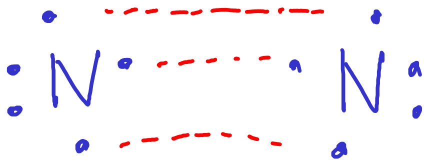
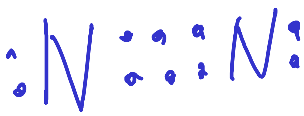
Let's look at NITROGEN ...

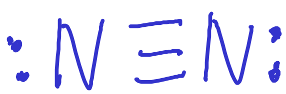


We know that nitrogen exists in air as the diatomic molecule N_2



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"

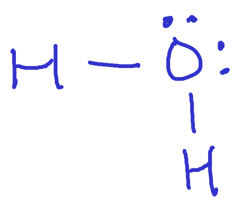
   - HYDROGEN will only end up with two electrons!

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

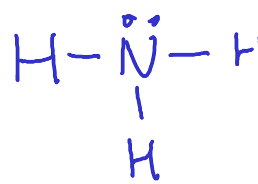
NOW, how could we come up with dot structures for some more complicated (and therefore, more interesting) molecules?

Examples:

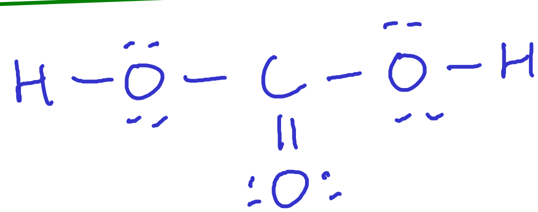
H_2O



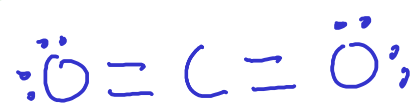
NH_3



H_2CO_3



CO_2



(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

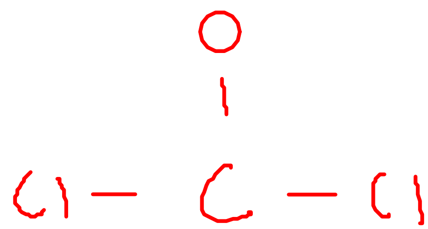
(3) Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

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

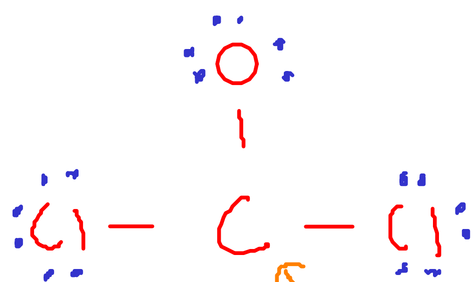
$COCl_2$

C : 4
O : 6
Cl : 7 x 2 = 14

24 e^-

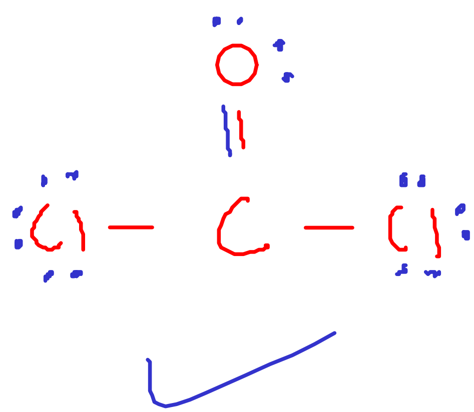


Choose CARBON as the central atom, since it needs to gain 4 more electrons (more than the others!)



Distribute remaining electrons ... stop when we have used 24.

... but CARBON only has a share in 6 electrons!



We'll make a double bond between carbon and oxygen. We pick oxygen for the double bond because it originally needed two electrons (which suggests it will form two bonds!)

1. Count valence electrons

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

NOCl

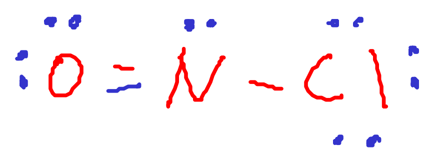
N: 5
O: 6
Cl: 7

$18e^-$

We 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 we put the last two electrons onto the central nitrogen atom.

