

Experiment 19

Bonding, Geometry and The Polarity of Molecules

Introduction

A key concept in chemistry is that the chemical and physical properties of a substance are determined by the the identity of bonded atoms and their arrangements in space relative to each other. In this lab, we will learn how chemists depict chemical bonding between atoms using Lewis structures to and how these Lewis structures can be used with valence shell electron pair repulsion theory (VSEPR theory) to predict the geometry of bonded atoms and lone pairs of electrons and the bond angles associated with a these geometries. We shall also see how geometry impacts whether a molecule is polar and how valence bond theory allows us to extend knowledge of geometry to specific sets of hybridized orbitals

Lewis Structures

A Lewis Structure is a depiction of covalent molecules (or polyatomic ions) where all the valence electrons from atoms or ions that make up a molecule (or ion) are shown distributed about the bonded atoms as either shared electron pairs (bonded pairs) or unshared electron pairs (non-bonded or lone pairs). A single bonds are represented as a line between atoms. Sometimes atoms can share two pairs or even three pairs of electrons and are therefore represented by two or three short lines. Pairs of dots or shorter lines are used to represent non-bonded electrons. The process of drawing a best Lewis structures follow the octet rule and minimize formal charges. Here is a basic recipe:

1. Write the molecular formula.
2. Determine the total number of valence electrons for the molecule by summing the number of valence e^- from each atom in the molecule. For polyatomic ions add $1 e^-$ for each negative charge or subtract $1 e^-$ for each positive charge for cations.
3. Select the central atom of the molecule by choosing the atom of lowest electronegative.
4. Arrange remaining atoms around the central atom bearing in mind that for oxyacids, H atoms are usually bonded to O atoms that are bonded to the central atom.
5. Using two electrons per bond draw single line to denote connect atoms with each line representing a pair of shared electrons (or 1 electron domain).
6. Satisfy the rule of octet or the octet rule then place any remaining electrons around the central atom as lone pairs. The octet rule must apply for central atoms C, N, O and F.
7. If several plausible structures are possible, choose the one with the least formal charge.

An Example Using Phosphorous Trichloride.

Let's apply these rules to the compound phosphorous trichloride.

1. First, we convert the name to formula.
2. The number of valence electrons is found from the group number and the number of P and Cl atoms.
No. valence $e^- = (1P)(5) + (3Cl)(7) = 26 e^-$
3. P is less electronegative than Cl, so P is the central atom. Place Cl atoms around P and begin drawing lines as shown below, which represent a single bond or a pair of shared electrons. Be mindful to account for all the valence e^- forming an octet of e^- 's around each atom. Left over e^- are placed around the central atom.

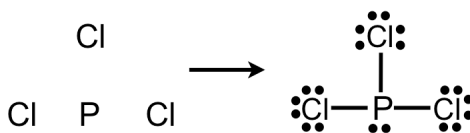


Figure 19.1: Generating the Lewis structure for PCl_3

From Lewis to AXE Designation

Chemists create short cuts to represent and communicate information. The AXE designation does just that by summarizing the number of bonded and non-bonded electron domains around a arbitrary central atom A in a Lewis structure. That information is then used to determine the electron domain and the molecular geometry around a central atom in a molecule using VSEPR theory.

Electron domains are either a non-bonding pair of electrons around a central atom, or a bonding-pair of electrons with the additional stipulation that all double or triple bonds count as one electron domain. The total number of bonding domains is represented by the subscript in the letter X_m , while the number of non-bonding domains is given as the subscript in the letter E_n .

We can apply the AXE designation to our PCl_3 example. Inspection of the Lewis structure of PCl_3 shows 3 different single bonds or 3-bonding domains, and 1 lone pair or non-bonding domain around the central atom P. PCl_3 AXE designation would be written AX_3E_1 . The total number of electron domains is $3 + 1 = 4$. We can use this construct to as an aid in VSEPR Theory.

VSEPR Theory Predicts Geometry

VSRPR theory says that the geometry adopted by electron domains around a central atom is the one that places domains as far apart from each other as possible thereby minimizing repulsive forces between domains. At first glance, one might think there are an infinite number of geometries, but in fact there are six possible electron domain geometries, and a total of 15 possible molecular geometries. These are shown in the diagram at the end of this lab. The logic of determining the geometry of any molecule is demonstrated in the schematic diagram below:

In words:

1. Determine the number of bonding electron domains and the number of non-bonding electron domains from a Lewis structure.

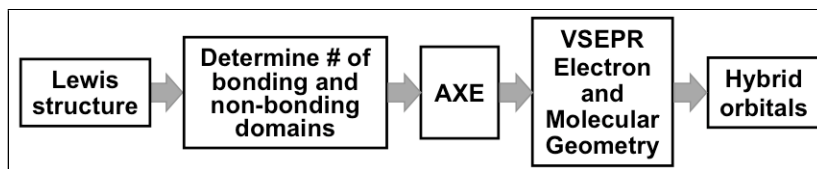


Figure 19.2: The flow for predicting molecular shapes

2. Establish the AX_mE_n designation. The total number of domains ($n + m$) determine the electron-domain geometry while the molecular geometry is determined only by the bonded domains.
3. Identify the bond angles that match the chosen geometry remembering that angles are reduced by non-bonded domains.
4. Handle the geometry of molecules with more than one central atom one at a time.

