

VSEPR THEORY

STUDENT LEARNING OUTCOMES:

- Learn how to draw Lewis structures for atoms which violate the octet rule.
- Learn how to use Lewis structures and VSEPR and to predict the shapes of molecules.
- Learn how to use the shape of a molecule to predict whether or not it is polar.

EXPERIMENTAL GOALS:

The purpose of this lab activity is to predict the VSEPR shape of those molecules, and whether or not the molecules are polar.

MATERIALS:

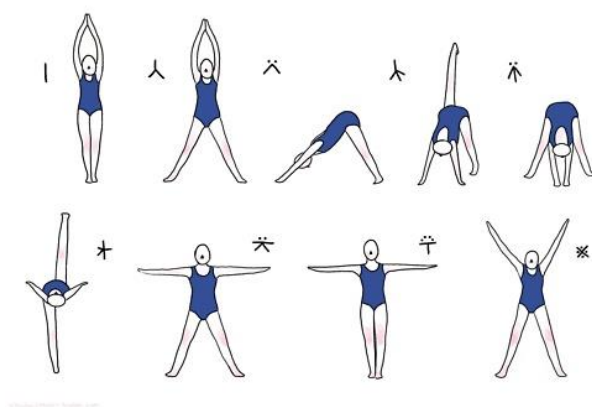
Each group of students will need a molecular modeling kit.

INTRODUCTION:

What information do you already have that can help you modify two dimensional Lewis structures into more accurate three dimensional models? You know that all electrons have the same charge and that like charges repel. It is reasonable to assume that the electron pairs in bonds will be oriented in a molecule as far from each other as possible. The valence electrons should be expected to occupy regions of space so that the shared pairs are evenly distributed around the central atom.

There are several theories in chemistry that suggest explanations for bonding in molecules. Each theory leads chemists to predict the shapes we will learn about today. The theory we will focus on is one that describes equal distribution of electron pairs around a central atom; this theory is known as the valence shell electron pair repulsion theory (VSEPR theory). To begin, we must delve into some of the exceptions that exist to the rules we learnt about in section 2.2.

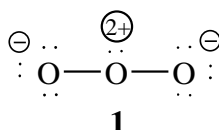
VSEPR YOGA



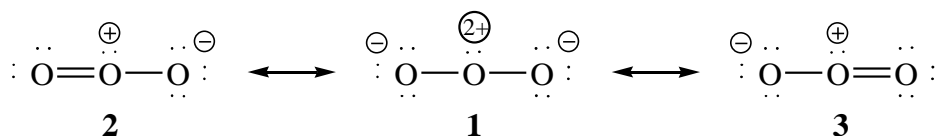
EXCEPTIONS to 2.2!**Resonance Structures — When One Lewis Structure Isn't Enough****O₃ (ozone)**

18 valence electrons (3×6)

Place one O in the center, and connect the other two O's to it. Drawing a single bond from the terminal O's to the one in the center uses four electrons; 12 of the remaining electrons go on the terminal oxygens, leaving one lone pair on the central oxygen:



We can satisfy the octet rule on the central O by making a double bond either between the left O and the central one (**2**), or the right O and the center one (**3**):

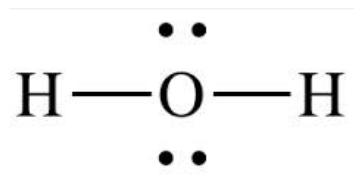


In this example, we can draw two Lewis structures that are *energetically equivalent* to each other — that is, they have the same types of bonds, and the same types of formal charges on all of the structures, and *both structures* (**2** and **3**) are used to represent the molecule's structure. The actual molecule is an *average* of structures **2** and **3**, which are called **resonance structures**. (Structure **1** is also a resonance structure of **2** and **3**, but since it does not satisfy the octet rule, it is a higher-energy resonance structure, and does not contribute as much to our overall picture of the molecule.) Structures **2** and **3** in the example above are somewhat “fictional” structures, in that they imply that there are “real” double bonds and single bonds in the structure for ozone; in reality, however, ozone has two oxygen-oxygen bonds which are equal in length, and are halfway between the lengths of typical oxygen-oxygen single bonds and double bonds — effectively, there are two “one-and-a-half” bonds in ozone. The real molecule does *not* alternate back and forth between these two structures; it is a *hybrid* of these two forms.

