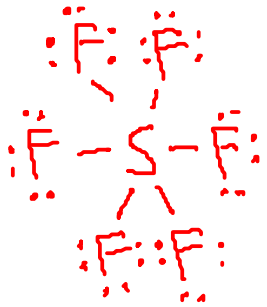
EXAMPLES:

SF_6



S: 6
F: 7 x 6
48

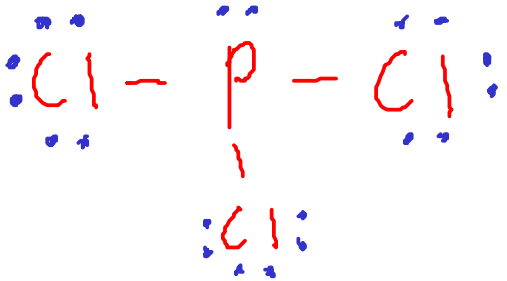
- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- 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

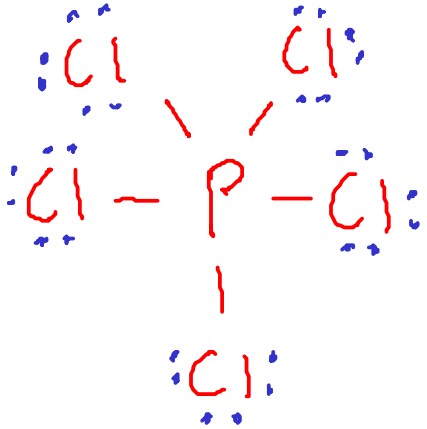
P : 5
Cl : 7 x 3 = 21
26



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.

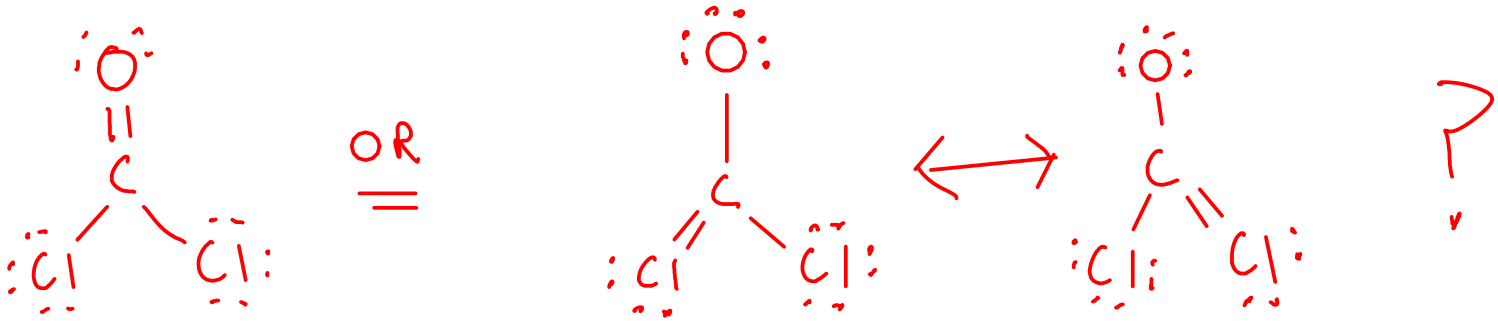
FORMAL CHARGE = ORIGINAL # OF VALENCE ELECTRONS − NUMBER OF BONDS − NUMBER OF UNSHARED ELECTRONS

* 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 structure on the right (the HCN one) is preferred, based on its lower formal charges.

Another bad thing about the HNC structure is that it seggests that carbon (-1 formal charge) is pulling electrons away from nitrogen (+1 formal chage) ... which is unlikely since N is more electronegative than C.

