CHEM 115
Models that Build onto Electron Dot (Lewis) Model

Lecture 23
Prof. Sevian

Reminder: Challenge problem is due at 2:00 promptly.

Agenda

Models of covalent bonding (still working on red one today)

1. Electron (Lewis) Dot Structures (explains stability of molecules)
2. VSEPR Theory (explains molecular shape)
3. Valence Bond Theory and Hybridization (reconciles the differences between the shapes of the s and p atomic orbitals with the geometries predicted by VSEPR)
4. Molecular Orbital Theory (explains the existence of excited electronic states of molecules)

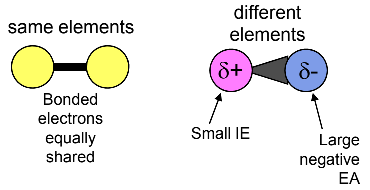
Models that explain properties of molecules based on distribution of electron density (can be used with first three models above)

- Formal charges model
  - Purpose: to predict which resonance structures are most and least stable, based on electron density distribution over the molecule or ion, when there are resonance structures that are not equivalent by symmetry
- Electronegativity model
  - Purpose: to predict how much ionic character a covalent bond has, based on unequal electron density distribution in the bond

Review of physical properties whose trends we generally explained (periodicity)

- Atomic radius
  Distance between nucleus at center of atom (protons) and most loosely bound valence electron
  - Increases down group (because more shells)
  - Decreases across (L→R) period (because Z_{eff} increases)
  - He is smallest atom
- Ionization energy
  Energy (endothermic) required to remove the most loosely bound electron
  - Decreases/become less endothermic down group (easier to remove e^- because farther away from + charged nucleus)
  - Increases across period (stronger force holding e^- to core because Z_{eff} increases)
  - Cs has smallest ionization energy, i.e., “wants” to get rid of electron the most (Fr would have smaller IE but is too radioactive to be useful)
- Electron affinity
  Energy change resulting from adding one e^-… in most cases it is exothermic (releasing heat energy), but sometimes endothermic (must input energy to force atom to accept the e^-)
  - Generally becomes less exothermic (smaller negative value) down group (more shells so new e^- not attracted as strongly)
  - Generally becomes more exothermic (larger negative value) across period (because Z_{eff} increases)
  - F has most exothermic electron affinity, i.e., “wants” electron the most

Why the physical properties are important to understand

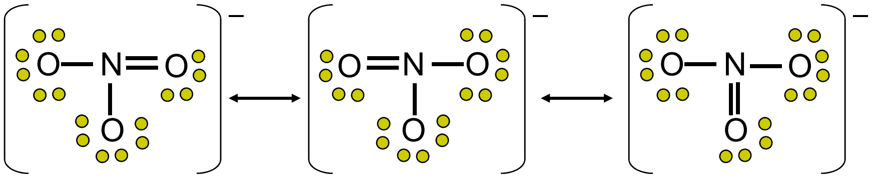


- Covalent bonding in molecules involves valence electrons of atoms
- Electrons in the bonds are shared (covalent bonding theories in chapter 9)
  - By the two atoms that the bond is holding together (electrons localized in *valence bonds*)
  - Across the entire molecule (electrons delocalized in *molecular orbitals*)
- Electrons in the bonds are not necessarily shared equally
  - The more unequally the electrons are shared, the more ionic character the bond takes on (*bond polarity*)
  - Bonds with more ionic character are stronger, due to additional attraction between δ+ pole and δ- pole
- You can predict qualitative comparisons of ionic character of bonds
  - The more exothermic an atom’s EA is (closer to F), the more easily it attracts the electrons in the bond and becomes stronger δ- pole
  - The smaller an atom’s IE is (closer to Cs), the more easily it allows electrons in the bond to be attracted away from it and becomes stronger δ+ pole

Stability predictions that can come from electron dot (Lewis) structures

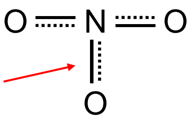
- Resonance
- Formal charge (when resonance structures are not equal, this is useful for predicting which resonance structures are most stable)
- Bond order (useful for comparing strengths of bonds)
- Bond length comparisons (comparing one molecule to another)

Resonance Structures (example where all equivalent)



- What do these structures have in common?
- How are they different?
- Which of these is the actual structure of NO_3^-?

$$\boxed{\text{Bond order} = \frac{\#\ of\ bonds}{\#\ of\ locations}}$$

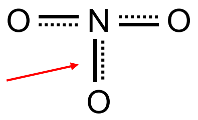


Average bond order = 4 bonds split over 3 locations = 4/3

Note: This is not a correct Lewis structure. It is drawn this way only to emphasize the bond order.

