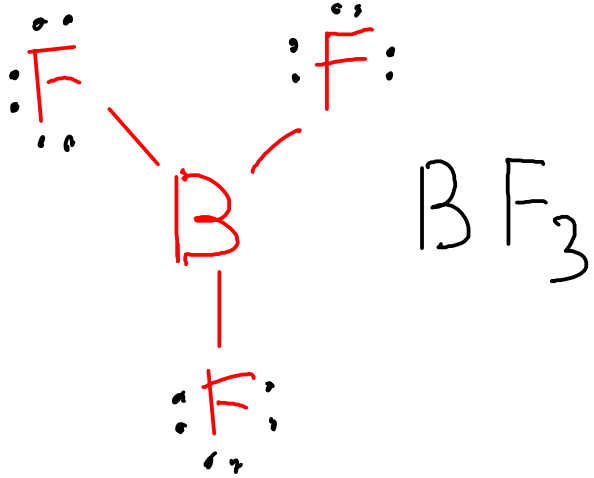
# EXPANDED VALENCE and other exceptions to the "octet rule"

- 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!

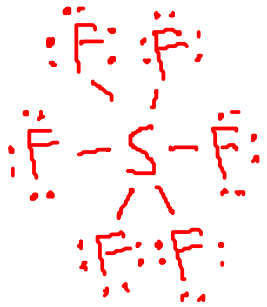
- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

... 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.

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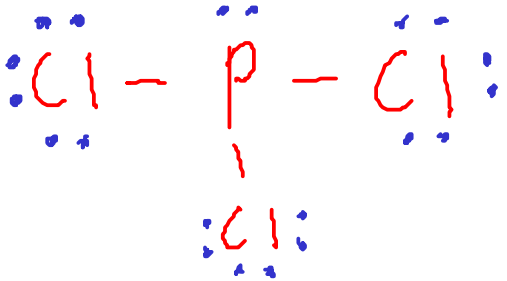
## $PCl_3$ vs $PCl_5$

$PCl_3$

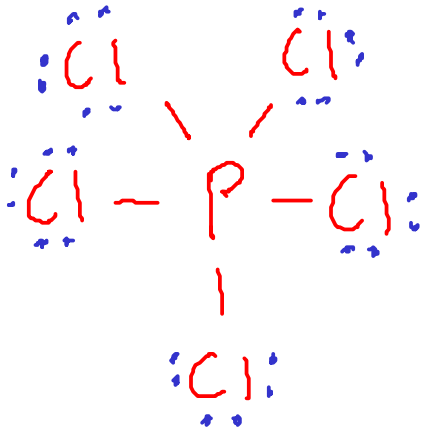
P : 5
Cl : 7 x 3 = 21
26



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.

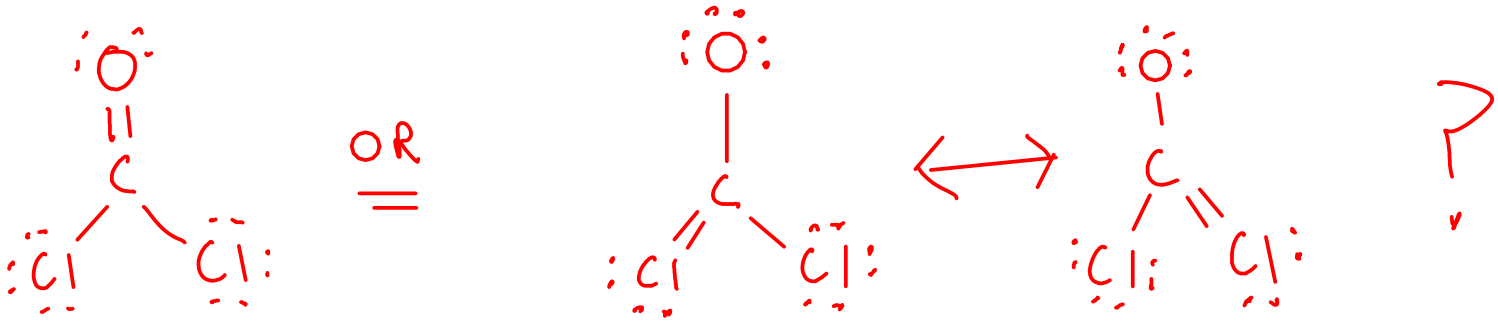
FORMAL CHARGE = ORIGINAL # OF VALENCE ELECTRONS − NUMBER OF BONDS − NUMBER OF UNSHARED ELECTRONS

* 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 resonance structures 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?

- Based on formal charge, the HCN structure is more likely than the HNC structure, since the formal charges are lower.

