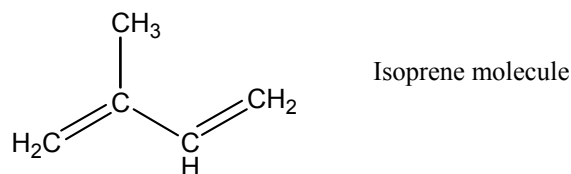


1. ATOMS, MOLECULES, ORBITALS AND BONDING: All the stuff you are not allowed to forget from general chemistry

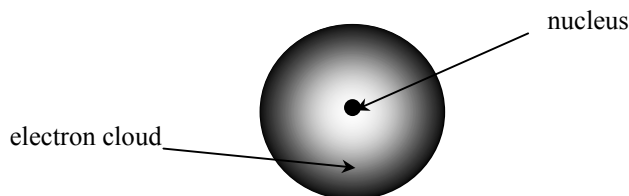
Ok, So now you are a sophomore. The last thing you did as a freshman was either burn your general chemistry textbook at a beach party and dance naked around the bonfire or, “sold” it back to the bookstore for enough money to buy a 5-5-5 pizza deal from Domino’s. My first words of advice...go get a new gen-chem book. Just because you are now taking organic chemistry, does not mean that you are allowed to forget an entire year of general chemistry. In fact, I will assume that you have complete mastery of it, as we are going to build on many of those ideas to which you were allegedly introduced. To that end, this first section is a very brief review to reacquaint you with the most important stuff you most likely forgot.

1.1 Atomic Structure

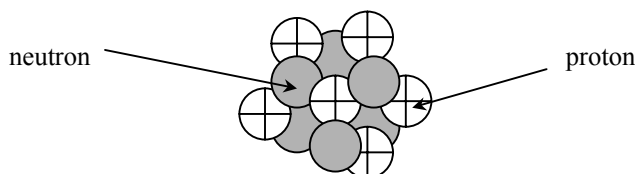
Molecules = atoms + bonds



Atoms = nucleus + electrons



Nucleus = protons + neutrons



Mass of proton:	1.6726×10^{-24} g
Mass of neutron:	1.6749×10^{-24} g
Mass of electron:	9.1094×10^{-28} g

*most of the mass of an atom resides in the nucleus

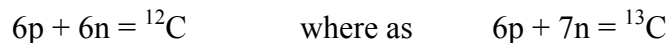
Atomic number (Z) = number of protons

Mass number (A) = number of protons + number of neutrons



Isotope = same atomic number, different number of neutrons.

Example: ^{12}C vs. ^{13}C



Atomic Weight = weighted average of the mass of all atomic isotopes

$$\begin{array}{r} .9888 * 12 = 11.8656 \\ .0112 * 13 = \underline{0.1456} \\ \hline 12.0112 \text{ amu} \end{array}$$

1 atomic mass unit (amu) is defined as 1/12 of ^{12}C .

The modern periodic table is based on carbon with an atomic weight of 12 amu. *Why is the modern periodic table not based on hydrogen?*

1.2 Electronic Structure

Why do we care so much about electrons?

Understanding organic chemistry boils down to understanding why compounds react the way they do. At the core of this is keeping track of electrons and understanding why they go where they do.

Two basic types of charged (ionic) chemical species:

Cation = a positively charged species



Anion = a negatively charged species



Ionization potential = The energy required to remove an electron from an atom and form a cation.

Electron affinity = The energy that is released by adding an electron to an atom to form an anion.

The bottom line driving force for every chemical interaction...every atom wants to have a noble gas electronic configuration...i.e., filled shells with 8 valence electrons (Octet Rule). This drive to satisfy the Octet Rule brings you to perhaps the most important concept you learned in general chemistry...ELECTRONEGATIVITY.

Electronegativity = the measure of an atom to draw binding electrons to itself.
Increasing electronegativity from the lower left to upper right of periodic table.
Scale of 0.7 to 4 (Pauling scale)

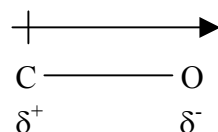
I	II	III	IV	V	VI	VII
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0					Br 3.0
						I 2.7

Electronegativities of common elements...

