Structural Formulas that Violate the octet rule

There are many types of covalent compounds that contain a central atom that violates the octet rule. Central atoms that violate are found in period 3 and below and may include, but are not limited to P, Cl, Mn, Cr, Br, I, Xe

To draw the structural formula you follow the same general rules:

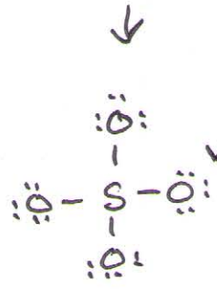
1) count total valence e^-
2) place e^- as bonding pairs, unshared pairs
3) extra pairs are used up as bonds and unshared pairs on the central atom.
4) A concept called formal charge (FC) is used to determine the correct or best structure.
5) $FC = \#\text{valence } e^- - \left(\frac{1}{2}\text{BE} + \text{total unpaired } e^-\right)$

(BE: bonding e^-)

6) Best structure is the structure where FC is zero for all atoms. If FC is not zero, then (->) FC should be on the most electronegative atom.

Example 1: SO_4^{-2}

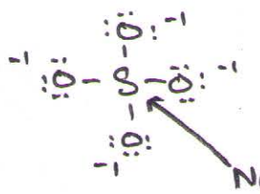
Normally if you follow the octet rule the structure would be: 32 valence e⁻



calc FC on O so

$FC = 6 - (1 + 6) = -1$

All the O's are -1.

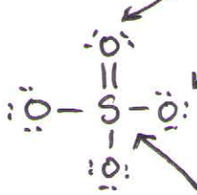


Now calc FC on S:

$FC = 6 - (4 + 0) = +2$

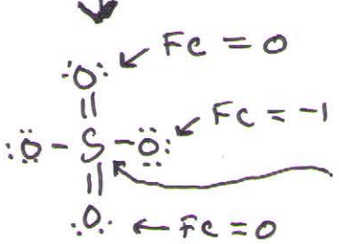
The FC on the S is +2. The FC on S should be zero. So there may be a better structure. So I try:

$FC = 6 - (2 + 4) = 0$



FC = -1

New $FC = 6 - (5 + 0) = +1$; not zero!

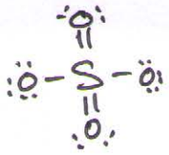


FC = 0

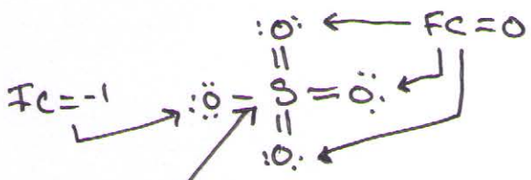
FC = -1

New $FC = 6 - (6 + 0) = 0$; yes!

FC = 0

So  is the best structure because the central atom has FC = 0, two of the O's are FC = 0 and 2 O's are -1 where the negative charge is on the more electronegative atom and sum of the net charge matches the polyanion charge of -2 where SO_4^{-2} ←***

what happens if we add another bond ?

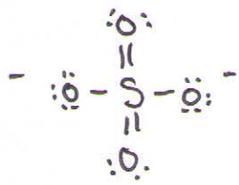


new FC = 6 − (7 + 0) = -1

↑ now a negative FC is on the less electronegative atom. Can't happen. Structure is not the best.

