

MOLECULAR GEOMETRY HANDOUT

Introduction

Much of the chemical behavior of matter can be related to the detailed structures and shapes of molecules. Structural theory is useful when we wish to relate experimental evidence to the more theoretical concepts of chemical bonding. The arrangement of atoms and ions in molecules and crystals is related to the distribution of bonding electrons within the structure.

Diagrams or line drawings often represent molecules. These drawings can be deceptive and it can be hard to interpret the three-dimensional nature of the structure. Molecular models are designed to reproduce molecular structures in three-dimensional space. If models are correctly assembled, many subtle features concerning shapes of molecules (such as dipole moment, polarity, and bond angle) will become clearer.

Because structure is so important, chemists have developed a number of theories to explain and predict molecular geometries. In 1916, G. N. Lewis developed a theory accounting for the significance of valence electrons in bonding. He proposed the "octet rule" in which atoms form bonds losing, gaining, or sharing enough electrons in order to have the same number of valence electrons (eight) as the nearest noble gas in the Periodic Table. The bond is ionic or covalent depending upon whether the electrons are transferred or shared. Many molecules and ions obey the octet rule but there are exceptions. If a molecule or ion can obey the octet rule then that is the most stable arrangement for that molecule or ion.

While Lewis-dot structures account for valence electrons on each atom, they only produce two-dimensional images. They do not explain how electrons are shared, nor do they predict any three-dimensional structure for the molecule. The valence shell electron-pair repulsion (VSEPR) theory provides some insight into the nature of the bonding between atoms and the three-dimensional structure of the molecule.

VSEPR theory proposes that the geometry of a molecule is determined by the repulsive interactions of electron pairs in the valence shell of its central atom. The orientation is such that the distance between the electron pairs is maximized so that the electron-electron interaction is minimized. The preferred arrangement of the bonding and non-bonding electron pairs around the central atoms give rise to the corresponding geometric shapes of the molecules. A multiple bond is considered one area of electron density for repulsive interactions to occur. Therefore, electrons on the central atom that contribute to a multiple bond (second or third bond between two atoms) do not affect the geometry of a molecule. There are three main electron geometries that are the framework of most molecular geometries (linear, trigonal planar, and tetrahedral). These are determined by the number of electron repulsions around the central atom (2, 3, or 4 respectively). When all the electron repulsions are bonds for the central atom (no lone pairs on the central atom), then the molecular and electron geometry is the same. If the central atom does have lone pairs then the molecular geometry changes. Possible electron and molecular geometries summarized in Table 1.1.

Once the geometry of a molecule is determined, its polarity vs. non-polarity can be estimated. A molecule is polar if there exists an unbalanced electron distribution in the molecule. This occurs as a result of atoms in the molecule having different electronegativities; the atom(s) having a higher electronegativity attracts the bonding electrons, creating a greater electron density and a partial negative charge, δ^- , relative to another portion of the molecule, δ^+ . The greater the electronegativity difference, and thus the greater distortion of the electron density, the more polar is the molecule. The polarity of the molecule is determined by finding the average of each charge. If the average (+) charge position is the same as the average (-) position the molecule is nonpolar. If the two averages fall in different positions then the molecule is polar. Remember not all partial charges have the same magnitude so an element that is more electronegative will have a partial charge greater than a less electronegative element.

If the partial charge magnitude is different the average favors the direction of the higher partial charge.

Table 1.1: Possible Electron and Molecular Geometries

Electron Repulsions	VSEPR Formula	Bonding Electron Pairs	Nonbonding Electron Pairs	Electron Geometry	Molecular Geometry	Bond Angle
2	MX_2	2	0	Linear	Linear	180°
3	MX_3	3	0	Trigonal Planar	Trigonal Planar	120°
	MX_3E	2	1	Trigonal Planar	Bent	$<120^\circ$
4	MX_4	4	0	Tetrahedral	Tetrahedral	109.5°
	MX_3E	3	1	Tetrahedral	Trigonal Pyramid	$<109.5^\circ$
	MX_2E_2	2	2	Tetrahedral	Bent	$<109.5^\circ$

Key: M – refers to the central atom
 X_m – refers to “m” number of bonding pairs of electrons on M
 E_n – refers to “n” number of non-bonding pairs of electrons on M

Example: Determine the Lewis Structure, Molecular Geometry and whether the molecule is polar or nonpolar for carbon tetrachloride, CCl_4 .

