

Lewis Structures and Molecular Shape

Objective: To draw Lewis dot structures and apply VSEPR theory to predict molecular shape and properties; to determine formal charges of atoms in Lewis dot structures

Materials: Molecular model kits

Safety/Waste: None

INTRODUCTION

Gilbert N. Lewis was one of the more prolific chemists of the twentieth century, with contributions ranging from thermodynamics to acid-base theory. He is best known, at least to chemistry students, for his work dealing with the electronic structure of molecules including Lewis dot structures and the “rule of eight,” or octet rule. The Lewis structure is elegant in its simplicity--it uses dots to represent valence electrons--but it provides us with a model to predict the type of bonding present in molecules. Knowledge of the bonding and shape of molecules is needed to explain the physical properties of molecules, and how they react.

In this lab exercise you will draw Lewis structures of a wide variety of molecules and build three dimensional molecular models to determine the shape of the molecules. You will also examine how bonding and shape can explain whether a molecule is polar or non-polar.

Lewis Structures

A Lewis dot structure is a two-dimensional sketch of a molecule that uses dots to represent valence electrons. The Lewis structure helps us identify the type of bonding that may be present in a molecule based on the number of valence electrons available and the octet rule. The **octet rule** states that atoms will gain, lose, or share electrons to attain a completely filled valence shell electron configuration (i.e., eight electrons). In molecular compounds, this is accomplished by sharing electrons to form covalent bonds.

Lewis structures for most molecules can be drawn by following a simple strategy:

1. *Determine the total number of valence electrons in the molecule or polyatomic ion.* Simply add up the number of valence electrons for each atom in the molecular formula, based on electronic configuration. For polyatomic ions, add an electron for each negative charge and subtract one electron for each positive charge.
2. *Draw a skeleton structure for the molecule.* Connect the atoms using single lines to represent covalent bond. Usually, the least electronegative element is the central atom. Hydrogen is

always on the outside, since it can only form one bond. Halogens are often on the outside as well, but can be in the center if paired with a more electronegative atom such as oxygen.

3. *Calculate the number of remaining electrons.* Subtract the number of electrons involved in covalent bonding from the total valence electrons in the molecule.
4. *Distribute the remaining electrons.* Typically, these electrons are distributed around the outside atoms until each atom has a complete octet, and then placing any remaining electrons on the central atom(s).
5. *If you run out of electrons before every atom has a complete octet, form multiple bonds.* Use pairs of non-bonding electrons from an outside atom to form double or triple bonds until each atom has a complete octet.

There are many exceptions to the octet rule. Beryllium and boron, for example, only have two and three valence electrons to share, respectively. As a result, these elements form compounds in which the Be or B atom has less than eight valence electrons. Elements in the third rows and higher ($n \geq 3$) can often form compounds in which the central atom has an **expanded octet**; because these elements have empty *d*-orbitals available, they can accommodate more than eight electrons in their valence shell.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Many chemical and physical properties depend on molecular shape or geometry. The Lewis structure can show us the basic structure in two dimensions but it cannot tell us the shape of the molecule. The three-dimensional arrangement of bonding and non-bonding electron pairs can be predicted using VSEPR theory. The basis for VSEPR theory is that negatively charged electron clouds (i.e., bonding and non-bonding e^- pairs) will arrange themselves around the central atom in order to minimize repulsive energies. In VSEPR, the electrons in a covalent bond count as one pair, regardless of whether it is a single, double, or triple bond. This makes sense, given that all the electrons in these covalent bonds are essentially oriented between the two atoms involved in the covalent bond. Non-bonding e^- pairs also count as an electron cloud.

The geometric orientation of electron clouds will depend on the number of electron clouds around the central atom. Two electron clouds, for example, will arrange themselves on opposite sides of the atom to form a linear geometry. Three electron clouds will form a triangular or trigonal planar configuration. Four electron clouds will assume a tetrahedral configuration. **Molecular geometry**, however, depends only on the arrangement of bonding electron clouds and may be different from the electronic geometry. Molecular geometries based on VSEPR theory are summarized in Table 1.