Since NITROGEN has a share in only six electrons, we will make a double bond between oxygen and nirtogen. (Why oxygen? Same reason as for the previous example.)



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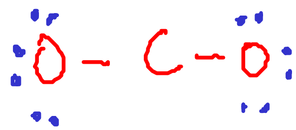
4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

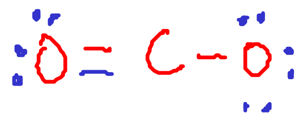
CO_2

C: 4
O: 6 x 2

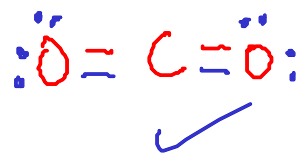
$16 e^-$



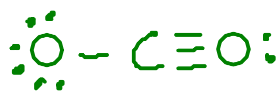
... but carbon has a share in only 4 electrons



... and now, six.



Adding a second double bond gives carbon a share in eight elecfrons.



The two oxygen atoms are in the same chemical environment, and should bond the same way to the central carbon atom.

EXPERIMENTALLY, we find that the bond distance between the two oxygen atoms and the central carbon is the SAME, supporting the double bond structure instead of the one drawn here in green.

1. Count valence electrons

2. Pick central atom and draw skeletal structure
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   - skeletal structure has all atoms connected to center with single bonds

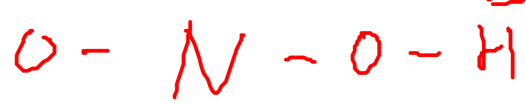
3. Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

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

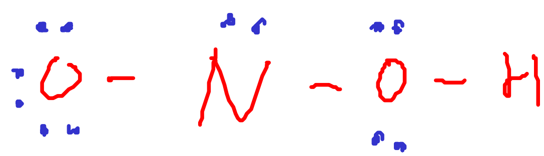
HNO_2 "nitrous acid"

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

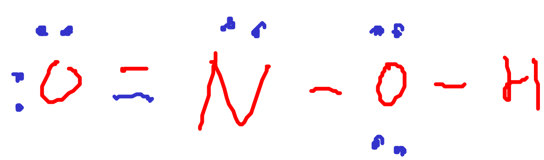
H: 1 x 1
N: 1 x 5
O: 2 x 6
18 e^-



Nitrogen is the central atom, but we know that the hydrogen has to be bonded to O in this OXYACID!



... but nitrogen has a share in only six electrons. We need a double bond.



We pick the oxygen atom on the left to share a second pair because the one on the right is already sharing two pairs (one with N, one with H)

These two oxygen atoms are in DIFFERENT chemical environments (compare to carbon dioxide)

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.

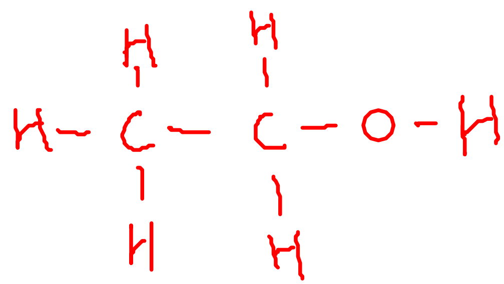
4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

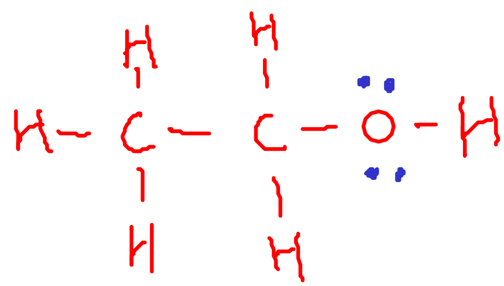
CH_3CH_2OH ETHANOL!

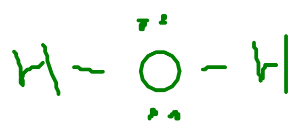
$C: 4 \times 2 = 8$
$H: 1 \times 6 = 6$
$O: 6 \times 1 = 6$
$| \; 20$

This formula gives us a hint to the structure of this large molecule, The molecule has three parts - three central atoms!

$CH_3 \quad CH_2 \quad OH$







Notice that the structures of ethanol and water are similar. Because of this similarity, ethanol and water molecules dissolve very well in one another.