Bond Order and Bond Length/Strength

- Bond order
  - Single bond is bond order 1
  - Double bond is bond order 2
  - Triple bond is bond order 3
  - Fractional bond orders occur when there are resonance structures



Average bond order = 4 bonds split over 3 locations = 4/3

- Bond strength
  - The greater the bond order, the stronger the bond (the more energy required to break the bond)
- Bond length
  - The greater the bond order, the shorter the bond length

Bond strength

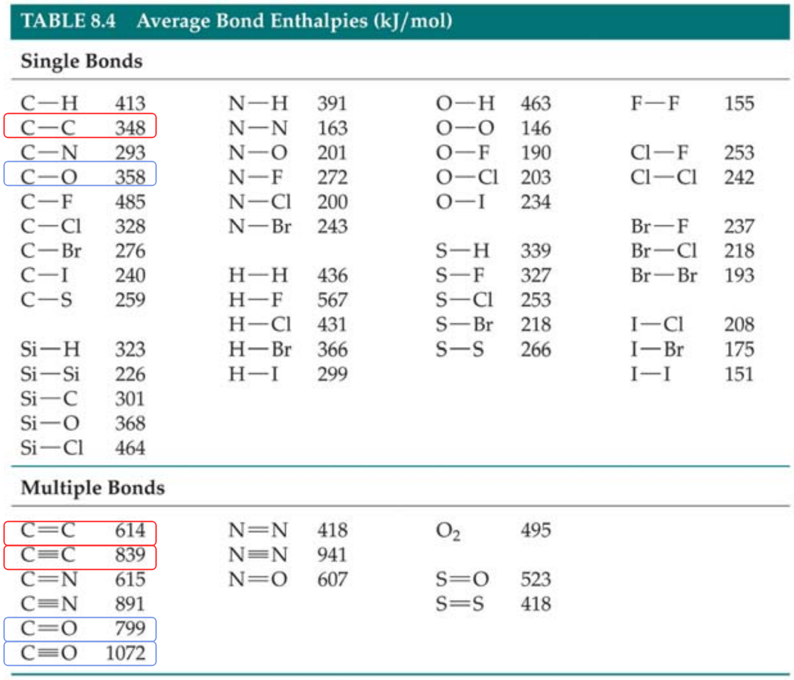


TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Bond length

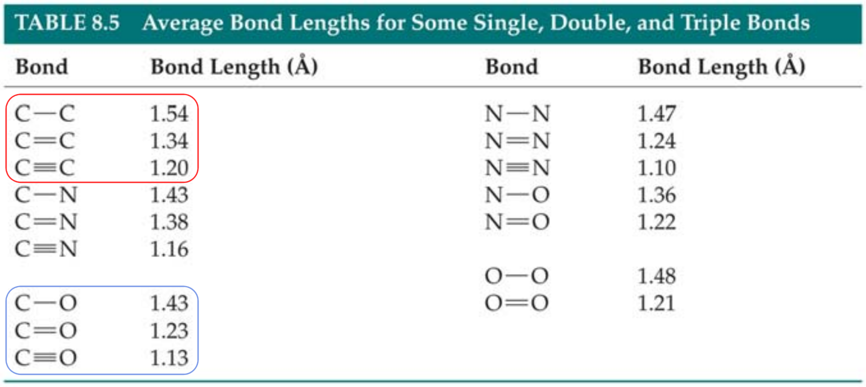
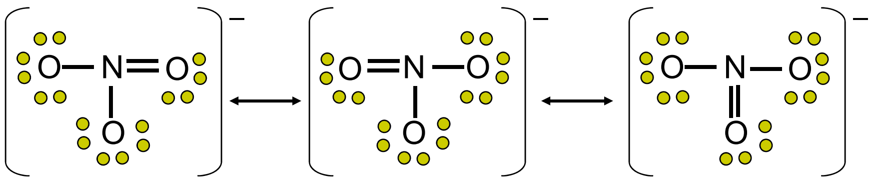


