

## 8.9 - 8.12 - Lewis Structures

### Lewis Structures

Thus far we've looked at individual bonds between atoms, delving into general characteristics that can be determined by differences in electronegativity.

Now we will be looking at the next level of complexity: dealing with the structures of entire molecules (rather than snippets)

We will use the **localized electron (LE) model**: which assumes that atoms are bound together by sharing pairs of electrons that do not move from the overlapping atomic orbitals of the bound atoms.

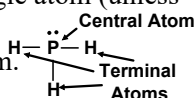
### Lewis Structure – Process

As with most things in chemistry, there is a stepwise process to make Lewis Structures.

1. From the formula, place atoms:

a. Central atom is a formula's single atom (unless the central atom is specified).

b. Hydrogen always terminal atom.



2. Add up all valence electrons (VE), PLUS or MINUS charge electrons (Ex:  $\text{NO}_3^-$  has 1 more  $e^-$ ).

3. Determine  $e^-$  pairs = divide VE by two.

### Lewis Structure – Process

4. Draw single bond b/w central and terminal atoms.

5. Count and place remaining  $e^-$  pairs:

a. Place on terminal atoms to satisfy octet rule.

b. Place **all** remaining pairs on central atom.

6. Does the central atom obey the octet rule?

If not, make double or triple bonds using lone pairs from terminal atoms (never hydrogen) to central atom.

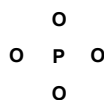
7. Check **formal charges** (to be defined) of all atoms if the central atom is in the third period or higher.

Determine the Lewis Structure with the lowest formal charge distribution by making double or triple bonds.

### 1. Polyatomic Ion Guided Example

Phosphate Ion  $\text{PO}_4^{3-}$

1. Phosphorus in middle.



2. Valence Electrons:

P  $\rightarrow$  5  $e^-$

O  $\rightarrow$  6  $e^-$  / atom x 4 atoms = 24  $e^-$

3 more  $e^-$  from charge

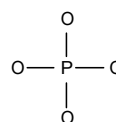
Sum of 32  $e^-$

### 1. Polyatomic Ion Guided Example

3. Electron pairs:

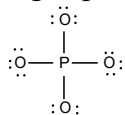
32 electrons / 2 = 16 pairs of  $e^-$

4. Connect terminal atoms:



**1. Polyatomic Ion Guided Example**

5. Place remaining  $e^-$  pairs around terminal atoms:



6. Does each atom have an octet?

Yes! Almost done, BUT we need to define and apply the formal charge concept.

**Formal Charges**

Earlier, we used *oxidation numbers* to assign charges to elements allowing us to solve redox reactions.

That practice leads to exaggerated estimates of charge distribution in molecules: does not work well enough for many molecules' actual Lewis Structures.

The **formal charge** is the difference between the number of valence electrons in the 'free' atom and the number of electrons 'belonging' to the atom in a molecule, and is only employed when the central atom is in the 3rd row of the Table or higher (more on that later). To assign charges:

1. Lone pair electrons belong entirely to the atom,
2. Shared electrons are divided evenly between the two sharing atoms.

**1. Guided Example: Continued**

7. In phosphate, we need to assign formal charges to the phosphorus atom, and each of the oxygen atoms:

Phosphorus: VE = 5.

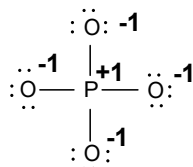
So far, it's assigned 4 VE: four single bonds divided by two. It's formal charge is:  $5 - 4 = +1$

Oxygen: VE = 6.

So far, it's assigned 7 VE: six from its lone pairs and one from its share of the single bond.

Formal charge:  $6 - 7 = -1$

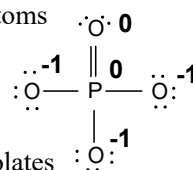
Assigning formal charges we get:



These charges can be lowered.

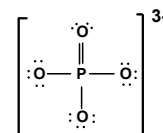
**1. Guided Example: Continued**

It's rare that all formal charges can be reduced to zero when the central atom is in period three or higher, but in this case any of the oxygen atoms can contribute a pair of electrons to phosphorus, lowering the charge distribution slightly:



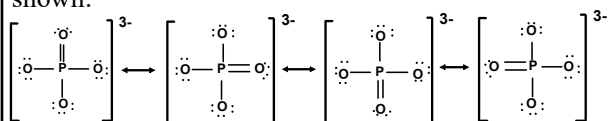
Note: it appears that phosphorus violates the octet rule. It has an expanded octet (more on that in a moment) and is OK.

Final Note: Ionic Lewis Structures are bracketed, with charge superscripted.

