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 x 5

H: 4 x 1

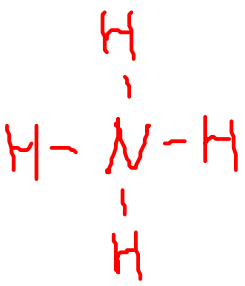
9 e⁻

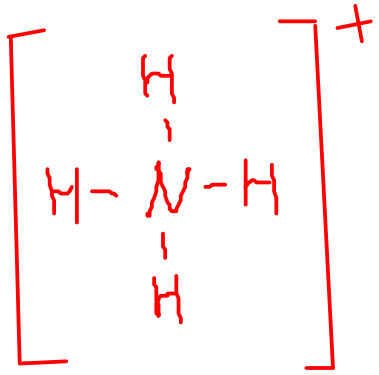
− 1 e⁻

8 e

An ODD number of electrons?
The dot structures we've seen so far all have EVEN electron counts.

Subtract one electron to account for the ion's +1 charge. (If this were an anion, we would add electrons!)

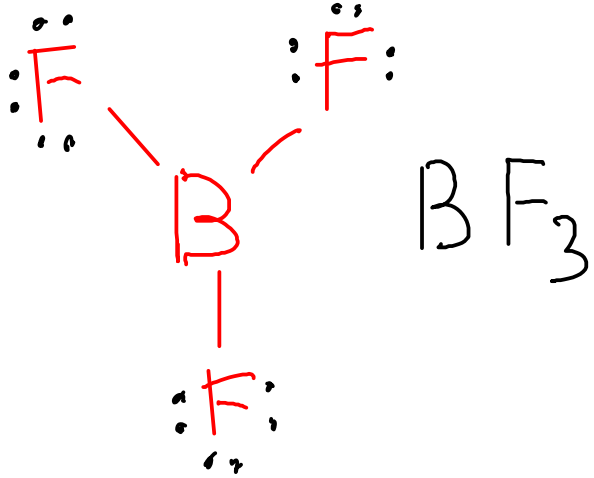




Draw brackets around the structure of the ion, and put the charge in the upper right-hand corner, in a similar way to how you'd indicate the charge of a monatomic ion.

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!

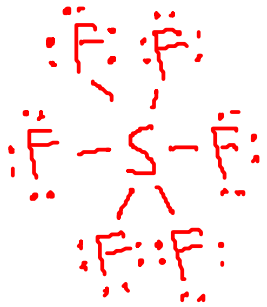
- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

... 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:

SF_6



S: 6
F: 7 x 6
48

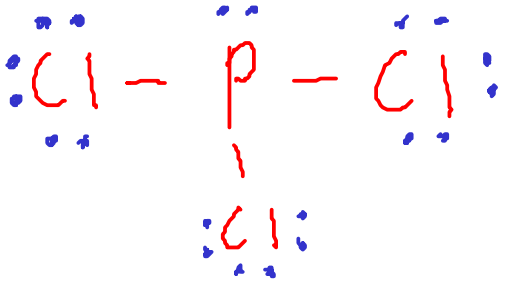
- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- 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

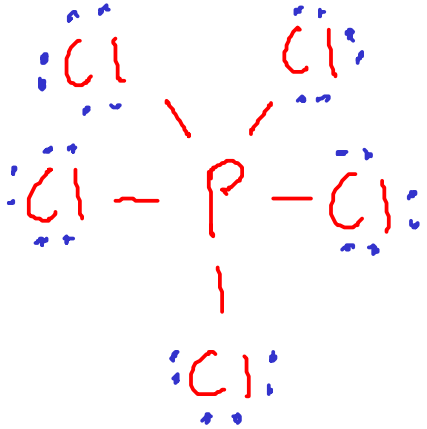
P : 5
Cl : 7 x 3 = 21
26



This structure obeys the octet rule.

PCl_5

P : 5
Cl : 7 x 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.

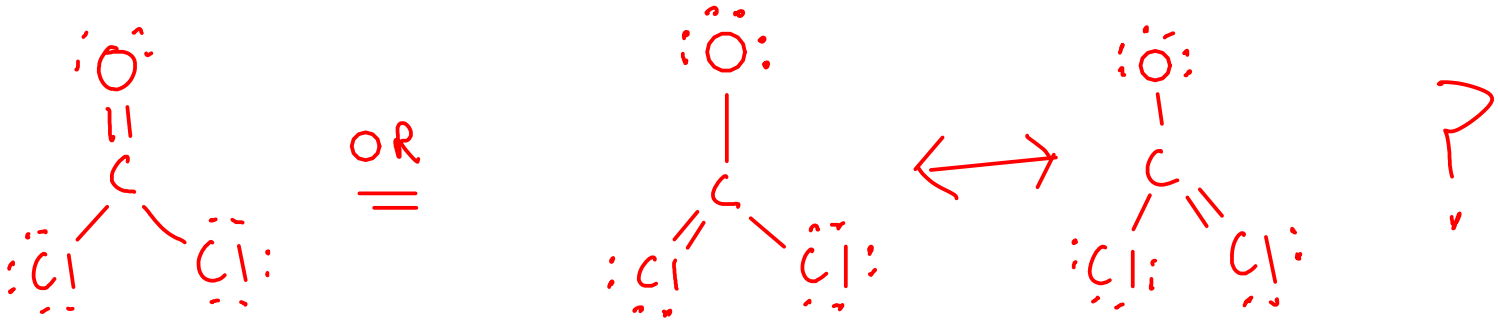
FORMAL CHARGE = ORIGINAL # OF VALENCE ELECTRONS − NUMBER OF BONDS − NUMBER OF UNSHARED ELECTRONS

* 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: $COCl_2$



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

O: 6 − 2 − 4 = 0

C: 4 − 4 − 0 = 0

Cl: 7 − 1 − 6 = 0

Cl: 7 − 1 − 6 = 0

O: 6 − 1 − 6 = −1

C: 4 − 4 − 0 = 0

=Cl: 7 − 2 − 4 = +1

−Cl: 7 − 1 − 6 = 0

BASED ON FORMAL CHARGE, the structure on the left is preferred. It has lower formal charges than the one on the right.