TABLE 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

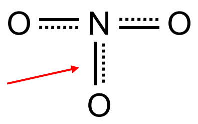
Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

Let's look again at our example of NO_3^- Resonance Structure (example where all equivalent)



- What do these structures have in common?
- How are they different?
- Which of these is the actual structure of NO_3^-?

$$\boxed{\text{Bond order} = \frac{\#\ of\ \ bonds}{\#\ of\ \ locations}}$$



Average bond order = 4 bonds split over 3 locations = 4/3

Note: This is not a correct Lewis structure. It is drawn this way only to emphasize the bond order.

Formal Charges

Warning: Two other models seem similar to the formal charges model but are completely different models.

- *Oxidation numbers model for understanding redox reactions*
- *Electronegativity model for explaining polarity (ionic character) in covalent bonds*

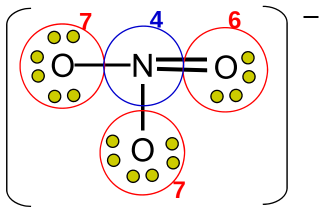
A comparison between the valence electrons originally contributed by an atom and the electrons that it looks like the atom would have if all bonds were broken and electrons reassigned democratically.

The valence electrons that were originally contributed:

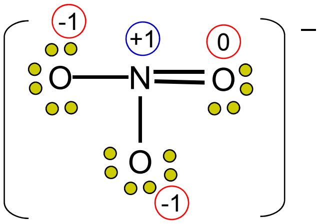
- each O had 6
- the N had 5

The formal charges model is used to explain why some resonance structures are more stable than others.

Electrons assigned democratically if bonds hypothetically broken



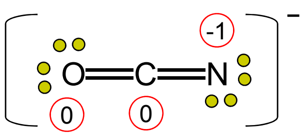
Therefore, the formal charges on each atom are

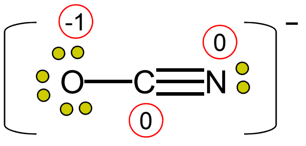


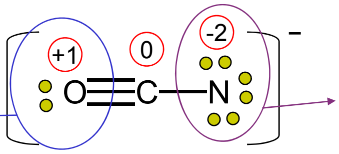
Notice that the sum of the formal charges must equal the ion charge

Formal Charges and Alternative Structures (example where resonance structures not equivalent)

- Formal charges give a picture of the electron density distribution so that you can predict which resonance structures contribute least or most to the actual structure
- If more than one Lewis structure exists, the most stable structure is the one in which the formal charges make most sense
  - Negative formal charges on atoms with large electron affinity
  - Positive formal charges on atoms with small ionization energies (small electron affinity)
- The most stable structure of the 3 structures below is the rightmost because O is more stable with negative formal charge on it because it has largest EA of the 3 elements (O, C and N)





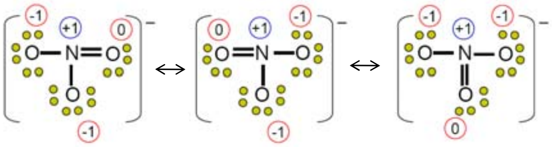


Oxygen's formal charge here is +1 because the democratically assigned electrons (5) are one short of the valence preference of oxygen (6)

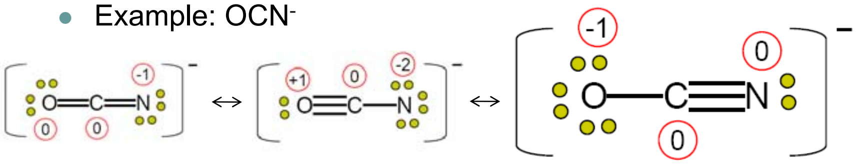
Nitrogen's formal charge here is -2 because the democratically assigned electrons (7) are two more than the valence preference of nitrogen (5)

