily) due to the amount of solute (i.e. concentration) but not necessarily on the nature of the solute
- Three main colligative properties:
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure

Freezing point depression and boiling point elevation

- Consider solutions where only the solvent is volatile, and the solute only dissolves in the liquid phase of the solvent



- $\Delta T_f = -\,iK_f m$
- $\Delta T_b = iK_b m$

i = van't Hoff factor (i = 1 for a non-electrolyte, ≈ 1 for a weak electrolyte, or # of particles for a strong electrolyte)

K_f = freezing-point depression (cryoscopic) constant

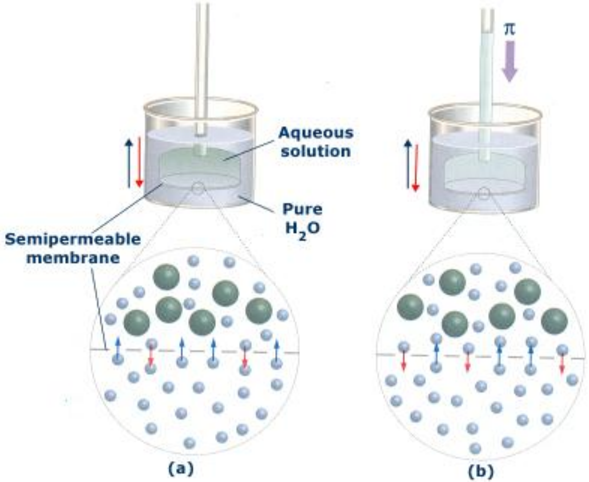
K_b = boiling-point elevation (ebullioscopic) constant

m = molality

https://www.boundless.com/chemistry/solutions/colligative-properties-nonelectrolyte-solutions/freezing-point-depression/

Osmotic pressure

- Osmosis - net flow of solvent molecules through a semipermeable membrane
  - Solvent molecules go from a solution of lower concentration to a solution of higher concentration (solute is not able to pass through)
- Osmotic pressure (π) = pressure required to stop osmosis
- π = MRT, where M = molarity



http://chemistry.tutorvista.com/physical-chemistry/osmotic-pressure.html

What is a bond?

- The “glue” that holds molecules together
- Really an electrostatic force between charged objects
- Coulomb’s Law
  - Attractive forces between protons and electrons
  - Repulsive forces between electrons
  - Repulsive forces between protons (can be ignored due to the Born-Oppenheimer approximation)
- Represents a minimum in a potential energy diagram

Ionic Compounds

- Ions – atoms that have gained or lost electrons (have + or – charge)
  - Can have very different properties than their corresponding elements
- Cations - + charge (lost electrons)
  - Usually originate from metals
- Anions - - charge (gained electrons)
  - Usually originate from nonmetals
- Ions can also be *polyatomic* (composed of more than one atom)

Types of bonded compounds

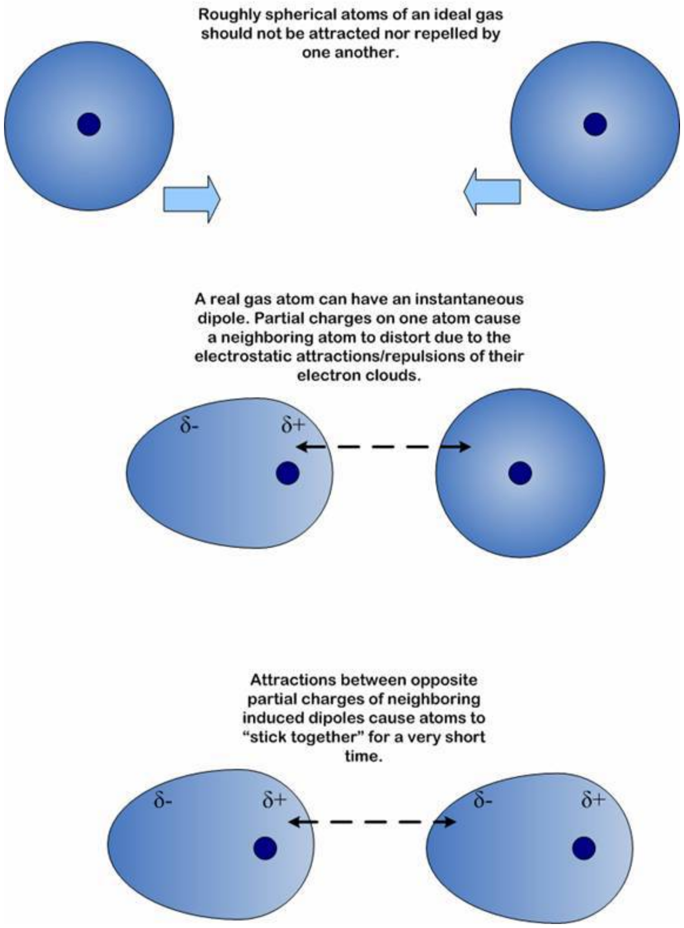
Type	Structural Particles	Intermolecular Forces
Nonpolar	Atoms or nonpolar molecules	Dispersion forces
Polar	Polar molecules	Dispersion forces, dipole-dipole and dipole-induced dipole
Hydrogen-bonded	Molecules with H bonded to N, O or F	Hydrogen bonds
Network Covalent	Atoms	Covalent bonds
Ionic	Cations and Anions	Electrostatic attractions
Metallic	Cations and delocalized electrons	Metallic bonds

Intermolecular Forces

- Present in ALL molecules
  - Explain why condensed phases can exist in the first place
- Strength of forces can vary
  - Electrostatics
  - Size
  - Shape
- Can be used to predict trends in stability
  - Melting point
  - Boiling point

van der Waals Forces

- Generally the weakest intermolecular forces (2-20 kJ/mol)
- Due to dispersion forces between instantaneous and induced dipoles
- *Polarizability* – measures the degree to which the electron density can be distorted by the presence of an external field
  - Related to strength of dispersion forces
  - Generally increase as the size (i.e. number of electrons) increases



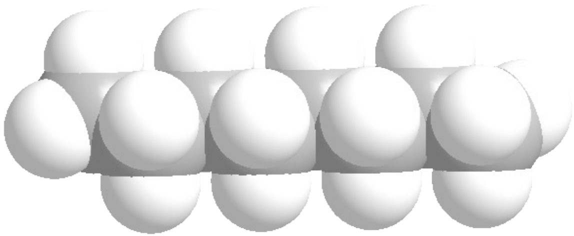
https://learnbiochemistry.wordpress.com/2011/09/11/chapter-2-water-non-covalent-bonds-van-der-waals-forces/

van der Waals Forces

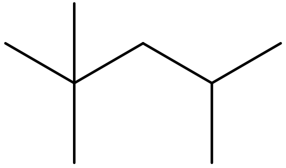
- Molecular shape can also affect the strength of these forces
  - Generally dispersion increases among elongated molecules (compared to more compact molecules)

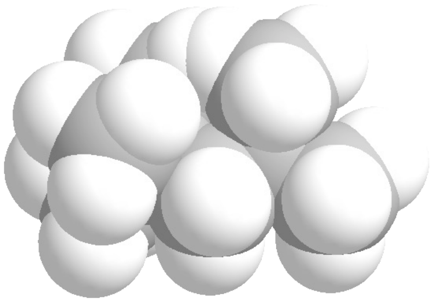
Example – alkane isomers

- Octane
  - mp = -56.8 ^{o}C
  - bp = 125.7 ^{o}C



- Isooctane
  - mp = -104.7 ^{o}C
  - bp = 99.2 ^{o}C



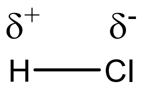


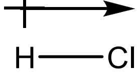
Types of covalent bonds

- Nonpolar – electrons are shared “equally”
- Polar – electrons are shared “unequally”
- Polarity within a bond is directly related to the electronegativity difference between the atoms of the bond
- Rough guidelines (there are always exceptions, and it is more of a continuum anyway)
  - $0 < \Delta\chi < 0.6$ = nonpolar
  - $0.6 < \Delta\chi < 1.6$ = polar
  - $\Delta\chi > 1.6$ = ionic

Polarity and dipole moments

- Partial charge (δ) – used to represent "slight" or small charge on an atom in a polar bond
  - Not quite ionic, but they do have a different tendency to have more or less electron density
- $\mu=\delta*d$, where δ is the (partial) charge and d is the distance between the charges
  - Usually expressed in Debyes (1 D = $3.34X10^{-30}$ C*m)
- μ is a vector quantity – has magnitude and direction
  - Can also be depicted using an arrow





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- μ is a vector quantity – has magnitude and direction
  - Can also be depicted using an arrow

Polarity revisited

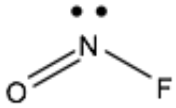
- Dipole moments can be defined between two atoms in a bond to determine the polarity of the bond (polar or nonpolar)
- Because dipole moments are vector quantities, we can also define a molecular dipole moment to be the sum of these individual dipole moments.

$$\mu_{molecule} = \sum \mu_{bond}$$

- It is possible that $\mu_{molecule} = 0$ even if $\mu_{bond} \neq 0$ because of symmetry!

Example: NOF and NO_2F

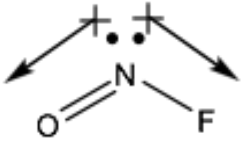
- First let's look at NOF. The number of valence electrons is 5+6+7 = 18
- Following the rules for Lewis dot structures we come up with the following:



- Following the rules for VSEPR we predict this to have an angular molecular geometry (though similar to a trigonal planar shape)

Example: NOF and NO_2F

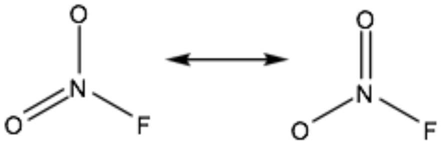
- Now let's consider electronegativities: F = 4.0, O = 3.5 and N = 3.0. The bonds are considered to be polar since $\Delta\chi$ = 1.0 for N-F bond and $\Delta\chi$ = 0.5 for a N-O bond.



- This results in a net dipole (downward) of a pretty substantial size (1.81 D)

Example: NOF and NO_2F

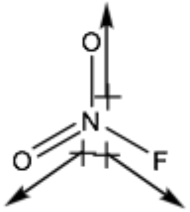
- Let's perform a similar analysis on NO_2F.
- The Lewis dot structure we predict is the following resonance form:



- VSEPR predicts that this molecule will also be in the trigonal planar family, with only slightly different bond angles from those of NOF.

Example: NOF and NO_2F

- The electronegativities are the same as before, so the bonds will still be polar
- However the overall dipole moment will be quite different!



- There is still a slight net dipole since F is more electronegative than O (μ = 0.47 D)

VSEPR theory

- Valence-shell electron-pair repulsion
- Predict molecular shapes based on the **total** number of (pairs of) electrons
  - Bonded and nonbonded (lone pairs) count, though they lead to different shapes
- Electrostatic interactions - molecules will arrange themselves in such a way as to minimize repulsion (keep the electrons as far away from each other as possible)
- Steric hindrance - molecules will arrange themselves in such a way as to have the largest (bulkiest) groups as far away from each other as possible

Electron group

- Any collection of valence electrons on a central atom that will affect the overall structure of a molecule
  - Single unpaired electron (radical)
  - Nonbonded electrons (lone pair)
  - One bonding pair of electrons (single bond)
  - Two bonding pairs of electrons (double bond)
  - Three bonding pairs of electrons (triple bond)

Electron group geometry

Number of electron groups	Geometry
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

- These represent ideal situations where all electron groups affect structure in the same fashion, regardless of whether they are a single electron (radical), single pair of nonbonded electrons (lone pair), or single/multiple pairs of bonded electrons (single, double, triple bonds)

Molecular geometry

- Attempts to distinguish between bonded and non-bonded electrons
- Lone pairs are believed to have a significant effect on the structure of the molecule
  - Their charge cloud is attracted to one nucleus (the central atom) rather than two (central atom and outer atom). Thus it is spread out further and able to exert a greater repulsion
  - LP-LP repulsions > LP-BP repulsions > BP-BP repulsions

Molecular geometry

- Designation
  - AX_nE_m
  - A = central atom
  - X = outer atom (bonded electron)
  - E = lone pair (non-bonded electrons)
  - n,m = integers ($2 \leq n \leq 6$, $0 \leq m \leq 3$)

Molecular geometry

Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	"Ideal" bond angles	Example
2	Linear	0	AX_2	Linear	180°	$BeCl_2$
3	Trigonal planar	0	AX_3	Trigonal planar	120°	BF_3
3	Trigonal planar	1	AX_2E	Angular (bent)	118°	SO_2
4	Tetrahedral	0	AX_4	Tetrahedral	109.5°	CH_4
4	Tetrahedral	1	AX_3E	Trigonal pyramidal	107°	NH_3
4	Tetrahedral	2	AX_2E_2	Angular (bent)	105°	H_2O

Molecular geometry

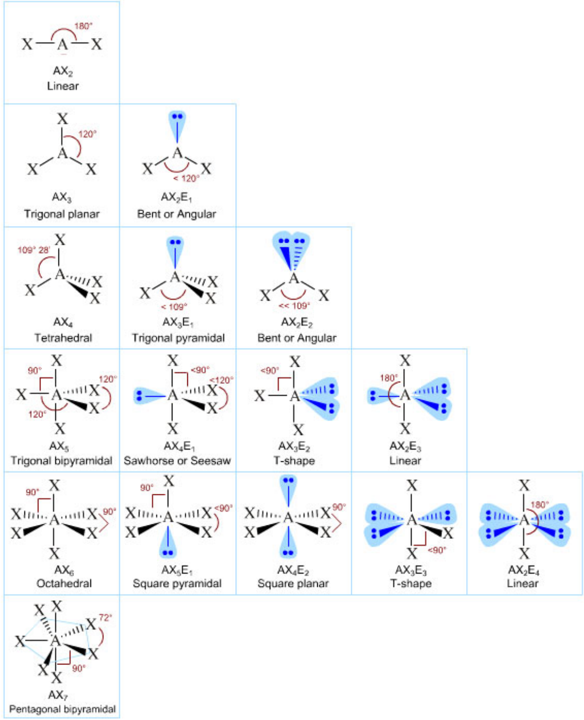
Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	Ideal bond angles	Example
5	Trigonal bipyramidal	0	AX_5	Trigonal bipyramidal	90°, 120°, 180°	PCl_5
5	Trigonal bipyramidal	1	AX_4E	See-saw	90°, 120°, 180°	SF_4
5	Trigonal bipyramidal	2	AX_3E_2	T-shaped	90°, 180°	ClF_3
5	Trigonal bipyramidal	3	AX_2E_3	Linear	180°	XeF_2

Molecular geometry

Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	Ideal bond angles	Example
6	Octahedral	0	AX_6	Octahedral	90^o, 180^o	SF_6
6	Octahedral	1	AX_5E	Square pyramidal	90^o	BrF_5
6	Octahedral	2	AX_4E_2	Square planar	90^o	XeF_4

Molecular geometry

- Shapes can be classified into families based on number of total pairs of electrons
- Geometries will vary slightly within a family, but less than from one family to another



http://www.chemistry-drills.com/VSEPR.php

Types of isomers

- Structural – have the same chemical formula but are attached differently
  - Donor atoms on ligands
    - Ex. Pentamminenitrito-*N*-cobalt(III) vs. Pentamminenitrito-*O*-cobalt(III)

    $[Co(NO_2)(NH_3)_5]^{2+}$ vs. $[Co(ONO)(NH_3)_5]^{2+}$
  - Ligands vs. free ions (outside of coordination sphere)
    - Ex. Pentamminesulfatochromium(III) chloride vs. Pentamminechlorochromium(III) sulfate

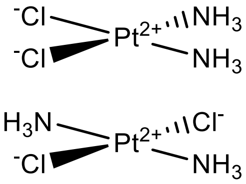
    $[Cr(SO_4)(NH_3)_5]Cl$ vs. $[CrCl(NH_3)_5]SO_4$

Types of isomers

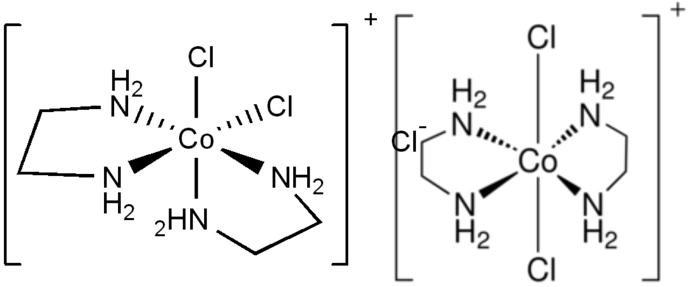
- Stereo – same atoms connected in the same way, but different 3-D shapes
  - Geometric – identical groups can be on the same side (cis) or opposite side (trans)
    - Have different chemical and physical properties
  - Optical - groups are oriented to form non-superimposable mirror images (enantiomers)
    - Racemic mixture – 1:1 ratio of two enantiomers
    - Have identical chemical and physical properties*
    - Can generally be distinguished by how they rotate the plane of polarized light in a polarimeter
    - Optical isomers are *chiral* molecules

