Chemistry 132.E2. Structure and Shape of Molecules

Objectives

To learn how to draw Lewis structures of molecules and ions.

To use VSEPR to predict the shapes of molecules.

To determine whether equivalent structures, called resonance structures, are present in molecules.

To determine whether the charge across a molecule is distributed evenly.

Introduction

This exercise provides procedures to determine the structure and shape of molecules. This information is important because the properties of molecules are dependent upon their structure. The first step in determining the structure (Lewis structure) of a molecule is to draw a structure accurately showing the location of all valence electrons. From this structure, you can use a method called valence shell electron pair repulsion (VSEPR) theory to predict the geometric shape of a molecule or ion. In order to use VSEPR, you need to be able to determine the number of electron groups bonded to the central atom and the number of atoms bonded to the central atom. Lastly, after you have determined the molecule's shape, you can determine whether charge in the molecule is arranged symmetrically (a nonpolar molecule) or asymmetrically (a polar molecule). The polarity of a molecule has important implications for the properties of molecules.

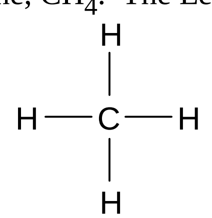
Theory of VSEPR

In order to use VSEPR, it is necessary to have a completed Lewis structure for the molecule. VSEPR is based on the principle that electron groups in a molecule tend to stay as far apart from each other as possible due to the repulsive forces that exist between like charges (the electrons). An electron group could be a lone pair of electrons, a single bond, a double bond or a triple bond around the central atom. It can be shown that the most probable arrangement of two, three, or four electron groups around a central atom are as follows:

Table 1. Electron Group Geometries

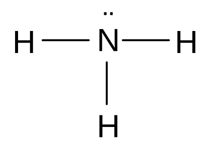
# of electron groups	Electron group geometry
2	linear
3	trigonal planar
4	tetrahedral

As an example, let's consider methane, CH_4. The Lewis structure for methane is given below:



In this case we can see that there are four electron groups (4 single bonds) surrounding the carbon atom, hence the geometric arrangement of the electrons about the carbon atom is tetrahedral.

Ammonia, NH_3, is a little more difficult,



The Lewis structure for ammonia shows that there are four electron groups (3 single bonds and 1 lone pair of electrons) therefore the electron group geometry is also tetrahedral. It should be noted however that CH_4 has 4 atoms bonded to the central atom and NH_3 only has 3 atoms bonded to the central atom therefore they will not have the same molecular geometry. Molecular geometry describes the arrangement of atoms about the central atom. When determining the molecular geometry, you must consider the electron group geometry and the number of atoms bonded to the central atom. The possible combinations of electron groups and bonded atoms are summarized below.

Table 2. Electron Group and Molecular Geometries

# of electron groups	# of bonded atoms	Electron group geometry	Molecular geometry
2	2	linear	linear
3	2	trigonal planar	120° bent
3	3	trigonal planar	trigonal planar
4	2	tetrahedral	109.5° bent
4	3	tetrahedral	trigonal pyramidal
4	4	tetrahedral	tetrahedral

Using Table 2, we can predict that CH_4 has a tetrahedral molecular geometry while NH_3 has a trigonal pyramidal molecular geometry.

After the geometries have been assigned to a molecule, we decide if there is more than one correct structure for it. These correct structures are called resonance structures. Lastly, we can use the molecular geometry to determine if charges are evenly distributed across the molecule. If charges are unevenly distributed across the molecule, the molecule is said to be polar. A molecule with a uniform charge distribution is nonpolar. But first you must learn how to draw Lewis dot structures…

Procedure

A. Drawing Lewis structures. This procedure will be illustrated by the use of SO_2 as an example.

1. Determine which atom is the central atom and place a pair of electrons between it and the other atoms. Generally, look for the atom that there is only one of in the formula. In SO_2, there is only 1 sulfur atom (and 2 oxygen atoms) therefore sulfur is the central atom. Knowing this, we an construct the following crude sketch:

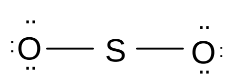
2. Determine the total number of valence electrons in the molecule. The number of valence electrons from an atom can be calculated by its location in the periodic table. So, in this case, S and O are both in group VIA, so each atom contributes 6 electrons. Hence the total number of valence electrons in SO_2 is 18 (3 atoms $\times$ 6 valence electrons).

For ions, it is necessary to add or subtract electrons depending on whether the charge is positive or negative. For anions, the magnitude of the charge should be added as additional valence electrons. For example, for OH^-, the total number of valence electrons is 8 (6 from oxygen + 1 from hydrogen + 1 for the charge). For cations, the magnitude of the charge should be subtracted from the number of valence electrons. For NO^+, the total number of electrons is 10 (5 for nitrogen + 6 for oxygen - 1 for the charge.

