How to Determine the Geometry of Molecules & Ions (Chapter 7 + 8)

A Draw Lewis dot formula using valence electrons (outer shell e^-) for each atom (same as Group No.)

* most atoms want 8 e^- around them (H wants 2 e^-) to be stable as noble gases

This is "octet" rule. Atoms will share e^- to form bonds or have lone pair of e^-

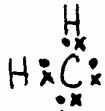
2 e^- shared is single bond, seen as : or —

4 e^- shared is double bond, seen as :: or =

6 e^- shared is triple bond, seen as ⁝ or ≡

Examples

CH_4



NH_4^+

N_2

$HClO$

H_2O

$HClO_4$

CO_2

CN^-

SO_2

CO_3^{2-}

$BeCl_2$

BF_3 PF_5

Rules of Thumb: (Step 0 - identify group number for each element)

(1) Put the atom needing most e^- to fill its octet in the middle, others are around it

(2) The most symmetrical skeleton is usually correct (doesn't always work)

(3) H and outside halogens always share 1 e^- to fill outer shell & never double or triple bond

(4) To keep things straight, it is useful to use different symbols for electrons "belonging" to atoms; eg. use • for C e^- and x for H e^-

(5) For ions, add or remove electrons from central atom.

(6) When forming multiple bonds between atoms (double & triple), both atoms donate the same number of electrons.

(7) In ternary acids, eg HClO, H bonds to O. They always obey octet rule.

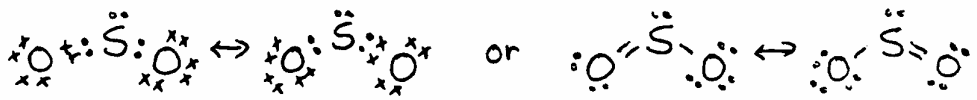
(8) O can bond in three ways:

* single bond by sharing an electron
* single bond by taking 2 e^- from another atom (O is very electronegative)
* double bond by sharing 2 e^-

(9) O atoms usually bond to another nonmetal, not to each other (except in peroxides H_2O_2)

(10) C compounds always obey octet rule. C never has lone pair(s) of e^- on it except when C is at end, eg CN^-

(11) Concept of resonance occurs when you have to make an arbitrary decision on where to put a double bond to fulfill octet rule. Write all structures and put double headed arrow between them.



The true structure is average of all resonance structures.

Compounds or ions disobey the octet rule only when they have to. It is the central atom that disobeys. The outer atoms always obey octet rule.

Formal Charges

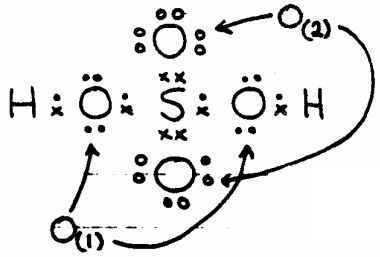
The concept of formal charges helps us choose the correct Lewis structure for a molecule.

Rules for assigning formal charges to Group A elements:

1. For a molecule, the sum of the formal charges for all elements is zero
   For an ion, the sum of the formal charges for all the elements equals charge on ion
2. Formal charge, FC = Group No. − (no. of bonds + no. unshared e^-)
   Note: Group Number of noble gases = VIII; double bond counts as 2 bonds.
3. A good (near zero) Lewis dot structure has
   - low or zero values of FC for all elements
   - adjacent atoms are not given FC values of the same sign
   - the more electronegative atom in a bond is given the more negative FC.

Consider two Lewis dot structures for sulfuric acid, H_2SO_4.