The ozone molecule, then, is more correctly shown with both Lewis structures, with the two-headed resonance arrow between them:



In these resonance structures, one of the electron pairs (and hence the negative charge) is “spread out” or *delocalized* over the whole molecule. In contrast, the lone pairs on the oxygen in water (to the right) are *localized* — i.e., they're stuck in one place. Resonance delocalization stabilizes a molecule by spreading out charges. Resonance plays a large role in our understanding of structure and reactivity in organic chemistry.

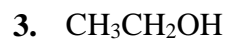
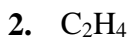
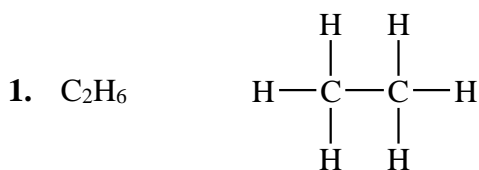


As a general rule, when it's possible to make a double bond in more than one location, and the resulting structures are energetically equivalent to each other, each separate structure must be shown, separated from each other by resonance arrows.

CO₃²⁻ (carbonate ion)

Multi-Center Molecules

Molecules with more than one central atoms are drawn similarly to the ones above. The octet rule can be used as a guideline in many cases to decide in which order to connect atoms.



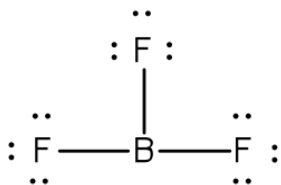
“Violations” of the Octet Rule

A number of species violate the octet rule by having fewer than eight electrons around the central atom or by having more than eight electrons around the central atom.

- **Electron deficient** species, such as beryllium (Be), boron (B), nitrogen (N), and aluminum (Al) can have fewer than eight electrons around the central atoms. Molecules with electron deficient central atoms tend to be fairly reactive (many electron-deficient species act as Lewis acids).
- **Free radicals** contain an odd number of valence electrons. One atom will have an odd number of electrons, and will not have a complete octet in the valence shell. As a result, these species are extremely reactive. When drawing these compounds, there are often several possible resonance structures than can be drawn.
- **Expanded valence shells** are often found in nonmetals from period 3 or higher, such as sulfur, phosphorus, and chlorine. These species can accommodate more than 8 electrons by shoving “extra” electrons into empty orbitals. Note that period 2 elements CANNOT have more than eight electrons.

Examples:**BF₃**

24 valence electrons ($3 + 3 \times 7$)



The octet rule is not satisfied on the B, but this is the correct Lewis structure.

NO (nitrogen monoxide, or nitric oxide)

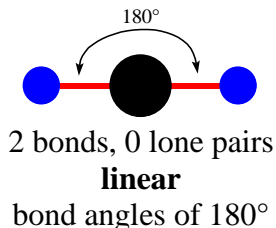
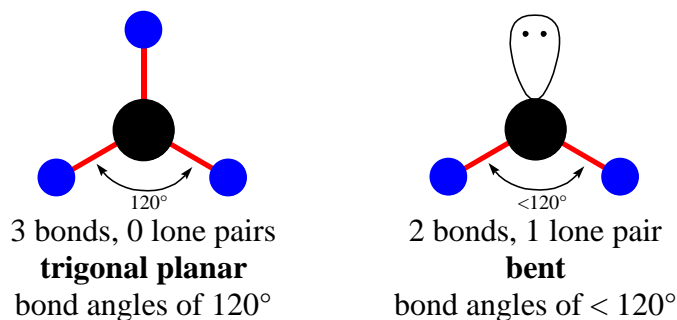


