

Molecules: Lewis Structures & VSEPR: Student Review Notes

G. N. Lewis suggested that atoms, by sharing electrons to form an electron-pair bond, can acquire a stable, noble gas electron configuration--this is the Octet Rule

Octet rule: Most atoms want eight valence electrons -- a full outer octet. This gives you an intuitive idea of what to expect. If you draw a Lewis diagram and one of the atoms in the molecule isn't surrounded by 8 electrons, either as lone pairs or shared in covalent bonds, you'd better make sure you haven't made a mistake. The octet rule doesn't hold 100% of the time, just most of the time.

Electron Bookkeeping:

- A methodical way to draw Lewis structures of molecules whose atoms follow the octet rule.
- It's also nice because when it breaks down it tips you off to exceptions to the octet rule like the expanded octet.

Step 1: Count the electron pairs needed

- * Hydrogen wants 1 pair
- * Group II's want 2 pairs
- * Group III's want 3 pairs
- * Everyone else wants 4 pairs

Step 2: Find the total number of covalent bonds possible

- * Total # of possible cov. bonds = sum of the valence e's divided by 2
- * Remember to add or subtract electrons according to any ionic charge

Step 3: Calculate the actual number of covalent bonds

$$\text{Actual Covalent Bonds} = \text{step 1} - \text{step 2}$$

If you don't get enough bonds to draw the molecule, it's likely an expanded octet.

Step 4: Calculate the number of σ bonds, π bonds, and nonbonding pairs

$$\text{No. of } \sigma \text{ (sigma) bonds} = \# \text{ of atoms in the molecule} - 1$$

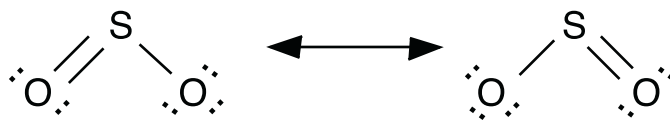
$$\text{No. of } \pi \text{ (pi) bonds} = \text{Actual covalent bonds (step 3)} - \text{No. of } \sigma \text{ bonds}$$

$$\text{No. of nonbonding pairs} = \text{possible bonds (step 2)} - \text{Actual bonds (step 3)}$$

Step 5: Draw the molecule here are some typical examples:

	CH₄	NH₃	H₂O	CO₂
step 1:	8	7	6	12
step 2:	4	4	4	8
step 3:	4	3	2	4
step 4:				
σ	4	3	2	2
π	0	0	0	2
nbp	0	1	2	4
step 5:				
	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{N} - \text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{..} \\ \text{H} - \text{O} - \text{H} \\ \text{..} \end{array}$	$\text{O} = \text{C} = \text{O}$

Resonance Comes up when there are more than one are equivalent Lewis structures.



Nothing tricky, when you draw a Lewis diagram just ask yourself if you could get an equivalent structure by moving one or more π -bonds.

Hit Parade: SO_2 , SO_3 , NO_3^- , CO_3^{2-}

Expanded Octet Once you get to period 3 and below, Group V, VI, VII atoms can use inner d orbital electrons for bonding, so the octet rule can be violated. They are either brutally obvious, SF_6 , or if they are subtle, I_3^- , Look for problems with the Lewis structure steps. Like for I_3^- , step 1 says that you need 12 pairs of electrons, step 2 says that the total number of covalent bonds possible is 11, step 3 says that the actual number of covalent bonds is $12 - 11 = 1$ <--- obviously you need more than 1 bond to hold together 3 atoms. and this kind of breakdown in the steps almost always indicates an expanded octet molecule.

Odd Electron Species

These are also called "free radical." The one you really need to know is the molecule NO. If you go through the Lewis steps: step 1 = 8 pairs needed, step 2 = 5.5 pairs available <-- obviously this is a problem. Given the total number of electrons, oxygen can obtain an octet with a double bond to nitrogen and that leaves nitrogen with only 7 electrons.