Electronegativity: Polar vs. Non-polar Molecules

Many physical properties depend on the strength of intermolecular forces, including vapor pressure, boiling point, and solubility in a polar or non-polar solvent. These properties will depend on whether the molecule as a whole has a permanent **dipole**, or a positive and negative end. In general, there are two criteria for a molecule to be polar:

1. *The molecule must contain polar bonds.* A polar bond is formed between two atoms having a significant difference in electronegativity. Remember the periodic trend for

electronegativity--it increases moving across a row and up a group. The most electronegative elements (N, O, F, Cl) are found in the upper right corner of the periodic table. While a covalent bond involves a sharing of electrons, they may not be shared equally. The electrons in a C-O bond, for example, will be more closely associated with the O atom because it is more electronegative. As a result, the carbon end of the bond will be slightly more positive while the oxygen end of the bond will be slightly more negative. We can represent the polarity of this bond by drawing an arrow pointing toward the more negative atom, with a "+" at the more positive end, for example $C + \rightarrow O$

2. *The polar bonds must be distributed asymmetrically.* In other words, the separation of charge associated with polar bonds must result in a permanent charge separation in the molecule. If the charge vectors are distributed symmetrically they will cancel out.

These first three concepts are illustrated in Example 1.

Example 1. BH₃ and NH₃ both have the general formula AB₃, yet they have very different shapes and properties. Explain these facts by determining the molecular shapes.

Solution: *Details are provided in the table below.*

Molecule	Total valence electrons	Bonding e ⁻ pairs	Non-bonding e ⁻ pairs	Molecular shape (from Table 1)
*BH ₃	B = 3; 3H = 3; total = 6	3	0	Trigonal planar
NH ₃	N = 5; 3H = 3; total = 8	3	1	Trigonal pyramid

*Remember that boron compounds are often exceptions to the octet rule

Based on the information in the table, the two molecules have different geometries. The BH₃ is a trigonal planar molecule. The bonds are non-polar and are distributed symmetrically around the central atom, so the molecule is non-polar. In NH₃, the N atom forms the apex of a trigonal pyramid and the H atoms form the triangular base. The N-H bonds are polar, with the N end (represented by the A atom in Table 1) being more negative. The molecular shape results in a molecule with a permanent dipole.

Isomers and Resonance Structures

In many instances, more than one Lewis structure can be drawn for the same molecular formula. In some cases, the different Lewis structures represent different molecules with different properties. Molecules having the same formula but different structures are called **isomers**, and are important in many areas of chemistry, especially organic and biochemistry. Consider, for example, the two molecules below having the molecular formula C₂H₄O.



Clearly, these are two completely different molecules, and we would expect them to have different physical and chemical properties.

In other cases, the different Lewis structures represent different ways of distributing the valence electrons, but the basic molecular skeleton is the same. Such structures are called **resonance structures**. Sometimes the real structure is an average of different resonance structures, but sometimes only one of the possible resonance structures makes sense chemically. In order to determine which resonance structure is most likely, it is helpful to calculate the formal charge associated with each atom in the Lewis structure.

Formal Charge

The concept of **formal charge** allows us to assign a nominal charge to each atom in a Lewis structure using Equation (1).

$$\text{Formal charge} = (\# \text{ of valence } e^-) - \frac{1}{2} (\# \text{ bonding } e^-) - (\text{non-bonding lone pair } e^-) \quad (1)$$

Since electrons in covalent bonds are shared, they are divided equally between the atoms in that bond, while lone pairs are assigned to the atom on which they are located. The sum of the formal charges for individual atoms must add up to zero for a neutral molecule, and must equal the ionic charge for a polyatomic ion. In many instances, two different resonance structures will result in different formal charges on the atoms. In such cases, the formal charges may help us decide which resonance structure makes more sense. In general, resonance structures that do not produce large differences in formal charge or put positive charges on electronegative atoms (such as O, N, F) are more reasonable. Such a case is illustrated in Example 2.

Example 2. Consider the two possible resonance structures for CO₂ provided below. Calculate the formal charge for each atom in the two structures. Which resonance structure is the more reasonable one? Explain.

