5.111 Lecture Summary #10   Monday, September 29, 2014

Readings for today: Section 2.5 – 2.8 Lewis Structures (Same sections in 5th and 4th ed.)
Read for Lecture #11: Section 2.9 – Radicals and Biradicals, Section 2.10 - Expanded Valence Shells, Section 2.11 - Group 13/III Compounds (Same sections in 5th and 4th ed.)

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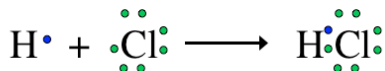

I. LEWIS STRUCTURES
G.N. Lewis (American scientist, 1875-1946). Twenty years prior to the development of quantum mechanics, Lewis recognized an organizing principle in bonding. Namely that:

The key to covalent bonding is **electron sharing**, such that each atom achieves a _____ valence shell (noble gas configuration).

OCTET RULE: electrons are distributed in such a way that each element is surrounded by eight electrons, an octet. Each dot in a Lewis structure represents a _____ e$^-$.

F + F $\longrightarrow$

EXCEPTION WITH H: special stability is achieved with _____ electrons.

H$\cdot$ + $\cdot$Cl: $\longrightarrow$ H:Cl:

Each valence e$^-$ in a molecule can be described as a bonding or a lone-pair electron.
For **Cl** in **HCl**

- _____ bonding electrons

- _____ lone-pair electrons   or   _____ lone pairs

Lewis structures correctly predict electron configurations 90% of the time. Our other option: solve the Schrödinger equation.

PROCEDURE FOR DRAWING LEWIS STRUCTURES

1. Draw a **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 number of **valence electrons**. If there is a negative ion, add the absolute value of total charge to the count of valence electrons; if positive ion, subtract.

3. Count 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. If bonding electrons remain, make some double or triple bonds. In general, double bonds form only between C, N, O, and S. Triple bonds are usually restricted to C, N, and O.

7. If valence electrons remain, assign them as lone pairs, giving octets to all atoms except hydrogen.

8. Determine the formal charge.

EXAMPLES

Hydrogen cyanide (HCN)   **Cyanide ion** (CN⁻)

1.   skeletal structure.
        (Atom in the middle for HCN is _____)

2.   # of valence e⁻s. (Don't forget charges)

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 (we will come back to this in a minute).

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.

$$FC = V - L - (½)B$$

V ≡ number of _____ electrons

L ≡ number of _____ electrons

B ≡ number of _____ 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 CN⁻.

$$\left[:C:::N:\right]^{-1} \qquad \left[:C\equiv N:\right]^{-1}$$

FC on C = **V − L - (½)B** = _____ - _____ - (½) _____ = _____

FC on N = **V − L - (½)B** = _____ - _____ - (½) _____ = _____

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 an ion of thiocyanate (a thiocyanate ion contains 1C, 1S, and 1N, and has a charge of -1). 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.
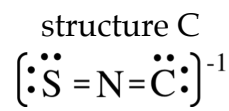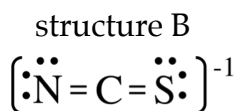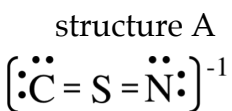
structure A	structure B	structure C
$\left[:C=S=N:\right]^{-1}$	$\left[:N=C=S:\right]^{-1}$	$\left[:S=N=C:\right]^{-1}$
FC_N = _____	FC_N= _____	FC_N = 5 – 0 - 4 = _____
FC_C = _____	FC_C= _____	FC_C = 4 – 4 - 2 = _____
FC_S = _____	FC_S = _____	FC_S = 6 – 4 - 2 = _____

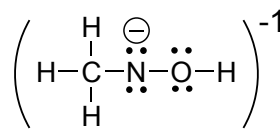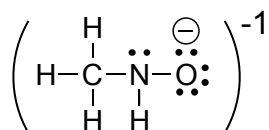The most stable structures is _____ .

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

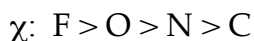CH$_3$ is a _____ group. These groups are <u>always</u> terminal.

CH$_3$NHO⁻

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

$$\left(\begin{array}{c} H \\ | \\ H-C-N-\overset{..}{\underset{..}{O}}{:}^{\ominus} \\ | \quad | \\ H \quad H \end{array} \right)^{-1}$$

$$\left(H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\ominus}{\underset{..}{\overset{..}{N}}}-\overset{..}{\underset{..}{O}}-H \right)^{-1}$$

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$_3$.

:Ö::Ö: Ö:
  A   B   C
   structure 1

:Ö: Ö::Ö:
  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:

$$:\ddot{O}::\ddot{O}:\ddot{\underset{\cdot\cdot}{O}}:$$

A   B   C

Structure 1

$$:\ddot{\underset{\cdot\cdot}{O}}:\ddot{O}::\ddot{O}:$$

A   B   C

Structure 2

$FC_{OA} =$ _____ $FC_{OA} =$ _____

$FC_{OB} =$ _____ $FC_{OB} =$ _____

$FC_{OC} =$ _____ $FC_{OC} =$ _____

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 $\left[:\ddot{O}=\ddot{O}-\ddot{\underset{\cdot\cdot}{O}}:\right] \longleftrightarrow \left[:\ddot{\underset{\cdot\cdot}{O}}-\ddot{O}=\ddot{O}:\right]$

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 ATOMS, but a different arrangement of ELECTRONS.

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