

## 5.111 Lecture Summary #11

**Readings for today:** Section 2.7 (2.8 in 3<sup>rd</sup> ed) – Resonance, and Section 2.8 (2.9 in 3<sup>rd</sup> ed) – Formal Charge.

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

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

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### 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<sup>s</sup>. 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<sup>s</sup> 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<sup>s</sup>? \_\_\_\_\_. 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.)

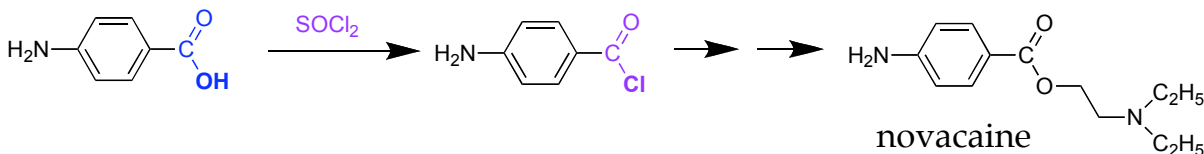
*EXAMPLE: Cyanide ion* ( $\text{CN}^-$ )

1. skeletal structure.
2. # of valence e<sup>-</sup>s. (Don't forget the -1 charge!)
3. # of e<sup>-</sup>s for each atom to have a full valence shell.
4. # of bonding e<sup>-</sup>s.
5. Assign 2 bonding electrons per bond.
6. remaining bonding electrons? \_\_\_\_\_
7. remaining lone pair e<sup>-</sup>s? \_\_\_\_\_
8. determine formal charge.

*EXAMPLE: Thionyl chloride* ( $\text{SOCl}_2$ )

*Thionyl Chloride,  $\text{SOCl}_2$*

$\text{SOCl}_2$  is a reagent used in organic and medicinal chemistry to convert carboxylic acid ( $\text{COOH}$ ) groups to acid chloride ( $\text{COCl}$ ) groups in molecules. One example of using  $\text{SOCl}_2$  in the synthesis of pharmaceuticals is for novacaine, a local anesthetic drug used in dentistry and to reduce pain in intramuscular injections of other drugs, such as antibiotics.



1. skeletal structure of  $\text{SOCl}_2$ .
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 charge, use the formula below.

$$\text{FC} = \text{V} - \text{L} - (\frac{1}{2})\text{S}$$

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.

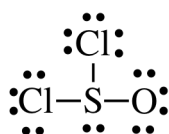
EXAMPLE:  $\text{CN}^-$



$$\text{FC on C} = \text{V} - \text{L} - (\frac{1}{2})\text{S} = \underline{\hspace{1cm}} - \underline{\hspace{1cm}} - (\frac{1}{2}) \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

$$\text{FC on N} = \text{V} - \text{L} - (\frac{1}{2})\text{S} = \underline{\hspace{1cm}} - \underline{\hspace{1cm}} - (\frac{1}{2}) \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

EXAMPLE:  $\text{SOCl}_2$



$$\text{FC on S} = \underline{\hspace{1cm}} - \underline{\hspace{1cm}} - (\frac{1}{2}) \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

$$\text{FC on O} = 6 - 6 - (\frac{1}{2})2 = \underline{\hspace{1cm}}$$

$$\text{FC on each Cl} = 7 - 6 - (\frac{1}{2}) 2 = \underline{\hspace{1cm}}$$

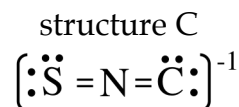
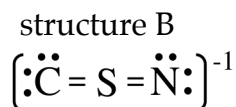
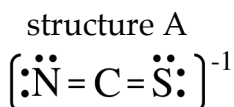
In general, more electronegative atoms should hold the negative charge.

Note: FORMAL CHARGE  $\neq$  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,  $\text{CSN}^-$ . The ionization energies in kJ/mol for C, S, and N are  $\text{IE}_\text{C} = 1090$ ,  $\text{IE}_\text{S} = 1000$ ,  $\text{IE}_\text{N} = 1400$ .

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



$$\text{FC}_\text{N} = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{N} = 5 - 4 - 2 = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{N} = 5 - 0 - 4 = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{C} = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{C} = 4 - 4 - 2 = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{C} = 4 - 4 - 2 = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{S} = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{S} = 6 - 0 - 4 = \underline{\hspace{2cm}}$$

$$\text{FC}_\text{S} = 6 - 4 - 2 = \underline{\hspace{2cm}}$$

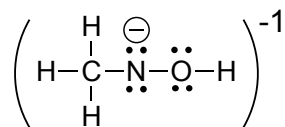
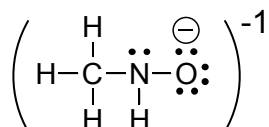
The most stable structures is \_\_\_\_\_ .

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<sub>3</sub> usually represents a \_\_\_\_\_ group. These groups are always terminal.

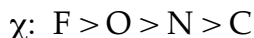


For “chain” molecules, atoms usually written in order. Terminal atoms usually follow the atom to which they are attached.



Zero FC on all other atoms

Zero FC on all other atoms



\_\_\_\_\_ 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<sub>3</sub>.



A B C  
structure 1



A B C  
structure 2

- 1) skeletal structure
- 2) valence e<sup>-</sup>s: 3(6) = \_\_\_\_\_
- 3) full shell e<sup>-</sup>s: 3(8) = \_\_\_\_\_
- 4) bonding e<sup>-</sup>s: \_\_\_\_\_ - \_\_\_\_\_ = \_\_\_\_\_
- 5) assign bonding e<sup>-</sup>s
- 6) remaining bonding e<sup>-</sup>s: 2
- 7) remaining valence e<sup>-</sup>s (assigned as lone pairs): 12
- 8) formal charges:

Structure 1

$$\text{FC}_{\text{OA}} = \underline{\hspace{2cm}}$$

$$\text{FC}_{\text{OB}} = \underline{\hspace{2cm}}$$

$$\text{FC}_{\text{OC}} = \underline{\hspace{2cm}}$$

Structure 2

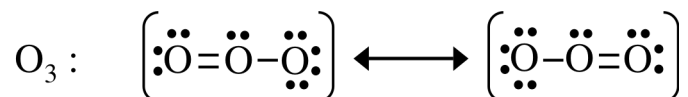
$$\text{FC}_{\text{OA}} = \underline{\hspace{2cm}}$$

$$\text{FC}_{\text{OB}} = \underline{\hspace{2cm}}$$

$$\text{FC}_{\text{OC}} = \underline{\hspace{2cm}}$$

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**.



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 \_\_\_\_\_.

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