- Also ... take a look at where the charges are in the HNC structure ... it seems that carbon (which isn't very electronegative) is pulling electrons away from nitrogen (which IS quite electronegative)

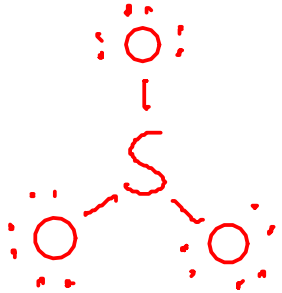
Let's look at sulfur trioxide. $SO_3$

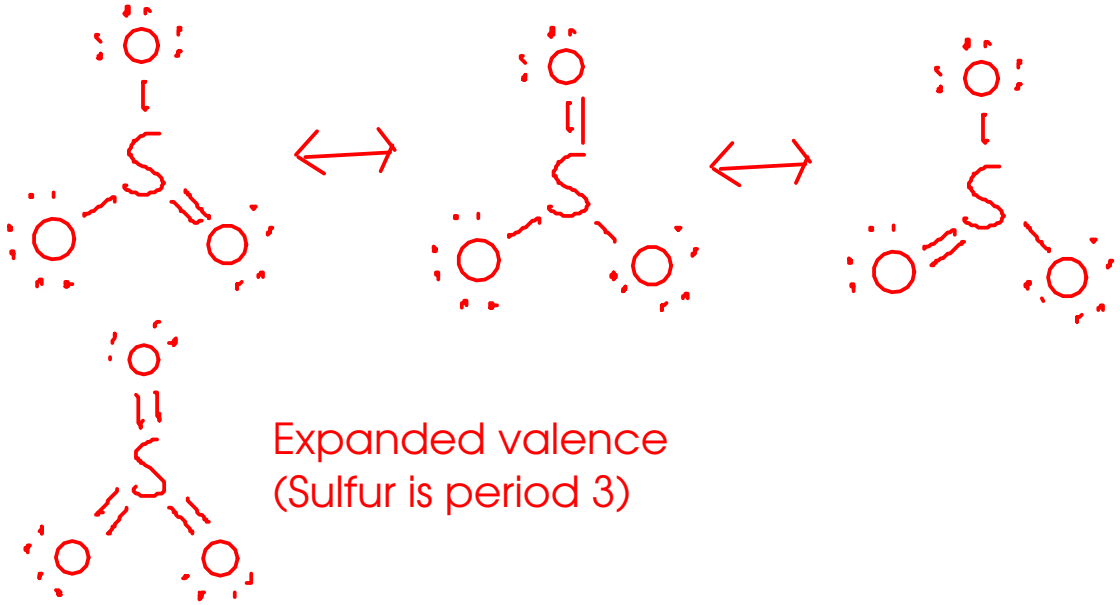
S: 6

O: 6 x 3 = 18

24 e⁻

Skeletal structure:

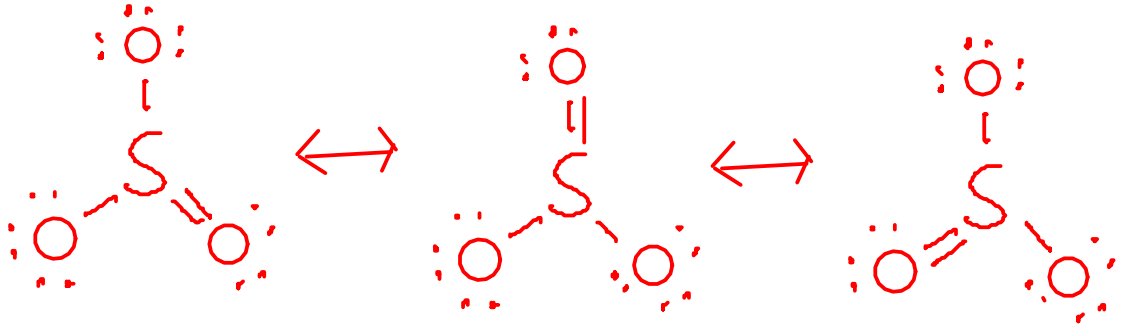




Resonance structures.

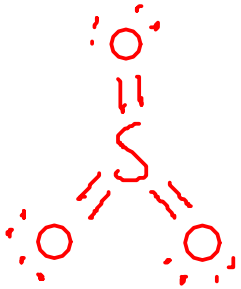
Expanded valence
(Sulfur is period 3)

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 charge, the expanded valence structure is more likely.

The correct (as in - explains more of the experimental data we have on sulfur trioxide) structure is also the expanded valence one, based on the data we have on bond lengths in sulfur trioxide.

In general, formal charge is a good way to decide which of two or more possible structures is the best fit for a molecule - even if one or mor eof the structures violate the octet rule. Just remember that elements in periods 1 and 2 never end up with more than eight outer shell electrons!