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

H: 1 – 1 – 0 = 0

C: 4 – 3 – 2 = –1

N: 5 – 4 – 0 = +1

H: 1 – 1 – 0 = 0

C: 4 – 4 – 0 = 0

N: 5 – 3 – 2 = 0

Which structure is more likely?

- The HCN (structure on the right) is preferred, since is has lower formal charges than the HNC structure.

- Notice that the HNC structure has another issue ... it seems that CARBON (-1) is withdrawing electrons from N (+1) ... this is unlikely, since N is more electronegative than C.

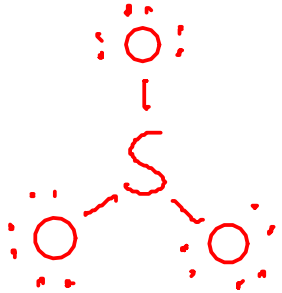
Let's look at sulfur trioxide. SO_3

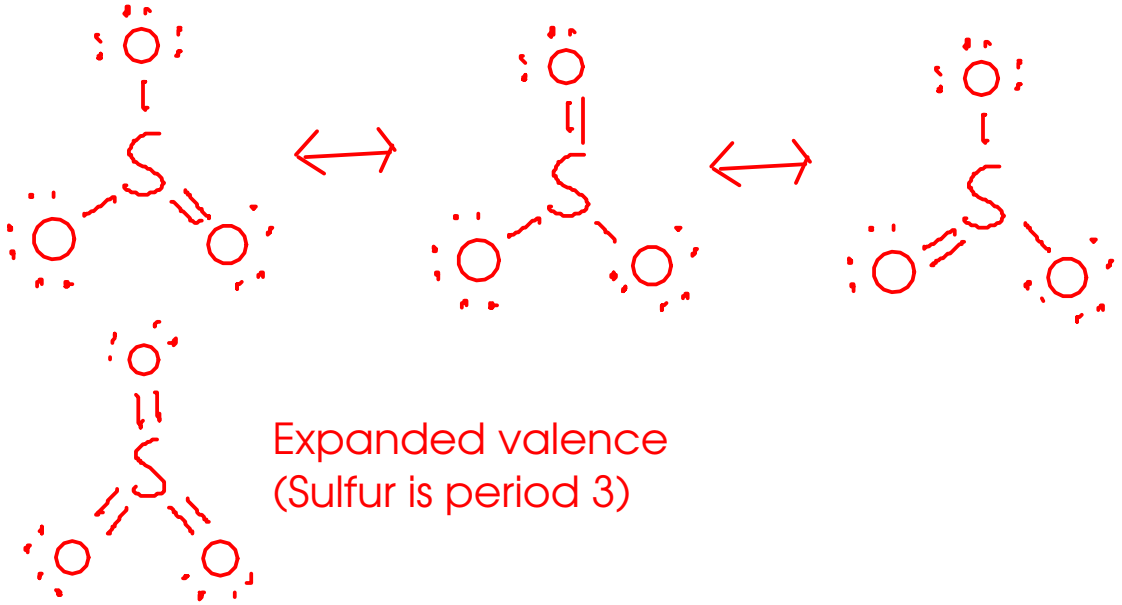
S: 6

O: 6 x 3 = 18

24 e⁻

Skeletal structure:

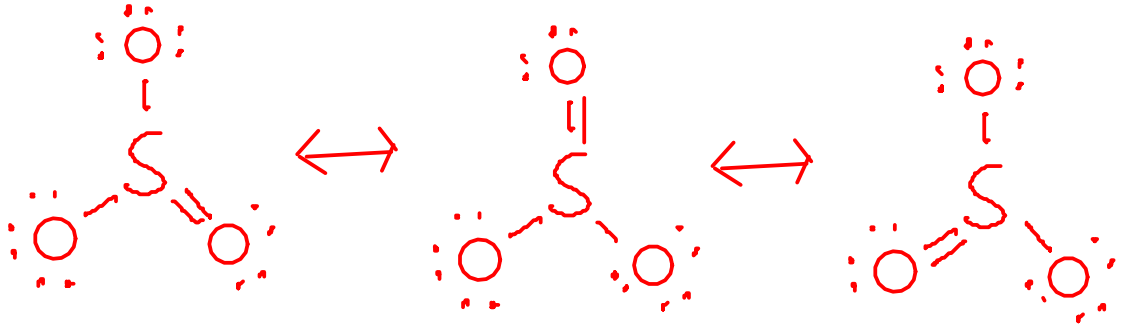




Resonance structures.

Expanded valence
(Sulfur is period 3)

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



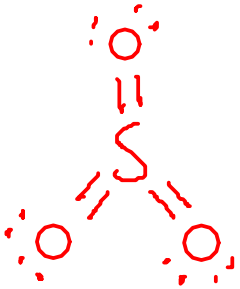
Resonance structures.

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 CHARGES, the expanded valence structure is the most likely structure for sulfur trioxide.

The correct (as in ... agrees with experimental data on bond lengths and bond energy) structure appears to be the expanded valence structure, too!

In general, the structure with lowest fotmal charges is correct - even if it violates the octet rule. Be aware, though, that expanded valence is NOT AN OPTION for atoms in period 2. (C, N, O, F, etc.)