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

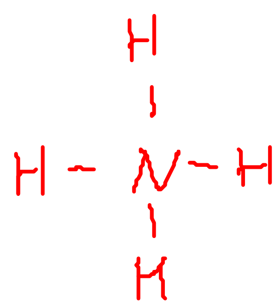
$9e^-$

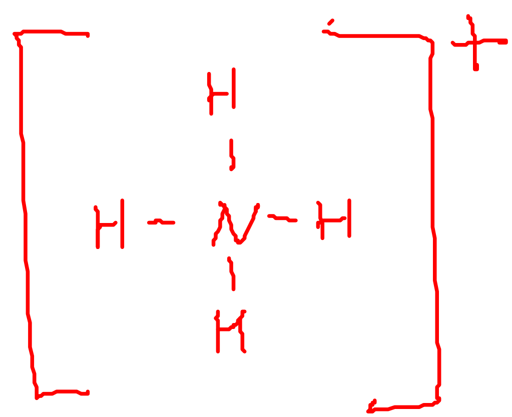
... but everything we have done with Lewis structures for molecules was in PAIRS ... so how do we deal with nine electrons?

-1

$8e^-$

... Since the ion has a +1 charge, we subtract an electron to find the true count!

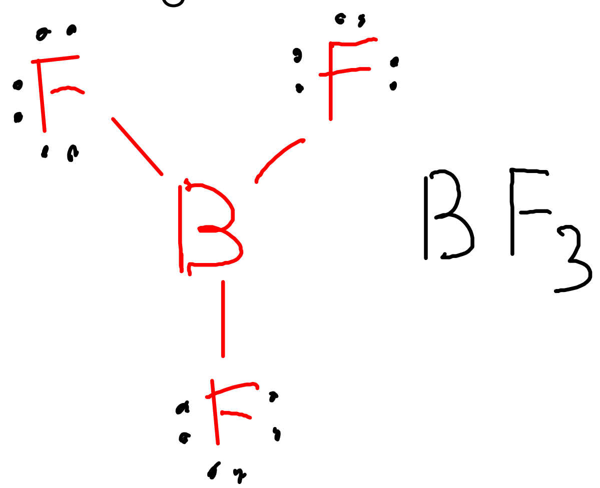




Draw brackets around the ion's strucure and indicate the charge at the upper right - similar to how you indicate the charge of other ions...

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!

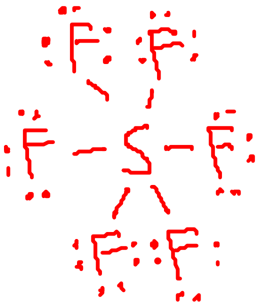
  ... these atoms have unfilled "d" orbitals that may participate in bonding!

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

EXAMPLES:

SF_6

S: 6
F: 7x6
48



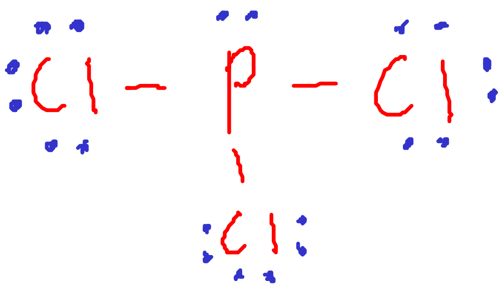
- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- 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

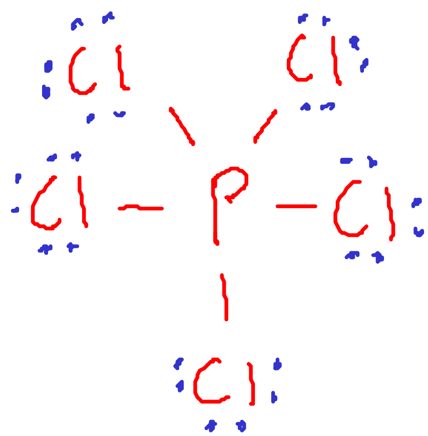
P : 5
Cl : 7x3 = 21
26



This structure obeys the octet rule.

PCl_5

P : 5
Cl : 7x5 = 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.

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

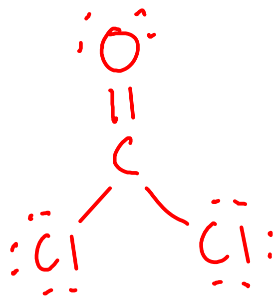
* The sum of the formal charges of all atoms in a structure should equal to the charge of the molecule (0 for neutral molecules)

The "better" Lewis structure will have:

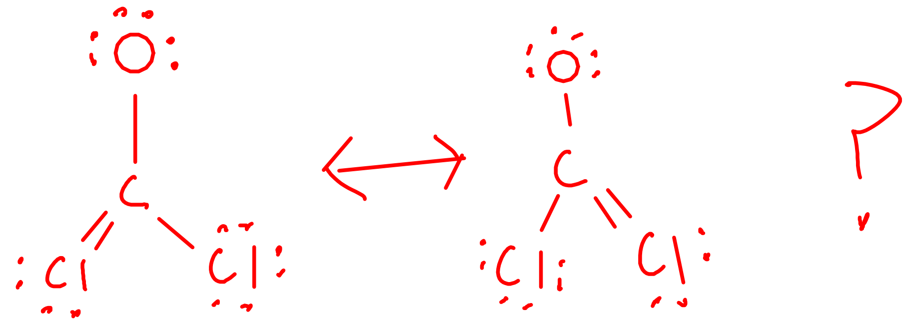
- Lower magnitudes of formal charge (0 0 is better than +2 -2)

- 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!