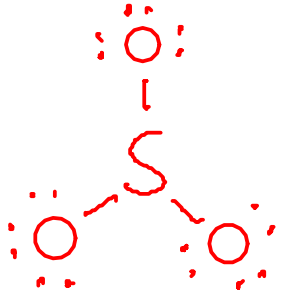
Let's look at sulfur trioxide. SO_3

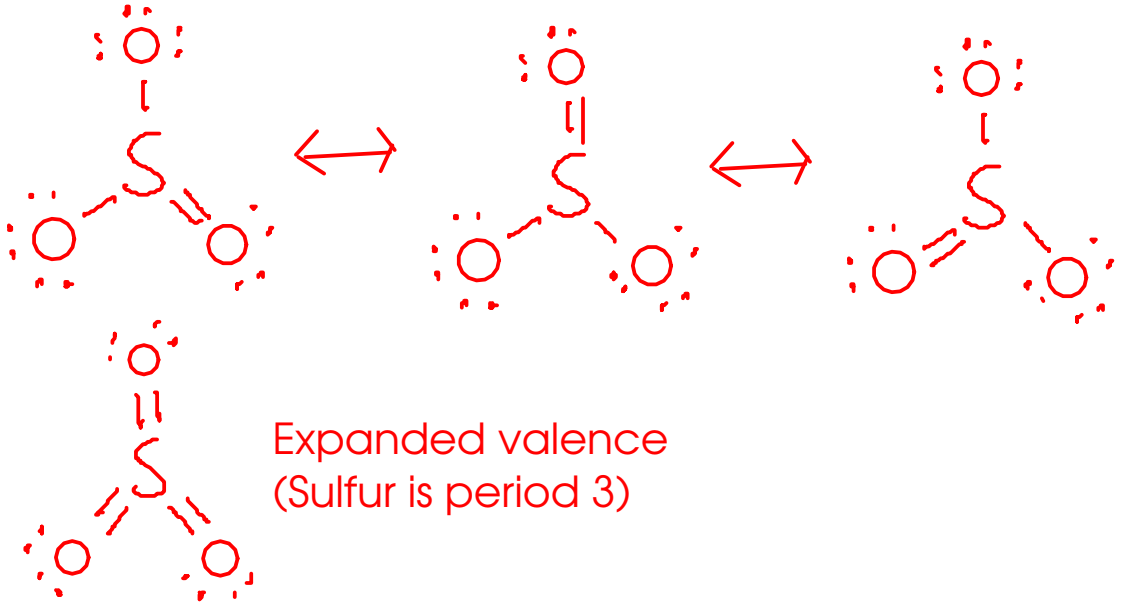
S: 6

O: 6 x 3 = 18

24 e⁻

Skeletal structure:

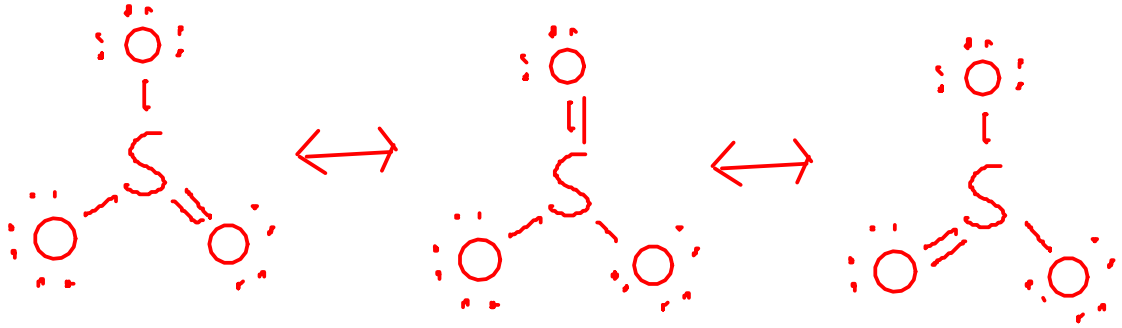




Resonance structures.

Expanded valence
(Sulfur is period 3)

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



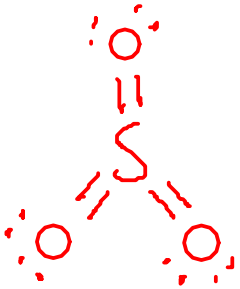
Resonance structures.

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 more likely one.

The correct (as in ... agrees with experimental data on bond length and bond energy) structure also appears to be the expanded valence structure.

In general, the structure with lower formal charges will be the correct one, whether it obeys the octet rule or not. BUT ... remember that period 2 atoms like C, N, O, and F CANNOT support expanded valence.