Lewis Dot Structures and Shapes of Molecules

What follows is a step-by-step tutorial on how to draw Lewis Dot Structures for molecules and polyatomic ions. We're going to be working with 6 different molecules or ions: CO_2, H_2O, BCl_3, PCl_3, NH_4^+, and NO_2^-.

Here are the five steps to success.

1) **Arrange the atoms appropriately and as symmetrically as possible** . The "odd" (i.e. different) atom usually goes in the middle. Usually, the arrangement that is most symmetrical is correct.
2) **Count up the total number of valence electrons that should be in the structure at the end**. If you're working with an anion, add an additional number of electrons equal to the anion charge. If you have a cation, subtract a number of electrons equal to the cation charge.
3) **Draw single bonds between the central atom and each surrounding atom**. Note that each single bond represents a shared pair of electrons.
4) **Place the remaining electrons, in pairs, around the atoms in the structure**. I usually start with the outer atoms. Note that H never gets lone pairs (it can only participate in a single bond)
5) **Move pairs around so that each non-metal element has an octet** (exceptions: H only needs 2 electrons, and B only needs 6 electrons). The final number of electrons in the structure should equal the number counted in Step 2.

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Determining Molecular Shapes using VSEPR Theory

VSEPR stands for Valence Shell Electron Pair Repulsion. The basic idea of VSEPR is that **electron groups** want to be as far apart as possible. There are only 2 kinds of electron groups:

1) Bonding groups – any single, double, or triple bond counts as one bonding group
2) Lone pair groups – a lone pair of electrons counts as one lone pair group

The following table tells how the number of electrons around the central atom influences the shape of the molecule or ion.

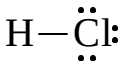
Number of electron groups around central atom	Best geometry to keep electron groups as far apart as possible
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

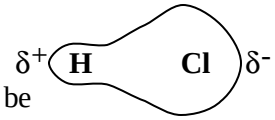
Now, it's important to distinguish between **electron group geometry** and **molecular geometry**. Molecular geometry is the shape formed only by the bonded groups. Electron group geometry is the shape including both the lone pair groups and the bonding groups. The only time that the electron group geometry and the molecular geometry are the same is if there are no lone pairs on the central atom. The following table summarizes the difference and introduces some new molecular geometries.

Total groups on central atom	# bonding groups	# lone pair groups	best group geometry	molecular geometry
2	2		linear	linear
3	3	0	trig. planar	trig. planar
3	2	1	trig. planar	bent (angular)
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent (angular)

Bond Polarity

Take a look at the dot structure for HCl



In a covalent bond, the more nonmetallic element "hogs" the shared electrons to itself → 

The unequal sharing creates a partial separation of charge, and the resulting bond is said to be **polar covalent.** A polar covalent bond has a dipole moment that can be measured experimentally.

We can symbolize a polar covalent bond in 2 ways: δ^+**HCl**δ^- or  The 2nd way, with the crossed arrow, is most useful. Note that the arrow points to the more nonmetallic element

How can you tell if a bond is polar? Look at the electronegativity difference (ΔEN) between the atoms in the bond

Electronegativity → a numerical measure of an atom's tendency to attract shared electrons to itself

The highest value of EN is 4.0 for fluorine; next is 3.5 for O. On the periodic table, whenever you are moving in a direction opposite of F, electronegativity decreases

The following is a table of electronegativity values for the representative (main group, i.e. Group A) elements:

Electronegativity

H = 2.1	x	x	x	x	x	x
Li = 1.0	Be = 1.5	B = 2.0	C = 2.5	N = 3.0	O = 3.5	F = 4.0
Na = 0.9	Mg = 1.2	Al = 1.5	Si = 1.8	P = 2.1	S = 2.5	Cl = 3.0
K = 0.8	Ca = 1.0	Ga = 1.6	Ge = 1.8	As = 2.0	Se = 2.4	Br = 2.8
Rb = 0.8	Sr = 1.0	In = 1.7	Sn = 1.8	Sb = 1.9	Te = 2.1	I = 2.5
Cs = 0.7	Ba = 0.9	Tl = 1.8	Pb = 1.9	Bi = 1.9	Po = 2.0	At = 2.2

How does the value of ΔEN tell you the polarity of the bond? We use the following approximate guidelines:

0.0 ------- nonpolar covalent ---- 0.5 -------polar covalent ---------2.0 ---------- ionic ----------4.0

Examples

H Cl	**C H**	**Na Cl**
2.1 3.0	2.5 2.1	0.9 3.0
ΔEN = 3.0 – 2.1 = 0.9 (polar)	ΔEN = 2.5 – 2.1 = 0.4 (nonpolar)	ΔEN = 3.0 – 0.9 = 2.1 (ionic)

Note that these guidelines are approximate. So, how can you really tell if a compound is ionic? As a good general rule…

***** A compound is ionic if it conducts electricity in the pure molten state *****

Molecular Polarity

Molecular (covalent) compounds in the liquid and solid phases are held together by intermolecular forces. The strength of these forces depends largely on the polarity of molecules.