Comparison of geometric and optical isomers

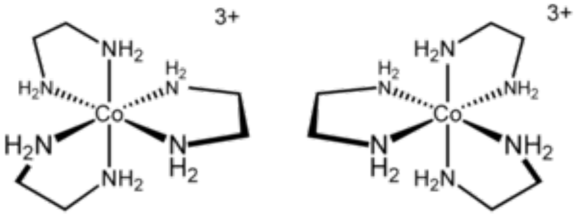
- Cisplatin and transplatin (square planar)



- *cis* and *trans*-dichloro bis(ethylenediamine) cobalt(III) ion (octahedral)



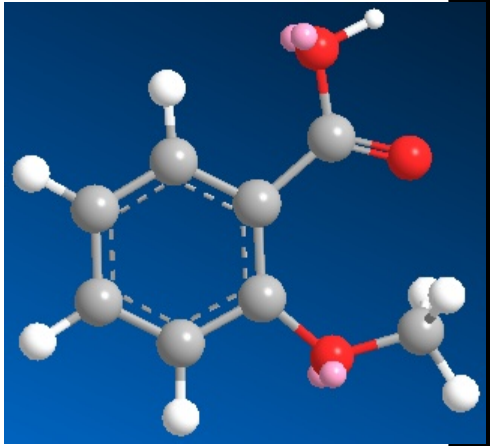
- Tris(ethylenediamine) cobalt(III) ion

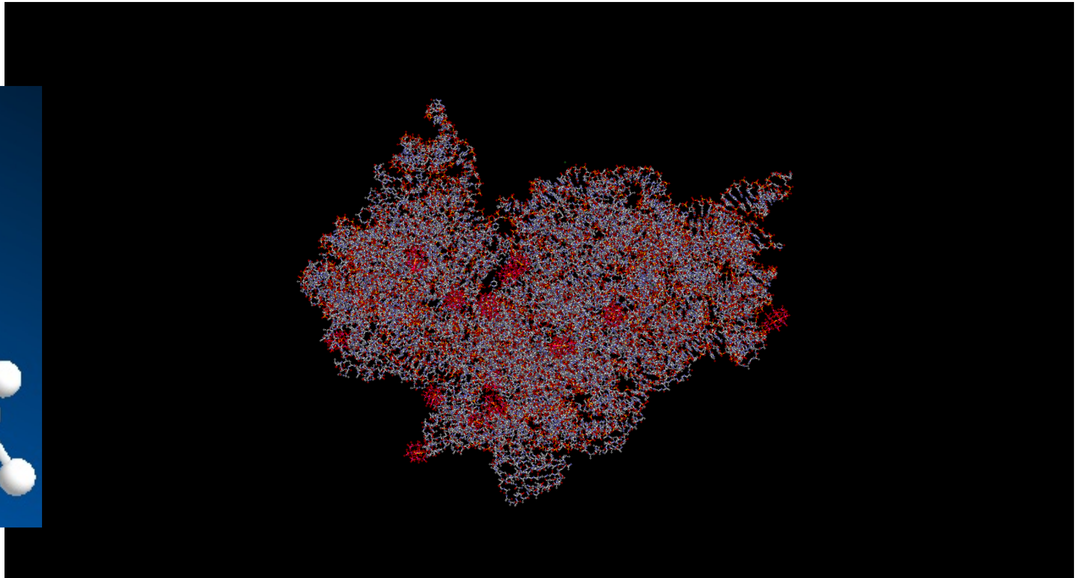


chloride anions omitted

Molecular Geometry

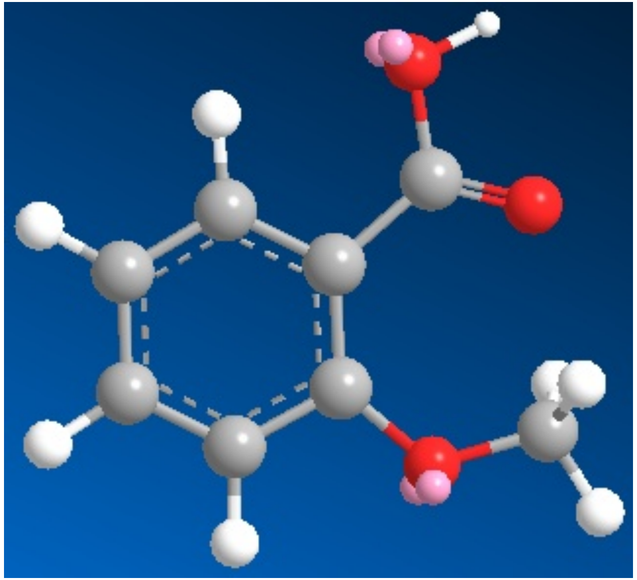
- Molecules can (and usually do) have well defined shapes, which can have a direct correlation to their function
- Ex. Aspirin



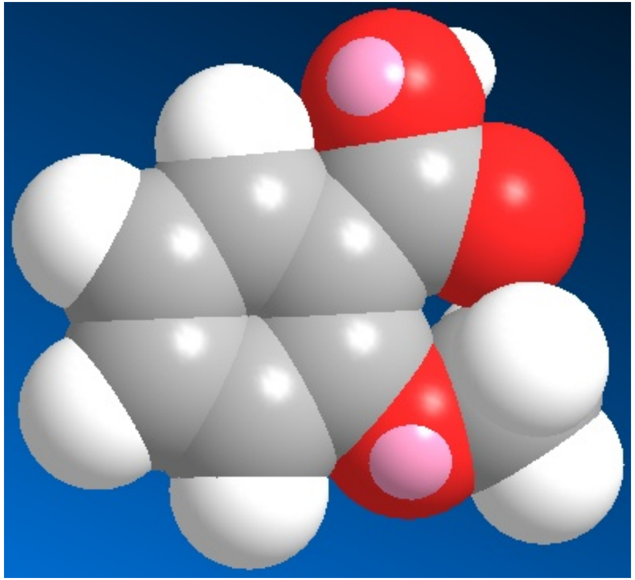


Visualizing Molecules (Aspirin)

Ball and Stick



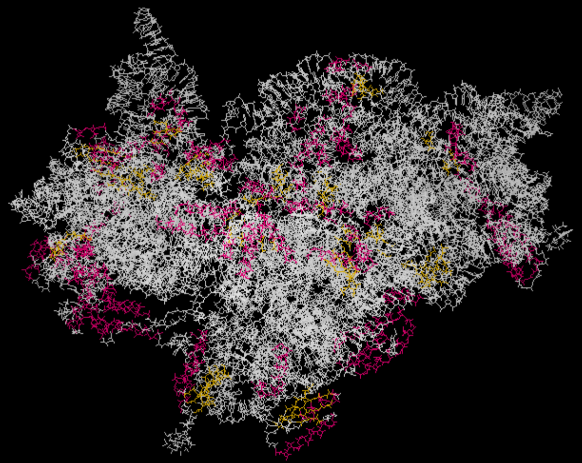
Space filling



Visualizing Molecules (16S ribosome)

Wireframe

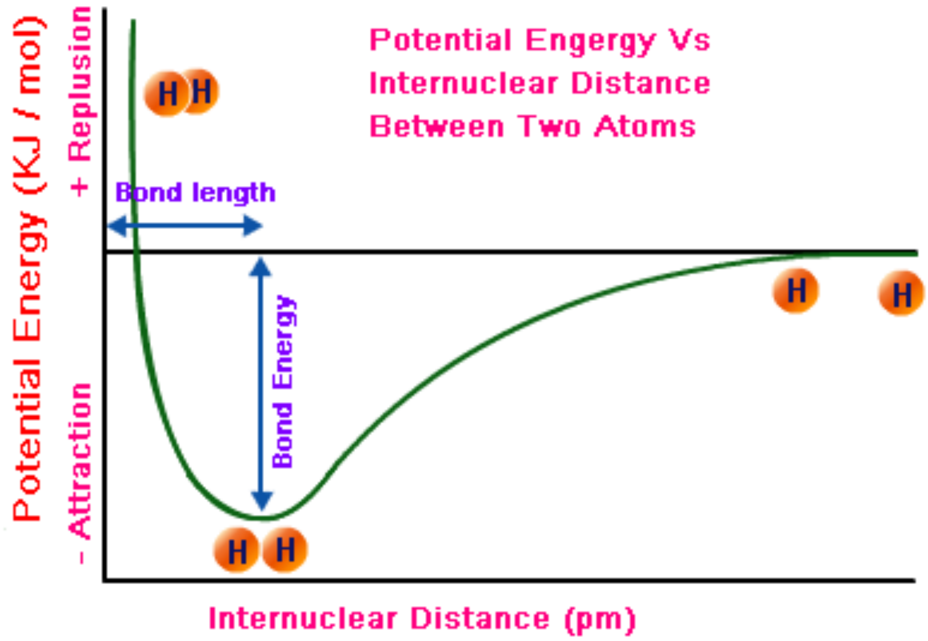
Cartoon (Structure color coded)



Valence bond theory

- Mathematically simpler
- Can be used to explain bonding in terms of orbital overlap
  - The more orbital overlap there is, the stronger the bond will be
- Also gives rise to bond lengths and bond strengths
  - Internuclear position and corresponding energy of maximum overlap

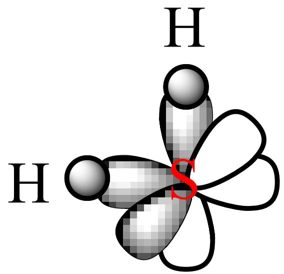
Valence Bond theory (in pictures)

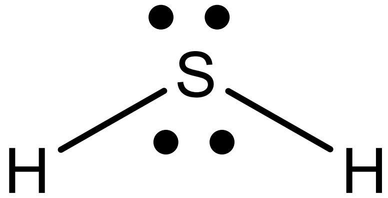


http://chemistry.tutorvista.com/organic-chemistry/chemical-bonds.html

Example: H_2S

- Predicted bond angle (VBT): 90^o
- Predicted bond angle (VSEPR): <109.5^o
- Experimentally determined bond angle: 92.1^o





Hybridization

- Problem – Atomic orbitals only work for atoms!
- Disagreement between theory and experimental data
  - Bond-dissociation energy
  - Bond angles
  - Bond length

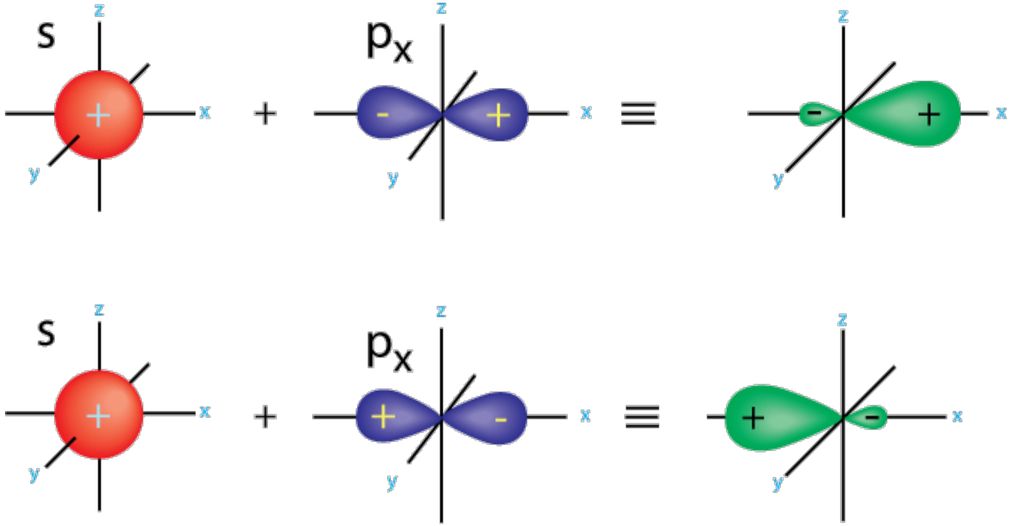
http://www.sparknotes.com/chemistry/organic1/orbitals/section1.html

Rules for hybridization

- Hybridization only exists on paper!
  - Atomic orbitals can be “combined” (mathematically, if nothing else)
- Hybrid orbitals can be constructed as long as two conditions are met
  - The total number of orbitals remains constant
  - The total energy of the system remains constant
- Hybridization can be used for bonding as well as non-bonding electron pairs

sp Hybridization

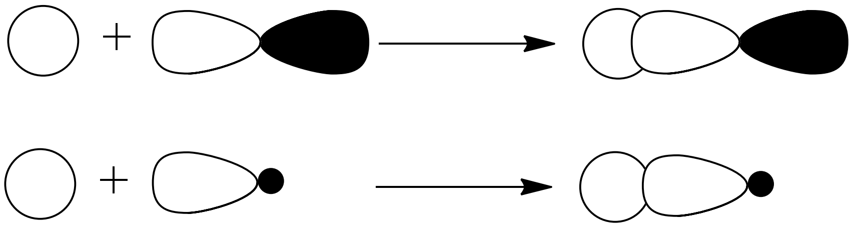
- Combination of an s orbital and a p orbital
- Result can be “constructive” or “destructive”



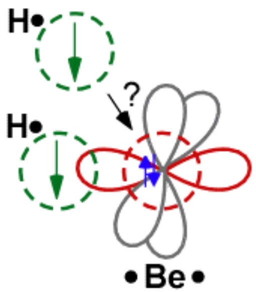
http://www.grandinetti.org/Teaching/Chem121/Lectures/Hybridization

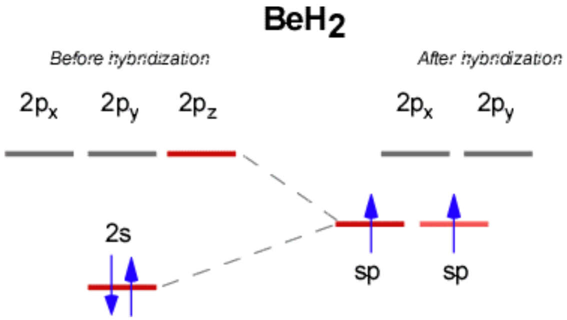
sp Hybridization

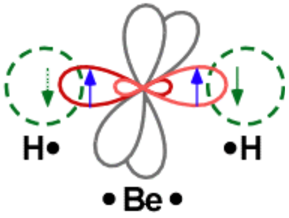
- “Character” - % of hybrid orbital that originated from a given atomic orbital
- 50% s character, 50% p character
- Leads to greater orbital overlap

