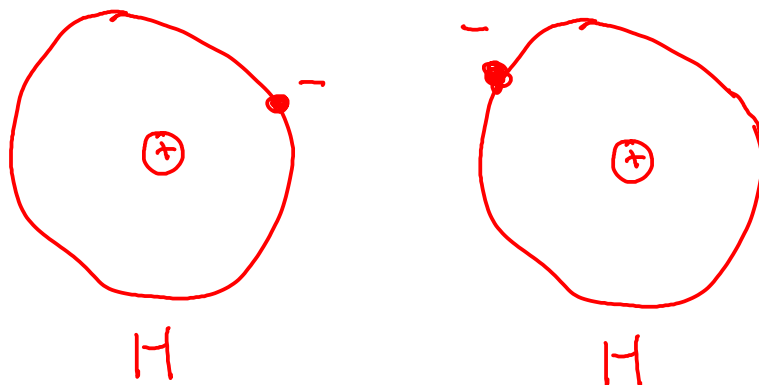


MOLECULAR COMPOUNDS

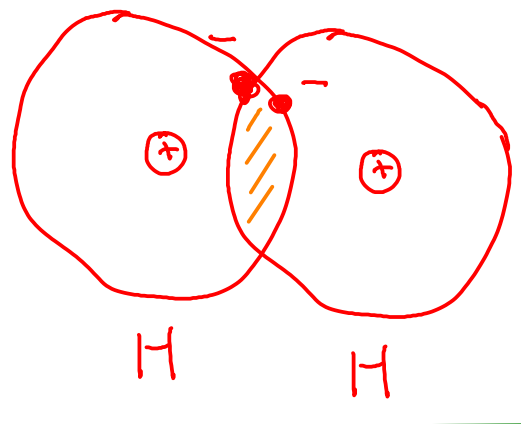
- Form when atoms SHARE electrons instead of transferring them. This results in the formation of MOLECULES ... groups of atoms held together by electron-sharing.

How might atoms SHARE electrons? By coming together close enough so that their atomic ORBITALS overlap each other:

This idea is called
VALENCE
BOND
THEORY!



Each hydrogen atom has a single electron in a 1s orbital.

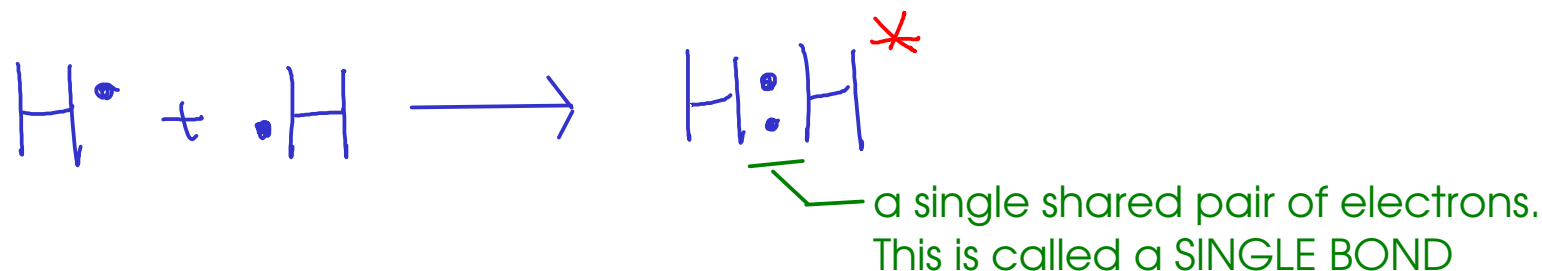


When hydrogen atoms come close enough to each other for these orbitals to OVERLAP, each hydrogen "sees" BOTH electrons, filling up the "s" orbitals of both atoms. This is a COVALENT BOND.

Co: together
Valent: valence shells

This is the DIATOMIC MOLECULE, H_2

... so how would this look using dot notation?

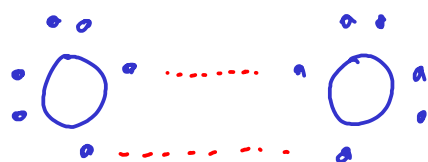


In dot structures, SHARED PAIRS of electrons are often written as DASHES to make the structures look neater.



* Why doesn't hydrogen end up with eight electrons? Because hydrogen has only the first shell, which contains only a single "s" subshell (NO "p" subshell). This "s" subshell is full with two electrons, and that's all hydrogen needs to get.