$O: 6 - 2 - 4 = 0$

$C: 4 - 4 - 0 = 0$

$Cl: 7 - 1 - 6 = 0$

$Cl: 7 - 1 - 6 = 0$

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

$C: 4 - 4 - 0 = 0$

$=Cl: 7 - 2 - 4 = +1$

$-Cl: 7 - 1 - 6 = 0$

The structure on the LEFT is preferred. It has lower formal charges tan the structure 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 suggests that CARBON pulls electron density away from NITROGEN, which is unlikely. (Nitrogen is more electromegative than carbon!)

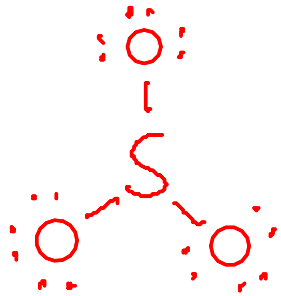
Let's look at sulfur trioxide. SO_3

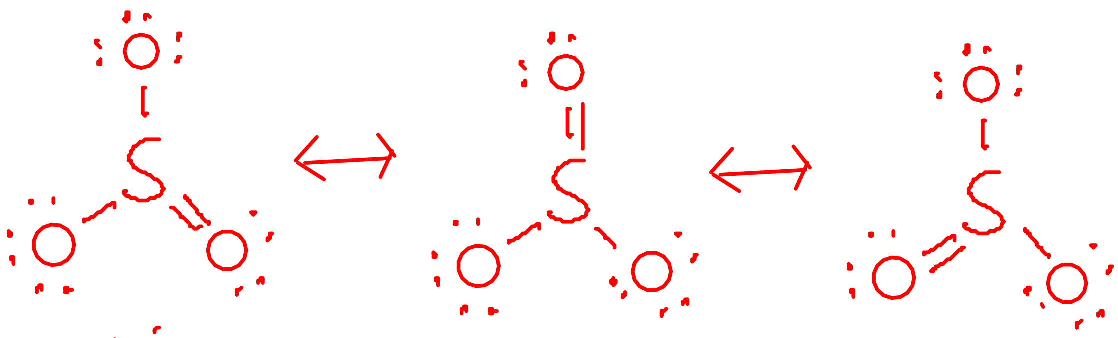
$S: 6$

$O: 6 \times 3 = 18$

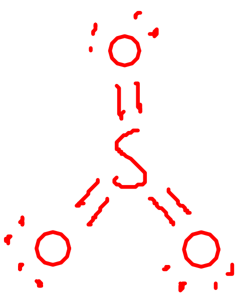
$24\ e^-$

Skeletal structure:



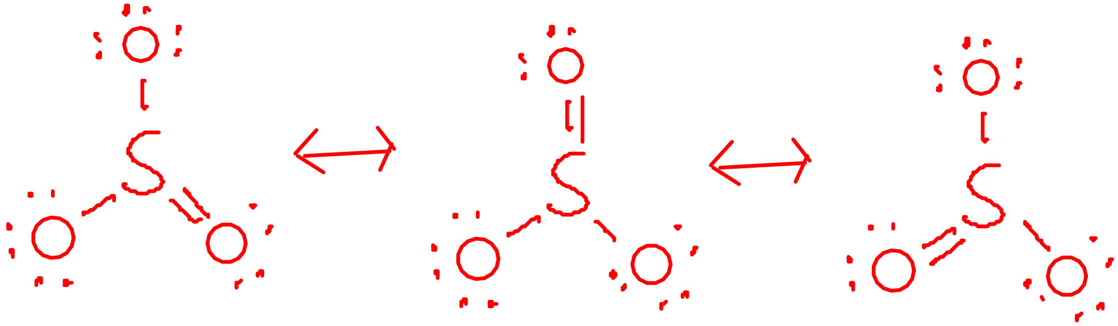


Resonance structures.



Expanded valence
(Sulfur is period 3)

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



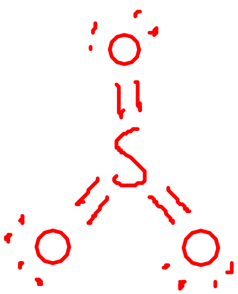
Resonance structures.

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

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

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

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



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 CHARGE, the expanded valence structure is more likely.

The correct - as in agrees with experiment - structure for this molecule is the expanded valence one, based on bond lengths.

In general, formal charge gives us a very reliable way of deciding which of a set of possible Lewis structures for a molecule is most likely. Sometimes, a structure that violates the octet rule is a better choice than one that obeys it! (Exception: Period 2 elements like C, N, O, F...)