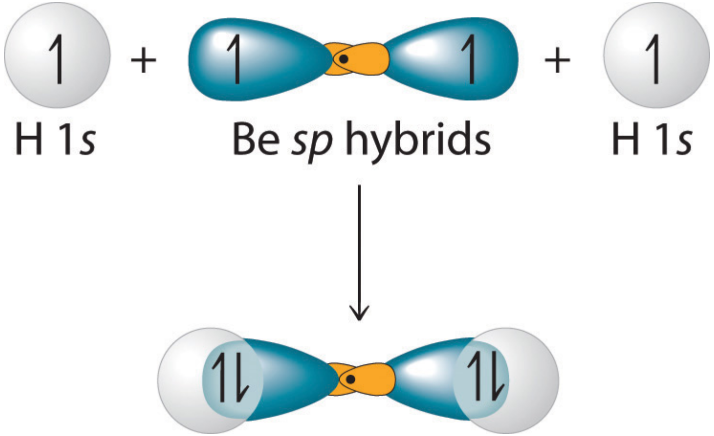


Example – BeH_2





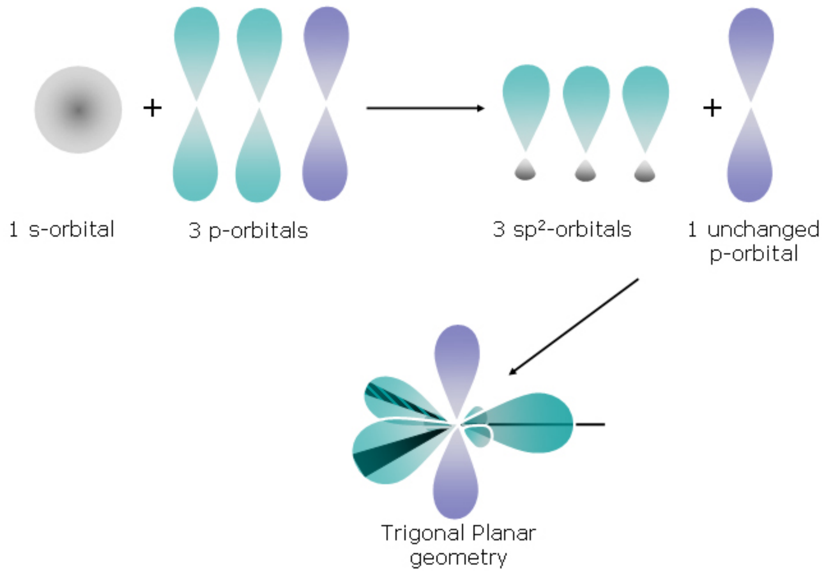




http://www.chem.umass.edu/~cmartin/Courses/GenChem/F08/CTMRsrcList.html
http://catalog.flatworldknowledge.com/bookhub/reader/4309?e=averill_1.0-ch09_s02

sp^2 Hybridization

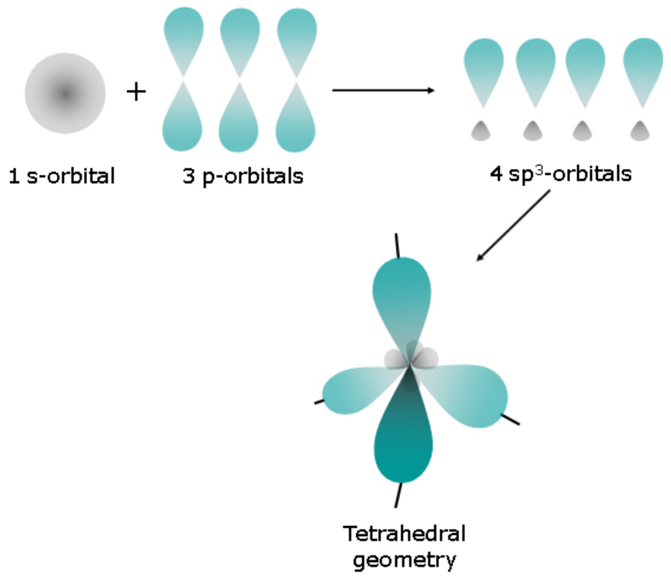
- Combination of one s orbital and two p orbitals (33% s character, 67% p character)



http://www.ntu.ac.uk/cels/molecular_geometry/hybridization/Sp2_hybridization/index.html

sp^3 Hybridization

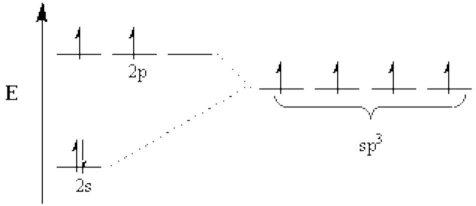
- 25% s, 75% p character

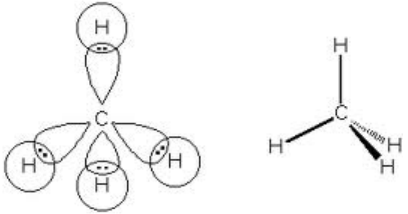


http://www.ntu.ac.uk/cels/molecular_geometry/hybridization/Sp3_hybridization/index.html

Why hybridization?

- Better overlap than if atomic orbitals are used
- Better agreement with experimental data





http://www.chemistry.ccsu.edu/glagovich/teaching/311/content/bond/bondhybrid.html
http://www.sparknotes.com/chemistry/organic1/orbitals/section1.html

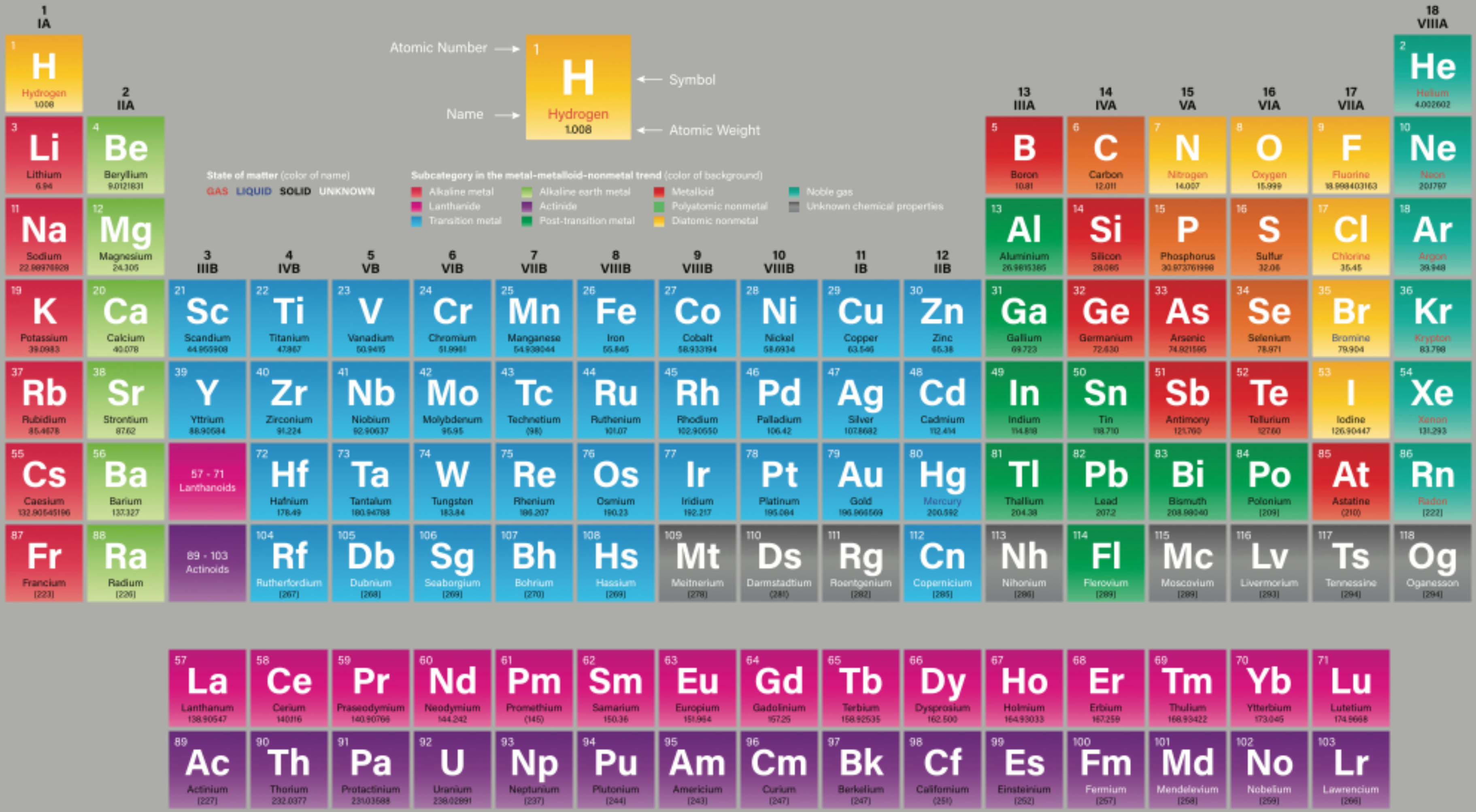
Hybridization involving d subshells

- For atoms in the 3rd period and beyond of the periodic table, it is possible for them to also use d orbitals for bonding
- An expanded octet rule argument is typically invoked
  - Experimental evidence is actually pretty weak!

Summary of hybridization schemes

Hybrid orbital type	Geometry	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3	Trigonal pyramidal	NH_3
sp^3	Bent (angular)	H_2O
sp^3d (or dsp^3)	Trigonal bipyramidal	PCl_5
sp^3d^2 (or d^2sp^3)	Octahedral	SF_6

Identify the hybridization of the central atom in Cl_2CO (C is the central atom)



Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Lanthanide
Transition metal
Alkaline earth metal
Actinide
Post-transition metal
Metalloid
Polyatomic nonmetal
Diatomic nonmetal
Noble gas
Unknown chemical properties
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
41 Nb Niobium 92.90637
42 Mo Molybdenum 95.95
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 112.414
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 131.293
55 Cs Caesium 132.90545196
56 Ba Barium 137.327
57 - 71 Lanthanoids
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 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium [209]
85 At Astatine (210)
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
89 - 103 Actinoids
104 Rf Rutherfordium [267]
105 Db Dubnium [268]
106 Sg Seaborgium [269]
107 Bh Bohrium [270]
108 Hs Hassium [269]
109 Mt Meitnerium [278]
110 Ds Darmstadtium (281)
111 Rg Roentgenium [282]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
114 Fl Flerovium [289]
115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
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 162.500
67 Ho Holmium 164.93033
68 Er Erbium 167.259
69 Tm Thulium 168.93422
70 Yb Ytterbium 173.045
71 Lu Lutetium 174.9668
89 Ac Actinium [227]
90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium [237]
94 Pu Plutonium [244]
95 Am Americium [243]
96 Cm Curium [247]
97 Bk Berkelium [247]
98 Cf Californium (251)
99 Es Einsteinium [252]
100 Fm Fermium [257]
101 Md Mendelevium [258]
102 No Nobelium [259]
103 Lr Lawrencium [266]

Molecular Orbital (MO) Theory

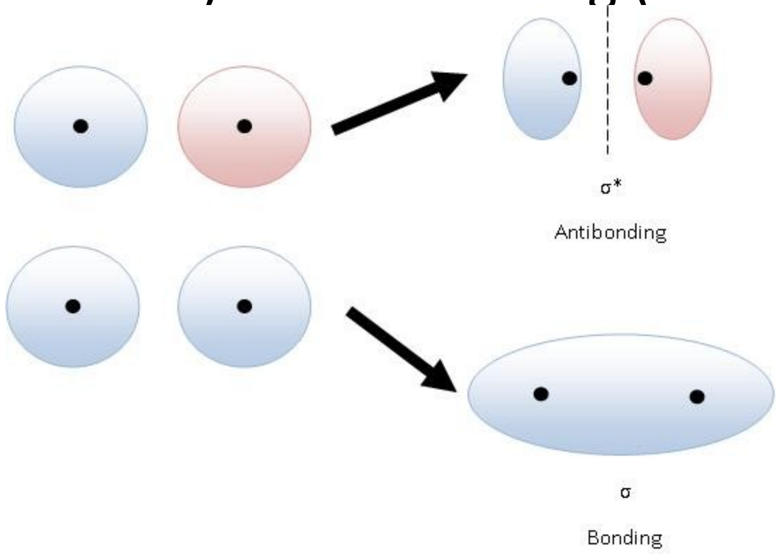
- If the electrons in an atom are described by atomic orbitals, then the electrons in molecules should be described by molecular orbitals!
- LCAO – MO is a linear combination of AO's
- Atomic orbitals can add constructively or destructively
- Generally only used for diatomic molecules

MO Theory (continued)

- Rules for Constructing MO's
  - The *total number of orbitals* must remain the same
  - The *total energy* must remain the same
- Bonding – MO is lower in energy than AO
- Antibonding – MO is higher in energy than AO
- Nonbonding – MO is equal in energy to AO
  - Due to orthogonal orbitals (noninteracting)

MO’s arising from s orbitals

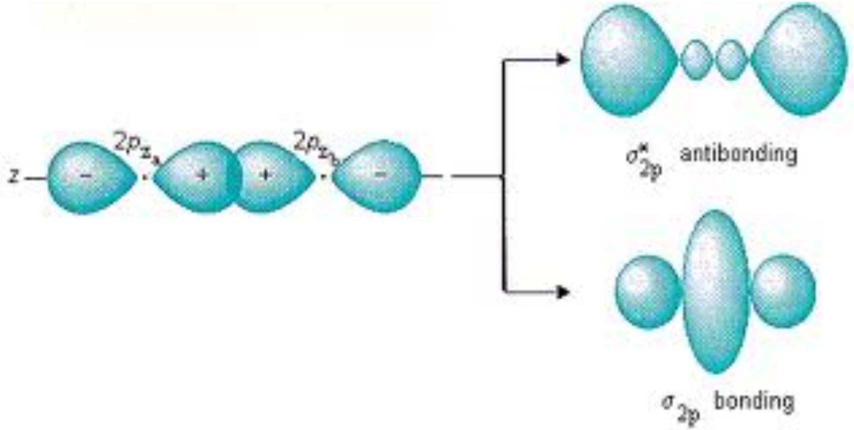
- Sigma bonds (σ) since orbitals are end to end
- Can be bonding (constructive) or antibonding (destructive)



http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Chemical_Bonding/Molecular_Orbital_Theory

MO's arising from p orbitals

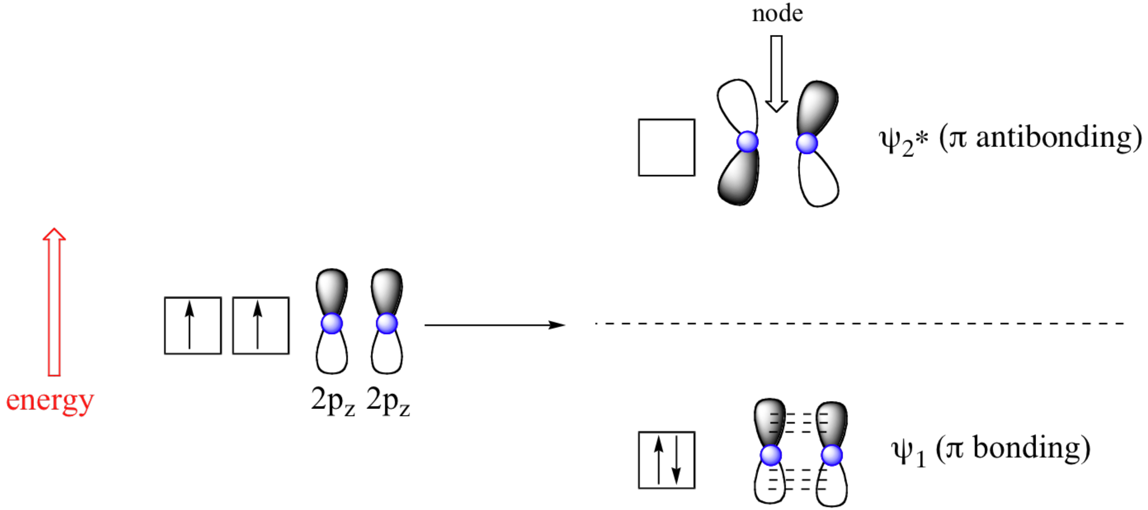
- Sigma bonds (σ) since orbitals are end to end
- Can be bonding or antibonding



chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/mo.html

MO’s arising from p orbitals

- pi bonds (π) since orbitals are parallel
- Can be bonding or antibonding



http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis/Chapter__2%3A_Introduction_to_organic_structure_and_bonding_II/Section_2.1%3A_Molecular_orbital_theory%3A_conjugation_and_aromaticity

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) bonding orbitals and antibonding orbitals

What it means to be non-ideal

- Intermolecular forces between solute and solvent molecules are <u>stronger</u> than other intermolecular forces
  - $\Delta H_3 > \Delta H_1 + \Delta H_2$
  - $\Delta H_{solution} < 0$, $\Delta V_{solution} < 0$
- Intermolecular forces between solute and solvent molecules are <u>weaker</u> than other intermolecular forces
  - $\Delta H_3 < \Delta H_1 + \Delta H_2$
  - $\Delta H_{solution} > 0$, $\Delta V_{solution} > 0$
  - If forces are much weaker, then a solution may not form at all!

Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

The concept of equilibrium

- Chemical reactions often involve a series of processes that may oppose each other.
- At some point the *rate* at which one process takes place will be equal to the *rate* at which another takes place. Thus there is no **net** change in the system, but changes are still happening!
  - Dynamic equilibrium (vs. static equilibrium)
- These reactions are usually indicated with two arrows to imply (microscopic) reversibility

Descriptions of dynamic equilibrium

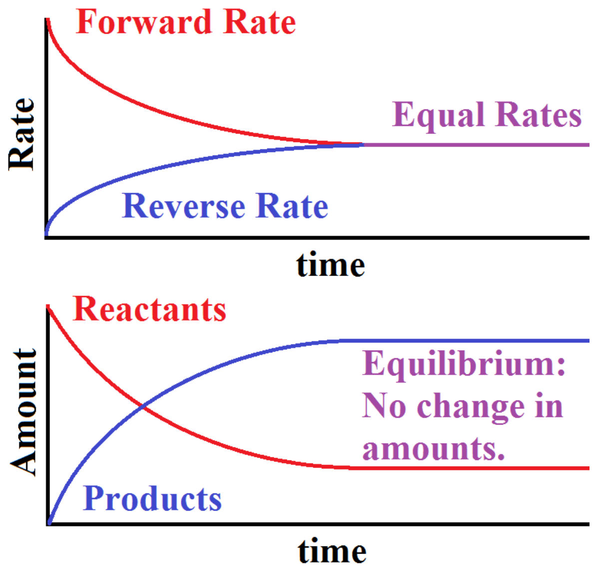
- In general we represent this as

$$\text{Reactants} \rightleftharpoons \text{Products}$$

- Mathematically the reaction rate is related to the rate of change of the concentration of a product or reactant

$$rate = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

- Graphically we can represent the change in reaction rate or amount



http://www.chem.queensu.ca/people/faculty/mombourquette/firstyrchem/equilibrium/

The equilibrium constant

- It turns out that the *ratio* of products to reactants in a reversible reaction is indicative of the state of equilibrium
- For a chemical reaction $aA + bB \rightleftharpoons cC + dD$

  The equilibrium constant K (K_{eq}, K_c) is defined as $K = \frac{a(C)^c a(D)^d}{a(A)^a a(B)^b}$ where a represents the activity. Typically the activities are replaced with concentrations in *M* (this assumes the concentrations are fairly dilute)

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

Notes on the equilibrium constant

- K is meant to give an impression of “how well” a reaction proceeds.
  - Large value of K means the reaction proceeds nearly to completion (products far outweigh reactants)
  - Small value of K means the reaction barely happens at all
- ALL reactions are really reversible, but practically reactions with very large K values ($>10^{10}$) are said to proceed irreversibly
- K is dimensionless because each term is really divided by a reference activity, which is equal to 1.

