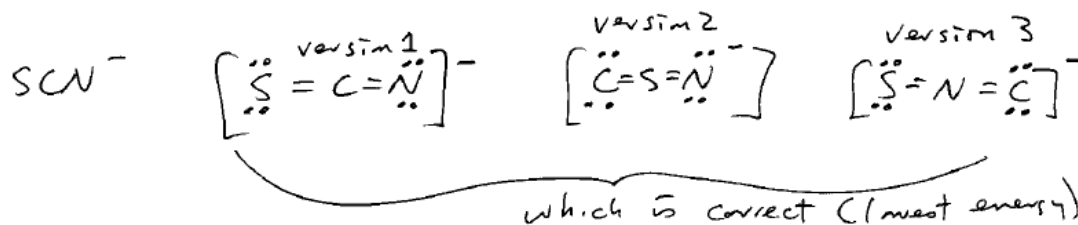
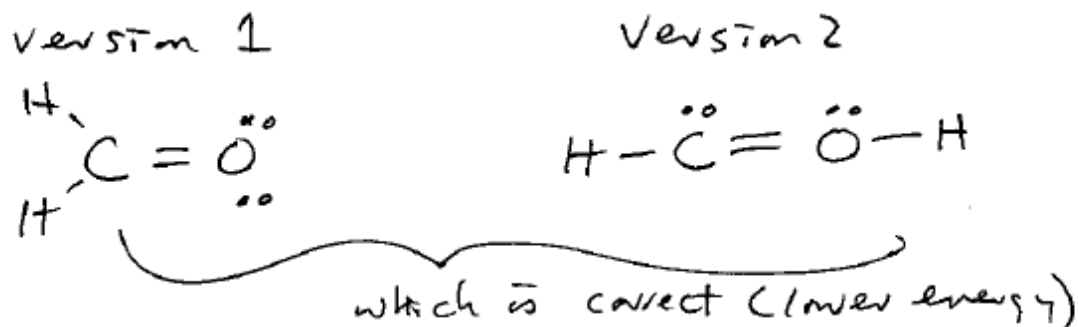


LECTURE 9. MORE SOPHISTICATED IDEAS IN LEWIS DOT STRUCTURES.

Can you make things more difficult?

Formal Charge

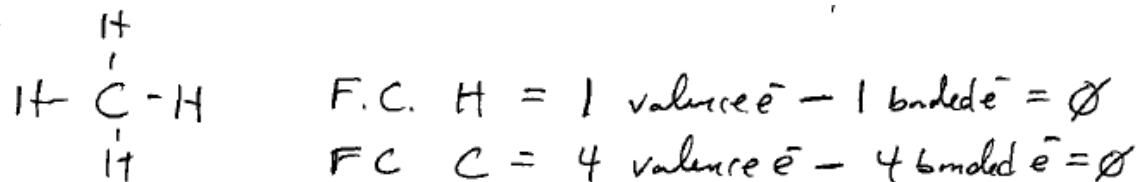
Sure, let's discuss Formal Charge. First, why do it? Consider the following examples of Lewis structures that seem to fit the rules, CH_2O :



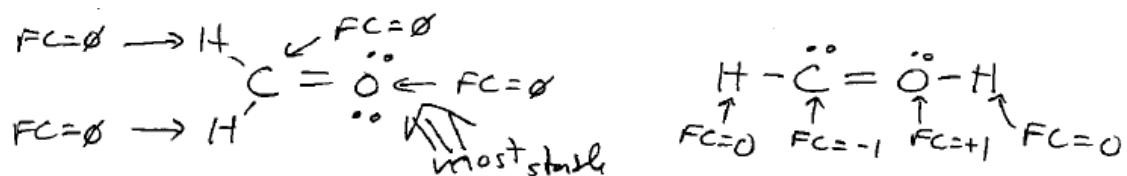
Solution, calculate the formal charge on each atom. The compound with the smallest formal charge values is the most stable. So how do you calculate formal charge?

$$\text{F.C.} = \# \text{ of valence } e^- \text{ s for an atom} - (2e^- \text{ s for every unbonded pair and } 1e^- \text{ from each bonded pair})$$

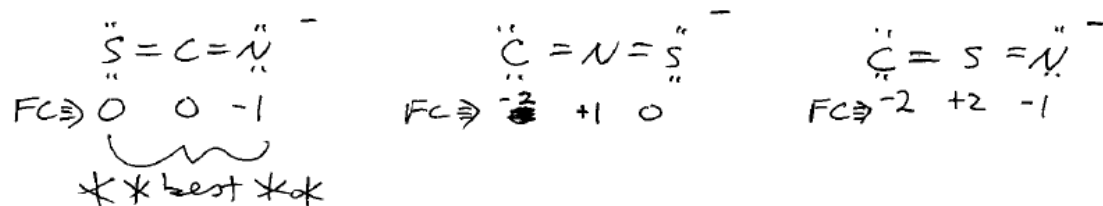
Example:



Example, which CH₂O is most stable:



Example, which SCN⁻ is most stable:



Electronegativity

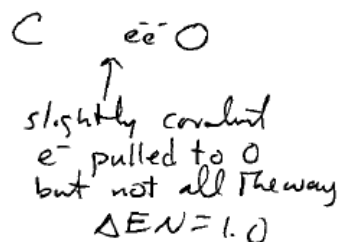
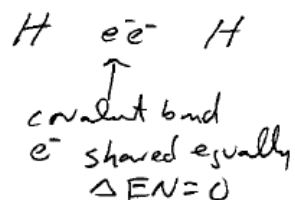
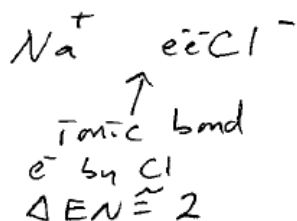
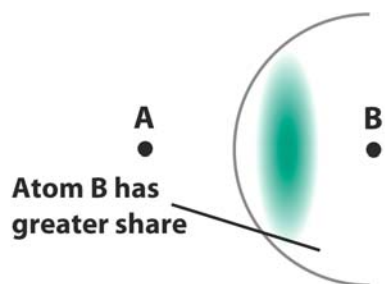
How do we distinguish whether a bond is ionic or covalent?

We can determine this in a quantitative manner:

$\Delta EN < 1.5$ is covalent

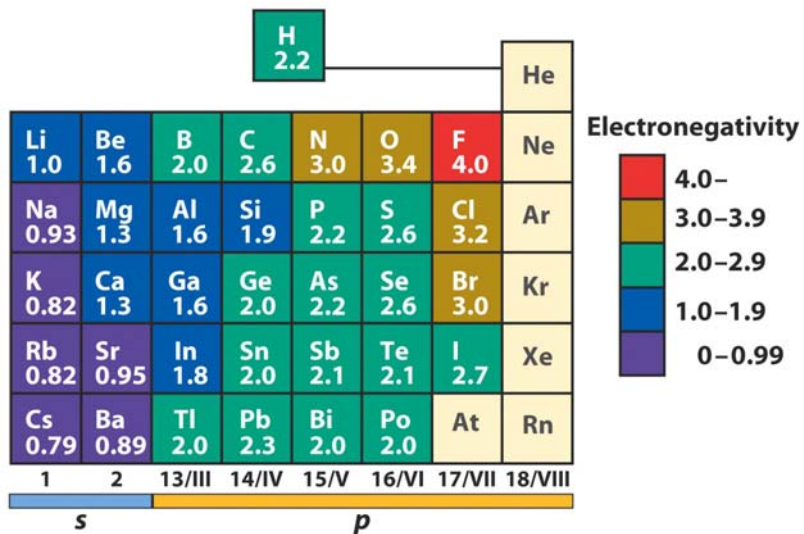
$\Delta EN > 1.5$ is ionic

But what is EN? Electronegativity is a measure of the pull by an atom for electrons. Atoms on the right pull more. Atoms on the left pull less.



So where do these numbers come from?

Both Pauling and Millikin made scales. Here is a rough version that makes calculations easy to remember. Start with Li = 1.0 and add a half as you go across the second row, all the way up to 4.0 for F.



Just like other trends, a diagonal from bottom right to top left parallels effective nuclear charge

**Note, the simple number in n=2 row can be memorized because they increase by about 0.5 and H is 2.2

Example, what is

$$\Delta \text{EN C-O} = |2-3| = 1.0 \text{ (covalent)}$$

$$\Delta \text{EN F-F} = |4-4| = 0 \text{ (covalent)}$$

$$\Delta \text{EN Li}_2\text{O} = |1-3.5| = 2.5 \text{ (ionic)}$$

Bond Energy and Length Trends

As we add more bonding (single->double->triple) the glue that binds the atom increases. The length between the atoms decreases.

TABLE 2.3 Average Bond Dissociation Energies (kJ·mol⁻¹)

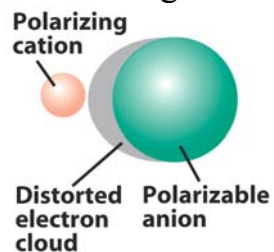
| Bond | Average bond dissociation energy | Bond | Average bond dissociation energy |
|-------------------|----------------------------------|------|----------------------------------|
| C-H | 412 | C-I | 238 |
| C-C | 348 | N-H | 388 |
| C=C | 612 | N-N | 163 |
| C [≡] C* | 518 | N=N | 409 |
| C=C | 837 | N-O | 210 |
| C-O | 360 | N=O | 630 |
| C=O | 743 | N-F | 195 |
| C-N | 305 | N-Cl | 381 |
| C-F | 484 | O-H | 463 |
| C-Cl | 338 | O-O | 157 |
| C-Br | 276 | | |

*In benzene.

- C-C Single bond, 154 pm, 348 kJ/mole → length goes down as bonding goes up
- C=C double bond, 134 pm, 612 kJ/mole
- C≡C triple bond, 120pm, 837 kJ/mole → energy goes up and bonding goes up

Polarizability

As we extend down the periodic table the electron density around the nucleus becomes more easily distorted. This results in a decrease in the ability to form strong bonds, hence the tendency for bond energies to go down, for example, in comparing the bond strength of HF > HCl > HBr > HI



| | | | |
|-------|-----|-----|---------|
| 17/VI | HF | 543 | 18/VIII |
| 16/VI | HCl | 419 | |
| | HBr | 354 | |
| | HI | 287 | |

