AT Chemistry
2012

POGIL on CHEMICAL BONDING

Part III: Localized Electron (LE) Model

The LE model assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. Those pairs of electrons localized on an atom are called lone pairs (nonbonding pairs), and those found in the space between atoms are called bonding pairs.

three parts:

a) Lewis structures - explained below

b) molecule geometry (VSEPR - valence shell electron pair repulsion theory) - count the number of effective pairs (EP) around the central atom. These EP's are subdivided into bonding pairs and nonbonding (lone) pairs). These will be arranged to minimize electron repulsions

c) types of hybridized atomic orbitals - discussed in the next chapter

<u>Lewis Structures</u> - depict bonding and lone pairs in molecules; concerned with valence electrons

recall drawing Lewis structures for individual atoms:

	EC	valence orbital notation	Lewis dot structure
a) N			
b) N^{3-}			
c) I			
d) Ba			
e) Ba^{2+}			

Strategy for Writing Lewis Structures for Molecules

1. Total number of valence electrons

    example CO_3^{2-}

2. Draw the structure

    Note: ***H and halogens can take only one dash (one shared pair)***

    a) draw in dashes (bonds - bonding pairs)
    b) add lone pairs (dots) to fill octets
    c) check that total valence electrons add up
    d) if Lewis structure drawn has too many electron pairs, remove one and make a double bond

Lewis Structures and Comments About the Octet Rule

- The second-row elements C, N, O, and F should always be assumed to obey the octet rule. Note that oxygen and nitrogen can and do form double and triple bonds, respectively.

- The second-row elements B and Be often have fewer than eight electrons around them in their compounds. These <u>electron</u> <u>deficient</u> compounds are very reactive.

- The second-row elements never exceed the octet rule, since their valence orbitals (2s and 2p) can accommodate only eight electrons.

- Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty d orbitals.

- Hydrogen can only single bond.

- Halogens can only single bond as ligands (atoms bonded to a central atom).

- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available d orbitals (elements in the third period or beyond).

Molecular Structure - The VSEPR Model

The Valence Shell Electron Pair Repulsion (VSEPR) model assumes that atoms will orient themselves so as to **minimize electron pair repulsions around the central atom**. The idea here is that the bonding and nonbonding (lone) pairs around an atom will be positioned as far apart as possible.

The rules for using the VSEPR model to predict molecular structure are:

1. Determine the Lewis structure for the molecule.

2. For molecules with resonance structures, use any of the structures to predict the molecular structure.

3. Sum the electron pairs around the central atom.

4. In counting pairs, count each multiple bond as one single effective pair.

5. The arrangement of the pairs is determined by minimizing electron pair repulsions. These arrangements are shown on the separate handout.

6. Lone pairs require more space than bonding pairs. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120^o.

Problem: Draw Lewis structures for the following molecules and predict the shapes and polarities and bond angles.

a) F_2

b) O_2

c) CO

d) CH_4

e) NH_3

f) H_2O

g) HF

h) $H_2\underline{C}O$

i) CO_2

j) $H\underline{C}N$

k) BeH_2

l) BF_3

m) SO_4^{2-}

n) $POCl_3$

o) XeO_4

p) $PO_4$3-

q) ClO_4^-

r) SCl_2

s) ClO_2^-

t) PCl_2^-

Writing Lewis Structures for Exceptions to the Octet Rule

To determine if you have an exception, proceed as if your molecule obeys the octet rule.

Example: ICl_3

total valence e-

structure:

To write the Lewis structure of exceptions, draw the structure with one bond to each ligand, complete the octets, and add any extra electrons to the central atom.

Problem: Write the Lewis structures for the following molecules and predict their shapes and polarities and bond angles:

a) IF_2^-

b) SF_6

c) XeF_4

d) ClF_5

e) PF_5

f) SF_4

g) ClF_3

h) Br_3^-

Resonance

Resonance occurs when more than one valid Lewis structure can be written for a particular molecule. The resulting electron structure of the molecule is given by the average of these resonance structures.

Example: carbonate ion

Measurements in bond lengths (via an infrared spectrum) suggest that all three C-O bond lengths are equivalent. Therefore, the actual structure is a time-average of all these structures.

Draw Lewis dot structures, predict shape, polarity and bond angle:

a) O_3

b) N_3^-

c) SO_2

d) SO_3

Odd-Electron Molecules

Relatively few molecules formed from two nonmetals contain odd numbers of electrons (e.g. NO, NO_2). Since the LE model is based on pairs of electrons, it does not handle odd-electron cases in a natural way. To treat odd-electron molecules, a more sophisticated model are needed – one called the Molecular Orbital Model MO model).

Formal Charge

Molecules or polyatomic ions containing atoms that can exceed the octet rule often have many nonequivalent Lewis structures. One method to determine which of these structures best describes the actual bonding is to estimate the charge on each atom in the various possible Lewis structures and use these charges to select the most appropriate structure. Formal charge is a computational device based on the LE model (and as such is not perfectly correct). To determine formal charge (a somewhat more realistic estimate of charge distribution in a molecule), follow these steps:

1. Take the sum of the lone pair electrons and one-half of the shared electrons. This is the number of valence electrons assigned to the atom in the molecule.
2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge (#2 - #1).
3. The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.
4. If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule.

Problem: Draw all the Lewis structures for CO_2 and SCN^- and select the most stable one based on formal charge.

CO_2

SCN^-

Counting Electrons in Molecules

a) Valence electrons:

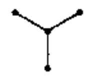
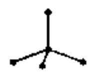
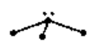
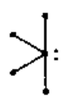
all lone pairs = 2
all shared pairs (dashes) = 2

b) Effective pairs (in determining shape/VSEPR)

lone pairs = 1
single
double all = 1
triple

c) Assigned electrons (when doing formal charge)

lone pairs = 2
shared pairs = 1

Hybdridization	# of σ Bonds	# of Non-Bonding Pairs	Molecular Shape		Bond Angles	Example
sp	2	0		Linear	180°	BeH_2, CO_2
sp^2	3	0		Trigonal planar	120°	SO_3, BF_3
sp^2	2	1		Angular	<120°	SO_2, O_3
sp^3	4	0		Tetrahedral	109.5°	CH_4, CF_4, SO_4^{2-}
sp^3	3	1		Trigonal pyramidal	<109.5°	NH_3, PF_3, $AsCl_3$
sp^3	2	2		Angular	<109.5°	H_2O, H_2S, SF_2
sp^3d	5	0		Trigonal bipyramidal	120°, 90°	PF_5, PCl_5, AsF_5
sp^3d	4	1		Sawhorse (irregular tetrahedron)	<120°, <90°	SF_4
sp^3d	3	2		T-shaped	<90°	ClF_3
sp^3d	2	3		Linear	180°	XeF_2, I_3^-, IF_2
sp^3d^2	6	0		Octahedron	90°	SF_6, PF_6^-, SiF_6^{2-}
sp^3d^2	5	1		Square pyramidal	<90°	IF_5, BrF_5
sp^3d^2	4	2		Square planar	90°	XeF_4, IF_4^-