Usefulness of formal charges model

- When resonance structures are equivalent, formal charges give a picture of how electron density is distributed on the molecule (or ion)
  - Example: NO_3^- (positive center negative edges)



- When resonance structures are not equivalent, formal charges are useful for predicting which of the resonance structures is most stable
  - Example: OCN^-

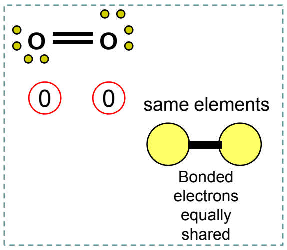


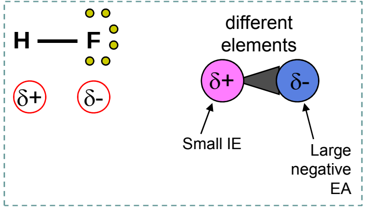
A Range of Bond Types

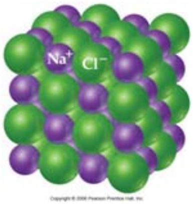
Bond "types" are not separable into a true dichotomy between covalent and ionic. Instead there is a range of covalent character vs. ionic character of bonds.

Increasing ionic character of bond
Increasing "bond polarity" →

nonpolar covalent	**polar covalent**	**ionic**
Perfectly covalently shared electrons	Bonding electrons exhibit greater electron density (δ-) on one atom in the bond than on the other (δ+)	Ions with full charges (unshared electrons)

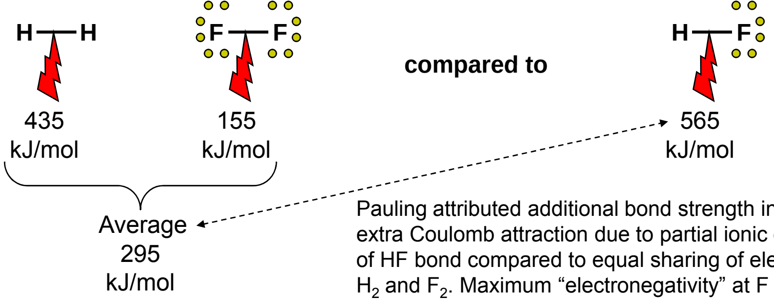






Electronegativity Model to Explain Bond Polarity

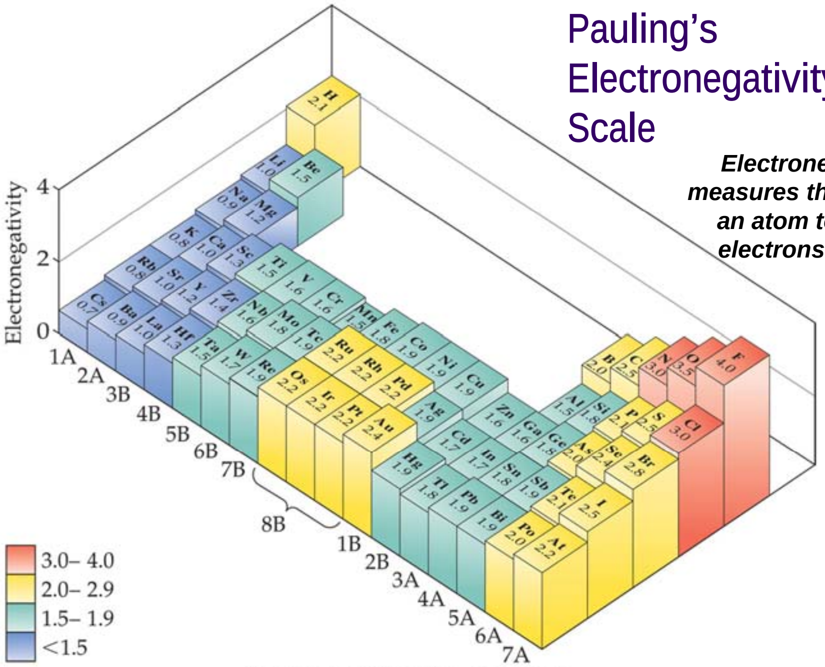
- Definition: the attraction that a given atom has for the electrons that are in a bond
- Early idea related to electron affinity (energy required to add an electron to an atom) and ionization energy (energy required to remove an electron from an atom)
- Linus Pauling invented an electronegativity scale of elements based on comparing bond energies of elements bonded to themselves and to other elements



Pauling attributed additional bond strength in HF to extra Coulomb attraction due to partial ionic character of HF bond compared to equal sharing of electrons in H_2 and F_2. Maximum "electronegativity" at F set to 4.0.

