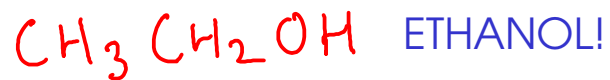


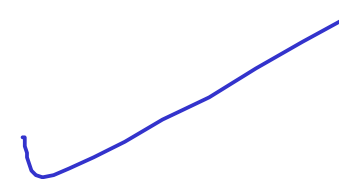
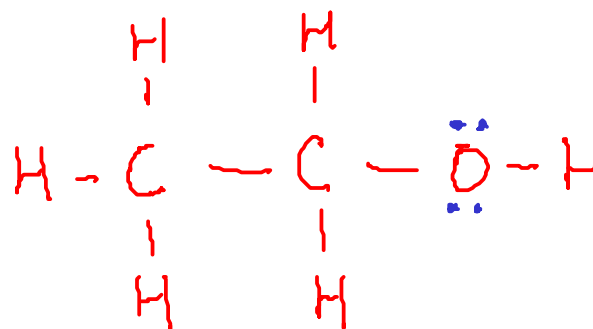
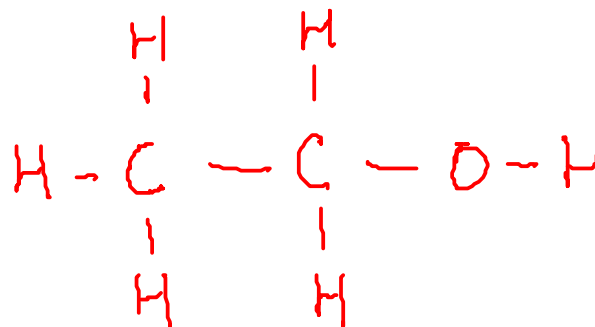
A DOT STRUCTURE FOR A LARGER MOLECULE

- ① Count valence electrons
- ② Pick central atom and draw skeletal structure
 - central atom is usually the one that needs to gain the most electrons!
 - skeletal structure has all atoms connected to center with single bonds
- ③ Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.
- ④ Check octet rule - each atom should have a share in 8 electrons (H gets 2). If not, make double or triple bonds.



$$\begin{array}{l|l} \text{C} : 4 \times 2 = 8 & \\ \text{H} : 1 \times 6 = 6 & 20 \\ \text{O} : 6 \times 1 = 6 & \end{array}$$

This formula gives us a hint to the structure of the molecule. Ethanol has THREE centers: the two carbon atoms and the oxygen atom.



A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS

$$O = 3 \times 6 = 18$$

See text, 9.7
p 350-352

① Count valence electrons

② Pick central atom and draw skeletal structure

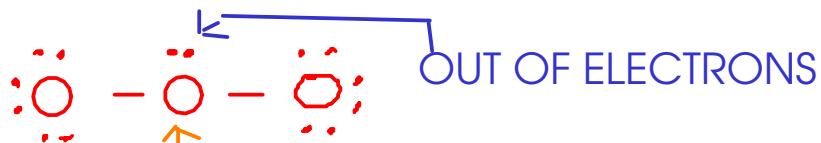
- central atom is usually the one that needs to gain the most electrons!

- skeletal structure has all atoms connected to center with single bonds

③ Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

④ Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

O_3 (OZONE)



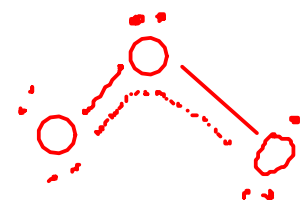
Central oxygen has only six electrons



The structure we drew implies that one of the outer oxygen atoms is closer to the central oxygen atom than the other one.

Experimentally, though, we find the two oxygen atoms to be the SAME distance from the center.

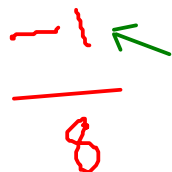
In the ozone molecule, electrons are actually being shared between ALL THREE oxygen atoms at the same time. This is called a DELOCALIZED BOND.



