

## Lecture 2

### General Chemistry Review

*Pease read chapter 1 and 2 of McSween et al. for this week*

- Periodic table & electronic configurations.
- Periodic properties: ionic radius, electron negativity, 1st ionization potential
- Covalent & ionic bonding
- Hybridization and molecular orbitals

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### Background-Elements and Atoms

*These are all terms you should already be familiar with:*

**atom** - smallest sub-divisible unit of matter that retains unique chemical properties. Composed of electrons, protons and neutrons.

**element** - a fundamental building block of matter defined by a specific number of protons in an atomic nucleus. All atoms of an element have the same number of protons.

**isotope** - different "flavors" of an element that have different numbers of neutrons in their nucleus (thus, they have different atomic masses).

**radioactive isotope** - isotope that decays away radioactively due to an unstable nuclear configuration.

**stable isotope** - one that does not decay radioactively.

**molecule** - a multi-atom material held together by chemical bonds.

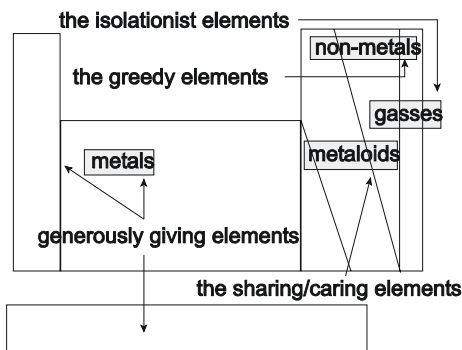
**compound** - a multi-element molecule.

**ion** - an atom or molecule that has gained or lost one or more valence or bonding electrons, giving it electronic charge.

**valence** - the outermost electron shell of an atom.

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**The Periodic Chart ala Ken**



The chemical elements display "periodic" (repeatable) properties governed by valence electron configurations.

The **Periodic Chart** is a 2d map of the elements that reflects their periodic behavior. There are many ways to draw the Chart but all are set up to classify like-chemistry elements. If you can read the map you will be able to predict an element's behavior in a range of environments.

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**PERIODIC TABLE OF THE ELEMENTS**

Periods	METALS										NONMETALS						NOBLE GASES	
	1 IA	2 IIA	TRANSITION ELEMENTS										13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H <sup>+</sup> Hydrogen																H <sup>+</sup> Hydrogen	He Helium
2	Li Lithium	Be <sup>2+</sup> Beryllium											B Boron	C Carbon	N <sup>3-</sup> Nitrogen	O <sup>2-</sup> Oxygen	F <sup>-</sup> Fluorine	Ne Neon
3	Na <sup>+</sup> Sodium	Mg <sup>2+</sup> Magnesium	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII B	9	10 VIII B	11 IB	12 IIB	Al <sup>3+</sup> Aluminum	Si Silicon	P <sup>3-</sup> Phosphorus	S <sup>2-</sup> Sulphur	Cl <sup>-</sup> Chlorine	Ar Argon
4	K <sup>+</sup> Potassium	Ca <sup>2+</sup> Calcium	Sc <sup>3+</sup> Scandium	Ti <sup>4+</sup> Titanium	V <sup>5+</sup> Vanadium	Cr <sup>3+</sup> Chromium	Mn <sup>2+</sup> Manganese	Fe <sup>2+</sup> Iron	Co <sup>2+</sup> Cobalt	Ni <sup>2+</sup> Nickel	Cu <sup>+</sup> Copper	Zn <sup>2+</sup> Zinc	Ga <sup>3+</sup> Gallium	Ge <sup>4+</sup> Germanium	As <sup>3-</sup> Arsenic	Se <sup>2-</sup> Selenium	Br <sup>-</sup> Bromine	Kr Krypton
5	Rb <sup>+</sup> Rubidium	Sr <sup>2+</sup> Strontium	Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd <sup>2+</sup> Cadmium	In <sup>3+</sup> Indium	Sn <sup>4+</sup> Tin	Sb <sup>3-</sup> Antimony	Te <sup>2-</sup> Tellurium	I <sup>-</sup> Iodine	Xe Xenon
6	Cs <sup>+</sup> Cesium	Ba <sup>2+</sup> Barium	La Lanthanum	Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au <sup>+</sup> Gold	Hg <sup>2+</sup> Mercury	Tl <sup>3+</sup> Thallium	Pb <sup>2+</sup> Lead	Bi <sup>3-</sup> Bismuth	Po <sup>2-</sup> Polonium	At Astatine	Rn Radon
7	Fr <sup>+</sup> Francium	Ra <sup>2+</sup> Radium	Ac <sup>3+</sup> Actinium	Rf Rutherfordium	Db Dubnium	Sg Seaborgium	Bh Bohrium	Hs Hassium	Mt Meitnerium	Uun Ununium	Uuu Ununium	Uub Unbinium	Uut Untrium	Uuq Unquadrium	Uuh Unhexium	Uuo Unoctium		