More notes on the equilibrium constant

- K is a measure of the thermodynamic stability of the products in comparison to the reactants.
- It says NOTHING about the speed of a chemical reaction, just which side (products or reactants) are favored. To understand the effects of concentration on the rates of a reaction, we have to look at kinetics
- Often there is a delicate interplay between kinetics and thermodynamics

Heterogeneous Equilibria

- Often chemical processes occur where various phases are present simultaneously.
- Although the amounts of liquids and solids may change throughout the course of a reaction, typically the activities for PURE liquids and solids are very close to one, which means that the concentration of a solid or liquid is close to one. Thus we ignore it in an equilibrium expression.
- The only quantities that appear in an expression for K are gases and concentrations in a solution.

Le Châtelier’s Principle (1888)

- When a system already at equilibrium is disturbed, the system will respond in such a way as to relieve the stress that was imposed on it.
- The disturbances include varying the concentration, pressure, and temperature.
- *Except for temperature, all disturbances are temporary and the system will revert back to the original equilibrium point!*

Effects of disturbances on the system

- Concentration
  - If the concentration of one of the reactants is increased, then the corresponding reaction quotient will decrease, meaning that the reaction will go forward to try to achieve equilibrium.
  - Conversely, if the concentration of one of the products is decreased (done by removing the product continuously as it is being formed), then Q will still decrease, so the reaction will still go forward!
  - Generally high concentrations of reactants are favored, but this may not be possible (economics, availability, safety, etc.)

Effects of disturbances on the system

- Volume of the container (gases only)
  - For a reaction involving gases, the volume is inversely related to the concentration. Thus decreasing the volume is akin to increasing the concentration, and vice versa.
  - Thus we can treat volume changes in an equivalent fashion to concentration changes.
  - Typically as small a container as possible is best – though this will also mean the pressure will increase… so it must still be safe and able to withstand this!

Effects of disturbances on the system

- Pressure (gases only)
  - Liquids and solids are fairly incompressible so reactions involving these are not typically affected by pressure.
  - If the total pressure is increased by decreasing the volume, then this has already been explained (effect of volume and concentration)
  - If the total pressure is increased by increasing the partial pressure of one of the components, then the reaction will shift in the direction of less moles of gas.
    - Higher P_i means greater number of moles, which need to occupy the same volume as before. The system would prefer to have as few moles as possible in the same volume (since $V \alpha n$) and so will shift to alleviate this stress.
  - If the total pressure is increased by adding an inert gas, then the equilibrium will be unaffected
    - The partial pressures of the components remain unchanged so K_p is the same!

Effects of disturbances on the system

- Catalyst
  - A catalyst helps to accelerate the course of a reaction by providing an alternate pathway. Although the kinetics (rate) of the reaction may be altered drastically, this will have **no effect** on the thermodynamics (stabilities) of the reactants and products (only the intermediates throughout the course of the reaction)

Effects of disturbances on the system

- Temperature
  - The effect of altering the temperature will be based upon the enthalpy change (ΔH) for the reaction.
    - If $\Delta H<0$ then increasing the temperature will cause the reaction to shift to the left
    - If $\Delta H>0$ then increasing the temperature will cause the reaction to shift to the right
  - This is the only factor that will **permanently** affect K since K=K(T)

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

Equilibria can be expressed in different ways

- For gases, sometimes it is more convenient to express quantities in terms of pressures than in terms of concentrations.
- Let K_c be the equilibrium constant for the reaction $aA + bB \rightleftharpoons cC + dD$ (using concentrations) and K_p be the equilibrium constant for the same reaction (using partial pressures).
- It can be shown that $K_p = K_c(RT)^{\Delta n}$ where $\Delta n = n_{gas}(\text{products}) - n_{gas}(\text{reactants})$

Convert the value of K_P to a value of K_c.

(d) $H_2O(l) \rightleftharpoons H_2O(g)$ K_P = 0.122 at 50 °C

Quantitative Aspects of the Equilibrium Constant

- The equilibrium constant is useful because it establishes a relationship between the initial concentrations and equilibrium ("final") concentrations of chemical species in a chemical reaction
- Fundamentally this approach can be used for ANY equilibrium process
  - Homogeneous/Heterogeneous reaction
  - Acid-Base
  - Solubility
  - Complexation

Quantitative Aspects of the Equilibrium Constant

- The key to all these problems is to set up a systematic relationship between the concentrations of all the reactants and products.
- This is most easily done using the "ICE" box.

$$aA + bB \rightleftharpoons cC + dD$$

Initial	A_o	B_o	C_o	D_o
Change	-ax	-bx	+cx	+dx
Equilibrium	A_o-ax	B_o-bx	C_o+cx	D_o+dx

$$K = \frac{[C_0 + cx]^c [D_0 + dx]^d}{[A_0 - ax]^a [B_0 - bx]^b}$$

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures:

$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

A Chemist's View of the Universe

- System – what we care about
- Surroundings – everything else
- Boundary – separates system from surroundings

Some basic definitions

- Work – motion against an opposing (external) force
- Heat – energy change associated with a change in temperature
  - *Exothermic* – releases heat to the surroundings
  - *Endothermic* – absorbs heat from the surroundings

Internal Energy (U or E)

- Total energy of the system (kinetic and potential)
- Internal energy is a state function, which means we can define a change in it as $\Delta U = U_f - U_i$.

Enthalpy (H)

- Total potential energy of the system
- Enthalpy is a state function, which means we can define a change in it as $\Delta H = H_f - H_i$.

1st Law of Thermodynamics

- The internal energy of an isolated system is constant.
- The only ways to change the internal energy of a system are heat and work
  - $\Delta U = Q + W$
- The change in internal energy for a system is equal and opposite to the change in internal energy for the surroundings
  - $\Delta U_{sys} + \Delta U_{surr} = \Delta U_{tot} = 0$

1^{st} Law of Thermodynamics

- “Greedy” convention (Ch and ChE’s)
  - Heat *absorbed* by system → $Q>0$
  - Heat *released* by system → $Q<0$
  - Work *done to* system → $W>0$
  - Work *done by* system → $W<0$

Hess's Law

- Direct application of the properties of state functions.
- The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided. (whether they are real or not)
- This can be extended to ANY thermodynamic variable

Phase Changes (Transitions)

- Any change of phase will have a corresponding change in enthalpy
- Because enthalpy is a state function, several useful properties emerge.
- Consider a change of phase (or state) from A to B with a change of enthalpy = ΔH. For the reverse process (going from B to A), the change in enthalpy will be $-\Delta H$.
- Consider a change from A to C. We can consider this as happening in two steps: first from A to B and then from B to C. Thus $\Delta H_{A \rightarrow C} = \Delta H_{A \rightarrow B} + \Delta H_{B \rightarrow C}$

Enthalpies of reaction

- A similar type of analysis can be performed for a chemical reaction. We can define the standard reaction enthalpy as the change in enthalpy between the products and the reactants, in the standard state:

$$\Delta H_{rxn}{}^{o} = \sum_{products} \nu_i H_{m,i}{}^{o} - \sum_{reactants} \nu_i H_{m,i}{}^{o}$$

where ν_i refers to the stoichiometric coefficient of species i, and $H_{m,i}$ refers to the molar enthalpy of species i (aka enthalpy of formation). The ^{o} indicates standard state.

The 2nd Law of Thermodynamics

- Used to predict spontaneity (tendency for a process to happen naturally)
- The 1st Law only talks about conservation of energy, it says **nothing** about the *direction* that a process will tend to go in!
  - Why don't balls leave the ground and bounce up?
  - Why doesn't shattered glass reform?
  - Why doesn't green pigment separate into blue and yellow pigments?

The 2nd Law of Thermodynamics

- The 2nd Law describes how spontaneity is related to the *distribution* of energy, **not** to the *total* energy.
- Energy tends to flow in a direction where it will be more “spread out”, or dispersed.

So What's Entropy?

- This leads to another view of the 2nd law: "The entropy of an isolated system increases in the course of a spontaneous change"
  - $\Delta S_{tot}>0$
- Related to chaos, randomness, disorder
- Notice that Q is not a state function but S is!

Phase transitions

- Previously we saw that for a phase transition occurring at a constant pressure, $Q=\Delta H_{tr}$
- This means that we can also calculate ΔS_{tr}:

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$

where T_{tr} is the temperature at which the transition occurs

Thus exothermic processes (freezing, condensing) have (-) changes in entropy, while endothermic processes (melting, boiling) have (+) changes in entropy

How is entropy measured?

- In an analogous fashion to enthalpy, we can define the reaction entropy change as:

$$\Delta S_{rxn}{}^{o} = \sum_{products} \nu_i S_{m,i}{}^{o} - \sum_{reactants} \nu_i S_{m,i}{}^{o}$$

- Note that unlike $H_m{}^o$, which can = 0 for substances in their standard state, $S_m{}^o$ is ≠ 0 (unless T=0)

Gibbs free energy

- let's define the Gibbs free energy as $G=H-TS$.
- For a macroscopic change, $\Delta G = \Delta H - T\Delta S$
- This also leads to the familiar conclusion that for a spontaneous process $\Delta G \leq 0$
- ΔG also represents the *maximum non-PV work* that can be done by a system

How can ΔG be measured?

- As for the other thermodynamic quantities we have encountered, we can define the standard free energy change for a reaction as:

$$\Delta G_{rxn}{}^{o} = \sum_{products} v_i G_{m,i}{}^{o} - \sum_{reactants} v_i G_{m,i}{}^{o}$$

- As with enthalpy of formation, $\Delta G_f{}^o$ for an element (or a naturally occurring diatomic molecule) = 0.
- Experimentally ΔG is often obtained by determining ΔH and ΔS separately.

Gibbs energy and the equilibrium constant

- What does ΔG_{rxn}^{o} represent? It is the difference in the (molar) Gibbs energies of products and reactants, in their standard state.

  $\Delta G_{rxn}^{o} = -RT \ln K$ is the crucial link between thermodynamics (energy) and chemical equilibrium

- Notice that if K>1 then the products are favored at equilibrium, while if K<1 then the reactants are favored.
- In general, where Q is the reaction quotient

$$\Delta G_{rxn} = \Delta G_{rxn}^{o} + RT \ln Q$$

Calculate $\Delta H°_{298}$ for the process $Sb(s) + 5/2\ Cl_2(g) \longrightarrow SbCl_5(g)$ from the following information:

$Sb(s) + 3/2Cl_2(g) \longrightarrow SbCl_3(g)$

$\Delta H°_{298} = -314$ kJ

$SbCl_3(s) + Cl_2(g) \longrightarrow SbCl_5(g)$

$\Delta H°_{298} = -80$ kJ

Calorimetry – it's da bomb!

- Experiments may be done at constant volume (bomb) or constant pressure (coffee-cup)
- Entire system is *adiabatic* – there is no heat lost between the system (sample) and the surroundings (water bath and metal casing)
- The change in temperature of the calorimeter will be proportional to the heat that it absorbs: $Q \propto \Delta T$, or $Q = C\Delta T$, where C is the heat capacity of the calorimeter.

Example

- In a preliminary experiment, the heat capacity of a bomb calorimeter assembly is found to be 5.15 kJ/^oC. In a second experiment, a 0.480 g sample of graphite (carbon) is placed in the bomb with an excess of oxygen. The water, bomb, and other contents of the calorimeter are in thermal equilibrium at 25.00 ^oC. The graphite is ignited and burned, and the water temperature rises to 28.05 ^oC. Calculate ΔH for the reaction: C (graphite) + O_2 (g) $\rightarrow$ CO_2 (g)

Solution

- The key to this problem is to realize that all the heat absorbed by the calorimeter must have come from the combustion reaction.
- First calculate the heat absorbed by the calorimeter using Q = CΔT:

$$Q_{cal} = 5.15\ \frac{kJ}{°C} * (28.05 - 25.00\ °C) = 15.7\ kJ$$

- The heat given up by the reaction must be equal and opposite to this: Q_{rxn} = -15.7 kJ

- We can then equate this to ΔU for the combustion of 1 mol of graphite:

$$\Delta U = \frac{-15.7\ kJ}{0.480\ g\ C} * \left(\frac{12.011\ g\ C}{1\ mol}\right) = -393\ kJ/mol$$

- Finally, recall that $\Delta H = \Delta U + RT\Delta n$ for an isothermal process. Since the temperature change is pretty small (3.05 ^oC) we can assume that it is isothermal. $\Delta n = (1-1) = 0$ so $\Delta H \approx \Delta U$. Thus $\Delta H = -393$ kJ/mol

Calorimetry revisited – that's one fancy coffee cup!

- For isobaric measurements, use a thermally insulated vessel that is open to the atmosphere
- More sophisticated calorimeters can be used
  - Adiabatic flame combustion
  - Differential scanning
  - Isothermal titration
- For solids and liquids, $\Delta H \approx \Delta U$ since their volume is negligible (at least compared to gases)

Example

- A 15.5 g sample of a metal alloy is heated to 98.9 ^{o}C and then dropped into 25.0 g of water in a calorimeter. The temperature of the water rises from 22.5 to 25.7 ^{o}C. Calculate the specific heat of the alloy.

Solution

- The key to solving this problem is to realize that all the heat lost by the hot solid must be gained by the water in the cup.
- First we will find the heat absorbed by the water: $Q_{H2O} = mc\Delta T$ so

$$Q_{H_2O} = 25.0g * 4.184\ \frac{J}{g\ °C} * (25.7 - 22.5\ °C) = 334\ J$$

- This must be equal and opposite to the heat lost by the alloy (remember the sign convention!) so Q_{alloy} = -334 J
- Finally calculate the specific heat of the alloy:

$$c = \frac{Q}{m\Delta T} = \frac{-334\,J}{15.5g * (25.7 - 98.9\,°C)} = 0.29\,\frac{J}{g\,°C}$$

Example

- A 50.0 mL sample of 0.250M HCl at 19.50 ^{o}C is added to 50.0 mL of 0.250M $NaOH$, also at 19.50 ^{o}C, in a calorimeter. After mixing, the solution temperature rises to 21.21 ^{o}C. Calculate the heat of this reaction.

Solution

- First recognize the reaction that is taking place: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$
- Now let's make a few assumptions/simplifications:
  - Take solution volumes to be additive so the total volume of solution is 50.0+50.0 = 100.0 mL
  - Consider the NaCl(aq) solution to be sufficiently dilute that the density and specific heat are the same as those for pure water (1.00 g/mL and 4.184 J/g^{o}C)
  - The system is perfectly insulated, so no heat escapes from the calorimeter
  - The heat required to warm any part of the calorimeter (other than the NaCl solution) is negligible)

- Find the heat retained in the calorimeter:

$$Q = mc\Delta T = \rho V c\Delta T = 100.0mL * 1.00\frac{g}{mL} * 4.184\frac{J}{g°C} * (21.21 - 19.50\ °C) = 715\ J$$

- Finally find the heat of reaction: $Q_{rxn} = Q_p = -Q_{cal} = -715$ J

Chemical Kinetics

- Study of the rates of chemical reactions
  - How quickly a process can take place
- Understanding of the mechanism of a reaction
  - How (on a molecular level) a process can take place
- Because these measurements are changing with respect to time and are sensitive to many variables, they are notoriously difficult experiments to carry out!

Factors affecting the rate of a chemical reaction

- Concentration
- Pressure (gases only)
- Temperature
- Presence of a catalyst
- Understanding the dependence of a reaction on these factors can aid our optimization of a chemical process

Measuring the rate of a reaction

- We can define the rate in terms of the loss of a reactant or the formation of a product:

$$v = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

  – Notice that this means the rate is related to the slope (tangent line) to the curve

- However this doesn't take into account the stoichiometry of the reaction (i.e. if the reaction is R→2P the rate of formation of a product will be twice as great as the loss of reactant).
- In terms of a given component i, $v = \frac{1}{\nu_i}\frac{d[i]}{dt}$ where ν_i is the stoichiometric number.