A difference greater than 2 between two elements is usually indicative of ionic bonding. Ionic bonds which are formed between species that are easily ionizable such as alkali metals and halogens (NaCl), i.e., a metal and a non-metal. A difference of less than 2 between two elements is usually indicative of covalent bonding. Covalent bonds are formed by the sharing of an electron pair...typically between two non-metals (C-O, C-C, C-N, C-H...etc)...between atoms which don't easily gain or lose electrons.

In truth, bonding between atoms spans a continuum of ionic and covalent character. In organic chemistry, we concern ourselves with primarily C, H, N, O, S and the halogens...and covalent bonds.

Despite the "sharing" of electrons between say, C and O, since O is more electronegative than C, the bond will be polar. The polarity of a covalent bond is expressed as δ^+ and δ^- ("partial positive" and "partial negative")...also seen as funny arrows...



The dipole moment of a molecule is the sum of all polarities in a molecule that results in partial positive and negative ends....symmetrical molecules tend to not have dipole moments (e.g., CH₄) while asymmetrical molecules have dipole moments (CH₃Cl). This idea rears its head in our discussions of solubility...polar compounds will dissolve in polar solvents, while non polar compounds prefer to dissolve in non-polar solvents. Hence, "oil and water don't mix."

1.3 Lewis Dot Structures

In general chemistry you learned how to draw molecule using Lewis Dot notation. Lewis structures are a convenient way to represent molecules with covalent bonds.

Do you remember how to do this???

- 1) total all valence electrons, + or – any extra charges.
- 2) Least electronegative in center (excluding H).
- 3) Orient other atoms radially.
- 4) Bonds = 2e-
- 5) Distribute remaining e- according to octet rule.
- 6) Extras are usually lone pairs.
- 7) Determine formal charge on atoms using octet rule.

Valence electrons = dots

Bond = two dots between two atoms

Observe the general bonding rules...

1 bond =	H	
1 bond =	F, Cl, Br, I	Group 7
2 bonds =	O, S	Group 6
3 bonds =	N	Group 5
4 bonds =	C	Group 4

Non-bonding electrons = lone-pair electrons

So, to draw Lewis structures from condensed structures... NH₃ and H₂O

N typically has 1 lone pair, O typically has 2 lone pair



Bonds can be (and are often) represented as lines instead of dots.

One line = one bond = one pair of electrons

Lone pairs are sometimes shown, but usually not. (just because they are not shown does not mean they are not there!)

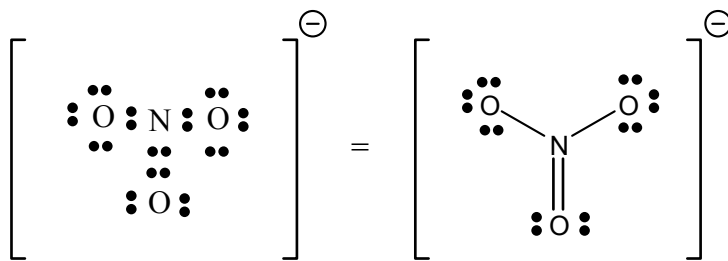


1.4 Formal Charge

$$FC = (\# \text{ of valence elec in atom}) - (\# \text{ of unshared elec. in atom}) - \frac{1}{2}(\# \text{ of shared elec. in atom})$$

For example... NO_3^- is the -1 charge on the N or one of the O's?

First, do a Lewis Dot diagram...

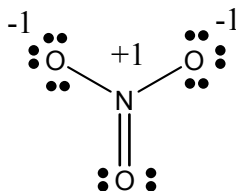


$$FC_{O1} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$FC_{O2,3} = 6 - 6 - \frac{1}{2}(2) = -1$$

$$FC_N = 5 - 0 - \frac{1}{2}(8) = +1$$

Therefore, the distribution of charges in nitrate anion looks like this...



It will be important for you to be able to recognize where charge is located on organic molecules...either as formal charge or as partial charge due to dipoles. Your ability to really understand chemical mechanisms will depend on it.

1.5 Atomic Orbital Theory

In organic chemistry, why do we care about atomic orbitals? Or valence bond theory, or MO theory for that matter??? Well, very shortly we will agonize over the overlap of p orbitals and where lone pairs of electrons lie and σ and π bonds and other all other such manner of things to which electrons are central. Remember, organic chemistry is ultimately about keeping track of electrons

THE RULE: no two electrons can occupy the same space and energy at the same time.