**ELEMENT KEY**

Atomic Number	Atomic Mass
Symbol of Element	Ion. Charge (if most common)
(Element Name)	

LEGEND Black ... Solid    Green ... Liquid    Blue ... Gas    Red Outline ... Synthetically prepared

Atomic masses appearing in parentheses are those of the most stable known isotopes. \* Names and symbols are under review; those listed are IUPAC temporary values and symbols.

Each element is defined by the number of protons in the nucleus, which in turn determines the number of electrons in a neutral atom. Electronic configuration determines chemical reactivity.

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## The importance of electrons

Elements that form the **columns** of the periodic table behave similarly largely because they have **similar electron configurations**.

Recall that **outer most electrons** are the most important in chemistry because these are more readily lost and/or shared.

In contrast, **inner electrons** are tightly bound to the nucleus by electrostatic forces.

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## Atomic orbitals

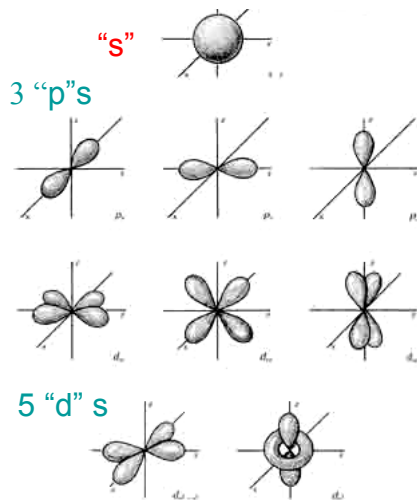


Figure 4.2 Electron clouds representing the  $s$ ,  $p$ , and  $d$  orbitals of the hydrogen atom according to the wave mechanical model of Schrodinger.

Note: the 14 "f"s are not shown

- Are a means of describing the likely spatial distribution of electrons about a nucleus.
- 2 electrons "fill" an orbital
- "s" orbitals are spherically symmetric; "p"s are pairs of "lobes" of electron density; d & f orbitals are geometrically more complex

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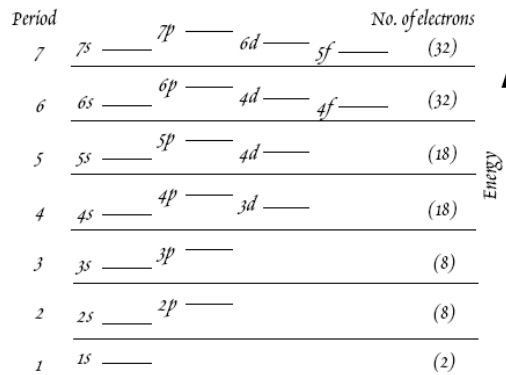
### The Aufbau Principle

**Table 4.1** Quantum Numbers and Orbitals of the Hydrogen Atom

Quantum numbers				Type of orbital
n	l	m	s	
1	0	0	+½, -½	1s
2	0	0	+½, -½	2s
2	1	0	+½, -½	2p
2	1	1	+½, -½	2p
2	1	-1	+½, -½	2p
3	0	0	+½, -½	3s
3	1	0	+½, -½	3p
3	1	1	+½, -½	3p
3	1	-1	+½, -½	3p
3	2	0	+½, -½	3d
3	2	1	+½, -½	3d
3	2	-1	+½, -½	3d
3	2	2	+½, -½	3d
3	2	-2	+½, -½	3d
etc.				