Solution. **Structure 1:** $\text{:O} \equiv \text{C} - \text{O:}$

$$\text{Formal charges: } \begin{aligned} \text{O \#1 (left)} &= (\text{valence } e^-) - \frac{1}{2}(\text{bonding } e^-) - (\text{lone pair } e^-) \\ &= 6 - \frac{1}{2}(6) - 2 = +1 \end{aligned}$$

$$\text{Carbon} = 4 - \frac{1}{2}(8) - 0 = 0$$

$$\text{Oxygen \#2 (right)} = 6 - \frac{1}{2}(2) - 6 = -1$$

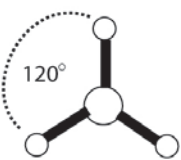
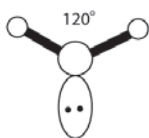

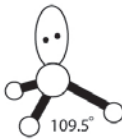
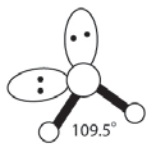
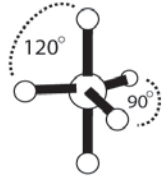
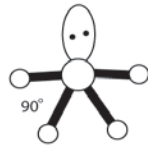
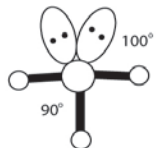
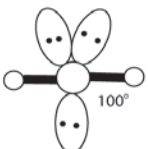
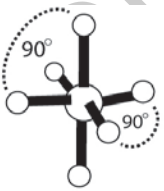
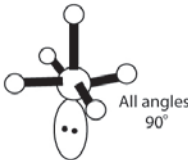
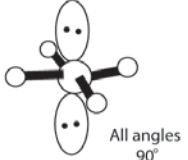
Structure 2: $\text{O} = \text{C} = \text{O}$

$$\text{Formal charges: } \text{O (both the same)} = 6 - \frac{1}{2}(4) - 4 = 0$$

$$\text{Carbon} = 4 - \frac{1}{2}(8) - 0 = 0$$

Structure # 2 is more reasonable because it does not result in a large difference in charges, or a positive charge on a very electronegative element (oxygen).

Table 1. Molecular Shapes Using Valence Shell Electron Pair (VSEPR) Theory

	Molecular Shape	General Formula
		AX_2E Bent or angular
		AX_3E Triangular pyramidal
		AX_2E_2 Bent or angular
		AX_4E See-saw
		AX_3E_2 T-shaped
		AX_2E_3 Linear
		AX_5E Square pyramidal
		AX_4E_2 Square planar

Pre-Lab Questions

- Using the strategy outlined in the Introduction, draw Lewis dot structures for the molecules in the Table.

Molecule	Total Valence electrons	Bonding e ⁻ clouds on central atom	Non-bonding e ⁻ clouds on central atom	Lewis Dot Structure
CS ₂				
NO ₃ ⁻ (Resonance structures)				
CH ₃ NH ₂ (C-N bond)				
SF ₄ *				

*Elements in the third row and higher can form compounds with “expanded octets” they can use empty *d* orbitals to accommodate more than 8 electrons in their valence shell.

- Based on the Lewis structure and the number of electron clouds, identify the molecular geometry for each of the Lewis structures you derived in Question 1.

Molecule	CS ₂	NO ₃ ⁻	CH ₃ NH ₂	SF ₄
Molecular Geometry				

- Draw the Lewis dot structure and calculate the formal charges for each atom in the cyanate ion, OCN⁻ (triple bond between C and N; single bond between O and C).

PREPARATION AND PROCEDURE

Review the rules for drawing Lewis dot structures and VSEPR theory and complete the pre-lab exercises before coming to lab!

The model kits use color-coded atom centers with pegs to represent electron pairs arranged in the more common geometries. The specific contents of your model kit may vary, but a typical kit composition is listed below, including color-codes for specific atoms and the types of connectors used to represent bonds.