Let's look at OXYGEN ...



We know that oxygen exists in air as the diatomic molecule O_2



The oxygen atoms share TWO pairs of electrons. This is called a DOUBLE BOND

OR

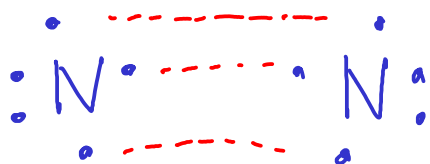


Each oxygen atom has a share in eight electrons!

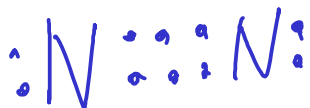
A few notes on the double bond:

- ① - For atoms to share more than one pair of electrons, they have to move closer to one another than they would if they were only sharing one pair of electrons. This BOND DISTANCE is measurable!
- ② - It takes more energy to break a double bond between two atoms than it would to break a single bond between the same two atoms. This BOND ENERGY is also measurable!

Let's look at NITROGEN ...



We know that nitrogen exists in air as the diatomic molecule N_2



The nitrogen atoms share THREE pairs of electrons. This is called a TRIPLE BOND

OR



Nitrogen gas is fairly inert ... it's hard to break the triple bond in nitrogen gas apart!

A few notes on the triple bond:

- ① - For atoms to share three pairs of electrons, they have to move closer to one another than they would if they were sharing one or two pairs of electrons. Triple bonds have the shortest BOND DISTANCE of all covalent bonds.
- ② - It takes more energy to break a triple bond between two atoms than it would to break either a single or double bond between the same two atoms. The triple bond has the largest BOND ENERGY of all three kinds of covalent bonds.

SO FAR, we've seen that ...

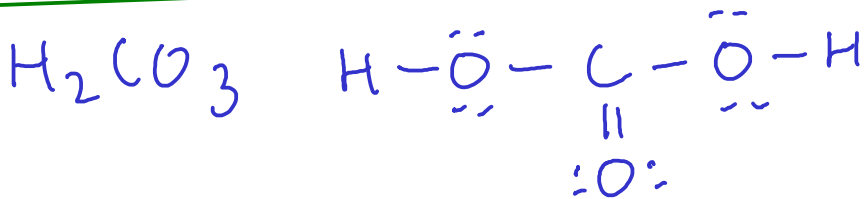
- ① Atoms may share one, two, or three pairs of electrons with each other.
- ② Atoms will usually share enough electrons so that each atom ends up with a share in EIGHT electrons - the "octet rule"

- HYDROGEN will only end up with two electrons!

- Some other atoms may end up with more or less than eight electrons. Exceptions to the octet rule are covered in Chapter 9.

NOW, how could we come up with dot structures for some more complicated (and therefore, more interesting) molecules?

Examples:



DRAWING DOT STRUCTURES FOR SIMPLE MOLECULES

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.

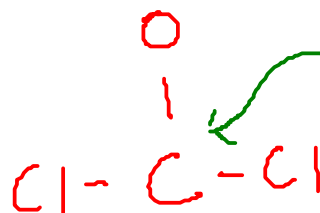


$$\text{C} : 1 \times 4$$

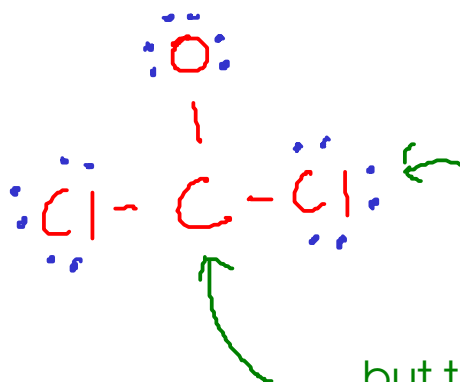
$$\text{O} : 1 \times 6$$

$$\text{Cl} : 2 \times 7 = 14$$

24 electrons



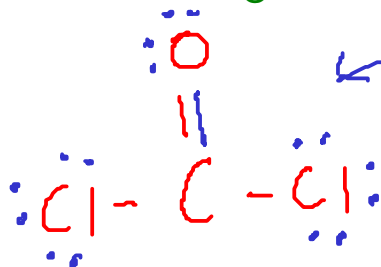
Choose CARBON as the central atom, since it needs to gain more electrons than either Cl or O.



Distribute remaining electrons, and stop when we run out (24 electrons here...)

... but the central carbon has only six valence electrons!