In pictures

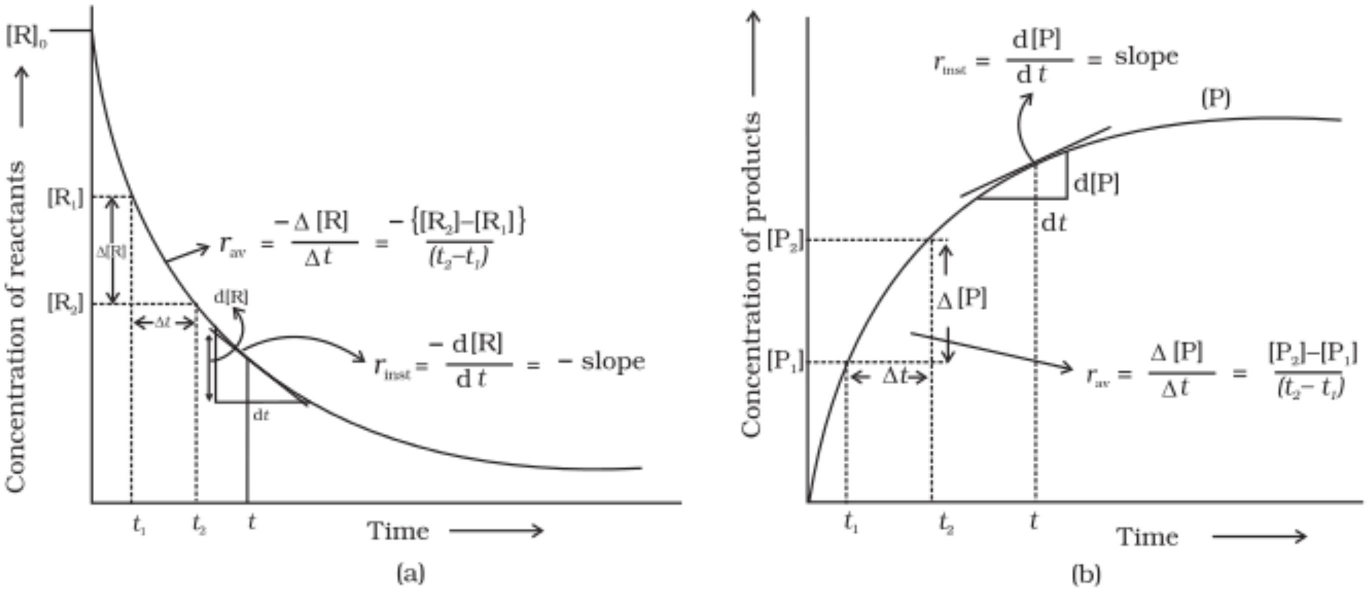


Fig. 4.1: *Instantaneous and average rate of a reaction*

http://textbook.s-anand.net/ncert/class-xii/chemistry/4-chemical-kinetics

Rate laws

- It is found experimentally that the rate of a reaction is usually proportional to the concentration of each reactant, raised to a certain power: $v = k[A]^x[B]^y$

  where x and y are the orders of the reaction with respect to A and B, respectively. The orders may be any real number (including 0 and fractions). The overall order is given by x+y.
- In general the orders must be determined experimentally and are NOT necessarily the stoichiometric coefficients of the reaction (unless the reaction is elementary).

Determination of the rate law for a reaction

- Isolation method – systematically vary the concentrations of the reactants so that all are in a large excess except for one. This allows the determination of the order of that one species.
- For example, if the general rate law is $v = k[A]^x[B]^y$ and B is present in a large excess, then its concentration can be assumed to be constant as the reaction proceeds, which means that d[B]/dt→0. Thus we can write the rate law as $v = k'[A]^x$ where $k' = k[B]^y$ and we can find the values of k' and x by curve-fitting.

Determination of the rate law for a reaction

- Typically the *initial* rates are measured. For example if B is in excess then the initial rate can be written as

$$v_o = k'[A]_o^{\,x}$$

- Thus we can plot v_o vs. $[A]_o$ and get k' and x by fitting the data nonlinearly (power law), or we can linearize the equation by taking the log of both sides:

$$\log v_o = \log k' + x \log[A]_o$$

- We can repeat this process where A is held in excess, and determine a new pseudo-rate constant k'' ($k'' = k[A]^x$) and y, and therefore also get the original rate constant k.

Example

- The recombination of iodine atoms in the gas phase in the presence of argon was investigated and the order of the reaction was determined by the method of initial rates. The initial rates of the reaction $2I(g)+Ar(g) \rightarrow I_2(g)+Ar(g)$ were as follows:

$[I]_o$ (10^{-5} mol/L)	**1.0**	**2.0**	**4.0**	**6.0**
v_o (mol/L*s)	a) 8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	b) 4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	c) 8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

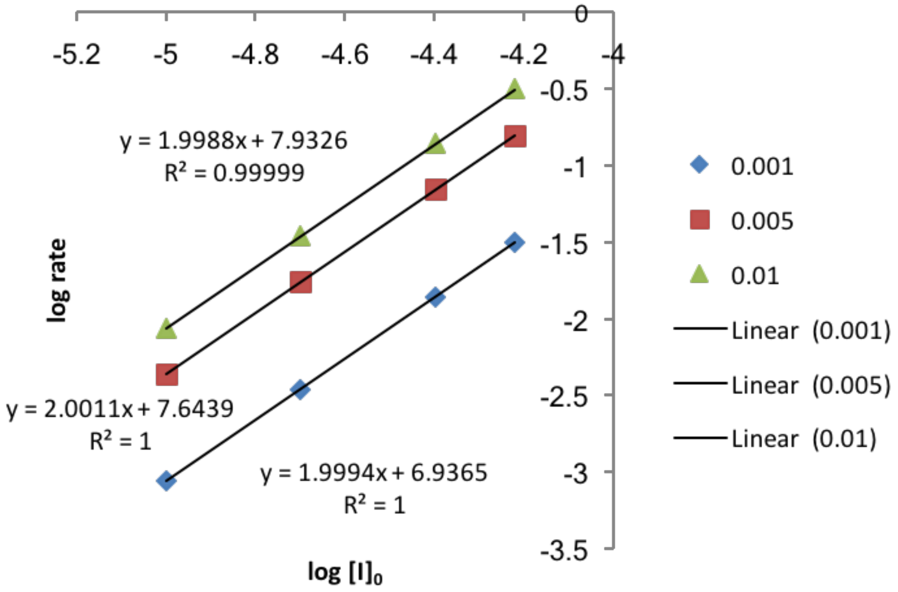
Example

- The Ar concentrations are a)1.0 mmol/L, b) 5.0 mmol/L and c) 10.0 mmol/L. Determine the orders of reaction with respect to the I and Ar atom concentrations and the rate constant.

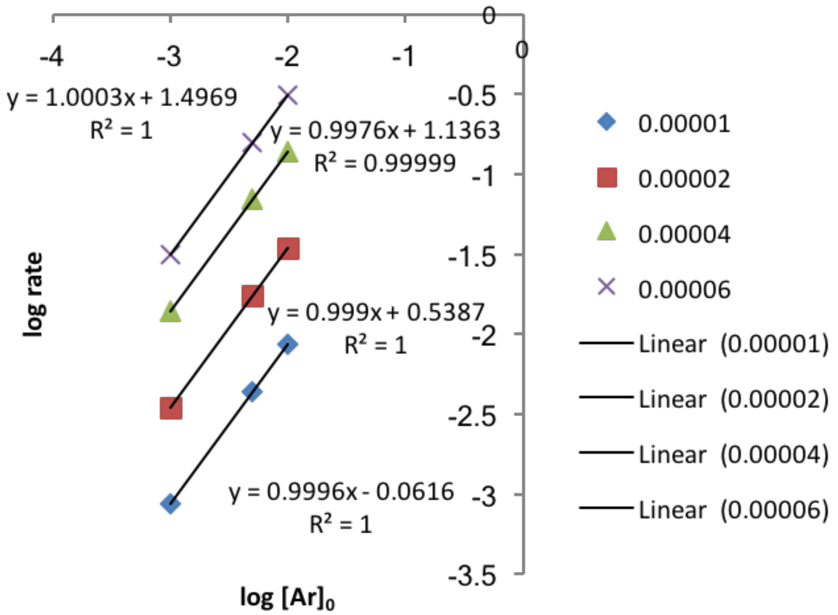
Solution

- Since the rate law will be of the form $v_o = k[I]_o{}^x[Ar]_o{}^y$, we need to plot the dependence of the rate on both $[I]_o$ and $[Ar]_o$. A log-log plot will be helpful as the slope will give us the order with respect to that substance.

Determination of Order With Respect to I At Various [Ar]



Determination of Order With Respect to Ar At Various [I]



Solution

- From the first graph, the slope is 2 which means that the reaction is 2nd order with respect to I. From the second graph, the slope is 1 which means that the reaction is 1st order with respect to Ar. Thus the rate law is
$$v_o = k[I]_o^{\,2}[Ar]_o$$
- Notice that this is the rate law only for the *initial rate* – it is possible that the reaction has a different rate law as the reaction proceeds.

Solution

- We can get the rate constant from the intercepts of either set of lines. In the first experiment, k' = k$[Ar]_0$. In the second experiment, k''=k$[I]_0^2$. In either case, k≈8.6*10^9 L^2/mol^2s.

log k'	k'	$[Ar]_0$	k
6.9365	8639727	0.001	8639726607
7.6439	44045343	0.005	8809068674
7.9326	85624885	0.01	8562488476

log k''	k''	$[I]_0$	k
-0.0616	0.867761	0.00001	8677607450
0.5387	3.457005	0.00002	8642512347
1.1363	13.68674	0.00004	8554212160
1.4969	31.39786	0.00006	8721626801

How will each of the following affect the rate of the reaction: $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is rate = $k\,[NO_2]\,[CO]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm

(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

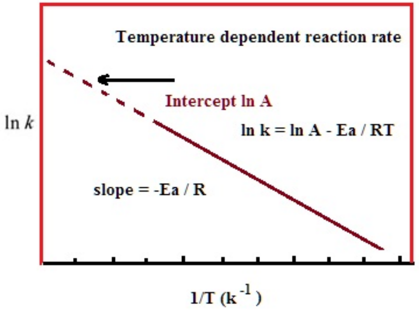
The Arrhenius equation

- A plot of ln k vs 1/T should give a straight line, with a slope of E_a/R and an intercept of ln A:

$$\ln k = \ln A - \frac{E_a}{RT}$$

- As T→∞, k→k_o (or A), which is called the *frequency factor*. It is also called the pre-exponential factor since the above equation can be written as

$$k = Ae^{-E_a/RT}$$



http://chemistry.tutorvista.com/inorganic-chemistry/arrhenius-equation.html

More on the Arrhenius equation

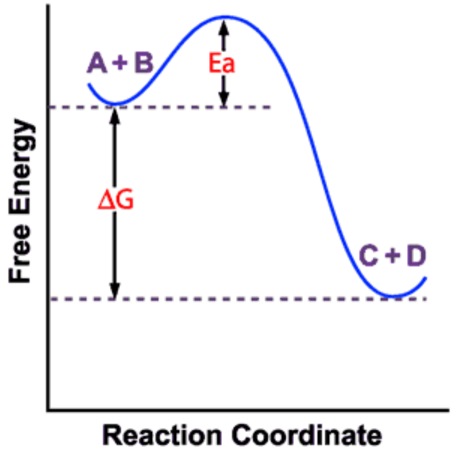
- The pre-exponential factor A represents the fastest possible rate for a reaction, which would only be limited by diffusion. This can be interpreted as being related to the rate of successful collisions between reactant molecules to yield product molecules.
- Notice that the fraction of molecules with an energy greater than E_a is given by an exponential decay, known as a Boltzmann distribution. Only those molecules with an energy that exceeds the activation energy will be able to react to form products.
- The higher the activation energy, the more the rate constant will depend on T.

Temperature dependence of the reaction rate

Arrhenius equation

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

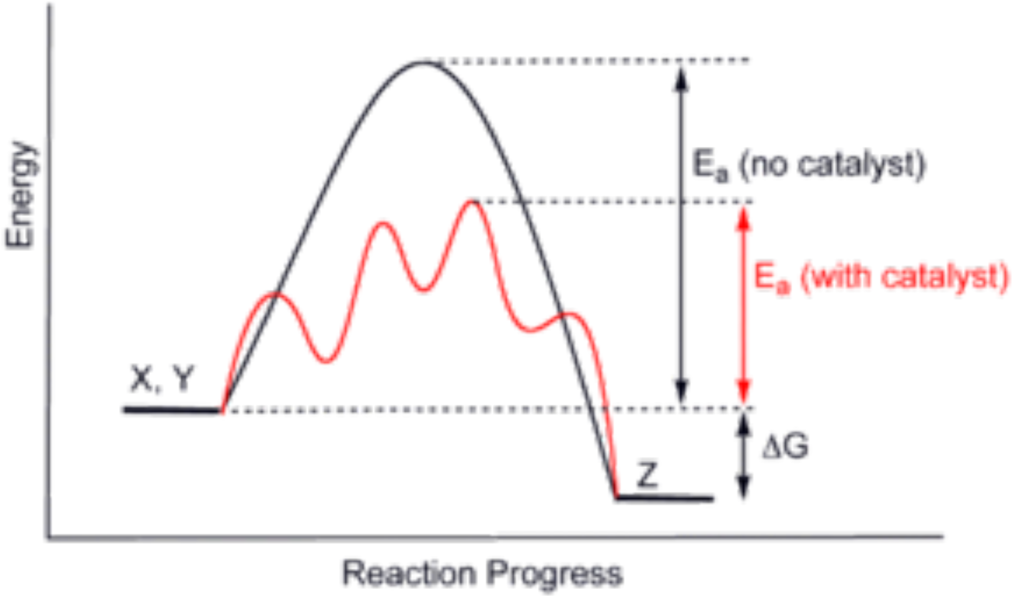
E_a is the activation energy of the reaction.

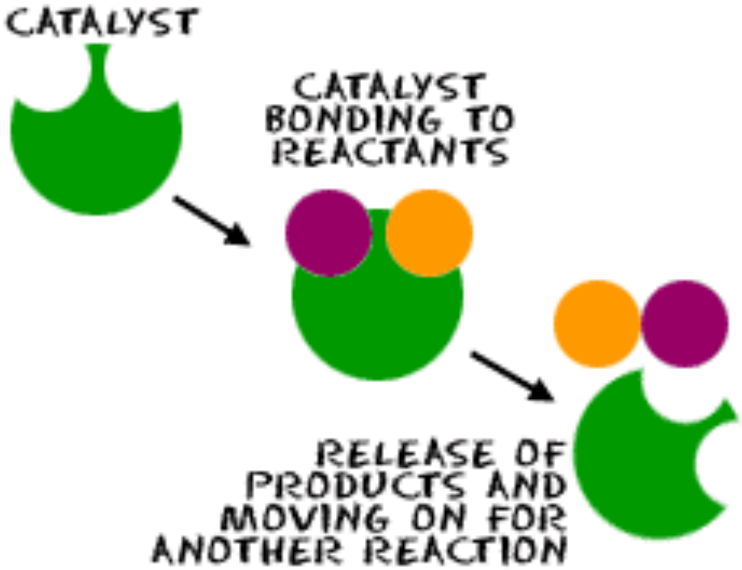


http://www.wiley.com/college/boyer/0470003790/reviews/kinetics/kinetics_stability.htm

Role of a catalyst

- Accelerate the rate of a reaction
  - Lower activation energy
  - Provide alternate path
- Does not change the thermodynamics or equilibrium of a reaction
  - ΔG, ΔH, ΔS and K are all the same as for the uncatalyzed reaction


Energy
E_a (no catalyst)
E_a (with catalyst)
X, Y
ΔG
Z
Reaction Progress


CATALYST
CATALYST BONDING TO REACTANTS
RELEASE OF PRODUCTS AND MOVING ON FOR ANOTHER REACTION

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Theoretical description of the rate laws

- Although the parameters for a rate law are experimentally determined, it is sometimes possible to calculate (or predict) them from first principles. This requires a knowledge of the way in which the reaction takes place, also known as the mechanism.
- Most reactions are thought to occur in a series of (relatively) well understood steps, each of which is known as an elementary reaction.
- In an elementary reaction, typically a small number (1-3) atoms, molecules or ions collide with each other and form a product.