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s,  
4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d

- Fill low energy orbital 1st.
- Distribute electrons among orbitals to minimize total energy of atom.
- Electron configurations with full or half-full orbitals are more stable or “preferred”.



There is a progression of quantum numbers and corresponding orbitals

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PERIODIC TABLE OF THE ELEMENTS

Group I 1A											NONMETALS						NOBLE GASES	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H Hydrogen	2 He Helium											13 B Boron	14 C Carbon	15 N Nitrogen	16 O Oxygen	17 F Fluorine	18 Ne Neon	
2 Li Lithium	Be Beryllium											B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine	Ne Neon	
3 Na Sodium	Mg Magnesium	3 Sc Scandium	4 Ti Titanium	5 V Vanadium	6 Cr Chromium	7 Mn Manganese	8 Fe Iron	9 Co Cobalt	10 Ni Nickel	11 Cu Copper	12 Zn Zinc	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon	
4 K Potassium	Ca Calcium	Sc Scandium	Ti Titanium	V Vanadium	Cr Chromium	Mn Manganese	Fe Iron	Co Cobalt	Ni Nickel	Cu Copper	Zn Zinc	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium	Br Bromine	Kr Krypton	
5 Rb Rubidium	Sr Strontium	Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium	I Iodine	Xe Xenon	
6 Cs Cesium	Ba Barium	La Lanthanum	Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au Gold	Hg Mercury	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium	At Astatine	Rn Radon	
7 Fr Francium	Ra Radium	Ac Actinium	Rf Rutherfordium	Db Dubnium	Sg Seaborgium	Bh Bohrium	Hs Hassium	Mt Meitnerium	Uun Ununilium	Uuu Ununnilium	Uu Ununium	Filling of “p” orbitals						
		Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium			
		Th Thorium	Pa Protactinium	U Uranium	Np Neptunium	Pu Plutonium	Am Americium	Cm Curium	Bk Berkelium	Cf Californium	Es Einsteinium	Fm Fermium	Md Mendelevium	No Nobelium	Lr Lawrencium			

Filling of the “f” orbitals!

Red Outline ... Synthetically prepared

Filled orbital assignment shorthand notation:  
Ne = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> and Ar = [Ne]2s<sup>2</sup> 3s<sup>2</sup> 3p<sup>6</sup>.

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Please review these **Periodic Properties** from your course in **Introductory Chemistry**

### 1. Atomic radius:

☞ Radii of the elements

increase down a column and  
decrease across a row (left to right).

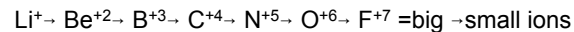
### 2. Ion size (ionic radius)

In general, a positive atomic ion is smaller and a negative atomic ion is larger than the neutral atom.

Atoms contract as they become positive ions because the "pull" of the positively charged nucleus is "felt" by fewer electrons than in a neutral atom.

☞ Like neutral atoms, radii of ions at a given charge increase down a column.

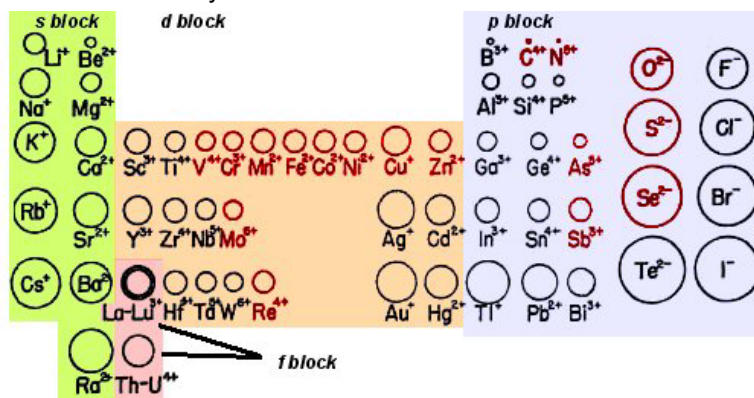
☞ An *iso-electronic series* contracts with increasing atomic mass:



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## Schematic representation of ionic radius of some common ions in common ionization state.