Formal Charge

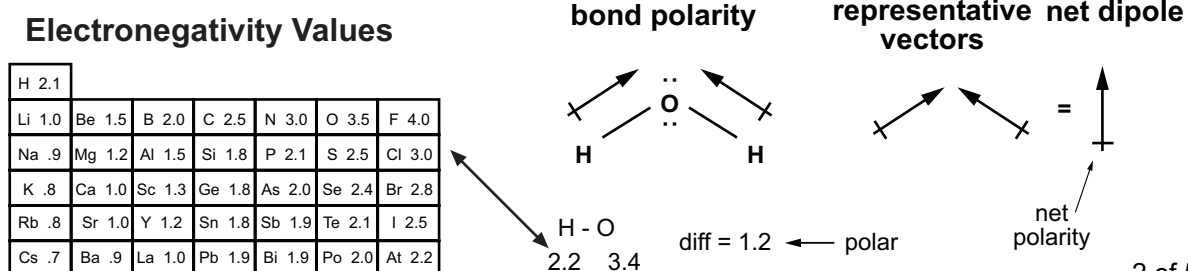
This is a rarely used calculation, but you kind of have to know how to answer the question "what is the formal charge of a particular atom in a molecule or of the molecule as a whole."

In a neutral molecule the sum of all the formal charges should equal zero, for an ion it should be the charge

$$\text{For an atom in a molecule formal charge} = \text{total number of valence electrons} - \text{total number of nonbonding electrons} - \frac{1}{2} (\text{total number of bonding electrons})$$

Bond Polarity/Electronegativity

Electronegativity is not a physical property. It is an assigned number between 0.8 and 4 for each element according to the element's ability to attract electrons (.8 to C and 4.0 to F). In a covalent bond, you have a pair of electrons being shared between two nuclei. By comparing the electronegativity values of the two elements in the bond, you can get a relative idea of how much time the electrons spend with each nucleus. Since electrons are negatively charged, the more electronegative atom in the bond will have more negative character than the other atom. Generally an electronegativity difference greater than 2.0 is an ionic bond, between .4 and 2.0 is a polar covalent bond and less than .4 is a nonpolar covalent bond. <-- Once you know the polarity of bonds, you can determine the molecule's net dipole. To look at the overall molecule you need to use representative vectors. For each bond in a molecule just draw arrows from positive to negative polarity and then add them all up vectorially to get an idea of the overall molecular polarity. For example, take a look at water



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VSEPR or valence shell electron pair repulsion theory accounts for molecular geometries due to the repulsion of the electron pairs that are around a central atom in a molecule.

- multiple bonds can be treated like single bonds in terms of electron pair repulsion.
- A single molecular geometry according to VSEPR is sufficient for resonance structures

Arrangement of bonding & nonbonding electron pairs	Molecular Geometry	Example	Central Atom		
			σ -bonds	π -bonds	n.b.p.s
	Linear	BeH ₂ CO ₂	2 2	0 2	0 0
	Trigonal planar	SO ₃ BF ₃	3 3	1 0	0 0
	Angular	SO ₂	2	1	1
	Tetrahedral	CH ₄	4	0	0
	Trigonal pyramidal	NH ₃	3	0	1
	Angular	H ₂ O	2	0	2
	Trigonal bipyramidal	PF ₅	5	0	0
	Seesaw (irregular tetrahedron)	SF ₄	4	0	1
	T-shaped	ClF ₃	3	0	2
	Linear	XeF ₂ I ₃ ⁻	2	0	3
	Octahedron	SF ₆	6	0	0
	Square pyramidal	IF ₅	5	0	1
	Square planar	XeF ₄ IF ₄ ⁻	4	0	2

Molecules: Lewis Structures & VSEPR: Student Review Notes

We know that opposite electrical charges attract according to the formula:

$$F = \frac{kq_1q_2}{r^2}$$

This basic idea of electrostatic attraction goes a long way to explain different physical properties of molecules. Because the atoms that make up molecules can have different electronegativities, i.e. greater or lesser ability to attract the electrons that are shared in a covalent bond, bonds can have polarity. Polarity means that there is a positive end to the bond (the less electronegative atom) and a negative end to the bond (the more electronegative atom). By examining the polarity of each of the bonds in a molecule adding it together, a net **dipole moment** can be determined for the molecule. Now, this is not a number, it's just the idea that the molecule as a whole may be seen in an electrical sense as a dumbbell with a positive end and a negative.

Being able to determine if a molecule is polar or non-polar tells you a lot of chemistry.

Know this: **"like dissolves like"**

Why? Because polar molecules have electrostatic attractions with one another--the opposite poles attract. If you try to mix in a non-polar molecule, there is not reason for the polar molecules to break the attraction they have with their polar neighbors. Essentially, the polar molecules don't let the non-polar molecules get between them. So, polar solvents will dissolve polar molecules and non-polar molecules will dissolve non-polar molecules. This is the **"oil and vinegar"** thing. Oil is non-polar and vinegar is polar.