Theoretical description of the rate laws

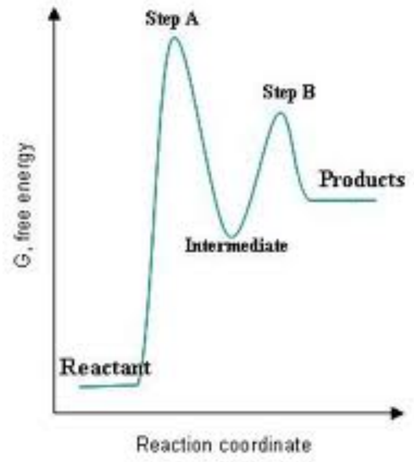
- Molecularity – the number of molecules (or atoms or ions) that come together in an elementary reaction
  - *Unimolecular*- one particle breaks apart or rearranges, i.e. dissociation or isomerization
  - *Bimolecular*- two particles collide with each other
  - *Termolecular* (rare)-three particles *simultaneously* collide with each other

Theoretical description of the rate laws

- Because elementary reactions are of a known molecularity, we can write down the rate laws for them simply by looking at how many species are present:
  - $A \rightarrow P$ $v=k[A]$
  - $A+B \rightarrow P$ $v=k[A][B]$
- A <u>mechanism</u> is a combination of elementary reactions that tries to explain the sequence of events (steps) of a chemical reaction

Rate-determining step

- The rate-determining step is the slowest "relevant" step in a chemical reaction, and determines the overall rate of the reaction. It also dictates how much product can be formed.
- Typically the slowest step in a chemical reaction has the highest activation energy since $k = Ae^{-E_a/RT}$
- In the diagram on the right, the local minima correspond to *intermediates* – this means that they can be (theoretically) isolated.
- The maxima correspond to *transition states* – they are very unstable and not isolable



http://chemwiki.ucdavis.edu/Wikitexts/UC_Davis/UCD_Chem_2C%3A_Larsen/Chem_2C%3A_Homework/Team_1/Chapter_24%3A_Kinetics

Equilibrium of Brønsted-Lowry reactions

- Acids $HA + H_2O \rightleftharpoons A^- + H_3O^+$ $K_a = \frac{[H^+][A^-]}{[HA]}$

- Bases $B + H_2O \rightleftharpoons BH^+ + OH^-$ $K_b = \frac{[BH^+][OH^-]}{[B]}$

- There is an inverse relationship between the strength of an acid (base) and its conjugate base (acid)
- Chemical reactions *always* proceed from a stronger acid (base) to a weaker acid (base).

Quantification of Acid/Base Strength

- Typically equilibrium constants vary dramatically (from <10^{-10} to >10^{10})
- Chemists thus look at the logarithms

$$pH = -\log[H^+] \qquad pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

  - Note that pH is not the same as pK_a!

	Acid	Approximate pK_a	Conjugate Base	
Strongest Acid	HSbF6	< - 12	SbF_6	Weakest Base
	HI	- 10	I^-	
	H_2SO_4	- 9	HSO_4	
	HBr	- 9	Br^-	
	HCl	- 7	Cl^-	
	$C_6H_3SO_3H$	- 6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	- 3.8	$(CH_3)_2O$	
	$(CH_3)_2C{=}\overset{+}{O}H$	- 2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	- 2.5	CH_3OH	
	H_3O^+	- 1.74	H_2O	
	HNO_3	- 1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF3CO_2^-$	
	HF	3.2	F^-	
	H_2CO_3	3.7	HCO_3^-	
Increasing acid strength	CH_3CO_2H	4.75	CH_3CO_2	Increasing Base strength
	$CH_3COCH_2COCH_3$	9.0	$CH_3CO\overset{-}{C}HCOCH_3$	
	NH_4+	9.2	NH_3	
	C_6H_5OH	9.9	$C_6H_5O^-$	
	HCO_3^-	10.2	$CO_3{}^{2-}$	
	CH_3NH_3+	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest Acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest Base

http://www.wonderwhizkids.com/popups/13040.html

Equilibrium calculations involving acids and bases

- Typically calculations involve weak acids or bases, as well as dilute solutions
- This means that the degree of dissociation x (how many ions are formed) will be small
- Rule of thumb: x will be small if $[HA]/K_a > 100$ for acids, or if $[B]/K_b > 100$ for bases

Example

- Calculate the pH of a 1.00M solution of acetic acid (CH_3COOH) given a K_a of $1.8X10^{-5}$.

Solution

- Although it may not seem obvious at first, there are really two (competing) acid-base reactions here because there are two components in the mixture – acetic acid and water. To decide which one will dominate, we need to look at the K_a's.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad K_a = 1.8X10^{-5}$$

$$H_2O + H_2O \rightleftharpoons HO^- + H_3O^+ \qquad K_w = 1.0X10^{-14}$$

- Because K_a is so much larger than K_w, we can ignore the small amount of H_3O^+ generated by the autoionization of water.

Solution

- Set up the ICE box for the reaction

	CH_3COOH	H_2O	H_3O^+	CH_3COO^-
Initial	1.00		0 (10^{-7})	0
Change	-x		x	x
Equilibrium	1.00-x		x	x

- Set up the expression for K_a and substitute the appropriate values

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

$$1.8X10^{-5} = \frac{x^2}{1.00 - x}$$

Solution

- This is a quadratic equation that must be solved for x. To simplify matters, invoke the "5% rule"
- $[CH_3COOH]/K_a = 1.00/1.8X10^{-5} > 100$ so we are justified in considering x to be a small number.
  - Therefore $1-x \approx 1$
- This simplifies the equation to $1.8X10^{-5} = \frac{x^2}{1.00}$ and so $x = 4.2*10^{-3}$ M.
- Since $x = [H_3O^+]$, $pH = -\log[H_3O^+] = 2.38$

Example

- The pH of a 0.164M aqueous solution of dimethylamine is 11.98. What are the values of K_b and pK_b? The ionization equation is

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$$

Solution

- In this problem we have to work backwards – we are not given the equilibrium constant but instead are indirectly told the final concentrations of all the species present at equilibrium.
- The expression for K_b will be:

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

- Since we are told the pH we can find $[OH^-]$.
  – pH = 11.98 so pOH = 14-11.98 = 2.02 and $[OH^-] = 10^{-2.02} = 9.5*10^{-3}$ M.

Solution

- By stoichiometry (or by setting up an ICE box) $[(CH_3)_2NH_2^+] = [OH^-] = 9.5*10^{-3}$ M
- Also, $[(CH_3)_2NH]$ at equilibrium will equal the initial concentration minus the amount that dissociates (x): $[(CH_3)_2NH] = 0.164 - 9.5*10^{-3}$ M = 0.1545.
- Thus by substituting into the expression for K_b, $K_b = 5.8*10^{-4}$ and $pK_b = -\log K_b = 3.24$

Theoretical description of the rate laws

- Although the parameters for a rate law are experimentally determined, it is sometimes possible to calculate (or predict) them from first principles. This requires a knowledge of the way in which the reaction takes place, also known as the mechanism.

Theoretical description of the rate laws

- Most reactions are thought to occur in a series of (relatively) well understood steps, each of which is known as an <u>elementary reaction</u>.
- In an elementary reaction, typically a small number (1-3) atoms, molecules or ions collide with each other and form a product.

Theoretical description of the rate laws

- Molecularity – the number of molecules (or atoms or ions) that come together in an elementary reaction
- Unimolecular- one particle breaks apart or rearranges, i.e. dissociation or isomerization
- Bimolecular- two particles collide with each other
- Termolecular (rare)-three particles simultaneously collide with each other

Theoretical description of the rate laws

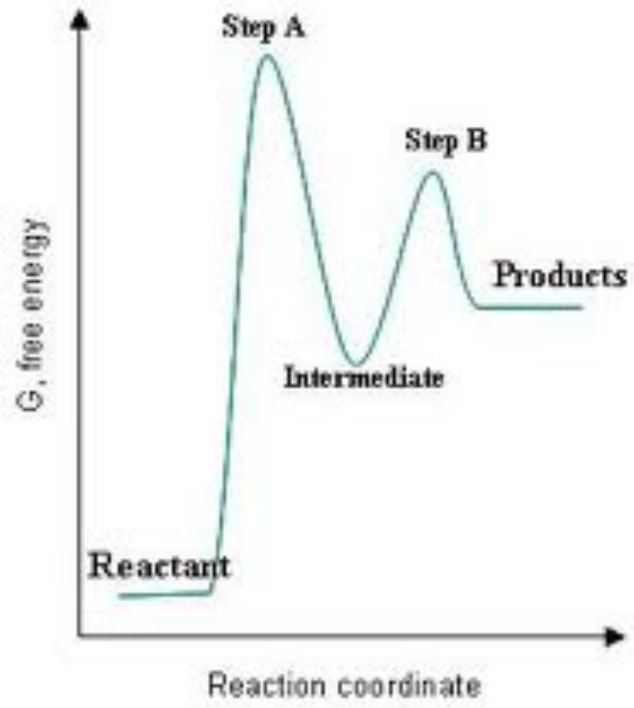
- Because elementary reactions are of a known molecularity, we can write down the rate laws for them simply by looking at how many species are present:
  - $A \rightarrow P$ $v=k[A]$
  - $A+B \rightarrow P$ $v=k[A][B]$
- A <u>mechanism</u> is a combination of elementary reactions that tries to explain the sequence of events (steps) of a chemical reaction

Rate-determining step

- The rate-determining step is the slowest "relevant" step in a chemical reaction, and determines the overall rate of the reaction. It also dictates how much product can be formed.
- Typically the slowest step in a chemical reaction has the highest activation energy since
- In the diagram on the right, the local minima correspond to *intermediates* – this means that they can be (theoretically) isolated.
- The maxima correspond to *transition states* – they are very unstable and not isolable

Rate-determining step

$$k = Ae^{-E_a/RT}$$



Deriving a rate law

- It is often possible to come up with a theoretical rate law, given a mechanism for a reaction (series of elementary reactions), though it might be necessary to invoke steady-state approximations or equilibrium conditions.

Deriving a rate law

- If the mechanism is correct, the rate law should “match” the experimentally determined rate law. However, it is IMPOSSIBLE to prove that the mechanism is correct! All we can say is that the mechanism is consistent with the given data. It is always possible that a different mechanism will also give a result that agrees with the experiment. This is the reason why mechanistic studies are so difficult!

A more complex mechanism

- Now let's consider a reaction where A and B react together, and form an intermediate I, which can then form product P. Furthermore let's assume that the 1st step is in equilibrium: $A{+}B \rightleftharpoons I \longrightarrow P$

- This is sometimes called a *pre-equilibrium*, because we have to establish equilibrium first between reactants and products before the product can form. It is only possible when the last step (product formation) is the slow step.

A more complex mechanism

- If the forward rate for the 1st step has rate constant k_a, the reverse rate has rate constant k_a' and the 2nd step has rate constant k_b, we can say that pre-equilibrium will exist when $k_a' >> k_b$.
- We can write down the equilibrium in terms of either the concentrations of A, B and I or in terms of the rate constants:

$$K = \frac{[I]}{[A][B]} = \frac{k_\alpha}{k_\alpha{}'}$$

A more complex mechanism

- The rate of formation of P will be $\frac{d[P]}{dt} = k_b[I]$
- Using the relationship above we can solve for [I] and express this in terms of more easily measurable quantities (A and B):

$$\frac{d[P]}{dt} = k_b K[A][B] = \frac{k_a k_b}{k_a{}'}[A][B]$$

- Thus we expect a 2nd order reaction overall, with $k = \frac{k_a k_b}{k_a{}'}$

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).

How many grams of $Zn(CN)_2$(*s*) (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2$(*s*) is 3.0×10^{-16}.

Solubility (an equilibrium perspective)

- Solubility product (K_{sp}) – related to the concentrations of the ions involved in a solubility equilibrium (raised to the stoichiometric coefficient)

  $K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2 = 1.0*10^{-25}$

  $$Mg_3(PO_4)_2\ (s) \rightleftharpoons 3\ Mg^{2+}\ (aq) + 2\ PO_4^{3-}\ (aq)$$

- K_{sp} is a function of temperature (like all equilibrium constants)

(Incomplete) Table of K_{sp} values

Name	Formula	K_{sp}
Barium carbonate	$BaCO_3$	2.6×10^{-9}
Barium chromate	$BaCrO_4$	1.2×10^{-10}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Calcium carbonate	$CaCO_3$	5.0×10^{-9}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}
Calcium sulphate	$CaSO_4$	7.1×10^{-5}
Copper(I) iodide	CuI	1.3×10^{-12}
Copper(II) iodate	$Cu(IO_3)_2$	6.9×10^{-8}
Copper(II) sulphide	CuS	6.0×10^{-37}
Iron(II) hydroxide	$Fe(OH)_2$	4.9×10^{-17}
Iron(II) sulphide	FeS	6.0×10^{-19}
Iron(III) hydroxide	$Fe(OH)_3$	2.6×10^{-39}
Lead(II) bromide	$PbBr_2$	6.6×10^{-6}
Lead(II) chloride	$PbCl_2$	1.2×10^{-5}
Lead(II) iodate	$Pb(IO_3)_2$	3.7×10^{-13}
Lead(II) iodide	PbI_2	8.5×10^{-9}
Lead(II) sulphate	$PbSO_4$	1.8×10^{-8}
Magnesium carbonate	$MgCO_3$	6.8×10^{-6}
Magnesium hydroxide	$Mg(OH)_2$	5.6×10^{-12}
Silver bromate	$AgBrO_3$	5.3×10^{-5}
Silver bromide	AgBr	5.4×10^{-13}
Silver carbonate	Ag_2CO_3	8.5×10^{-12}
Silver chloride	AgCl	1.8×10^{-10}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver iodate	$AgIO_3$	3.2×10^{-8}
Silver iodide	AgI	8.5×10^{-17}
Strontium carbonate	$SrCO_3$	5.6×10^{-10}
Strontium fluoride	SrF_2	4.3×10^{-9}
Strontium sulphate	$SrSO_4$	3.4×10^{-7}
Zinc sulphide	ZnS	2.0×10^{-25}

- Notice that most values are very small!

http://www.highschool247.com/chem12/solubility/unit4notes.html

Acids and Bases – An Overview

- Arrhenius (1887)
  - Acid = H^+ donor
  - Base = OH^- donor
- Brønsted-Lowry (1923)
  - Acid = H^+ donor
  - Base = H^+ acceptor
- Lewis (1923)
  - Acid = e^- acceptor
  - Base = e^- donor

Arrhenius Theory

- Simplest definition
  - Still commonly used
- Only works for aqueous solutions
- Only works for substances that can generate H^+ (H_3O^+) and OH^- ions
- Based on dissociation
  - Can be used to quantify the *strength* of an acid or base

Brønsted-Lowry

- Equilibrium reactions
  - Acid $HA + H_2O \rightleftharpoons A^- + H_3O^+$
  - Base $B + H_2O \rightleftharpoons BH^+ + OH^-$
- Conjugates
  - Acid and base for reverse reaction
- Conjugate pairs always differ by a single H^+

Brønsted-Lowry

- Amphoterism
  - A substance can sometimes act as either an acid or a base (amphiprotic)

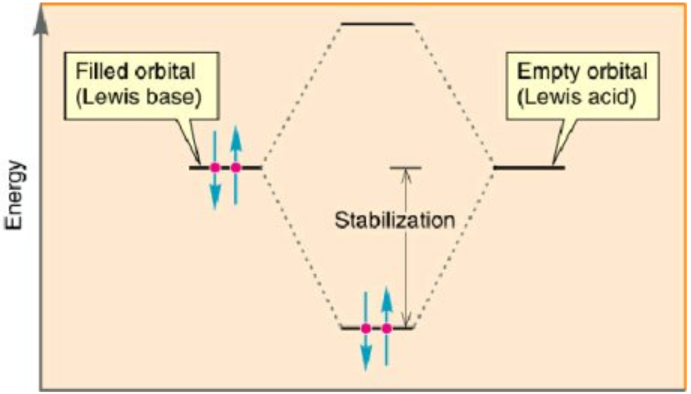
$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

- How do we know which one will happen?
  - Based on *relative strengths* of acids and bases
  - Reactions always go (spontaneously) in the direction of weaker acids/bases

Lewis theory – the MO point of view

- A filled orbital is a Lewis base in that it donates electrons to an unfilled (empty) orbital, which is a Lewis acid



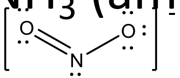
http://chemistry.umeche.maine.edu/CHY252/HOMO-LUMO.html

Basic definitions

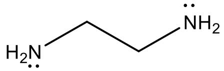
- Complex – central atom surrounded by ligands
  - Complexes may be neutral or charged (ions)
- Ligands may be neutral or charged
  - Ex. $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$
- Coordination number – total number of points that ligands connect to central atom
  - Most common numbers are 2, 4 and 6
  - Shapes are given by VSEPR theory (typically linear, tetrahedral, square planar or octahedral)
- Coordination compound – consists of one or more complexes
  - Ex. $[Co(NH_3)_6]Cl_3$, $[CoCl[NH_3)_5]Cl_2$

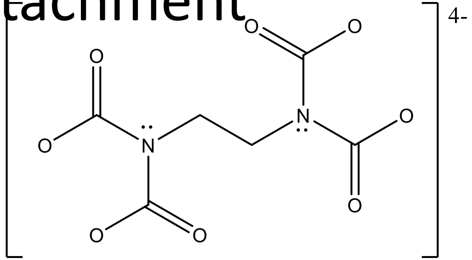
Ligands

- Generally have lone pairs that can be donated to central atom (Lewis acid)
- The donor atom on the ligand contains the lone pair (Lewis base)
  - Ex. Cl^-, OH^- (hydroxo), H_2O (aqua), NH_3 (ammine), NO_2^- (nitrito-N or nitrito-O)



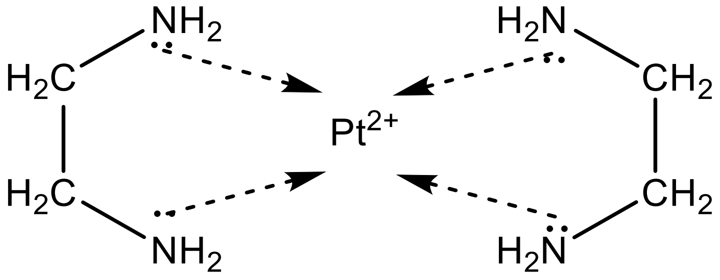
- Ligands can be monodentate, bidentate or polydentate, depending on number of points of attachment
  - Ex. Ethylenediamine (en), EDTA





Chelation

- Complex that forms between ligand and metal ion
  - Ex. $[Pt(en)_2]^{2+}$
  - Square planar geometry



Naming coordination compounds and complex ions

- Name the ligands, followed by the metal
  - Ex. $[Cu(NH_3)_4]^{2+}$ = tetraamminecopper(II) ion
- Name the ligands in alphabetical order (ignoring prefixes), listing anionic ligands before neutral ones
  - Ex. $[CoCl_2(H_2O)_2(NH_3)_2]^+$ = diamminediaquadichlorocobalt(III) ion
- If the ligand contains a prefix already, use a different prefix for how many ligands there are (bis = 2, tris = 3, tetrakis = 4)
  - Ex. $[Pt(en)_2]^{2+}$ = bis(ethylenediamine)platinum(II) ion
- Name complex ions by adding –ate at the end (use Latin names for Cu, Au, Fe, Pb, Ag)
  - Ex. $[CuCl_4]^{2-}$ = tetrachlorocuprate(II) ions
- Common common names – $K_4[Fe(CN)_6]$ = potassium ferrocyanide (has Fe^{2+}) and $K_3[Fe(CN)_6]$ = potassium ferricyanide (has Fe^{3+})

Common-ion Effect?