Remember: many elements have more than one stable "valance".



Elements **lettered in red** have active "redox" chemistry in nature.  
oxidation = loss of electrons; reduction = gaining electrons.

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Why does size matter?

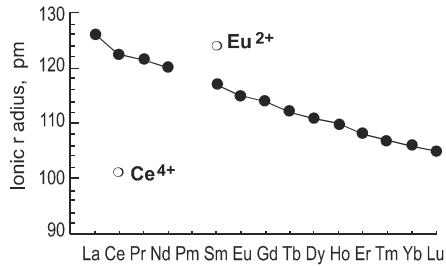


Figure 7.5. Ionic radii of the lanthanide rare earth elements (3+ state except where noted). Promethium (Pm) has no isotope with a half-life longer than 5 years.

modified from White, Geochemistry

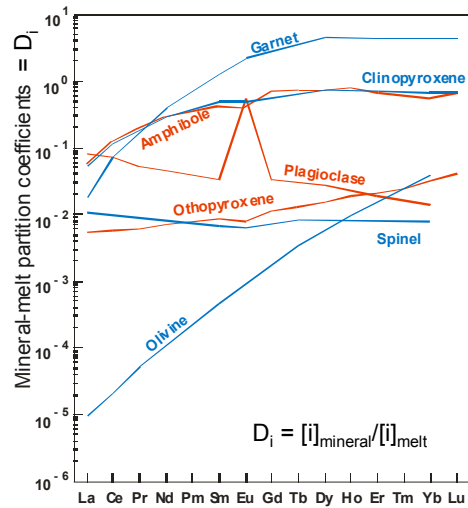
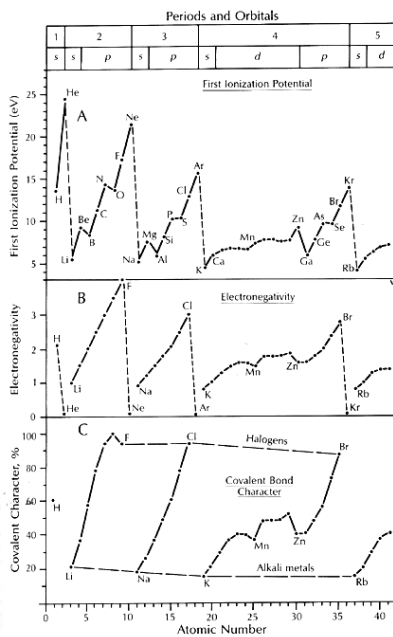


Figure 7.15. Rare earth mineral-melt partition coefficients for mafic magmas. Data from Table 7.5. from: White, Geochemistry

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Periodicity is also obvious in several other important measures of how the elements "feel" about electrons.