Is It Polar or Non-Polar?

Atoms as a result of differences in shielding by inner electron shells and differences in nuclear charges have different affinities for electrons. This ability of an element to attract electrons to itself is called *electronegativity*. A polar bond results when there is a difference in electronegativity between two bonded atoms in a covalent compound. Thus, a first step in predicting whether a molecule is polar or non-polar is to assess if there are polar bonds in a molecule by looking for difference in electronegativity in bonded atoms. This is done by having some notion of the electronegativity trends in the periodic table. Fluorine, oxygen and chlorine in that order have the greatest electronegativity of all the elements, and the heavier alkali metals such as potassium, rubidium and cesium have the lowest electronegativities. Carbon is about in the middle of the electronegativity scale range, and is just slightly more electronegative than hydrogen.

In general, a molecule will be polar if it contains polar bonds that are distributed in a non-symmetrical arrangement around the central atom. A polar molecule is said to have a net dipole moment. A molecule will be non-polar if it contains all non-polar bonds or if there are polar bonds that are distributed in a symmetrical arrangement around the central atom. The symmetry causes the individual bond polarities to cancel giving a net non-polar molecule. A symmetrical arrangement typically results when there are no lone pairs on the central atom, and if all the outer atoms are identical.

Consider for example carbon dioxide. Its Lewis structure is $O=C=O$. It has 2 bonded electron domains (and no non-bonding domains). Its AXE designation is AX_2 . VSEPR theory predicts a linear electron-domain geometry and a linear molecular geometry. Because O is more electronegative than C, both $C=O$ bonds are polar. This information might tempt some to believe that the CO_2 molecule must be polar, but *it is not*. It must be remembered that the *net dipole moment* of a molecule, is the sum of the polar-bond vectors taking into account the geometry of the molecule and the direction the bond vectors point. In the case of linear carbon dioxide, the bond vector of the $O=C$ on the left points in the opposite direction as the $C=O$ bond on the right. The sum of the two vectors cancel and the net dipole is zero. The molecule is non-polar despite being made of two polar bonds. On the other hand, if we take another linear molecule like $H-Cl$ the net dipole moment of a molecule is not zero and HCl is polar.

Valence Bond Theory

While VSEPR theory works well for predicting the geometries of many molecules, it does not do so in the context of atomic orbital theory and the theory of quantum mechanics. This is a shortcoming limits its applicability. Valence Bond Theory is a complementary model of covalent bonding that asserts that covalent chemical bonds are formed by the spatial overlap of atomic orbitals, or hybridized atomic orbitals

on bonding atoms, with the sharing of electron pairs overlapped orbitals. Because Valence Bond theory and hybridization is central to organic chemistry we summarize how the VSEPR theory geometry matches up with hybridized orbitals required in VB theory.

Electron Geometry	Molecular Geometry	AX_nE_m	Hybridization
Linear	Linear	AX_2	sp
Trigonal planar	Trigonal planar V-shaped bent	AX_3 AX_2E_1	sp^2
Tetrahedral	Tetrahedral Trigonal pyramidal V-shaped bent	AX_4 AX_3E_1 AX_2E_2	sp^3
Trigonal bipyramidal	Trigonal bipyramidal Seesaw T-shaped Linear	AX_5 AX_4E_1 AX_3E_2 AX_2E_3	sp^3d
Octahedral	Octahedral Square pyramidal Square planar	AX_6 AX_5E_1 AX_4E_2	sp^3d^2

Figure 19.3: Connecting VSEPR to VBT Hybrid Orbitals

Procedure

Obtain some modeling clay and shape it into a 2-cm ball. If a toothpick represents a bonding domain (one pair of electrons), stick two toothpicks into the clay ball such that the two toothpicks are as far away from each other as possible. What shape or geometric figure is it? Now do the same procedure 3 toothpicks which represents 3-bonding domains remembering to find locate the toothpicks into the clay ball as far away from one another stick as possible. Then try 4, then 5 then 6 toothpicks. For some assistance of geometries and their corresponding names use the table at the end of this experiment.

Putting It All Together

The following table is a list of substances for which you are to convert the names to Lewis structures showing arrows indicating polar bonds when appropriate, assign the AXE designation, determine the electron and molecular geometry, bond angles, and the VBT hybridization. You should find the Figure 2 and the on the following page to be helpful.

Table 19.1: Putting It Together

Molecule	Lewis Structure	AXE	Molecular Geometry	Polarity	Hybridization
water					
methane					
beryllium dichloride					
selenium hexafluoride					
iodine trichloride					
arsenic pentachloride					
sulfur dioxide					
sulfur trioxide					
sulfur hexafluoride					
sulfur pentafluoride					
xenon difluoride					
xenon pentafluoride					
boron trichloride					
silicon dioxide					
nitrate ion					
ammonia					
ammonium ion					
chloromethane					
hydrogen bromide					
methanol					

Reference

Gillespie, R.J., Journal of Chemical Education, 40, 295-301 (1963) and 51, 370-387 (1974).

Figure 19.4: The 5 fundamental electron-domain geometries and the 15 molecular geometries.