To get carbon more electrons, we'll make a double bond between C and O. We choose O because it needed two electrons initially, and is likely to form two bonds to get them!



This structure looks better, since all atoms have a share in eight valence electrons!

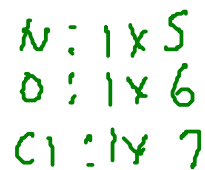
① Count valence electrons

② Pick central atom and draw skeletal structure

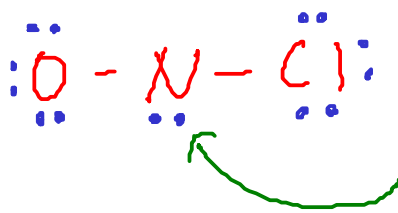
- central atom is usually the one that needs to gain the most electrons!
- skeletal structure has all atoms connected to center with single bonds

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.



We will pick NITROGEN as our central atom, since it needs to gain more electrons than O or Cl.



We ran out of space on the outer atoms, so the last pair of electrons goes on the central NITROGEN atom!

Even with the extra pair, N still has a share in only six electrons. Time to make a double bond!



We pick OXYGEN here for the double bond since it initially needed two more electrons - and is likely to share two of its own electrons to get two!

Now all atoms have a share in eight valence electrons!

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!

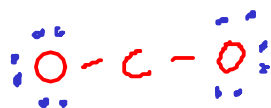
- skeletal structure has all atoms connected to center with single bonds

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.



$$\begin{array}{r} \text{C: } 1 \times 4 \\ \text{O: } 2 \times 6 \\ \hline 16e^- \end{array}$$



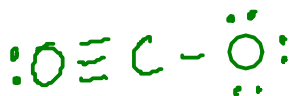
... but the carbon atom only has a share in four valence electrons.



... now six!



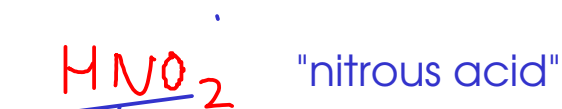
Adding a second double bond with the other oxygen atom gives carbon a share in eight valence electrons!



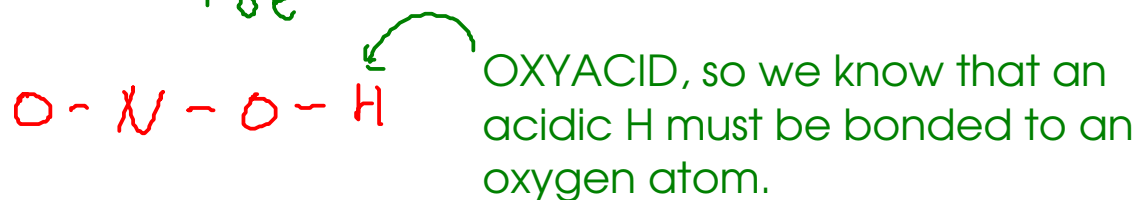
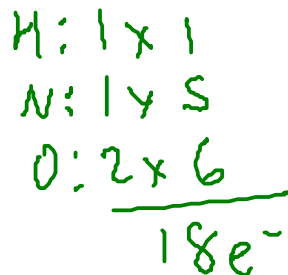
This structure implies that the two oxygen atoms (which should be chemically identical) will bond in different ways.

For this molecule, we can find experimentally (through x-ray diffraction experiments) that there's only one bond distance - not two. That supports the $\text{O}=\text{C}=\text{O}$ structure!

- 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.



In oxyacids, the acidic hydrogen atoms are attached to OXYGEN atoms in the structure!



We don't end up seeing two double bonds like the carbon dioxide molecule because one of the oxygen atoms is already sharing two of its electrons (the one on the right!)

A DOT STRUCTURE FOR A LARGER MOLECULE

① Count valence electrons

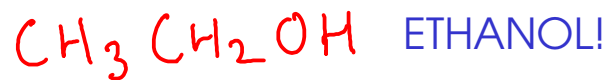
② Pick central atom and draw skeletal structure