Schrodinger: Some peoples hero, some peoples Satan. From the observation of both wave and particulate nature of electrons, he described an electron interacting with a proton with a wave equation. Solutions to this evil bit of calculus are called wave functions (Ψ). A one-electron wave function is called an orbital and is the square of the wave function (Ψ^2) and is proportional to electron density...and therefore the probability of finding an electron with a given energy somewhere in space. Ugh.

Quantum numbers = Set of numbers that determine the wave function (orbital)

n = principle quantum number, distance from nucleus, larger number = higher energy, integer value (1,2,3,4...)

l = angular quantum number, related to shape of orbital, integer, $n-1$ to 0

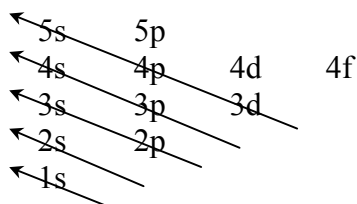
m = related to orientation in space, integer value $+l$ to $-l$.

s = spin, $+1/2$, $-1/2$

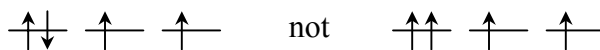
...from the angular quantum number l , $0 = s$ $1 = p$ $2 = d$ $3 = f$

gives, 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p....do you remember how they fill?

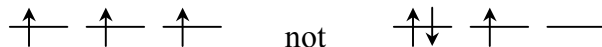
Can you say Aufbau?



...and Pauli? No more than two electrons in one orbital, must have opposite spin.



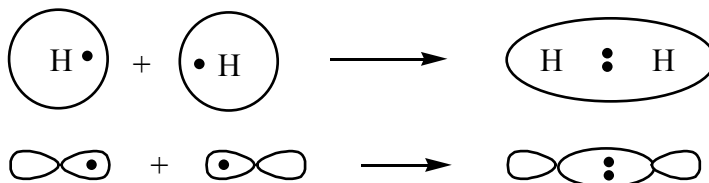
...and Hund?



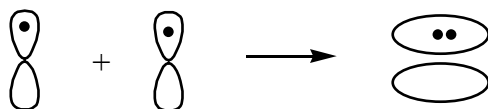
1.6 Valence Bond Theory

Covalent bonds result from the overlap of two atomic orbitals. This requires that there be 1 electron in each atomic orbital. Each atom retains its own atomic orbitals and the pair of electrons are “shared” by both atoms.

σ bond: results from the head-to-head overlap of orbitals



π bond: results from the lateral interaction of p orbitals

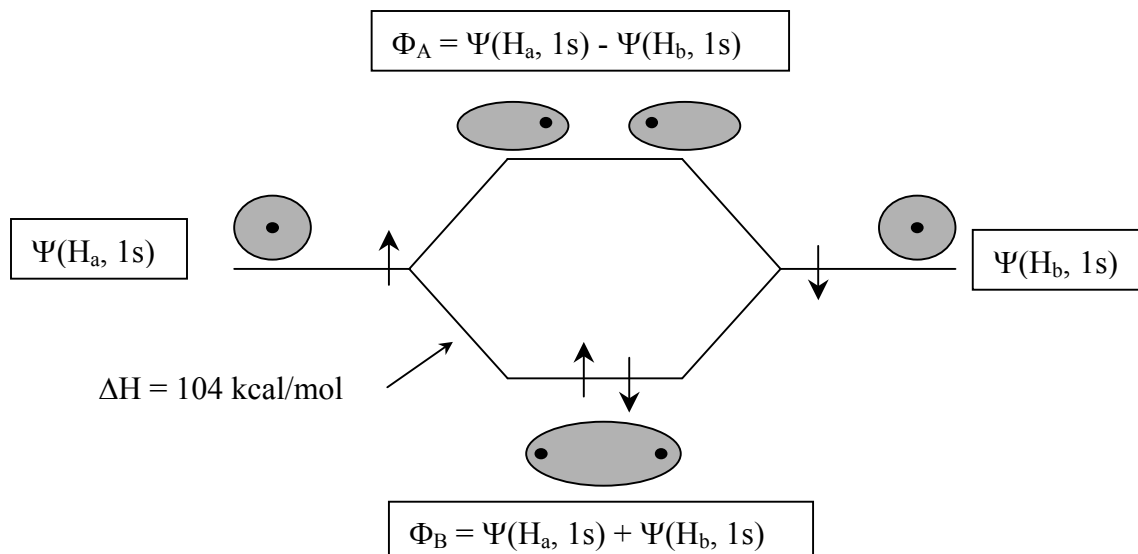


1.7 Molecular Orbital Theory

The atomic orbitals of each atom combine to form a new molecular orbital (unlike VB where the original atomic orbitals are retained). The number of molecular orbitals formed = the number of atomic orbitals involved.