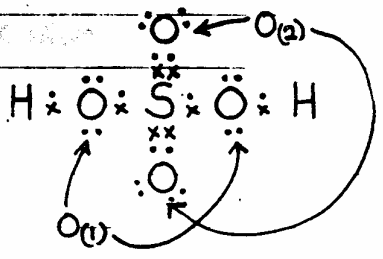
(a)



FC H = 1 − (1 + 0) = 0
$O_{(1)}$ = 6 − (2 + 4) = 0
$O_{(2)}$ = 6 − (1 + 6) = −1
S = 6 − (4 + 0) = +2

This is an OK dot structure, but there might be a better one where FC of S is closer to zero. Consider

(b)



Note: sulfur does not obey the octet rule

FC H = 1 − (1 + 0) = 0
$O_{(1)}$ = 6 − (2 + 4) = 0
$O_{(2)}$ = 6 − (2 + 4) = 0
S = 6 − (6 − 0) = 0

Structure is a little strange, but all elements have zero FC. Good!!
There is data to support this structure for H_2SO_4.

(B) Count the "regions of high electron density" around the central atom

One region is a single bond, double bond, triple bond or lone pair of e^-.
This tells you the Electronic Geometry, hybridization, bond angles.

Regions	Electronic Geometry	Hybridization	Bond Angles
2	linear	sp	180°
3	trigonal planar	sp^2	120°
4	tetrahedral	sp^3	109° 28'
5	trigonal bipyramidal	sp^3d	90°, 120°, 180°
6	octahedral	sp^3d^2	90°, 180°

Note on hybridization - to account for these ~~weird~~ geometries, we say that atomic orbitals mixed together ie "hybridized" to form new orbitals called hybrid orbitals. They all look like a cross between an s + p orbital

For example: sp^3 means we mixed 1 s and 3 p orbitals to get 4 new hybrid orbitals called sp^3 orbitals, which formed a tetrahedron with bond angles of 109° 28'. This is just a theory for explaining what we see to be true.

(C) Look at the number of lone pairs of electrons on the central atom - this will set the Molecular Geometry - what the molecule or ion really looks like

Use models to see shapes.

Regions	Electronic Geometry	# Lone Pairs e^-	Molecular Geometry
2	linear	0 or 1	linear
3	trigonal planar	0	trigonal planar
		1	bent/angular
4	tetrahedral	0	tetrahedral
		1	pyramidal
		2	bent/angular
5	trigonal bipyramidal	0	trigonal bipyramidal
		1	seesaw
	lone pairs go on trigonal planar part because they need more room	2	T-shaped
		3	linear
6	octahedral	0	octahedral
		1	square pyramidal
		2	square planar
		3	T-shaped (distorted)

(D) A molecule is nonpolar if its bond polarities + unpaired electrons (if any) around central atom cancel out. (the molecule is symmetrical).

So what makes a bond polar or nonpolar?

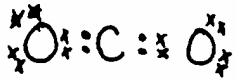
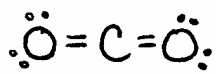
- a bond between 2 atoms is polar if 2 atoms have different electronegativities

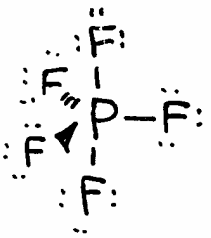
$\underset{\text{EN } 2.5}{C}-\underset{3.5}{O}$ polar bond

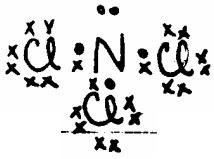
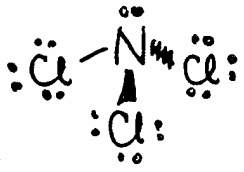
- a bond between 2 atoms is nonpolar if 2 atoms have same electronegativity

$\underset{\text{EN } 4.0}{F}-\underset{4.0}{F}$ or $\underset{3.0}{N}-\underset{3.0}{Cl}$

Examples:

CO_2 (1)   bonds are polar, but cancel out molecule CO_2 is nonpolar

PF_5 (2)   bonds are polar, but cancel out PF_5 is nonpolar

NCl_3 (3)   bonds are not polar, but lone pair of electrons has polarity associated with it, so molecule is polar.

(E) Better explanation in class, but

(1) all single bonds are sigma (σ) bonds
(2) all double bonds have 1 sigma bond + 1 pi (π) bond.
(3) all tiple bonds have 1 sigma bond + 2 pi bonds.