A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS

$O: 3 \times 6 = 18$

See text, 9.7
p 350 - 352

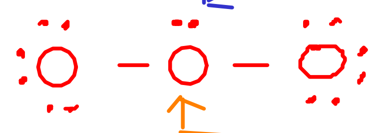
1. Count valence electrons

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.

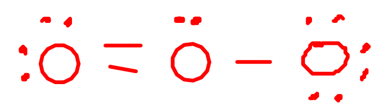
4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

O_3 (OZONE)



OUT OF ELECTRONS

Central oxygen has only six electrons

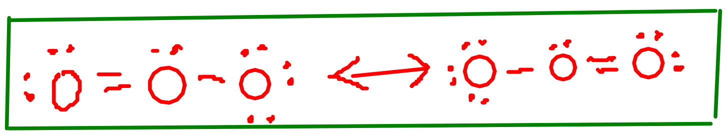


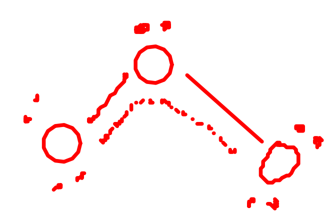
All atoms have a share in eight electrons!

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 resonsnce 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.

NH_4^+

N: 1 × 5
H: 4 × 1

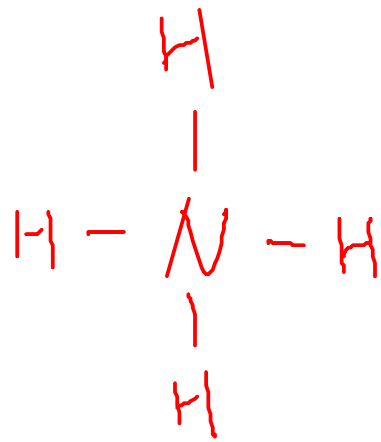
$9e^-$

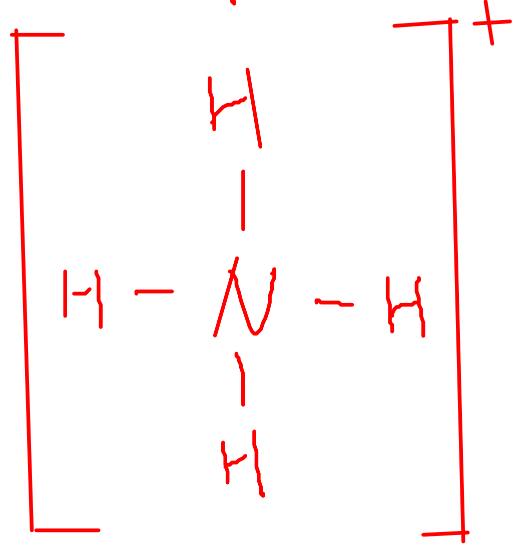
−1

$8e^-$

Wait ... NINE electrons? All the molecules we've drawn so far have an EVEN number of electrons!

Since the ion has a charge of +1, it must've lost an electron.

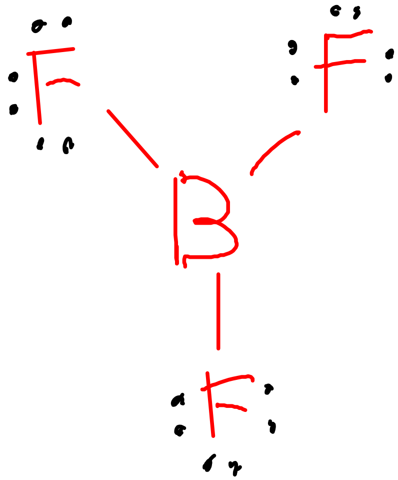




For ions, draw brackets around the structure and indicate the charge in the upper right corner.

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.