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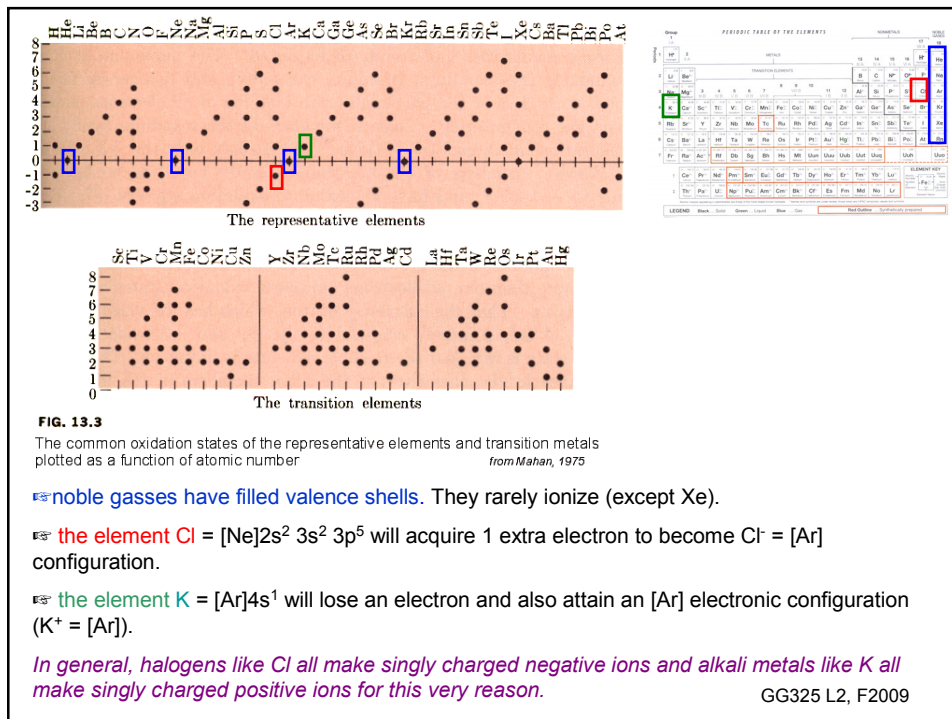
### 3. Ionization and Ionization Energy (aka ionization potential):

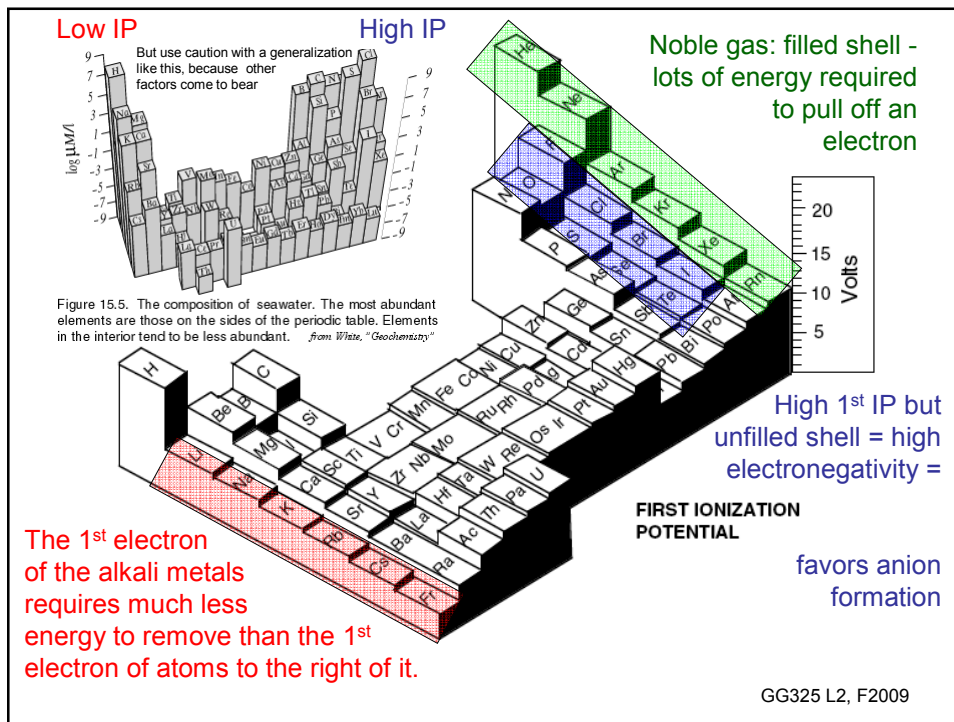
Ionization is the removal or addition of one or more electron(s) from a neutral atom or molecule, making a charged (ionized) species.

IE measures how easy or hard it is to remove an electron from an element or ion.

Energies of filled electronic orbitals give rise to common oxidation states for individual elements. Electronic structure determines ionic charge and IE.