The Shapes of Molecules (or Molecular Geometry): The VSEPR Model

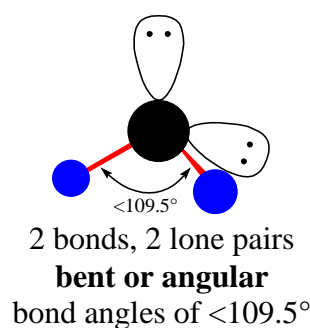
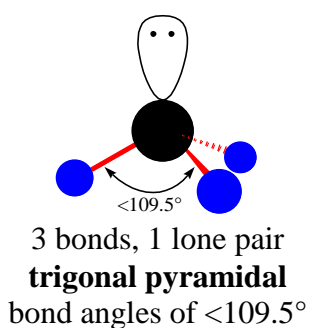
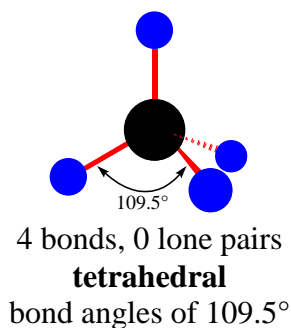
Drawing a Lewis structure is the first steps towards predicting the three-dimensional shape of a molecule. The shape of molecules strongly affect their physical properties, and is very important in the way that biological molecules interact with each other.

Steps to determine the shape of a molecule:

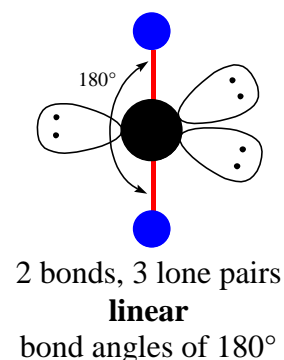
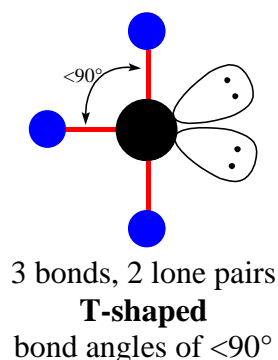
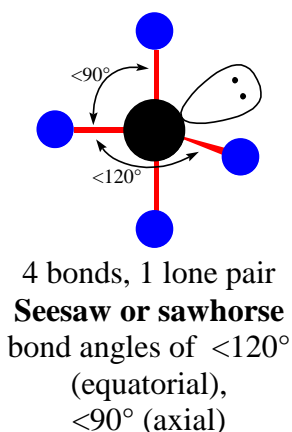
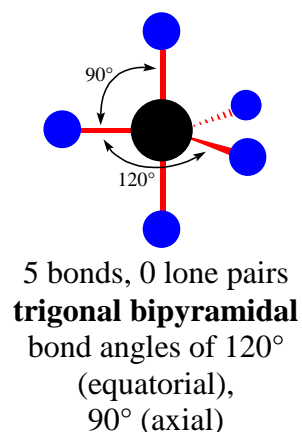
1. Draw the Lewis structure for the molecule of interest and count the number of electron groups surrounding the central atom. Each of the following constitutes an electron group:
 - a single, double or triple bond (multiple bonds count as one electron group)
 - a lone pair
 - an unpaired electron
2. Predict the arrangement of electron groups around each atom by assuming that the groups are oriented in space as far away from one another as possible.
3. The shapes of larger molecules having more than one central are a composite of the shapes of the atoms within the molecule, each of which can be predicted using the VSEPR model (this is a larger scope that we will touch on in unit 3).

Two Electron Groups***Three Electron Groups***

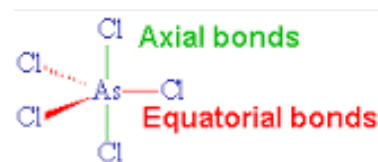
Lone pairs take up more room than covalent bonds; this causes the other atoms to be squashed together slightly, decreasing the bond angles by a few degrees.

Four Electron Groups****Note****

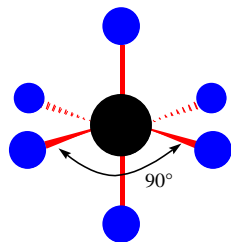
A dashed line means that bond is going backwards into the page you are viewing. A solid line means that bond is found on the same plane as the page you are looking at. A bolded line means that bond is coming forward out of the page you are viewing.

Five Electron Groups

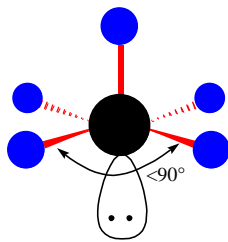
The trigonal bipyramidal shape can be imagined as a group of three bonds in a trigonal planar arrangement separated by bond angles of 120° (the *equatorial* positions), with two more bonds at an angle of 90° to this plane (the *axial* positions).