- Consider the solubility of AgCl in NaCl solutions. You might predict that the aqueous solubility would decrease as the [Cl^-] increases due to addition of more NaCl. It does, but only up to a point!

[Cl^-] (M)	Predicted Solubility of AgCl (X10^5 M)	Measured Solubility of AgCl (X10^5 M)
0.000	1.3	1.3
0.0039	0.0046	0.072
0.036	0.00050	0.19
0.35	0.000051	1.7
1.4	0.000013	18
2.9	0.0000063	1000

Complex ions

- A complex ion is a polyatomic ion (cation or anion) consisting of a central metal atom (Lewis acid) that has ligands bonded to it (Lewis base) via coordinate covalent bonds.
  - Common ligands include halides, NH_3 and H_2O, with coordination taking place via lone pairs.
- We can describe its formation with a formation constant K_f.
- Ex. $[AgCl_2]^-$

$$Ag^+ (aq) + Cl^- (aq) \rightleftharpoons [AgCl_2]^- \qquad K_f = \frac{[[AgCl_2]^-]}{[Ag^+][Cl^-]} = 1.2X10^8$$

(Incomplete) Table of K_f values

Table 17.1 Formation Constants for Some Metal ComplexIons in Water at 25°C

Complex Ion	K_f	Equilibrium Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq + 4Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4OH^- \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$
$Ni(NH_3)_6^{2+}$	5.5×10^8	$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^3+(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$

- Notice that the K_f's are >>1

http://wps.prenhall.com/wps/media/objects/3312/3392202/blb1705.html

Common Ion Effect

- Specific application of Le Châtelier's Principle to acid-base equilibria.
- If a water-soluble salt is added to a solution that contains a weak acid or base, *and the salt has a common ion with the acid or base*, then the dissociation will be affected by its presence.
- Leads to the idea of a buffer – a solution that contains both forms of a substance (acid and its conjugate base or base and its conjugate acid)

The magical world of buffers

- Buffer (biology definition) – a solution that resists change in pH
- Buffer (chemistry definition) - a solution that is composed of a weak acid and the salt of its conjugate base, or a weak base and the salt of its conjugate acid
- Why are these different ways of saying the same thing?
  - When a small amount of acid(base) is added to a buffer, it will react with the conjugate base(acid) that is present, which will neutralize the solution and only *slightly* change the concentrations of acid and base that are present in the solution

Buffer capacity

- Even though buffers appear to be magical, they cannot resist changes in pH forever!
- In general, the more concentrated a buffer is, the better it will be able to neutralize an incoming acid or base.
- Also in general, the buffer will work best when the concentrations of the conjugate pair (acid and base) are approximately equal.
  - Thus typically buffers are prepared to have a pH $\approx$ pK_a.

Oxidation Numbers

- Refers to the charge on a chemical species
  - Ion – charge on ion
  - Atom – charge = 0
  - Polyatomic ion or compound – what the charge on *each* individual atom would be if it were an ion.

Determining the charge for an ion

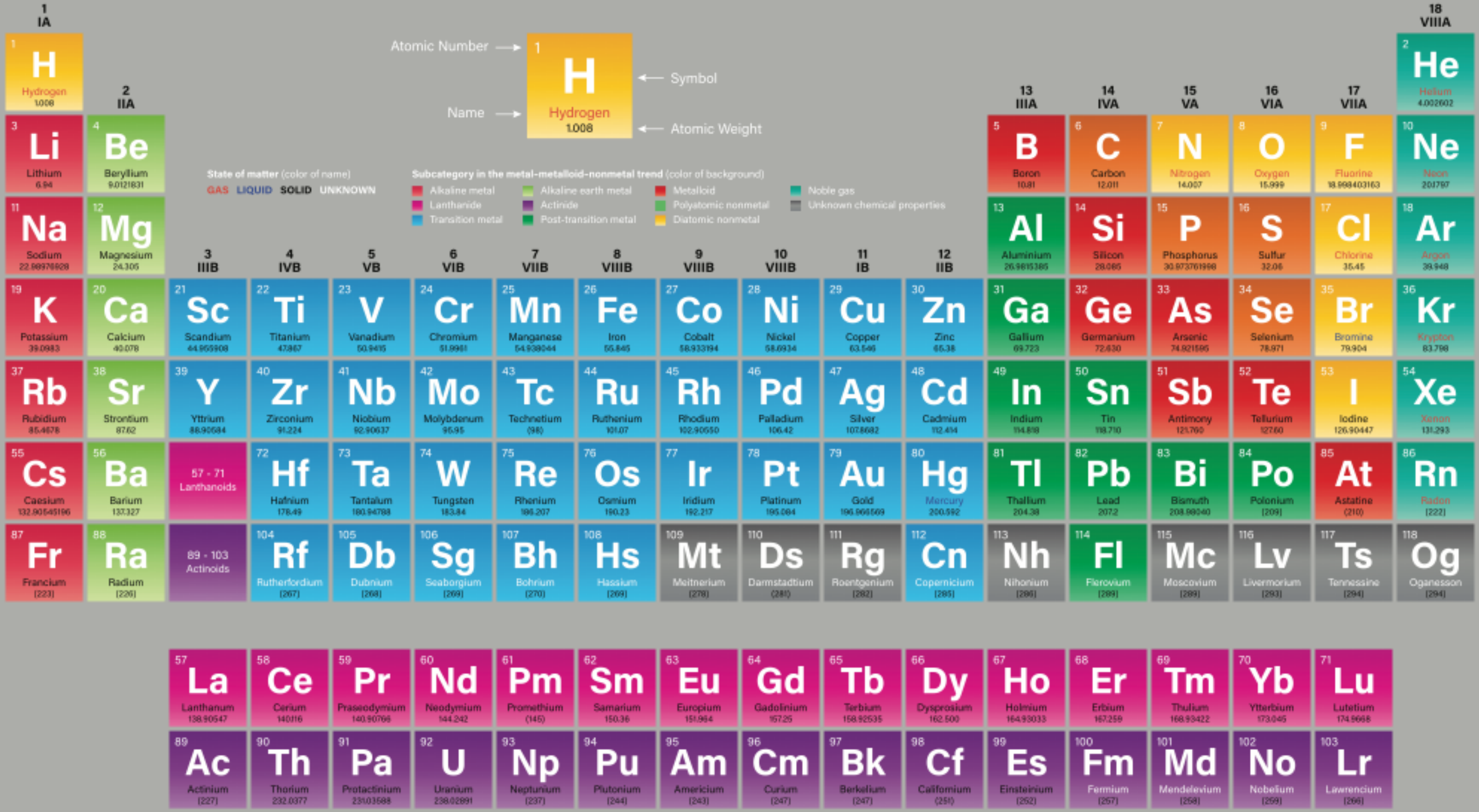
- For Groups IA-VIIIA the “usual” charge of an ion is based on its position
  - +1, +2, +3, +/-4, -3, -2, -1, 0
- For Group B (transition metals), use the Stock system
  - Roman numerals represent charges
  - Ex. Fe(II) ion = Fe^{2+}

"Rules" for oxidation numbers

- The sum of the oxidation numbers must equal the overall charge on the species (0 if neutral)
- Can usually use the groups of the periodic table to determine oxidation numbers for ions.
  - IA = +1, IIA = +2, IIIA = +3, IVA = +/-4, VA = -3, VIA = -2, VIIA = -1, VIIIA = 0.
- F is usually -1 (as are most halogens)
- H is usually +1 (except if combined with IA or IIA metal to form a hydride, in which case it will be -1)
- O is usually -2 (except if combined to form a peroxide (-1) or superoxide (-1/2))

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in the following equation:

$$2K_2S_2O_3(s) + I_2(s) \longrightarrow K_2S_4O_6(s) + 2KI(s)$$



1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
Atomic Number
Symbol
Name
Atomic Weight
1 H Hydrogen 1.008
State of matter (color of name)
GAS LIQUID SOLID UNKNOWN
Subcategory in the metal-metalloid-nonmetal trend (color of background)
Alkaline metal
Alkaline earth metal
Metalloid
Noble gas
Lanthanide
Actinide
Polyatomic nonmetal
Unknown chemical properties
Transition metal
Post-transition metal
Diatomic nonmetal
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.0121831
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
41 Nb Niobium 92.90637
42 Mo Molybdenum 95.95
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 112.414
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 131.293
55 Cs Caesium 132.90545196
56 Ba Barium 137.327
57 - 71 Lanthanoids
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 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium [209]
85 At Astatine (210)
86 Rn Radon [222]
87 Fr Francium [223]
88 Ra Radium [226]
89 - 103 Actinoids
104 Rf Rutherfordium [267]
105 Db Dubnium [268]
106 Sg Seaborgium [269]
107 Bh Bohrium [270]
108 Hs Hassium [269]
109 Mt Meitnerium [278]
110 Ds Darmstadtium (281)
111 Rg Roentgenium [282]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
114 Fl Flerovium [289]
115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Oganesson [294]
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
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 162.500
67 Ho Holmium 164.93033
68 Er Erbium 167.259
69 Tm Thulium 168.93422
70 Yb Ytterbium 173.045
71 Lu Lutetium 174.9668
89 Ac Actinium [227]
90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium [237]
94 Pu Plutonium [244]
95 Am Americium [243]
96 Cm Curium [247]
97 Bk Berkelium [247]
98 Cf Californium (251)
99 Es Einsteinium [252]
100 Fm Fermium [257]
101 Md Mendelevium [258]
102 No Nobelium [259]
103 Lr Lawrencium [266]

Redox reactions (an introduction)

- Redox reactions involve a simultaneous *red*uction and *ox*idation.
- Reduction – gain of electrons
  - oxidation number is decreased
- Oxidation – loss of electrons
  - Oxidation number is increased
- Disproportionation – redox reaction where the same species is both oxidized and reduced.
  - Ex. $2H_2O_2 \rightarrow 2H_2O + O_2$

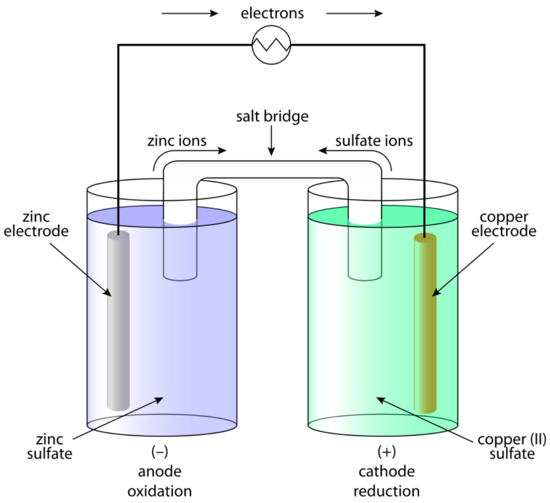
Agents

- Reducing agent – causes a reduction
  - Gets oxidized
  - Usually metal
- Oxidizing agent – causes an oxidation
  - Gets reduced
  - Usually nonmetal

Types of electrochemical cells

Galvanic/Voltaic

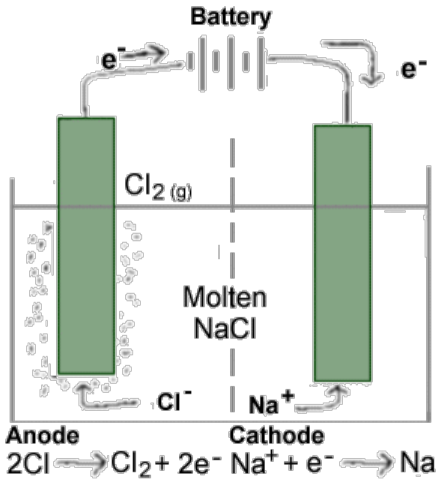
- Produces electricity as a result of a spontaneous reaction



https://en.wikipedia.org/wiki/Galvanic_cell

Electrolytic/Battery

- Electricity is used to carry out a non-spontaneous reaction



https://www.chem.tamu.edu/class/majors/tutorialnotefiles/electrolytic.htm

Standard potentials

- Since all electrochemical cells contain two electrodes, we can only measure the overall potential, which is the combination of the potential of the anode and that of the cathode.
- We can define a reference electrode to have a voltage of 0 V so that all values are relative to this number.
- The standard hydrogen electrode (SHE) is $H_2(g)$ adsorbed on Pt, an inert metal:

$$Pt(s) \mid H_2(g) \mid H^+(aq) \qquad E^o = 0\ V$$

The Nernst equation

- We know that $\Delta G_{rxn} = \Delta G_{rxn}{}^{o} + RT \ln Q$
- Dividing both sides by -νF, and using the equation we just derived: $E = -\frac{\Delta G_{rxn}{}^{o}}{\nu F} - \frac{RT}{\nu F} \ln Q$
- The 1st term represents the standard emf E^{o}: $\Delta G_{rxn}{}^{o} = -\nu F E^{o}$
- This leaves us with the Nernst equation:

$$E = E^{o} - \frac{RT}{\nu F} \ln Q$$

- At a temperature of 25^{o}C, RT/F=25.7 mV, so we can write the equation as:

$$E = E^{o} - \frac{25.7\ mV}{\nu} \ln Q$$

- Sometimes it is also kept in SI units but with a common logarithm:

$$E = E^{o} - \frac{0.0591}{\nu} \log Q$$

The Nernst equation

- At equilibrium, Q=K, ΔG_{rxn}=0 and so E=0. Substituting this into the Nernst equation gives:

$$0 = E^o - \frac{RT}{\nu F}\ln K$$

- Rearranging a bit, $$\ln K = \frac{\nu F E^o}{RT}$$
- This means that we can calculate equilibrium constants by measuring cell potentials.
- This has important practical consequences, as a typical voltmeter can easily measure fractions of a volt, which translate into enormous K's (10^{30} or greater) which can't be determined otherwise (at least not easily)

Final thoughts on electrochemical cells

- Note that for a spontaneous reaction, $\Delta G<0$ and so $E>0$. That is, we can determine which half reaction occurs at the anode and which occurs at the cathode by looking at the corresponding potentials and rewriting them (remember we always have to flip one since they are both given as reductions!) so that the overall voltage is positive.

For the reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.