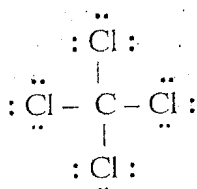
Solution:

- Determine the number of valence electrons for each atom and the octet that it wants. Add the valence electrons together including any charge that is present then add the octet electrons together. The valence electrons are how many electrons you have, the octet electrons are how many you want for each atom to have an octet. The difference between the two is how many electrons have to be shared. Dividing this by 2 will give how many bonds are present in the structure.

	Have	Want	
C	$4 \times 1 = 4$	$8 \times 1 = 8$	
4Cl	$7 \times 4 = 28$	$8 \times 4 = 32$	
Total	32	40	
Difference	$40 - 32 = 8$ electrons shared		# Bonds: $8/2 = 4$ bonds

- To draw the Lewis Structure you start with the central atom and draw a single bond between it and each bonding atom. If there are bonds left over then there will be at least one multiple bond in the structure. After all bonds distributed then fulfill the octet of each atom by assigning lone pairs of electrons.

There are four bonds in the structure with carbon as the central atom and four bonding chlorine atoms. Drawing one bond to each chlorine atom uses up all the bonds therefore there are no multiple bonds in the structure. The central carbon has four bonds (2 electrons for every bond) so it has its octet. The chlorine atom has one bond representing 2 electrons so still needs 6 more electrons for its octet so needs 3 lone pairs of electrons. All chlorines are the same.



3. Once the Lewis Structure is drawn determine the Molecular Geometry by first determining the number of electron repulsions around the central atom. An electron repulsion is a bond whether it is single, double or triple and any lone pairs of electrons on the central atom.

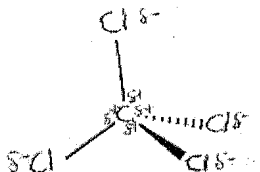
CCl_4 has 4 single bonds and no lone pairs of electrons on the central carbon atom. This leads to 4 repulsions on the central carbon atom.

4. Once the number of repulsions is determined, assign the electron geometry that corresponds to that number of repulsions then determine the molecular geometry of the bonds in the structure.

CCl_4 has 4 repulsions on the central carbon atom, 4 repulsions corresponds to the electron geometry of tetrahedral. Since all repulsions are bonds then the molecular geometry and the electron geometry are the same. Therefore the molecular geometry is tetrahedral.

5. The last step is to determine whether the structure is polar or nonpolar. Determine whether the bonds in the structure are polar or nonpolar bonds by comparing their electronegativities. If the bonds are polar, assign partial charges to the atoms involved in the bond. Partial negative to the more electronegative atom and partial positive to the less electronegative atom. Find the average of all the negative charges and the average of all the positive charges. If the averages appear in the same spot the molecule is nonpolar, if they appear separated then the molecule is polar.

CCl_4 has 4 carbon-chlorine bonds (the electronegativities are $\text{Cl} = 3.0$ and $\text{C} = 2.5$). Since the electronegativities are not the same so each $\text{C} - \text{Cl}$ bond are polar bonds. The chlorine in each bond will have a partial negative (δ^-) and the carbon will get a partial positive (δ^+). All δ^+ charges are on the carbon so the average "+" is on the carbon. The δ^- charges are on the chlorines, which are on the corners of a tetrahedral so the average "-" is at the center of the tetrahedral, on the carbon. Therefore the average (+) and average (-) are in the same spot so the molecule is nonpolar.



EXPERIMENTAL PROCEDURE:

A. Molecular Geometry for Known Molecules and Ions

Students can work in small groups.