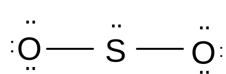
3. Subtract the number of electrons used to connect the atoms from the total number of valence electrons. Remember each single bond is composed of 2 electrons. For SO_2, 18 electrons (total) - 4 electrons (from the two bonds in step 1) = 14 electrons. Therefore we have 14 electrons left to place around the molecule.

4. Add the appropriate number of electrons around each atom. Hydrogen requires 2 electrons, , boron requires 6 electrons, and all other elements require 8 electrons. Start by placing electrons on the outermost atoms and then work to the center.

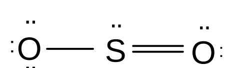
In our example, S and O both require 8 electrons. So first we put 6 electrons around one O (which gives us 8 including the two in the bond) and another 6 electrons around the other O. At this point our structure will look like this:



Now we have only two electrons left to place around the S atom. The question is, do we have enough electrons? If we place the two electrons around the S atom, we only have 6 electrons around S (as shown in the following structure), and we need 8.



We need to use the electrons more efficiently by making one of the lone pairs on an O atom a double bond. If we move a lone pair to make a double bond, we get the following structure.



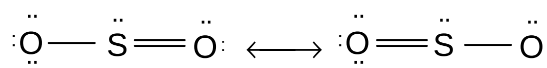
This is the completed Lewis structure for SO_2 because all of the atoms are surrounded by eight electrons (octet rule!)

B. Procedure to Determine the Electron Group and Molecular Geometries of a Molecule. The electron group geometry can be determined by counting the number of groups of electrons around the central atom and then looking up the appropriate geometry in Table 1. In the case of SO_2, we count three groups from the Lewis structure (1 single bond + 1 lone pair + 1 double bond). From Table 1, the electron group geometry is trigonal planar.

The molecular geometry can be determined by counting the number of bonded atoms to the central atom, and using the number of electron groups determined above to select the appropriate geometry from Table 2. SO_2 has two bonded atoms and three electron pairs, so Table 2 indicates that the molecular geometry is 120° bent.

C. Resonance Structures. Some molecules have more than one correct Lewis structure. These are called resonance structures. In order for a molecule to have resonance structures, it must have at least one multiple bond. Molecules with only single bonds cannot have resonance structures.

In the case of SO_2, the molecule has been drawn above with the double bond to the oxygen to the right of the sulfur. However, it could have also been drawn between the sulfur and the oxygen on the left, as shown below. These are the resonance structures for SO_2.

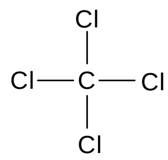
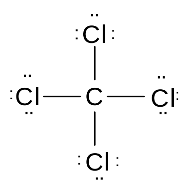


D. Polarity of a Molecule. The last piece of information to be obtained about a molecule concerns the arrangement of charges around the molecule. A molecule with a uniform charge distribution is nonpolar; and one with an asymmetrical distribution is polar. A molecule is nonpolar only if it has no lone pair electrons about the central atom <u>and</u> all groups attached to the central atom are identical (both conditions must be met to be nonpolar). Another way to state this is if the electron group and molecular geometries are the same and the atoms attached to the central atom are identical, then the molecule is nonpolar.

In the case of SO_2, the Lewis structure shows us that the molecule is polar because the sulfur atom has a lone pair.

The Assignment

You are to determine the Lewis structure, electron group and molecular geometries, presence or absence of resonance structures, and the polarity of a series of molecules given on the succeeding pages of this handout. Feel free to work on this exercise in a group to help you learn the procedure. Carbon tetrachloride is worked out as an example.

	CCl_4	BF_3	SO_3	CO_2	ClO_2^-
Crude Sketch					
Calculations (# of valence electrons, # of bonds, etc.	1(4) + 4(7) =32 32-4(2) = 24				
Lewis Structure					
# electron groups, electron group geometry	4 tetrahedral				
# of bonded atoms, molecular geometry	4 tetrahedral				
Resonance structures (if any)	none				
Polar or nonpolar	nonpolar				

	H_2O	SO_4^{2-}	NO_2^+	PO_4^{3-}	NO_3^-
Crude Sketch					
Calculations (# of valence electrons, # of bonds, etc.					
Lewis Structure					
# electron groups, electron group geometry					
# of bonded atoms, molecular geometry					
Resonance structures (if any)					
Polar or nonpolar					

	CO_3^{2-}	SO_2	NO_2^-	PF_3	SiI_4
Crude Sketch					
Calculations (# of valence electrons, # of bonds, etc.					
Lewis Structure					
# electron groups, electron group geometry					
# of bonded atoms, molecular geometry					
Resonance structures (if any)					
Polar or nonpolar					

	NH_3	H_3O^+	NH_4^+	SO_3^{2-}	$CHCl_3$
Crude Sketch					
Calculations (# of valence electrons, # of bonds, etc.					
Lewis Structure					
# electron groups, electron group geometry					
# of bonded atoms, molecular geometry					
Resonance structures (if any)					
Polar or nonpolar					