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

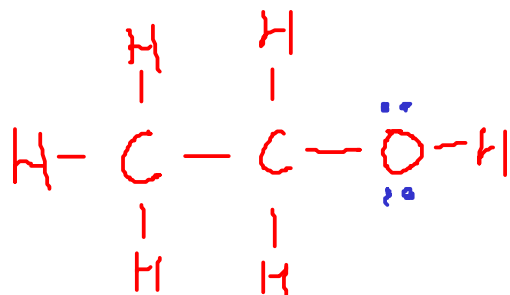
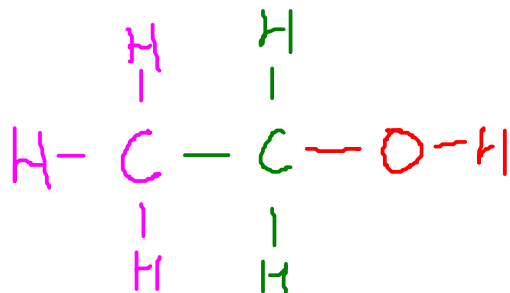
- skeletal structure has all atoms connected to center with single bonds

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.



This formula gives us a hint to the structure of ethanol. Ethanol has THREE central atoms chained together.



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

A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS

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

See text, 9.7
p 356-357

① Count valence electrons

② Pick central atom and draw skeletal structure

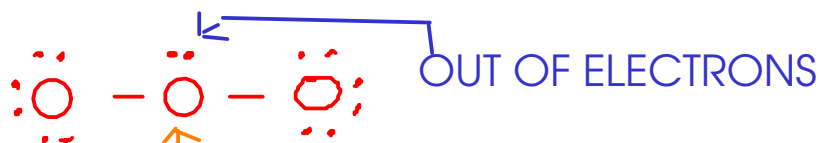
- central atom is usually the one that needs to gain the most electrons!

- 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)



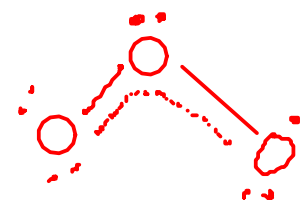
Central oxygen has only six electrons



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

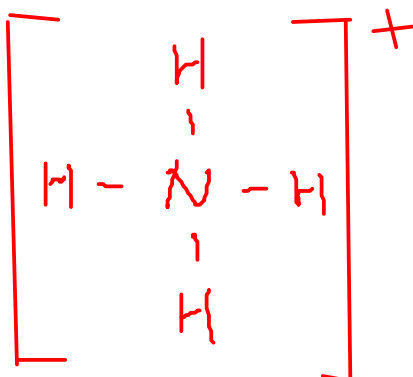
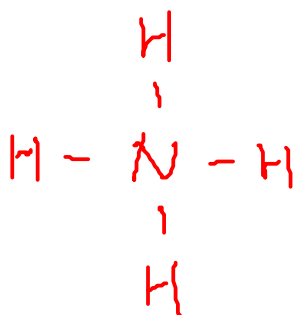
A DOT STRUCTURE FOR A POLYATOMIC ION

- 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? The dot structures we work with all have pairs ... even numbers of electrons!

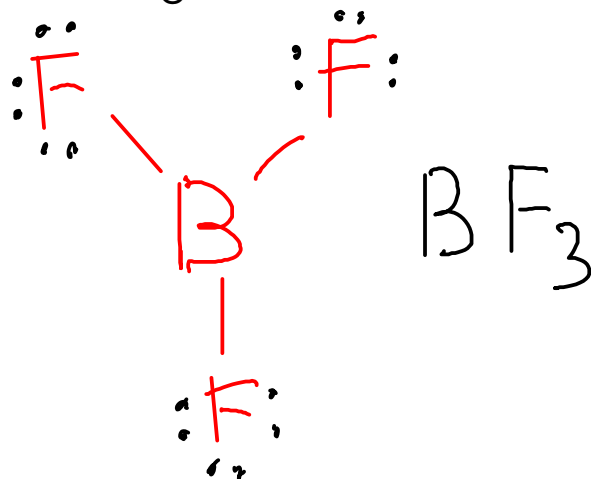
Subtract an electron because the ammonium ion has a +1 charge!



Draw brackets around the structure, then indicate the charge on the upper right just like we do for chemical formulas.

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.



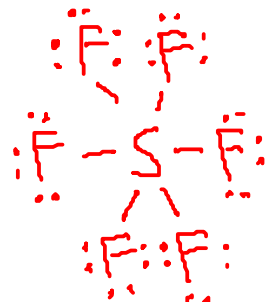
... but many more bond in such a way that they end up with a share in MORE THAN EIGHT electrons!