Perform the following operations on each molecule or ion provided on the report sheet.

1. Draw the correct Lewis structure. The central atom is indicated by being bold and italicized.

Use the Have/Want method to determine the number of bonds in the structure. Subtract the total valence electrons (Have) from the total of full octets (Want); this determines the number of shared electrons. Then divide this value by two to determine the number of bonds present. Start with the central atom and make single bonds between it and the bonding atoms. If you have more bonds than bonding atoms then a multiple bond is needed. From your knowledge of what elements tend to form multiple bonds, draw the multiple bond to that element. Once you have the correct number of bonds represented in your structure make sure every atom has a complete octet by assigning lone pairs of electrons where necessary.

2. Determine the electron geometry of the central atom(s) by determining the number of electron repulsions for that central atom.
3. Assemble a molecular model for the compound.

Choose a central atom from the model kit that has the correct electron geometry. Depending on the model kit, attach tubes to represent bonds and balls to represent bonding atoms

4. Sketch a 3-D representation of the compound.

Use a solid line to represent a bond in the plane of the paper, a wedge bond for a bond coming out of or in front of the plane of the paper, and a dashed bond for a bond in back of the plane of paper. Include the lone pairs in 3-D representation.

5. Indicate the following for each Lewis structure
 - a. Molecular geometry of central atom(s).
 - b. Whether the molecule is polar or nonpolar.

B. Molecular Geometry for Unknown Molecules or Ions

Each student should obtain an unknown set from the instructor and perform the previous operations on each of the given molecules or ions:

SHOW ALL WORK

1. Draw the Lewis Structure for PF_3 .
2. When selecting a central atom from the model kit to represent the phosphorus atom in the above question, what electron geometry should it have? Explain why.
3. Determine the total number of valence electrons for COF_2 , ClO_3^{1-} , and H_3O^+ .
4. What is the molecular geometry of the central atom in CH_2F_2 and in COF_2 ? Are the molecules polar or non-polar?

A. Molecular Geometry for Known Molecules or Ions

Molecule or Ion	Lewis Formula	Data	Sketch the 3-D Geometry
1. CF_4		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
2. CF_3Cl		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
3. H_2O		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	

Molecule or Ion	Lewis Formula	Data	Sketch the 3-D Geometry
4. H_2S		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
5. NH_3		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
6. NH_4^+		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	

On separate sheets of paper, construct the same table for the following molecules and ions.

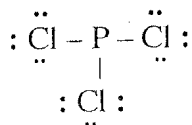
- | | | | | |
|-----------------|------------------|-----------------|-----------------|------------------|
| 7. H_3O^+ | 10. O_3 | 13. CH_2O | 16. SO_2 | 19. C_2H_2 |
| 8. PO_4^{3-} | 11. $COCl_2$ | 14. $OPCl_3$ | 17. SO_4^{2-} | 20. AsF_3 |
| 9. BrO_2^{1-} | 12. ClO_3^{1-} | 15. Cl_3CCF_3 | 18. NO_3^{1-} | 21. ClO_2^{1-} |

B. Molecular Geometry for Unknown Molecules or Ions

Molecule or Ion	Lewis Formula	Data	Sketch the 3-D Geometry
1.		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
2.		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
3.		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	
4.		Bonding Electron Pairs _____ Non-bonding Electron Pairs _____ Total repulsions _____ Electron Geometry _____ Molecular Geometry _____ Polar or Non-polar _____	

Post-Lab Question

1. If a student determined the Lewis Structure of PCl_3 to be as below is it the correct Lewis Structure? If not what is the correct structure?



2. What would the molecular geometry be for the given Lewis Structure in question 1? Would the molecule with that structure be polar or non-polar?
3. What would the molecular geometry be for the correct Lewis Structure in question 1? Would the molecule with that structure be polar or non-polar?
4. Determine the electron geometry and the molecular geometry around the central atom in SeO_2 . Is it polar or non-polar?