The structures in the green box are called RESONANCE STRUCTURES. The "real" structure of ozone is an "average" of the two resonance structures. The "double bond" electrons in these structures are actually shared between all three oxygen atoms

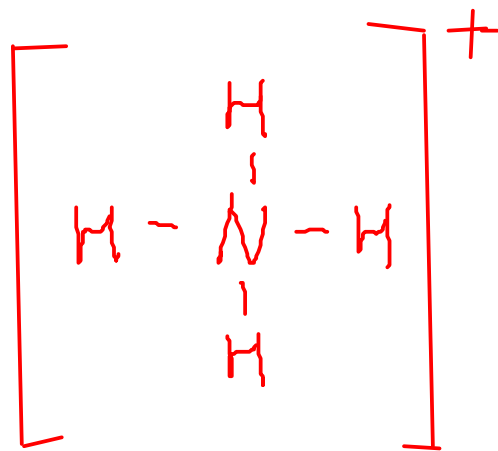
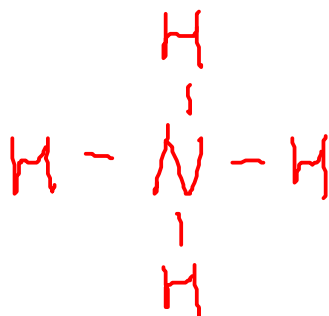
A DOT STRUCTURE FOR A POLYATOMIC ION

- ① Count valence electrons
- ② Pick central atom and draw skeletal structure
 - central atom is usually the one that needs to gain the most electrons!
 - skeletal structure has all atoms connected to center with single bonds
- ③ Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.
- ④ Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.



An ODD number of electrons? But Lewis structures for MOLECULES generally have even numbers of electrons!

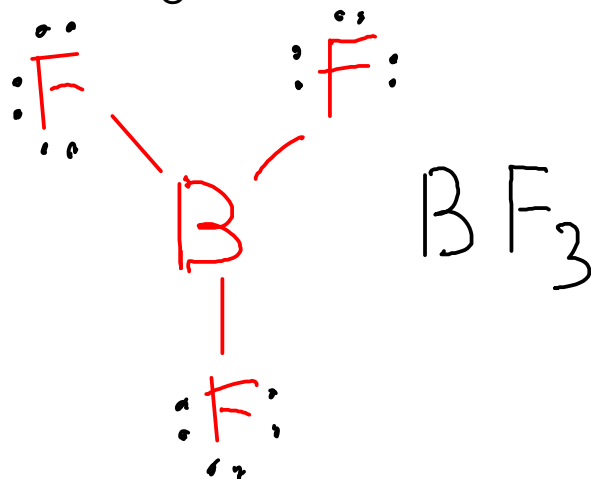
← Subtract an electron from the total to account for the +1 charge.



← Draw brackets around the structure of the ion, then indicate the charge in the upper-right corner - just like we normally do with ions.

EXPANDED VALENCE and other exceptions to the "octet rule"

- Some atoms do not always obey the octet rule. A few, like BORON, will bond in such a way that they end up with less than eight electrons.



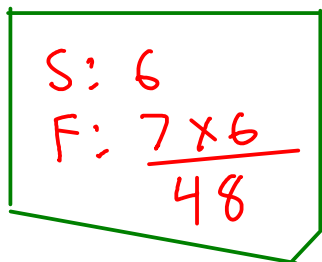
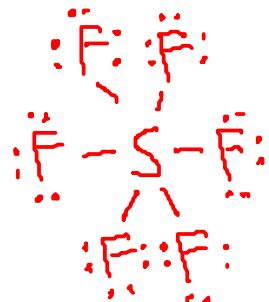
... but many more bond in such a way that they end up with a share in MORE THAN EIGHT electrons!

- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

... these atoms have unfilled "d" orbitals that may participate in bonding!

- All noble gas compounds (example: XENON compounds with oxygen and fluorine) exhibit this behavior!