$Ni^{2+}(aq) + 2e^{-} \longrightarrow Ni(s)$

$E^{o} = -0.257$ V

$Mn^{2+}(aq) + 2e^{-} \longrightarrow Mn(s)$

$E^{o} = -1.185$ V

$Mn(s) + Ni^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Ni(s)$

Quantitative electrolysis

- The quantity of reactant consumed (or product formed) during electrolysis can be calculated using stoichiometry
  - Related to molar mass of substance ($n = m/M$)
  - Related to number of electrons transferred in the electrode reaction (ν)
  - Related to the quantity of electric charge used ($Q = It$)

Example

- We can use electrolysis to determine the gold content of a sample. The sample is dissolved, and all the gold is converted to $Au^{3+}(aq)$, which is then reduced back to Au(s) on an electrode of known mass. What mass of gold will be deposited at the cathode in 1.00 hour by a current of 1.50 A?

Solution

- First find the total charge:

$$Q = (1.5\,A)(1.00\,hour)\left[\frac{1\frac{C}{s}}{1\,A}\right]\left[\frac{60\,min}{1\,hour}\right]\left[\frac{60\,s}{1\,min}\right] = 5.40 * 10^3 C$$

- Next find the moles of e^-s transferred:

$$v = \frac{Q}{F} = \frac{5.40 * 10^3 C}{96485\,C/mol} = 0.0560\,mol\,e^-$$

Solution

- Use stoichiometry to determine the moles of Au produced:

$$n = 0.0560\ mol\ e^{-}\left(\frac{1\ mol\ Au}{3\ mol\ e^{-}}\right) = 0.0187\ mol\ Au$$

- Finally calculate the mass of Au deposited:

$$m = n * M = 0.0187\ mol\ Au\left(\frac{197.0\ g}{1\ mol\ Au}\right) = 3.68\ g\ Au$$

Hydrogen

- Makes up <1% of the mass of the Earth's crust, but about 90% of the atoms in the Sun and outer space
- Can be formed via reactions that typically require high temperatures (1000 ^{o}C) and a catalyst
  - Water-gas reaction: $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
  - Water-gas shift reaction: $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
  - Reforming of methane (but in principle any hydrocarbon): $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$
    - Principal commercial source of hydrogen
  - Catalytic reforming: $C_6H_{14} \rightarrow C_6H_6 + 4H_2$

Uses for hydrogen

- About ½ of the H_2 manufactured is used to make NH_3 (Haber process), which can be used to fertilizers, plastics and explosives.
- A significant amount is also used in the petrochemical industry
  - Hydrogenation of unsaturated compounds: $C_6H_6 + H_2 \rightarrow C_6H_{12}$
  - Synthesis of methanol: $CO + H_2 \rightarrow CH_3OH$
- Metallurgy: $WO_3 + H_2 \rightarrow W + H_2O$

Carbon compounds (inorganic)

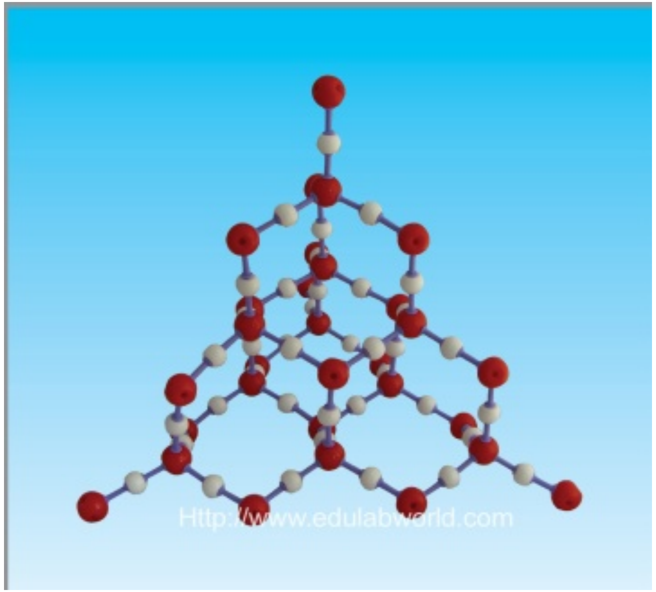
- Reaction with metals (oxides) to form carbides (acetylides) at high temperatures:
  - $CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$
  - $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$
- Methane can be converted to inorganic compounds:
  - $CH_4 + 4S \rightarrow CS_2 + 2H_2S$
  - $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$
- CN^- reacts much like a halide:
  - Dimerization to cyanogen $(CN)_2$
  - Disproportionation in basic solution: $(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$

Silicon compounds

- Si is the 2nd most abundant element in the Earth's crust (after O)
- Si can make four bonds, but is incapable of making extended systems like C can
  - Si is significantly larger than C
  - Si-Si and Si-H bonds are relatively weak
- Si crystallizes in a cubic arrangement similar to diamond (tetrahedral, sp^3 hybridized)
  - Can't form π bonds so cannot form sheets the way graphite can (p orbitals are too large for efficient overlap)

Silica and silicates

- SiO_2 is really a network covalent solid where each Si atoms is bonded to 4 O atoms, and each O atom is bonded to 2 Si atoms
- SiO_4^{4-} and $Si_2O_7^{6-}$ can arrange tetrahedrally with cations to form minerals (ex. Th^{4+}, Zr^{4+}, Sc^{3+})



http://www.edulabworld.com/product/265-sio2-crystal-model-31046-1-d1a7/

Nitrogen compounds

- Ammonia can be synthesized by the Haber process: $N_2 + H_2 \rightarrow NH_3$
  - Generally used to make fertilizer:

$NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 + (NH_4)_2HPO_4$

  - Can be converted to NO using the Ostwald reaction, which can then form nitric acid:

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Properties of oxygen

- Most abundant substance in Earth's crust
- Can form compounds with all elements except He, Ne and Ar
- Generally has an oxidation number of -2 in compounds (oxide), but it can also be -1 (O_2^{2-}, peroxide) or -1/2 (O_2^-, superoxide)
- Can exist as O_2 or O_3
- O_3 is a strong oxidizing agent (acidic solutions):

$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \quad E^o = 2.075$ V

Synthesis of oxygen

- Generally made by decomposition reactions:

$HgO \rightarrow Hg + O_2$

$KClO_3 \rightarrow KCl + O_2$

$H_2O_2 \rightarrow H_2O + O_2$

- Reaction involving superoxide:

$KO_2 + CO_2 \rightarrow K_2CO_3 + O_2$

- Can also be made by electrolysis:

$H_2O \rightarrow H_2 + O_2$

Compounds with fluorine

- Fluorine reacts with every element except He and Ne
- Reaction with U allows for separation of U-235 and U-238 isotopes by gaseous diffusion:

$U + F_2 \rightarrow UF_6$

- Reaction with S forms a gaseous electrical insulator:

$S + F_2 \rightarrow SF_6$

- HF can be synthesized from a fluoride and concentrated sulfuric acid:

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + HF$

- HF can be used for etching:

$SiO_2 + HF \rightarrow H_2O + SiF_4$

Compounds with chlorine

- Chlorine reacts with hydrocarbons:
  - Ex. $CH_4 + Cl_2 \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$
- Chlorofluorocarbons (CFCs) are volatile liquids that are commonly used as refrigerants, although they are known to damage the ozone layer
  - Ex. $CFCl_3$ and CF_2Cl_2
- HCl can be synthesized from a chloride and concentrated sulfuric acid:

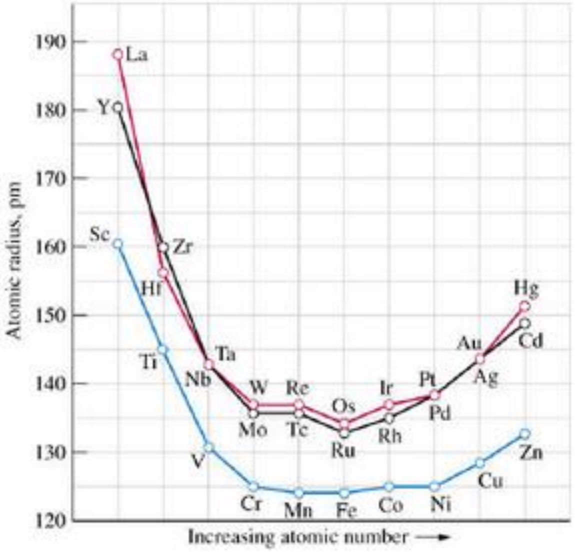
$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl$

Interesting facts about the d-block elements

- In the 4th period, Cu^{2+} is the only divalent cation that has a positive reduction potential
  - $Cu^{2+} + 2e^- \rightarrow Cu$ $E^o = 0.340$ V
- In the 4th period, Sc is the only metal reactive enough to react with water and displace hydrogen
  - $Sc + H_2O \rightarrow Sc^{3+} + H_2$
- Going from top to bottom, the number of oxidation states generally increases
  - As the oxidation number increases, the covalent nature of the compound also increases
- Sc and Cr hydoxides are amphoteric:
  - $Sc(OH)_3 + H^+ \rightarrow Sc^{3+}$ $Sc(OH)_3 + OH^- \rightarrow Sc(OH)_6^{3-}$
  - $Cr(OH)_3 + H^+ \rightarrow Cr(H_2O)_6^{3+}$ $Cr(OH)_3 + OH^- \rightarrow Cr(OH)_4^-$

Periodic trends – atomic radius

- Going from left to right, atomic radius decreases, then increases
  - greater attraction between nucleus and inner e^-s then greater repulsion between inner e^-s
- Going from top to bottom, atomic radius increases then stays approximately constant (or even decreases slightly)
  - Greater number of energy levels (shells), but then lanthanide contraction occurs since the 6th period contains 4f orbitals, which are not very good at screening (shielding) valence e^-s from the nucleus



http://gwapchem.wikispaces.com/23.7+Transition+Metals

Lanthanide (rare-earth) metals

- f-block elements
- Inserted between d-block elements
- Very similar properties to each other and to 3B metals
  - Difficult to separate and isolate
- $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$ has a greater E^{o} than for reductions involving $Cr_2O_7^{2-}$ or MnO_4^{-}

Magnetic properties of metals

- Most d-block metals are paramagnetic because they have unpaired d electrons
  - Individual magnetic moments that can (temporarily) align in the presence of an external field
- Fe, Co and Ni are also ferromagnetic
  - Domains that can (permanently) align in the presence of an external field, even after the field is removed!
  - Requires certain interatomic distances
  - Can also occur in alloys (Al-Cu-Mn, Ag-Al-Mn, and Bi-Mn)

Properties of Fe, Co and Ni

- Fe can form +2 or +3 ions with $[Ar]3d^6$ and $[Ar]3d^5$ electron configurations (particularly stable)
- Co and Ni form primarily +2 ions ($[Ar]3d^7$ and $[Ar]3d^8$, respectively)
  - Co can have an oxidation number of +3 in complex ions such as $[Co(NH_3)_6]^{3+}$

Properties of Cu, Ag and Au

- Relatively unreactive (filled d orbitals)
  - Do not displace H_2 from H^+ solutions (but can react to form SO_2 or NO_x by reacting with H_2SO_4 or HNO_3)
- Highest electrical and thermal conductivities of all the metals
- Au does not react with any single acid to form H^+, but it does with *aqua regia* (1:3 HNO_3:HCl):

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow [AuCl_4]^- + 2H_2O + NO$$

- Au is resistant to oxidation, while Ag can tarnish (Ag_2S) and Cu can corrode ($Cu_2(OH)_2CO_3$)

Organic compounds

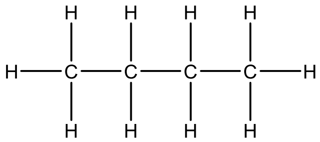
- C, H, N, O – about 95% of Earth's living things
- C, H, N, O, P, S – about 99%
- Carbon is king!
  - 4 covalent bonds (with itself or other elements)
  - Optimum size and valence
- Functional group
  - Collection of certain atoms that confer characteristic chemical (and biological) activities

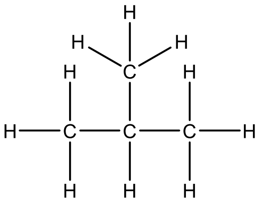
Hydrocarbons - alkanes

- Simplest organic molecules
- Saturated
- General formula C_nH_{2n+2}

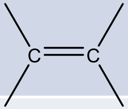
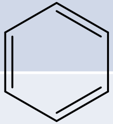
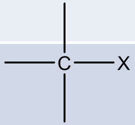
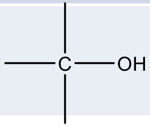
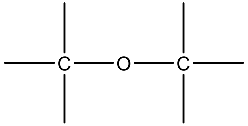
Constitutional Isomers

- Same chemical formula, different structural formula
- Leads to ENORMOUS diversity

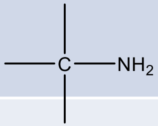
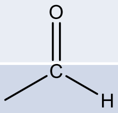
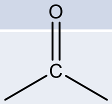
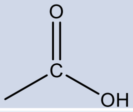
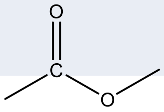
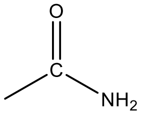




Functional Groups

Functional Group	Structure
Alkene	
Alkyne	
Aromatic Ring (arene)	
Halide (X = F, Cl, Br, I)	
Alcohol	
Ether	

Functional Groups

Functional Group	Structure
Amine	
Aldehyde	
Ketone	
Carboxylic Acid	
Ester	
Amide	

Recrystallization

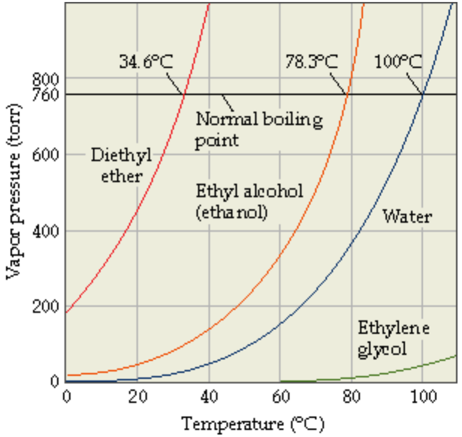
- Common technique for the purification of solids
- Principle: Solid and solid impurities can be separated from each other by selective dissolution
  - Dissolve solid in a liquid (solvent) so that it is insoluble at low temperature but soluble at high temperature
  - The impurities will remain undissolved, and so can be filtered off
  - Upon cooling, recrystallization will occur
  - May be an iterative process

Distillation

- Separation of liquids based on boiling points
- Vapor pressure – pressure that a gas exerts on a liquid at equilibrium
- Boiling occurs when the atmospheric (outer) pressure is equal to the vapor pressure (VP)

Dependence of Vapor Pressure on Temperature and External Pressure

- Normal bp = T at which equilibrium is reached when the external pressure is 1 atm
- At a reduced pressure (vacuum), the temperature required for boiling is lower



http://chemistry.umeche.maine.edu/~amar/Spring2001/vaporpressure.html

Simple Distillation

- "Quick and dirty"
- Useful if the boiling points of the liquids in the mixture differ greatly (> 40^{o}C)
- The more volatile component will be eluted, the less volatile will remain in the flask (pot)

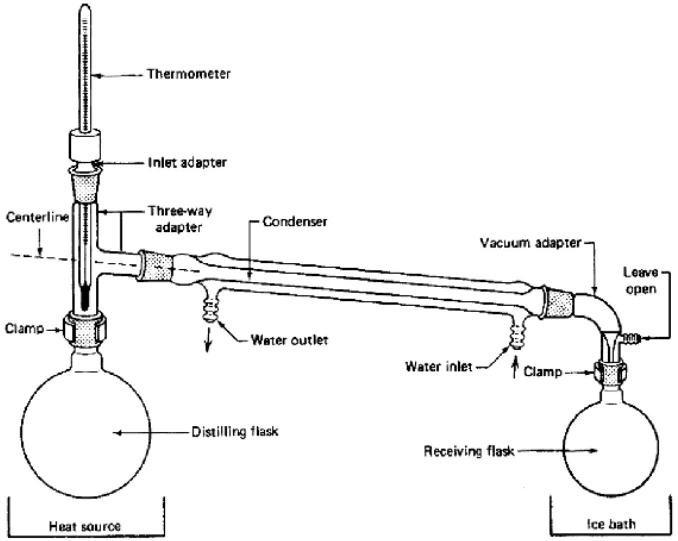


Fig. 98 A complete, entire simple distillation setup.

http://designerdrugs.com/pte/12.162.180.114/dcd/chemistry/equipment/distillation4dummies.html

Fractional Distillation

- Used when the mixtures contains liquids that are closer together in bp (> 10^{o}C)
- Typically fractions are collected which contain (hopefully) pure compounds
- A greater separation is achieved by a better distillation column
  - Greater surface area

Extraction

- Technique used to purify liquid-liquid or liquid-solid systems
- Primarily based on intermolecular forces and polarity
- Used extensively in "work-up" of organic reactions
- Can be used iteratively
  - Same conditions – increase recovery
  - Different conditions – extract different compounds from complex mixtures (ex. natural product isolation)

Chromatography

- Separation of compounds based on polarity
- More effective than extraction in terms of identifying the *number* of components in a mixture
- Can also be used to separate compounds that are very similar in nature (though it becomes more difficult the more similar they are)