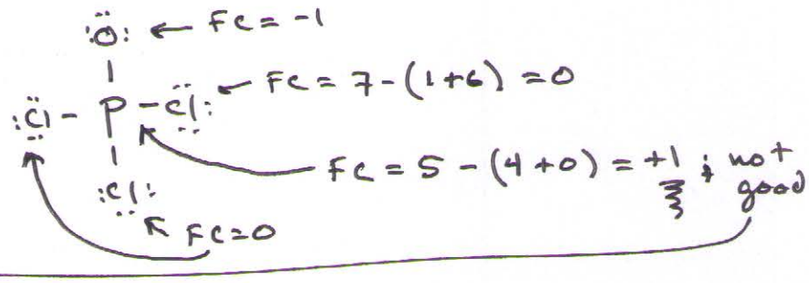
Best structure SO_4^{-2}

↓

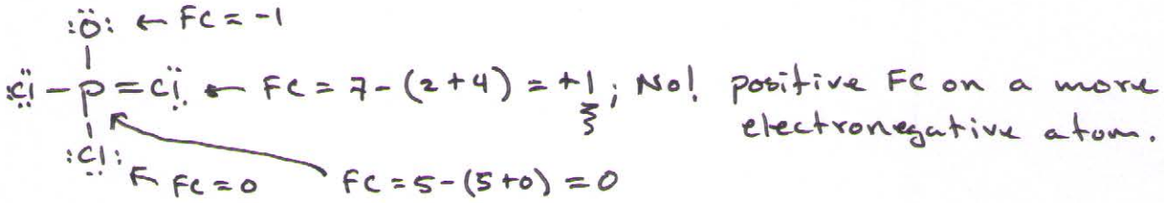


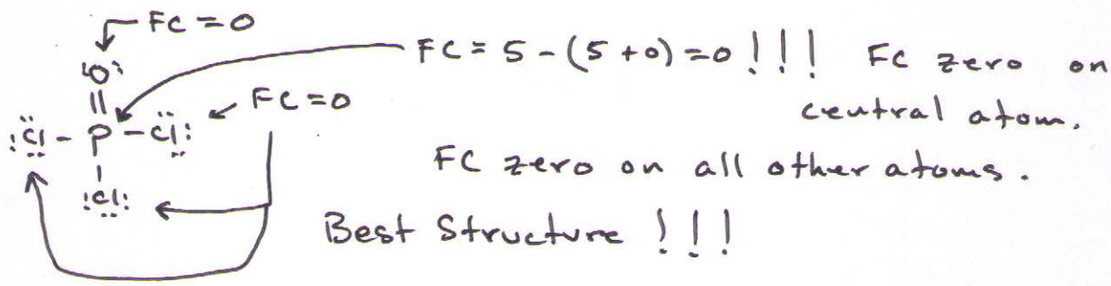
Example 2 $POCl_3$ total valence is 32 e^-

with octet:



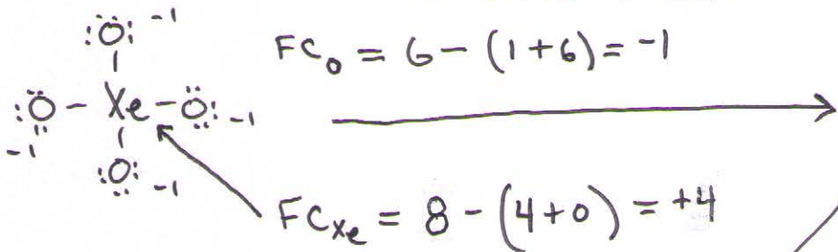
So we try some options:

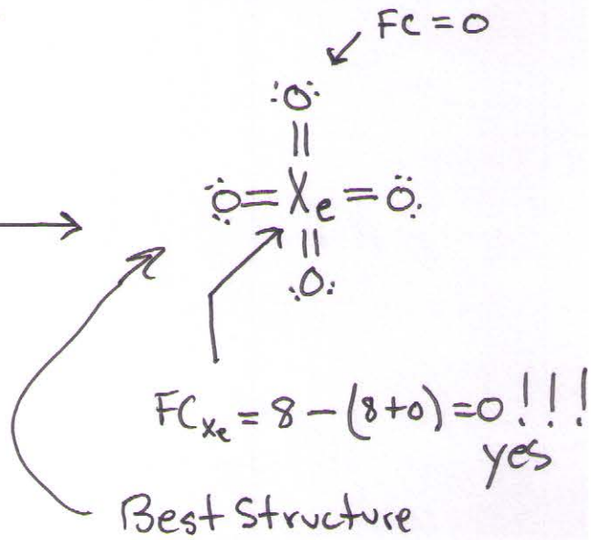




Example 3 XeO_4 32 valence e^-

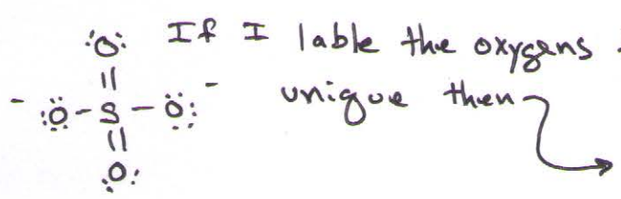
Draw structure via octet rule:



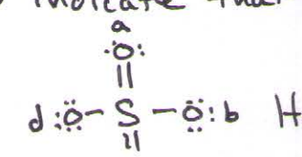


Resonance : A situation when more than one equivalent structure is possible for a molecule.

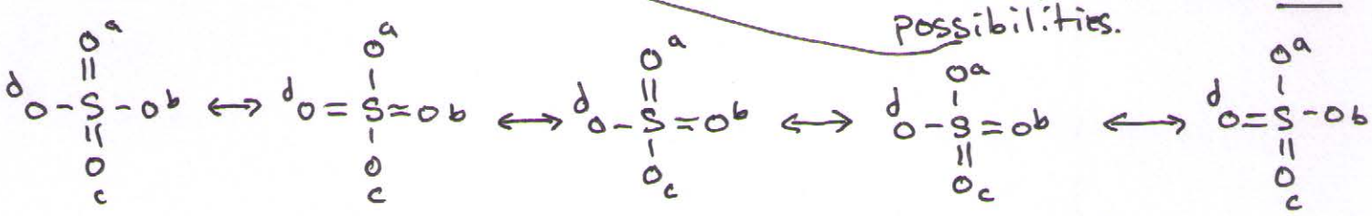
Lewis structures are a way for chemists to model the actual physical structure of a molecule. Drawings allow us another method to communicate what we know or what we can predict about the physical and/or chemical behavior of a molecule. Sometimes our model systems break down. Let's look at SO_4^{-2} again: The best structure is,



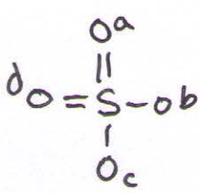
If I lable the oxygens to indicate that each O is unique then



Hopefully you can see that we could have placed the double bonds in other locations. There are six possibilities.



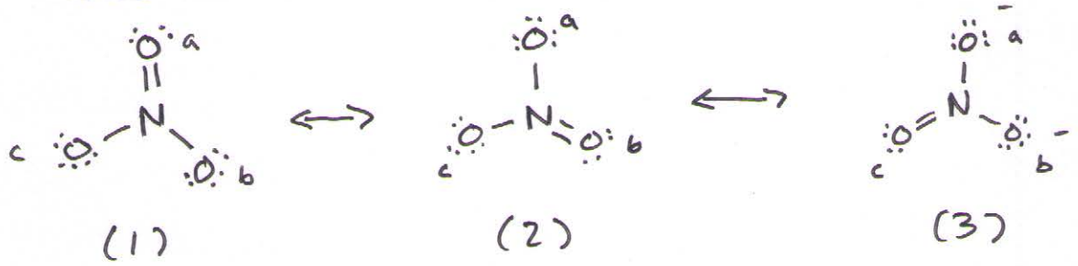
Each of the six structures are equivalent = same # double bonds, single bonds, etc. we call the 6 structures resonance structures. what this means is that the real structure is an average of the structures shown above. There are no double bonds in this molecule. The two pairs of double bond e^- are delocalized over the surface area of the molecule. So each bond is about 1.5 bonds.



Resonance

Example 1 — nitrate NO_3^- — 24 valence e^-

By octet rule since N is period 2



(1) (2) (3)

Nitrate has 3 resonace structures. Note that you cannot argue that the structures are simply being rotated - they are not. The double bond pair of e^- are delocalized over the surface area of the molecule so the actual structure is the average of all three structures. So each bond is about 1⅓.