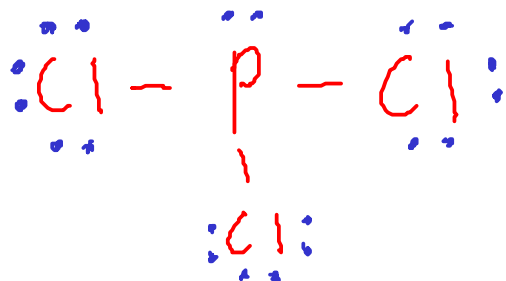
EXAMPLES:



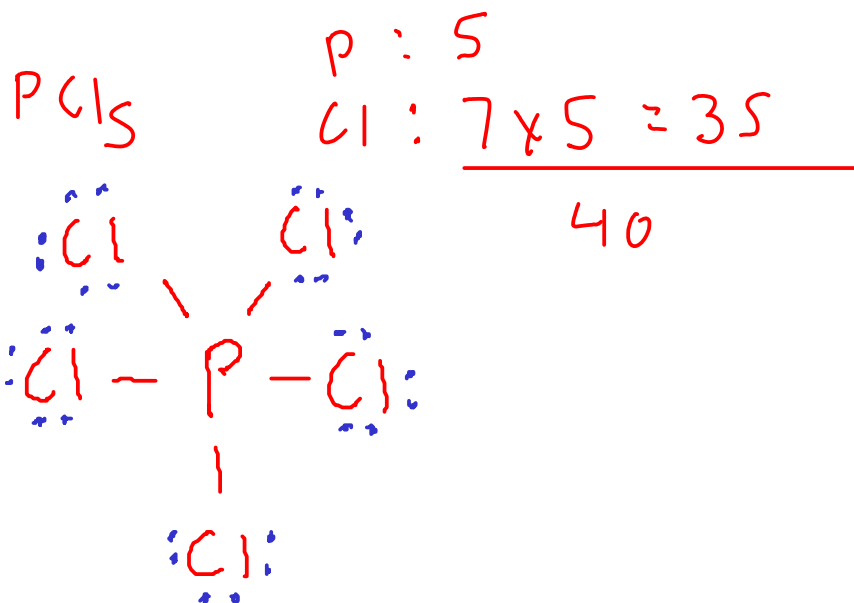
- The central SULFUR atom has a share in TWELVE total electrons, not eight!
- The SHAPE of the sulfur hexafluoride molecule in three dimensions agrees with the picture of six fluorine atoms each sharing a pair of electrons with a sulfur center.



$$\begin{array}{r} \text{P: } 5 \\ \text{Cl: } \frac{7 \times 3 = 21}{26} \end{array}$$



This structure obeys the octet rule.



This molecule does NOT obey the octet rule. Phosphorus ends up with ten electrons instead of eight.

FORMAL CHARGE

- You can often draw more than one structure for a molecule that appears correct. How can you determine which one is more likely?

- USE FORMAL CHARGE!

- Formal charge is a hypothetical charge on each atom in a structure. It assumes:

- ① All bonding electrons are shared EQUALLY between atoms
- ② Lone pairs are NOT shared.

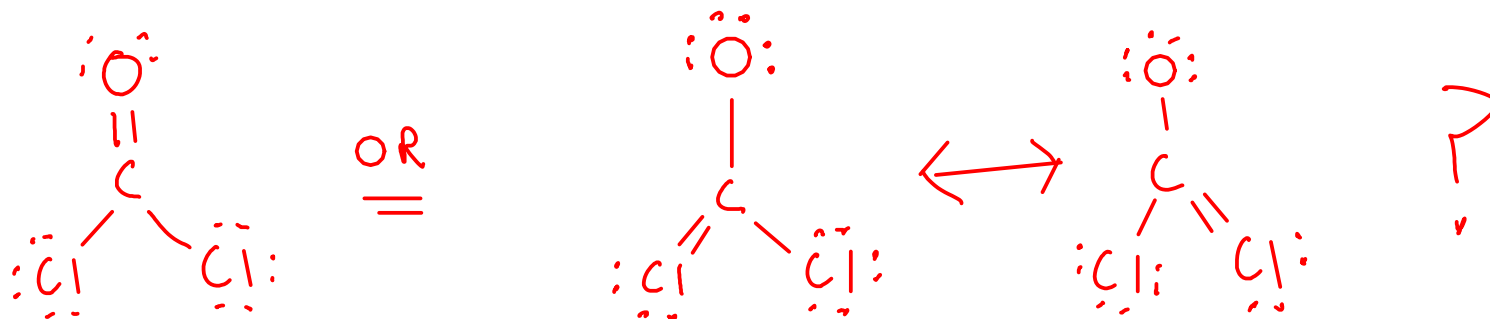
$$\text{FORMAL CHARGE} = \text{ORIGINAL \# OF VALENCE ELECTRONS} - \text{NUMBER OF BONDS} - \text{NUMBER OF UNSHARED ELECTRONS}$$