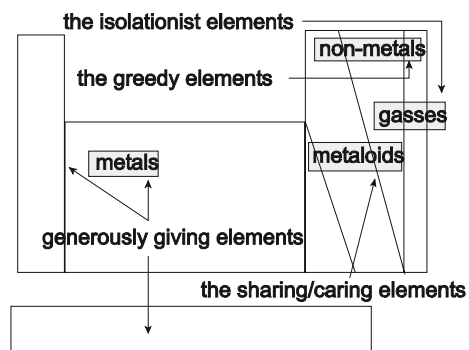
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**4. Electronegativity** is a measure of an atom's desire to gain an electron, forming a negative ion. Atoms can be classified in terms of their electron affinities with respect to their peers in the periodic chart as:

- a. donors** ("generously giving" and "sharing/caring")  
 Low electronegativity  
 = mostly or entirely empty valence shell  
 = conductor = **metal** (gives up electrons easily)
- b. acceptors** ("greedy")  
 high electronegativity  
 = mostly or entirely filled valence shell  
 = insulator = **non-metal**
- c. inert** ("isolationists").



Electronegativity  $\geq 2.5$  is somewhat of a chemical dividing line for the very “greedy elements”, but element near that boundary (like C and N) don’t always behave a certain way in the presence of other chemical elements.

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.5	Br 2.8	K
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.2	At 2.2	Rd
Fr 0.7	Ra 0.9	Ac 1.1															
			La 1.0	Ce 1.0	Pr 1.0	Nd 1.0	Pm 1.0	Sm 1.0	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.2	Yb 1.2	Lu 1.2
			Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np 1.4	Pu 1.4									

Figure 1.5. Electronegativities of the elements.

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#### Background - Chemical Bonds

Bonds allow multiple elements to form *molecules*.

#### Lewis dot configurations

are useful for predicting ionization behavior during the formation of some compounds, but they only work rigorously for s + p block electrons.

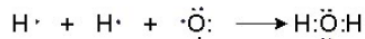
Lewis dot configurations for molecular bonding are based upon an element's desire to ultimately attain some sort of noble gas (filled shell) configuration, e.g., He, :Ne:, :Ar:

where • represents an e<sup>-</sup> and : represents an e<sup>-</sup> pair.

Each element brings some # of valence electrons in s and p orbitals to a compound that combine to form a *Lewis dot product* containing noble gas configurations around all the elements (2 or 8 electrons, = He or other noble gasses)

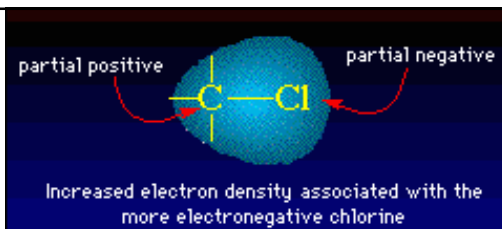
H has 1 electron = H•  
 C has 4 electrons = •C• [same as Si], etc..  
 N has 5 electrons = •N• [same as P], etc..  
 O has 6 electrons = •O: [same as S], etc..

We can use Lewis dot product logic to demonstrate why H<sub>2</sub>O is a more common and stable combination of elements than other H and O combinations such as HO<sub>2</sub>. O has e<sup>-</sup> structure like Ne, each H has e<sup>-</sup> structure like He.



**Bond Character**

Although there is electron sharing going on in all chemical bonds, not all bonds share e<sup>-</sup> equally.



Two end members:

☞ **Pure Covalent Bond** = exact same electronegativity of two bonded atoms

☞ **Pure Ionic Bond** = largest possible electronegativity difference of two bonded atoms

There is a spectrum of electron distribution in chemical bonds related primarily to the electronegativity difference of the two bonded atoms.

☞ If electronegativity difference is < 50% maximum, *bond is more covalent*.

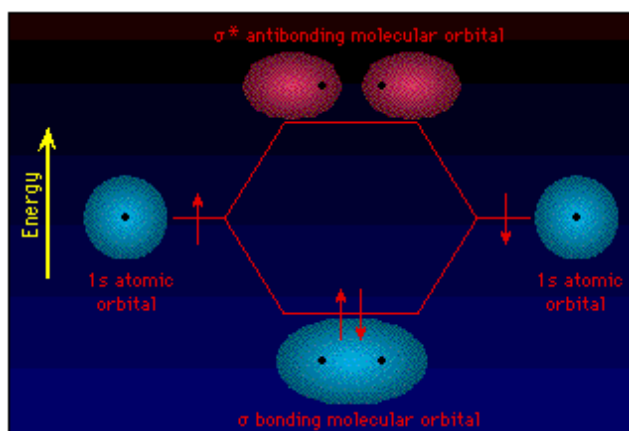
☞ If electronegativity difference is > 50% maximum, *bond is more ionic*.

