5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #11

Readings for today: Section 2.7 (2.8 in *3rd ed*) – Resonance, and Section 2.8 (2.9 in *3rd ed*) – Formal Charge.
Read for Lecture #12: Section 2.9 (2.10 in *3rd ed*) – Radicals and Biradicals, Section 2.10 (2.11 in *3rd ed*) - Expanded Valence Shells, Section 2.11 (2.12 in *3rd ed*) - Group 13/III Compounds, Section 2.3 (2.1 in *3rd ed*)- The Energetics of Ionic Bond Formation, Section 2.12 (2.13 in *3rd ed*) – Electronegativity.

Topics: **I.** Lewis structures
II. Formal charge
III. Resonance structures

I. LEWIS STRUCTURES

Lewis structures share the total number of valence electrons between atoms so that each atom achieves a noble gas configuration.

EXAMPLE: **Hydrogen cyanide** (HCN)

1. Draw skeleton structure. H and F are always terminal atoms. The element with the lowest ionization energy goes in the middle (with some exceptions).

2. Count the total # of valence e^-s. If there is a negative ion, add the absolute value of total charge to count of valence electrons; if a positive ion, subtract.

3. Calculate the total # of e^-s needed for each atom to have a full valence shell.

4. Subtract the number in step 2 (valence electrons) from the number in step 3 (total electrons for full shells). The result is the **number of bonding electrons**.

5. Assign 2 bonding electrons to each bond.

6. Are there any remaining bonding e^-s? _____________. If bonding electrons remain, include double or triple bonds.

7. Are there any remaining valence electrons? _____________. If valence electrons remain, assign as lone pairs, giving octets to all atoms except H.

8. Determine the formal charge. (We'll learn to do this in Section II of the notes.)

EXAMPLE: **Cyanide ion** (CN^-)

1. skeletal structure.

2. # of valence e^-s. (Don't forget the -1 charge!)

3. # of e^-s for each atom to have a full valence shell.

4. # of bonding e^-s.

5. Assign 2 bonding electrons per bond.

6. remaining bonding electrons? _________

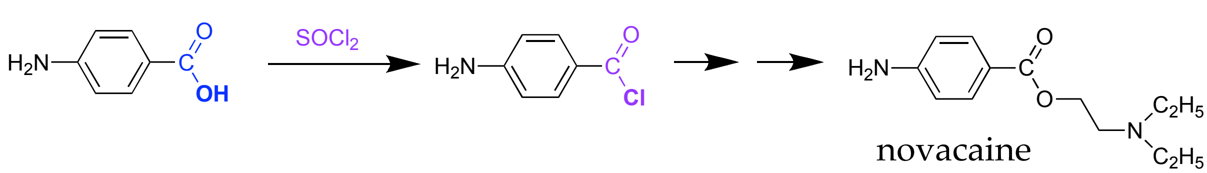
7. remaining lone pair e^-s? _________

8. determine formal charge.

EXAMPLE: **Thionyl chloride** ($SOCl_2$)

Thionyl Chloride, $SOCl_2$

$SOCl_2$ is a reagent used in organic and medicinal chemistry to convert carboxylic acid (COOH) groups to acid chloride (COCl) groups in molecules. One example of using $SOCl_2$ in the synthesis of pharmaceuticals is for novacaine, a local anasthetic drug used in dentistry and to reduce pain in intramuscular injections of other drugs, such as antibiotics.



novacaine

1. skeletal structure of $SOCl_2$.

2. # of valence e^-s.

3. # of e^-s for each atom to have a full valence shell.

4. # of bonding e^-s.

5. Assign 2 bonding e^-s per bond.

6. remaining bonding e^-s? ________

7. remaining lone pair e^-s?

8. determine formal charge.

II. FORMAL CHARGE (FC)

Formal charge is a measure of the extent to which an atom has gained or lost an _______________ in the process of forming a covalent bond.

To assign formal change, use the formula below.

$$\mathbf{FC = V - L - (½)S}$$

V ≡ number of _______________ electrons
L ≡ number of _______________ electrons
S ≡ number of _______________ (bonding) electrons

For an electronically-neutral molecule, the sum of the formal charges of the individual atoms must be ___________.

For a molecule with a net charge of -1, the sum of the formal charges of its atoms must be ______.