* The sum of the formal charges of all atoms in a structure should equal to the charge of the molecule (0 for neutral molecules)

The "better" Lewis structure will have:

- Lower magnitudes of formal charge (0 is better than +2 -2)
- Negative formal charges on ELECTRONEGATIVE atoms, or positive formal charges on atoms that are less electronegative.

EXAMPLE: COCl_2



... calculate formal charges to tell which structure is more likely!

$$\text{O}: 6 - 2 - 4 = 0$$

$$\text{C}: 4 - 4 - 0 = 0$$

$$\text{Cl}: 7 - 1 - 6 = 0$$

$$\text{Cl}: 7 - 1 - 6 = 0$$

$$\text{O}: 6 - 1 - 6 = -1$$

$$\text{C}: 4 - 4 - 0 = 0$$

$$=\text{Cl}: 7 - 2 - 4 = +1$$

$$-\text{Cl}: 7 - 1 - 6 = 0$$

The structure on the LEFT is preferred. It has lower formal charges than the structure on the right.



... we can determine which of these structures is more likely by calculating formal charges!

$$\begin{aligned} \text{H}: & 1 - 1 - 0 = 0 \\ \text{C}: & 4 - 3 - 2 = -1 \\ \text{N}: & 5 - 4 - 0 = +1 \end{aligned}$$

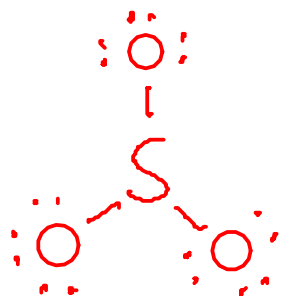
$$\begin{aligned} \text{H}: & 1 - 1 - 0 = 0 \\ \text{C}: & 4 - 4 - 0 = 0 \\ \text{N}: & 5 - 3 - 2 = 0 \end{aligned}$$

Which structure is more likely?

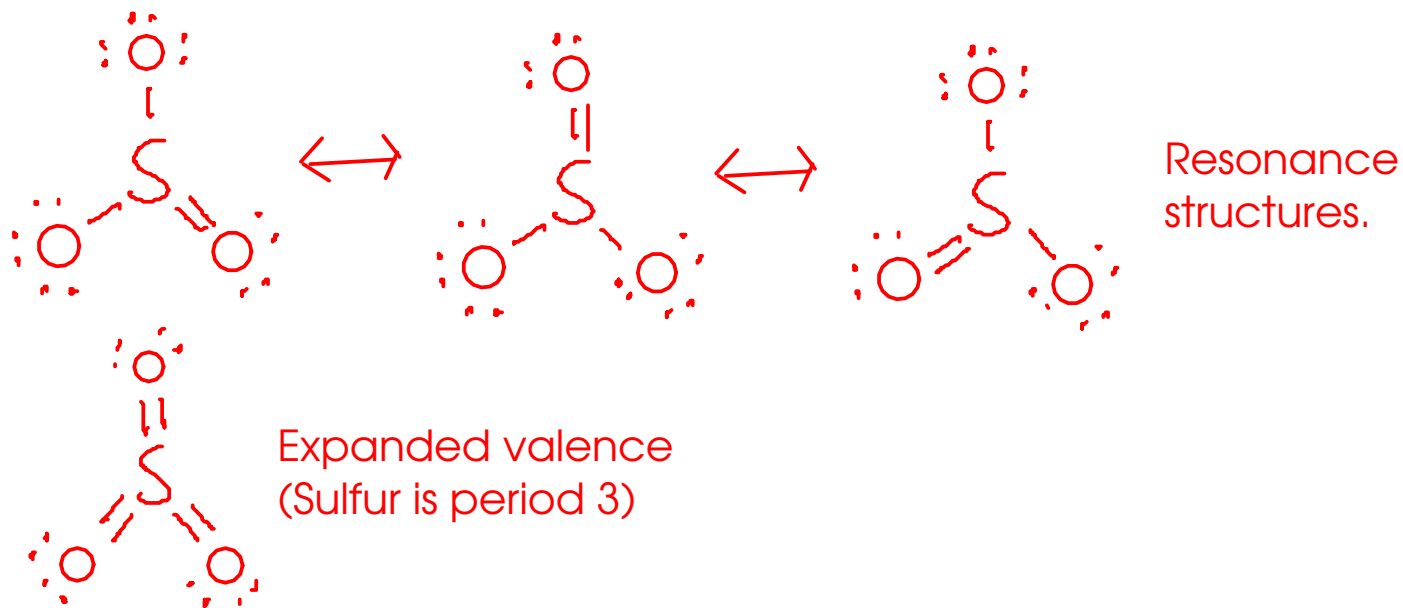
- * The HCN structure is more likely. It has lower formal charges than the HNC structure does.
- * the HNC structure has another problem. It puts a positive formal charge on the nitrogen atom, while putting a negative formal charge on the much less electronegative carbon atom.