Bonding orbitals = addition of orbitals, no node between atoms, lower energy than the atomic orbitals from which they arose. This is very often an important driving force in a reaction...lower overall energy in the molecule.

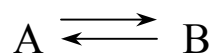
Antibonding = a node (zero electron probability) between the atoms therefore no bonding.



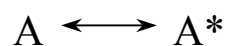
1.8 The Arrows

In general chemistry, you learned about 4 different kinds of arrows shown below. In organic chemistry, we are going to put these arrows to full use. Know them, live them, love them.

Two distinct chemical species...two straight arrows, one head each. This example shows a reversible reaction.



One species, two resonance forms...one straight arrow, two heads



One electron moving...single-barbed, curved arrow



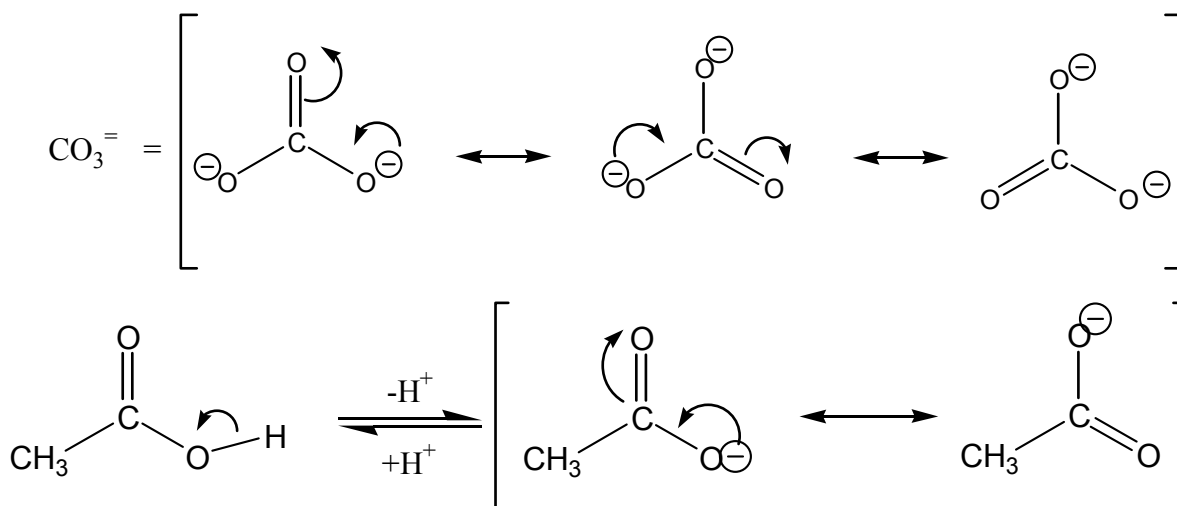
A pair of electrons (or bond) moving...double-barbed, curved arrow

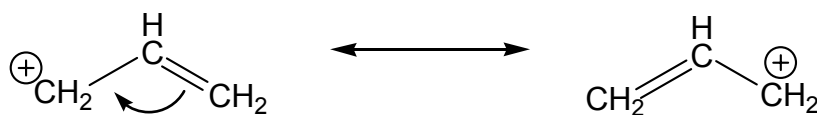


1.9 Resonance

For many charged and uncharged molecules, there is more than one possible structure. The different structures that arise from different electron configurations are called resonance structures. Different resonance structures sometimes have different chemical properties.

Examples...





More specific information on resonance will be presented when specific examples arise throughout the year...

And lastly,

Dissociation energy = energy required to break a bond homolytically

Homolytic cleavage = break a molecule into two neutral species

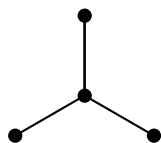
Heterolytic cleavage = break a bond so that an anion-cation pair are formed.

...Oops, one more...Shapes.

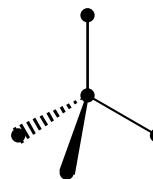
You learned at least three basis shapes of molecules; linear, trigonal planar and tetrahedral.



linear



trigonal planar



tetrahedral

...for organic chemistry, it is important that you learn them, know them, live them.