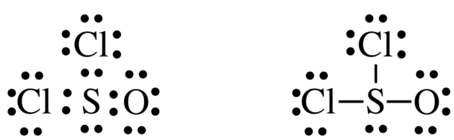
The sum of individual formal charges must equal the total charge on the molecule!

Let's go back to two of Lewis structure examples.
EXAMPLE: CN^-

FC on C **= V – L - (½)S** = _____ - _____ - (½) _____ = _____

FC on N = **V – L - (½)S =** _____ - _____ - (½) _____ = _____

EXAMPLE: $SOCl_2$



FC on S = _____ - _____ - (½) _____ = _____

FC on O **=** 6 - 6 - (½)2 = _____

FC on each Cl = **7** – 6 - (½) 2 = _____

In general, more electronegative atoms should hold the negative charge.

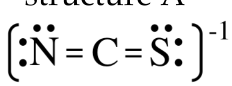
Note: FORMAL CHARGE ≠ OXIDATION NUMBER

Formal charge is very helpful in deciding between possible Lewis structures. **Structures with lower absolute values of FC are the _________ stable (lower energy) structures.**

For example, consider the three possible structures for the thiocyanate ion, CSN^-. The ionization energies in kJ/mol for C, S, and N are IE_C = 1090, IE_S 1000, IE_N = 1400.

Based on IE alone, we would predict _____ to be the central atom.

structure A

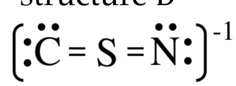


FC_N = _________________

FC_C = _________________

FC_S = _________________

structure B

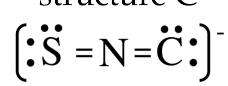


FC_N = 5 – 4 - 2 = _______

FC_C = 4 – 4 - 2 = _______

FC_S = 6 – 0 - 4 = _______

structure C



FC_N = 5 – 0 - 4 = _______

FC_C = 4 – 4 - 2 = _______

FC_S = 6 – 4 - 2 = _______

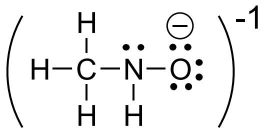
The most stable structures is _______ .

If two valid Lewis structures have the same absolute value of formal charges, the more stable structure is the one with a negative charge on the more electronegative atom.

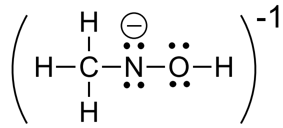
CH_3 usually represents a ____________ group. These groups are always terminal.

CH_3NHO^-

For "chain" molecules, atoms usually written in order. Terminal atoms usually follow the atom to which they are attached.



Zero FC on all other atoms



Zero FC on all other atoms

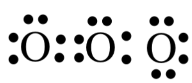
χ: F > O > N > C

_____________ energy structure

III. RESONANCE STRUCTURES

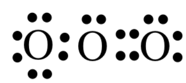
For certain molecules, more than one Lewis structure is needed to correctly describe the valence electron structure of the molecule.

For example, consider the Lewis structure(s!) of ozone, O_3.



A B C

structure 1



A B C

structure 2

1) skeletal structure
2) valence e^-s: 3(6) = ______
3) full shell e^-s: 3(8) = ______
4) bonding e^-s: ______ – ______ = ______
5) assign bonding e^-s
6) remaining bonding e^-s: 2
7) remaining valence e^-s (assigned as lone pairs): 12
8) formal charges:

Structure 1

FC_{OA} = ______

FC_{OB} = ______

FC_{OC} = ______

Structure 2

FC_{OA} = ______

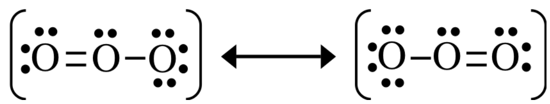
FC_{OB} = ______

FC_{OC} = ______

We might expect one short O=O bond and one long O-O bond, but experimental evidence demonstrates that the two bonds are __________________.

Thus, the two structures are equivalent. A better model is to blend the structures as denoted with the brackets and arrows below, a **resonance hybrid**.

O_3 :



Electrons in resonance structures are ________________. Electron pairs are shared over several atoms, not just two.

Resonance structures are two (or more) structures with the same arrangement of ____________, but a different arrangement of ________________.