Black = Carbon (3-bond and 4-bond centers)

Red = Oxygen (2-bond and 4-bond centers)

Green = Halogens (1-bond and 4-bond centers)

Purple = Variable (5-bond centers)

Clear plastic tubes = single bonds

White flexible tubes = multiple bonds

White = Hydrogen (1-bond)

Blue = Nitrogen (4-bond centers)

Yellow = Sulfur (4-bond centers)

Grey = Variable (6-bond centers)

In this lab you will draw Lewis dot structures of many common substances, and use these structures and VSEPR theory to build molecular models. From the models you can identify the molecular geometry or shape of the molecules. You will also calculate formal charges of atoms in the structures, and predict whether or not the molecule is polar or non-polar. Finally, you will investigate compounds that can have more than one molecular structure (isomers) or the same molecular structure but different Lewis dot structures (resonance structures).

While you may not have discussed these subjects in your lecture class, there is adequate information provided in the Introduction section to successfully complete the lab exercise. Working with a partner, complete one section at a time. Have your TA check your work before moving on to the next section.

1. Draw the Lewis dot structures for the compounds having four electron clouds in Table 2, and complete the table.
2. Draw the Lewis dot structures for compounds having multiple bonds in Table 3, and complete the table.
3. Draw the Lewis dot structures for compounds that do not follow the octet rule in Table 4, and complete the table.
4. Draw Lewis dot structures for the compounds in Table 5 (isomers and resonance structures), and complete the table.

Data Sheet

A. Compounds with four electron clouds.

1. Following the rules for drawing Lewis dot structures, draw structures for the compounds in Table 2.
2. Based on the Lewis dot structures, build molecular models for these molecules. Have your TA or instructor check your models.
3. Based on your models, identify the molecular geometry for each compound.
4. Based on the geometry, identify the molecule as polar or non-polar.

Table 2. Lewis Dot Structures and Geometries of Molecules with Four Electron Clouds

Molecule	Lewis Structure	Bonding e ⁻ clouds on central atom	Non-bonding e ⁻ clouds on central atom	Shape/Geometry	Polar/Non-polar?
CH ₄					
NH ₃					
H ₂ O					
HCl			(NA)		

Data Sheet (con't.)

B. Compounds having multiple bonds.

Following the same steps outlined in Part A, draw structures for the compounds in Table 3 and complete the table.

Table 3. Compounds Having Multiple Bonds

Molecule	Lewis Structure	Bonding e ⁻ clouds on central atom	Non-bonding e ⁻ clouds on central atom	Shape/Geometry	Polar/Non-polar?
CO ₂ (2 double bonds)					
Cl ₂ CO (1 double bond)					
HCN (1 triple bond)					
SO ₃ (1 double bond)					

Data Sheet (con't.)

C. Exceptions to the Octet Rule

Draw structures for the compounds in Table 4 and complete the table.

Table 4. Exceptions to the Octet Rule

Molecule	Lewis Structure	Bonding e ⁻ clouds on central atom	Non-bonding e ⁻ clouds on central atom	Shape/Geometry
BF ₃ (3 e ⁻ pairs)				
PCl ₅ (5 e ⁻ pairs)				
SF ₆ (6 e ⁻ pairs)				
IF ₃ (5 e ⁻ pairs)				
XeF ₄ (6 e ⁻ pairs)				

Data Sheet (con't.)

D. Isomers and Resonance Structures

Complete the Table below, providing the suggested number of structures for each molecule.

Table 5. Isomers and Resonance Structure

Molecule	Lewis Structure	
C_2H_6O (2 isomers)	1.	
	2.	
SCN^- (2 resonance structures)	1.	Formal Charges: S = C = N =
	2.	Formal Charges: S = C = N =
COS (2 resonance structures; C in center)	1.	Formal Charges: S = C = O =
	2.	Formal Charges: S = C = O =

Post-Lab Questions

1. The compounds in Table 1 all have four electron clouds (i.e., same electron cloud geometry), but different molecular geometries. Explain.
2. The molecules CO_2 and SCl_2 are both of the general molecular type AB_2 , but one is polar and one is not. Which molecule is polar? Draw the Lewis structures for these molecules to illustrate your reasoning.
3. Based on the formal charges you calculated in Table 5, which resonance structures for the SCN^- ion and the COS molecule would you expect to be more stable? Explain.
4. Explain the difference between isomers and resonance structures.
5. Why is it difficult to construct a Lewis Dot structure for the molecule NO ?