Because ionically-bonded solids ("salts") and covalently-bonded solids (quartz, octane, etc..) behave differently in H<sub>2</sub>O and air, bond character is very useful in determining how a compound will behave in natural environments.

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**Bond orbitals**

Atomic orbitals combine and "hybridize" to make bonding and non-bonding orbitals that define electron density between atoms.



<http://chipo.chem.uic.edu/web1/ocol/SB/1-2.htm>

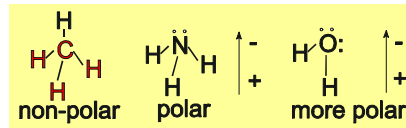
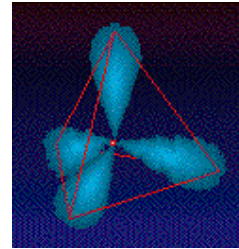
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**sp<sup>3</sup> hybridization**

This simplest combo includes all 3 p orbitals and the s orbital of a valence. This mix produces 4 equal sp<sup>3</sup> orbitals in tetrahedral coordination (angle of 109.5° between each bond). Methane, CH<sub>4</sub>, and the [SiO<sub>4</sub>] unit in silicate minerals have this geometry.

In molecules with one sp<sup>3</sup> bonding orbital containing an electron pair rather than a bond (such as ammonia, H<sub>3</sub>N:), the lone pair causes the 3 bonds to contract somewhat to an angle of 107.3°.

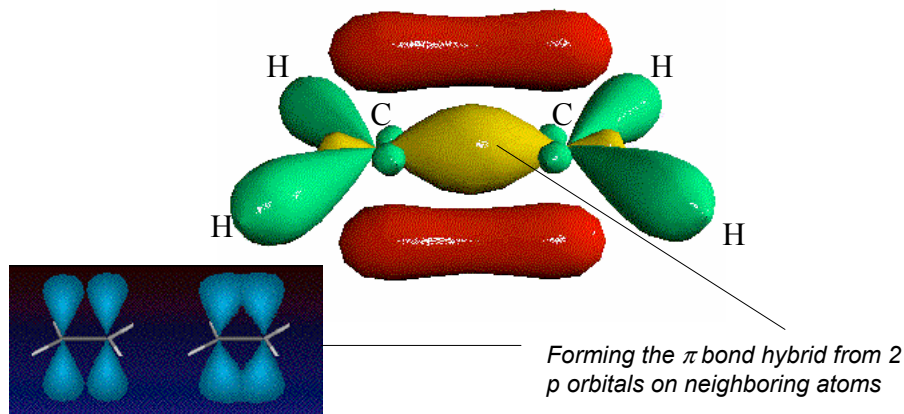
The case is more severe for water, with two e<sup>-</sup> pairs and the H-O-H bond angle reduces further to 104°. This makes water (and ammonia) *polar* molecules as charge is not evenly distributed about them and methane *non polar* as charge is symmetrically distributed about it.



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**Another hybrid type is sp<sup>2</sup> (planar geometry).** It involves 1 s orbital and 2 p orbitals, leaving one unhybridized p orbital to do something else.