Let's look at sulfur trioxide. SO_3

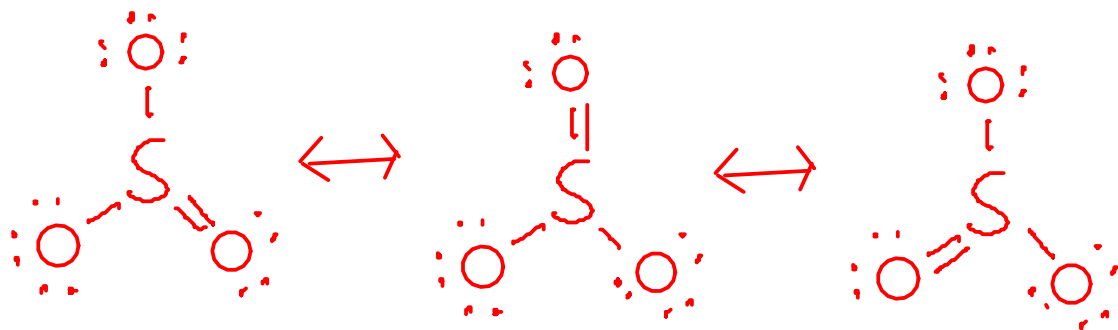
Skeletal structure:



$$\begin{array}{r} \text{S: } 6 \\ \text{O: } 6 \times 3 = 18 \\ \hline 24 e^- \end{array}$$



To decide which structure is preferred, let's look at formal charges.



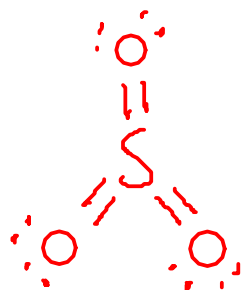
Resonance structures.

$$S: 6 - 4 - 0 = +2$$

$$O - : 6 - 1 - 6 = -1$$

$$O - : 6 - 1 - 6 = -1$$

$$O = : 6 - 2 - 4 = 0$$



Expanded valence
(Sulfur is period 3)

$$S: 6 - 6 - 0 = 0$$

$$O = : 6 - 2 - 4 = 0$$

$$O = : 6 - 2 - 4 = 0$$

$$O = : 6 - 2 - 4 = 0$$

BASED ON FORMAL CHARGE, the expanded valence structure is the more likely one.

The correct (as in - agrees with experimental data on bond lengths) structure is the expanded valence one - even though it violates the octet rule.

In general, the structure with lower formal charges is preferred EVEN IF it violates the octet rule. HOWEVER, remember that period 2 elements NEVER end up with more than eight outer electrons.