**Resonance**

In the phosphate example, more than one correct Lewis structure was possible.

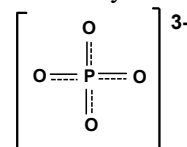
Resonance occurs when one or more double bonds are present: because any one of the doubly bonded terminal atoms is no more likely to be double bonded than any other, multiple correct structures must be shown:

**Resonance Hybrid**

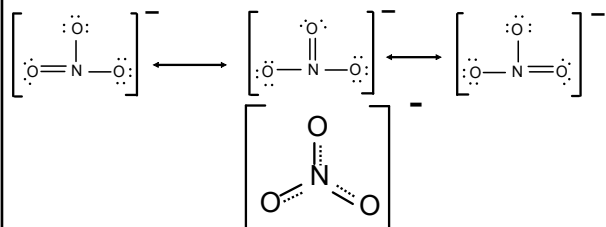
It is tedious to draw all a compound's resonance structures.

A quick way exists called a resonance hybrid, using solid and dashed lines to show possible configurations.

2. Draw the resonance hybrid of the phosphate  
Example:

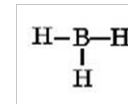
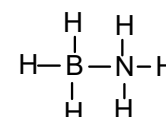


Note: no electrons are drawn around terminal atoms. It's implied that they will form an octet regardless of the number of bonds they have to the central atom.

3. Draw the Nitrate ion:  $\text{NO}_3^-$ **Resonance Example****Sub-Octets**

Some compounds are stable with less than an octet. This happens when the central atom is smaller than carbon (B, Be, Li, H).

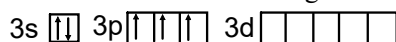
Note: compounds like this are reactive: the central atom readily combines with molecules having a lone pair of electrons, forming what's known as a coordinate covalent bond, and achieving an octet.

4. Draw  $\text{BH}_3$ .5. Draw the structure of the product of  $\text{BH}_3 + \text{NH}_3$ .**Expanded Octet**

Some atoms can have more than eight electrons in their valence shell.

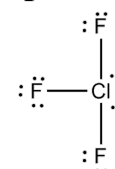
Happens in elements with available d orbitals (period three and higher).

Consider the valence orbital diagram of phosphorus:

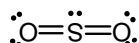


The localized electron model assumes that the empty 3d orbitals can be used to accommodate extra electrons.

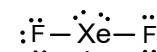
In sequential aufbau filling during element building, the 3d sublevel is not filled until after 4s, but 3d bonding orbitals can be occupied to minimize energy in more complex molecules.

**Expanded Octet Example**6. Draw chlorine trifluoride,  $\text{ClF}_3$ **7.  $\text{SO}_2$  Example:**

- Sulfur in middle.      O S O
- How many valence electrons? = 18 (O = 6 X 2, S = 6).
- Total pairs = 9 (18/2 = 9).
- Placement: single bonds first.      O—S—O
- Place remaining seven pairs first on terminal atoms, then the rest on the central atom.       $\text{:}\ddot{\text{O}}\text{—}\ddot{\text{S}}\text{—}\ddot{\text{O}}\text{:}$
- Make double bonds so central atom obeys octet rule (oxygen shares with sulfur):  $\text{:}\ddot{\text{O}}\text{—}\ddot{\text{S}}\text{=}\ddot{\text{O}}\text{:}$  OR:  $\text{:}\ddot{\text{O}}\text{=}\ddot{\text{S}}\text{—}\ddot{\text{O}}\text{:}$
- Formal charge check: sulfur has a formal charge of +1, and the single bonded oxygen has a charge of -1. Therefore, the central sulfur must be double bonded:

**8. Xenon Example!**

Draw the Lewis Structure of  $\text{XeF}_2$ .



**9. Carbon Monoxide Example!**

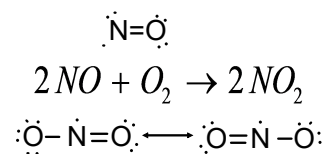
Draw the Lewis Structure of CO.

**10. Odd Electron Example!**

It is rare that odd-numbered electron molecules form. One example is nitrogen monoxide, which is a byproduct of automobile exhaust.

Such a molecule is called a free radical (like in the '60s, man!), and is very reactive (also like the '60s, man!)

Draw the Lewis Structure of NO, then write the reaction of NO with O<sub>2</sub>, forming NO<sub>2</sub> (another free radical, although a less reactive one). Finally, draw the Lewis structure of NO<sub>2</sub>. Include resonance if necessary.

**Homework**

Preview 8.13

8.9 - 8.12 Problems in your Booklet  
Due: Next Class