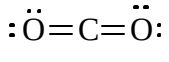
What does it mean for a molecule to be polar? It means that the molecule has a net dipole (separation of charge)

How do you determine the polarity of molecule? There are 2 steps:

Step 1: determine if the molecule has polar bond by evaluating the electronegativity differences between atoms for each bond individually.

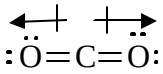
Step 2: determine if the individual bond polarities cancel each other out, which will only happen if the molecule has a perfectly symmetrical shape (linear, trigonal planar, tetrahedral) and identical polarity bonds

Examples

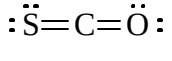
Look at CO_2 → 

Step 1: Are the bonds polar? The electronegativity of C is 2.5 and O is 3.5. Thus the difference is 3.5 - 2.5 = 1.0, so the CO bonds are highly polar.

Step 2: Do the bond dipoles cancel each other? You would show the bond dipoles on the molecule as follows:

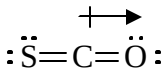


*** Notice the perfect symmetry of the CO_2 molecule! You can picture the bond dipoles "pulling" directly against each other. Because CO_2 has perfect linear symmetry and both bonds involved in the linear shape have identical polarity, the strong CO dipoles cancel each other and thus CO_2 is a nonpolar molecule.

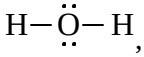
What about this molecule →  (it's just like CO_2 except one of the oxygen atoms is now a sulfur)

Step 1: Are the bonds polar? As we saw in the first example, the CO bond is highly polar. But the CS bond in nonpolar, because C and S both have electronegativity of 2.5.

Step 2: Do the bond dipoles cancel each other? You would show the bond dipoles on the molecule as follows:

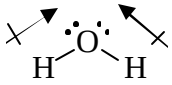


In this case, the strong CO bond dipole is not "opposed" by another bond dipole. Even though the molecule is liner, it is NOT perfectly symmetrical because the CO and CS bonds have different polarity. Thus, CO bond dipole is not cancelled out so CSO is a polar molecule.

One more example: H_2O; most people write the Lewis dot structure of H_2O as  , which is fine

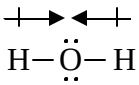
Step 1: Are the bonds polar? The electronegativity of H is 2.1 and O is 3.5. The difference is 1.4, so the OH bond is highly polar.

Step 2: Do the bond dipoles cancel each other? **To see this, you should draw the geometric picture of the molecule, so you can see how the dipoles interact.** Since H_2O is MX_2E_2, the molecule is <u>bent</u> and drawing with dipoles would look as follows:



Because the molecule is bent, it is not perfectly symmetrical, so the two OH bond dipoles do not cancel each other. Electrons in both OH bonds are pulled toward O, causing the oxygen side of H_2O to be partially negative and the hydrogen side to be partially positive. H_2O is a highly polar molecule.

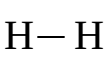
What if you didn't draw the H_2O "geometrically" when you did the polarity analysis? Then you would have

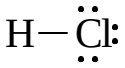


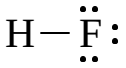
and it would look like the bond polarities would be opposing, and canceling, each other. This is not what happens, because H_2O is not a linear molecule.

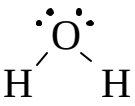
Here's a good, general rule of thumb: If a molecule has <u>one or more lone pairs</u> on a <u>central atom</u> and at <u>least one of the bonds to that central atom is polar</u>, then the molecule is most likely polar.

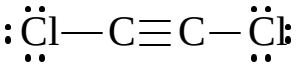
<u>Examples to go over in class</u>

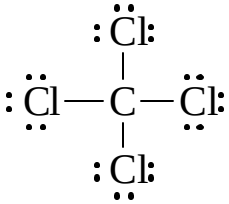


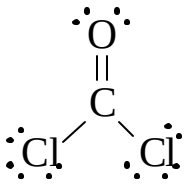












In general, a molecule is nonpolar only if:

1) All bonds are nonpolar
2) The molecule is <u>perfectly symmetrical</u> (linear, trig planar, tetrahedral, octahedral, or square planar) <u>and has identical polarity bonds</u>, so that all bond dipoles ("pulls" or "pushes") cancel