Pauling's Electronegativity Scale

Electronegativity measures the ability of an atom to attract electrons to itself



Predicting Bond Polarity Using Electronegativities

- Electronegativity is a measure of the ability of an atom to attract electrons to itself
- Bond polarity depends on the **difference** between the electronegativities of the two elements that are in a bond

No difference in electronegativies of atoms in bond

Large difference in electronegativies of atoms in bond

Increasing bond polarity

Electronegativities Allow You to Compare Bond Polarity

- Which bond is most polar? Which bond is least polar?
- Which end of the bond is the negative pole (greater electron density)? Which end is the positive pole (less electron density)?

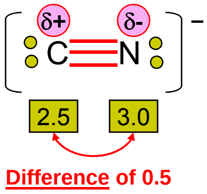
The bond between C and N in CN^-

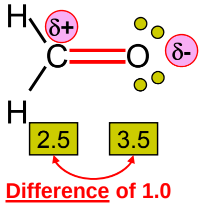
Is less polar than

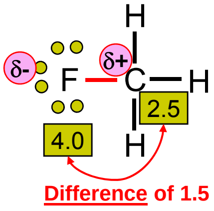
The bond between C and O in H_2CO

Is less polar than

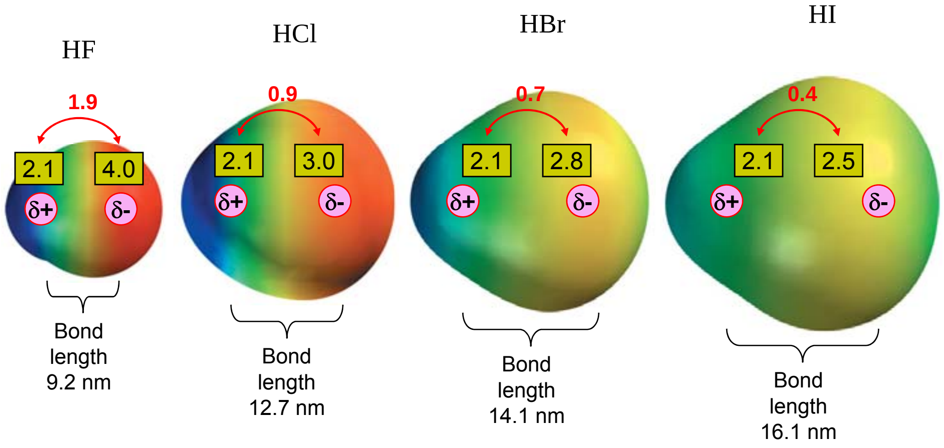
The bond between C and F in CH_3F







Comparing a series



Use the information above to explain why the dipole moments of this series of hydrogen halides exhibits the following behavior:

Dipole moments are HF = 1.82 *D*, HCl = 1.08 *D*, HBr = 0.82 *D*, HI = 0.44 *D*

Note: “*D*” stands for Debyes, the S.I. units in which dipole moment is measured in the laboratory.

What we’ve learned so far today

- Formal charges model:
  - The distribution of electron density in a molecule or ion
  - Useful for comparing different resonance structures to see which is most stable and which is least stable
  - Can be used to predict which resonance structures contribute most and least to the actual structure of a molecule or ion
- Electronegativity model:
  - Provides a way of understanding the gray area between covalent bonding and ionic bonding: ranging from not polar at all, to so completely polar that the electron transfers completely
  - Use the difference between electronegativity values of two atoms in a bond to estimate ionic character of the bond
    - Zero difference = perfectly polar
    - The larger the difference, the more ionic character the bond has
  - Ultimately you can predict the overall polarity of a molecule (by a vector sum of all the bond polarities in a molecule)
  - When a molecule is more polar, it responds more to an electric field – you can measure the dipole moment of a molecule