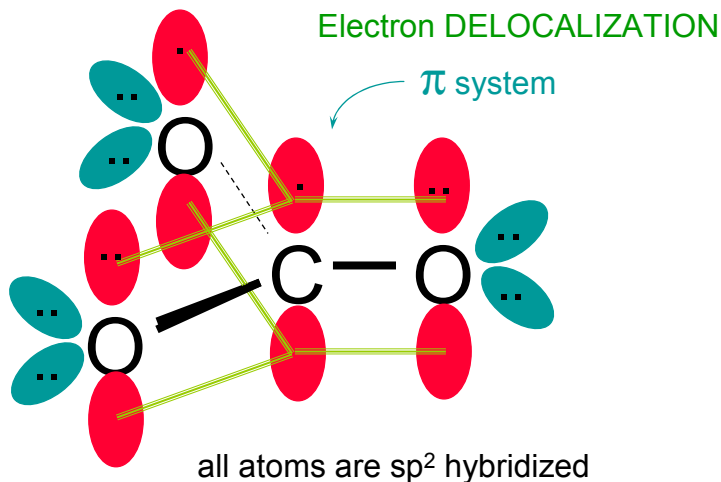
This is common in carbon-carbon double bonds in molecules like C<sub>2</sub>H<sub>4</sub>, ethene: The primary (σ) bond is from an sp<sup>2</sup> + sp<sup>2</sup> molecular hybrid (in yellow) and a second bond forms from the unhybridized p-orbitals out of the plane of the molecule (also called a π bond), shown in red.



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Another example:

$sp^2$  hybridization in the carbonate anion =  $CO_3^{2-}$

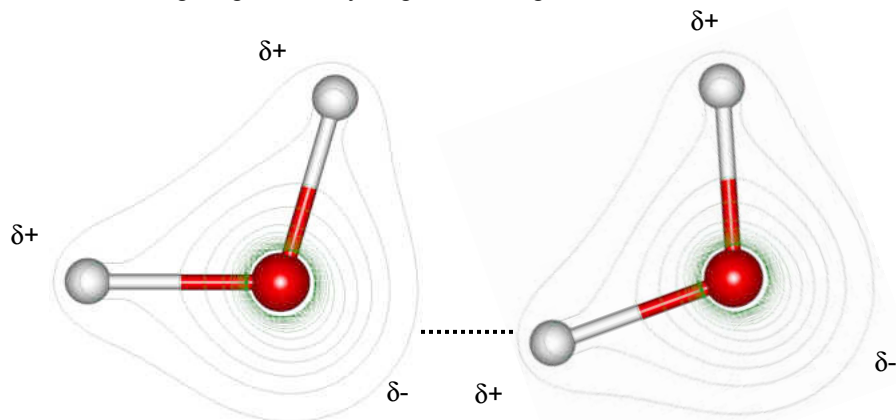


[www.chem.wvu.edu/harvey/Chemistry-351/Chapter-6.ppt](http://www.chem.wvu.edu/harvey/Chemistry-351/Chapter-6.ppt)

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### Other bonding interactions

Average electron density around oxygen in  $H_2O$  is 10 times greater than around the hydrogen atoms. This nearly completely exposes the “naked” protons of the H atoms, giving the molecule a partial positive charge in this area, in turn giving rise to hydrogen bonding between molecules.



Modified from <http://www.sbu.ac.uk/water/index.html>

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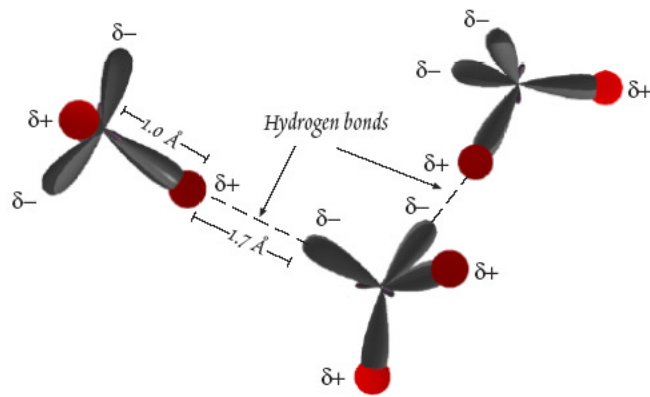


Figure 1.8. Hydrogen bonding between water molecules. Hydrogen positions shown as red;  $sp^3$  hybrid orbitals in oxygen shown as dark gray. The  $\delta^+$  and  $\delta^-$  indicate partial positive and negative charges respectively.

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