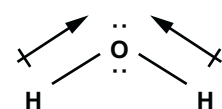
This is also why **water is known as the Universal Solvent**. Water is very polar and most most molecules have some dipole moment. Water therefore dissolves lots of things.

Okay, so take a look at how you use electronegativity values and representative vectors (the arrowhead points to the more electronegative element) to determine if a molecule is polar. As an a first example, look at water:

Electronegativity Values

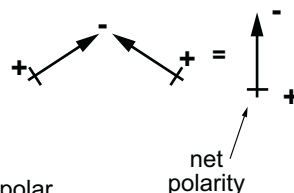
H 2.1							
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na .9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K .8	Ca 1.0	Sc 1.3	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb .8	Sr 1.0	Y 1.2	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs .7	Ba .9	La 1.0	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	

bond polarity



H - O
2.2 3.4
diff = 1.2 ← polar

representative net dipole vectors



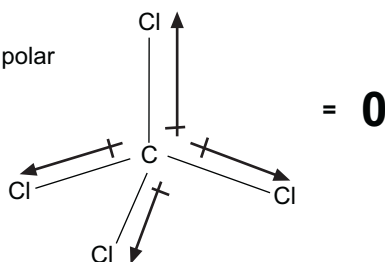
net polarity

Now how about CCl_4 ? We know from VSEPR or VB Theory that this molecule is a tetrahedron with carbon in the center and the chlorine at the ends of four single bonds. Let's do the same analysis by first looking at bond polarity using electronegativity values.

Draw the representative vectors and add them up

C - Cl
2.5 3.0

diff = .5 ← polar



Because of symmetry, all the representative vectors cancel out. Get that? Even though there is bond polarity in CCl_4 , there is no dipole for the molecule.

Remember that the picture here is like a dumbbell with a positive end and a negative end. In non-polar molecules, there is either no bond polarity, H_2 for example or as in the case of CCl_4 , the symmetry of the polar bonds sums in a way that doesn't create a positive and negative pole.

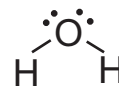
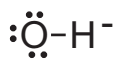
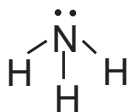
Coordinate Covalent Bonds

Transition metals can behave like Lewis Acids (electron pair acceptors) in the formation of what are called **complex ions**. A **coordination compound** typically consists of a complex ion and counter ion.

The molecules or ions that surround the metal in a complex ion are called **ligands**. The ligands act like a Lewis Base in that they donate a pair of electrons. A ligand must therefore have at least one unshared pair of electrons. The type of bond between the metal and the ligand is a **coordinate covalent bond**. In a coordinate covalent bond, one of the bonding atoms supplies both of the electrons.

The atomic in a ligand that is bound to the metal is called the donor atom. The coordination number is defined as the number of donor atoms surrounding a metal in a complex ion.

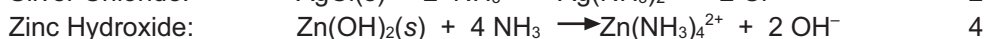
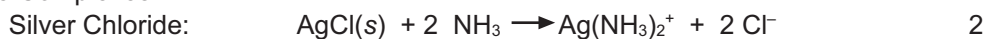
Here are some molecules that commonly act as ligands:



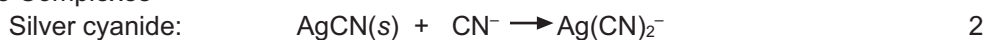
Here are some common examples of complex ions:

Coordination Number

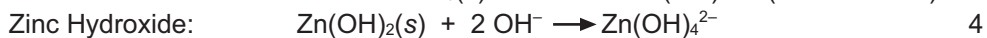
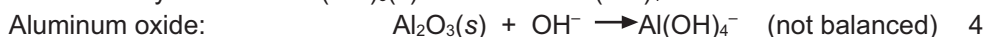
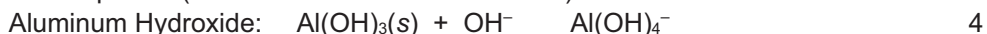
A. Ammine Complexes



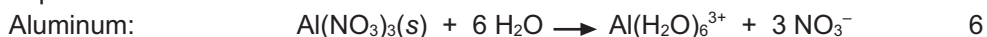
B. Cyanide Complexes



C. Hydroxide Complexes (mixed with a concentrated base)



D. Aqua Complexes



There are four common geometries for complex ions.

Coordination Number

2

4

6

Structure

Linear

Tetrahedral or square planar

Octahedral

The metal ion is always at the center and the ligands are at the corners of the structure.