BF_3

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

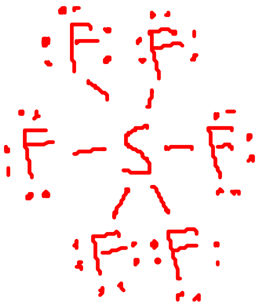
- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

    ... 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:

SF_6



$S: 6$
$F: 7 \times 6$
48

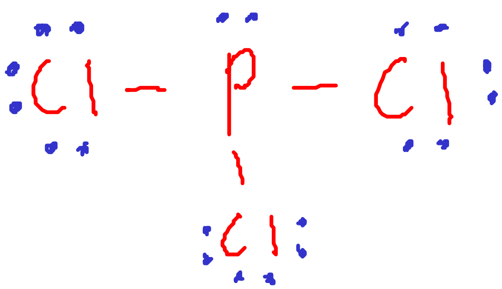
- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- 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.

PCl_3 vs PCl_5

PCl_3

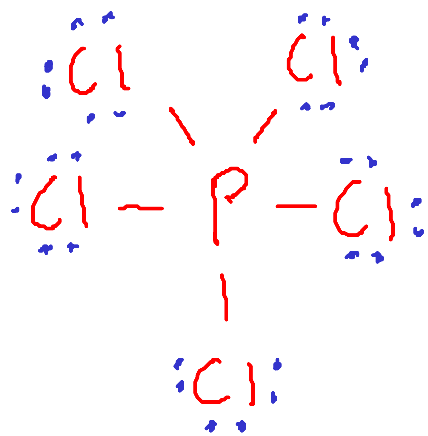
$P: 5$
$Cl: 7 \times 3 = 21$
26



This structure obeys the octet rule.

PCl_5

$P: 5$
$Cl: 7 \times 5 = 35$
40



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.

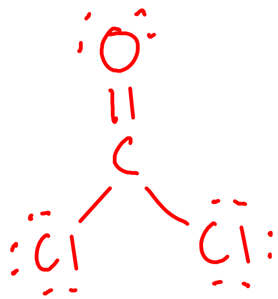
$$\text{FORMAL CHARGE} = \text{ORIGINAL \# OF VALENCE ELECTRONS} - \text{NUMBER OF BONDS} - \text{NUMBER OF UNSHARED ELECTRONS}$$

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

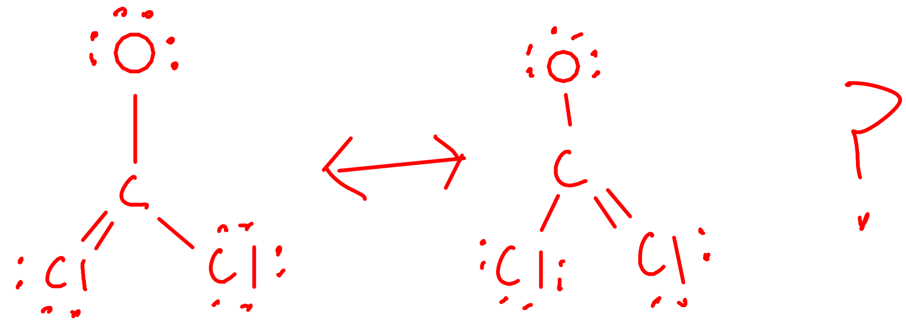
The "better" Lewis structure will have:

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

EXAMPLE: $COCl_2$



OR



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

O: $6 - 2 - 4 = 0$	O: $6 - 1 - 6 = -1$
C: $4 - 4 - 0 = 0$	C: $4 - 4 - 0 = 0$
Cl: $7 - 1 - 6 = 0$	=Cl: $7 - 2 - 4 = +1$
Cl: $7 - 1 - 6 = 0$	−Cl: $7 - 1 - 6 = 0$

The structure on the LEFT is preferred, since all the formal charges are zero (lower in magnitude than the structures on the right)

H–N≡C: vs H–C≡N: ?

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

H–N≡C:	H–C≡N:
H: 1 – 1 – 0 = 0	H: 1 – 1 – 0 = 0
C: 4 – 3 – 2 = –1	C: 4 – 4 – 0 = 0
N: 5 – 4 – 0 = +1	N: 5 – 3 – 2 = 0

Which structure is more likely?

- The HCN structure is more likely, based on lower formal charges than the HNC structure.

- Also, the HNC structure has a positive formal charge on nitrogen and a negative formal charge on the adjacent carbon - suggesting that carbon is pulling electrons away from nitrogen. This is unlikel - since nitrogen is more electronegative than carbon..