- 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:

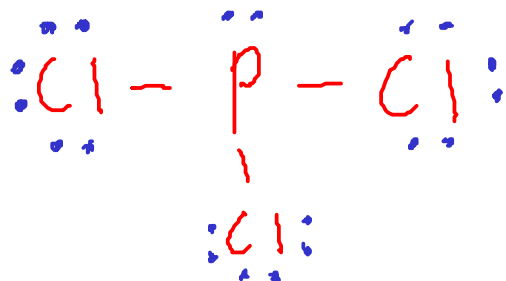


$$\begin{array}{r} \text{S: } 6 \\ \text{F: } \frac{7 \times 6}{48} \end{array}$$

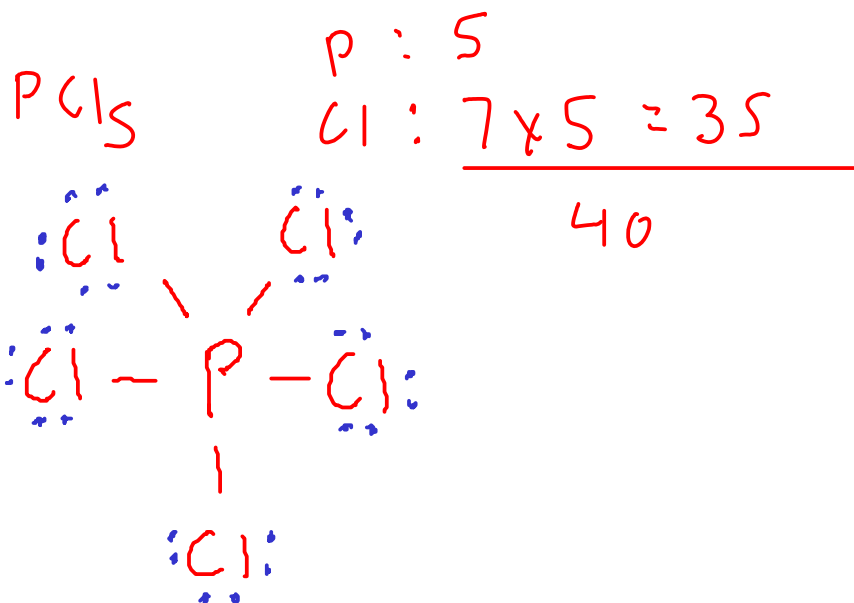
- The central SULFUR atom has a share in TWELVE total electrons, not eight!
- The SHAPE of the sulfur hexafluoride molecule in three dimensions agrees with the picture of six fluorine atoms each sharing a pair of electrons with a sulfur center.



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



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.

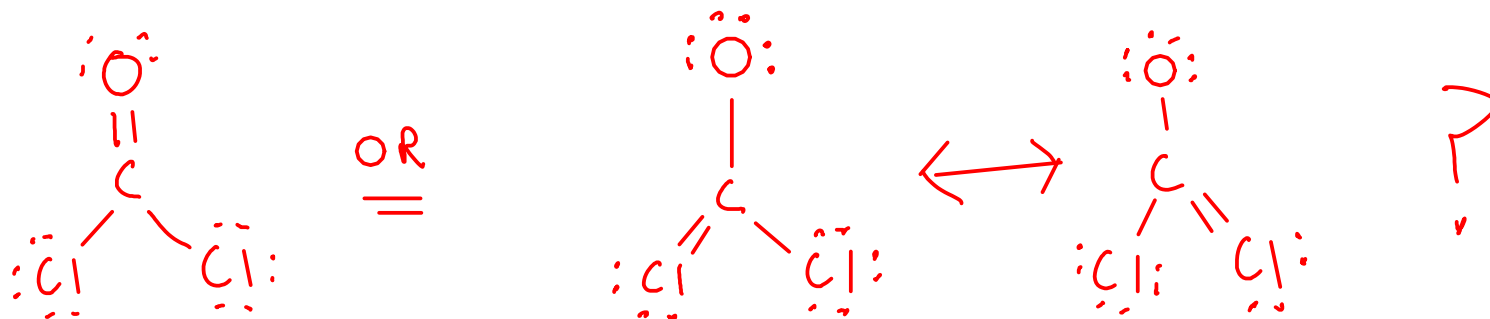
$$\text{FORMAL CHARGE} = \text{ORIGINAL \# OF VALENCE ELECTRONS} - \text{NUMBER OF BONDS} - \text{NUMBER OF UNSHARED ELECTRONS}$$

* 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!

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

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

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

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

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

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

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

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

Based on formal charge, the structure on the left is preferred. It has overall lower formal charges.