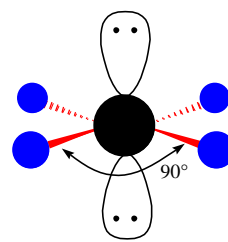
Lone pairs go in the equatorial positions, since they take up more room than covalent bonds. In the equatorial position, lone pairs are $\sim 120^\circ$ from other bonds, while in the axial positions they would be 90° away from other bonds.

Six Electron Groups

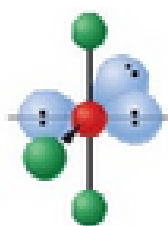
6 bonds, 0 lone pairs
octahedral
bond angles of 90°



5 bonds, 1 lone pair
square pyramidal
bond angles of $<90^\circ$

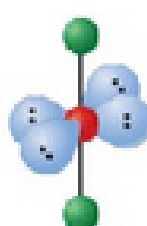


4 bonds, 2 lone pairs
square planar
bond angles of 90°



T-shaped

3 bonds, 3 lone pairs
T-shaped
bond angles of $<90^\circ$



Linear

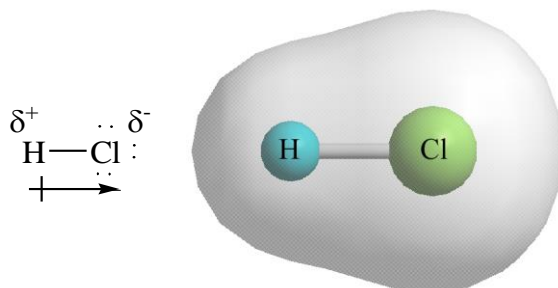
2 bonds, 4 lone pairs
Linear
bond angles of 90°
and 180°

Examples

Methane (CH_4)

Carbon Dioxide (CO₂)**Polar and Nonpolar Covalent Bonds**

Remember that when two bonded atoms have a difference of between 0.5 and 1.69 electronegativity units, the electrons are shared *unequally*, and the bond is a **polar covalent bond** — there is an *unsymmetrical* distribution of electrons between the bonded atoms, because one atom in the bond is “pulling” on the shared electrons harder than the other, but not hard enough to take the electrons completely away (as in an ionic bond). The more electronegative atom in the bond has a **partial negative charge (δ^-)**, because the electrons are pulled slightly towards that atom, and the less electronegative atom has a **partial positive charge (δ^+)**, because the electrons are partly (but not completely) pulled away from that atom. For example, in the HCl molecule, chlorine is more electronegative than hydrogen by 0.96 electronegativity units. The shared electrons are pulled slightly closer to the chlorine atom, making the chlorine end of the molecule very slightly negative (indicated in the figure below by the larger electron cloud around the Cl atom), while the hydrogen end of the molecule is very slightly positive (indicated by the smaller electron cloud around the H atom), and the resulting molecule is polar:

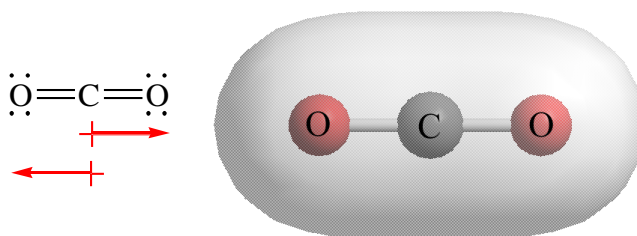


Molecular Shape and Polarity

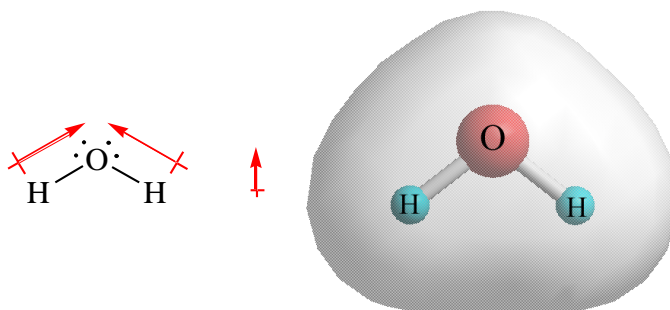
In a diatomic molecule, there is only one bond, and the polarity of that bond determines the polarity of the molecule: if the bond is polar, the molecule is polar, and if the bond is nonpolar, the molecule is nonpolar.

In molecules with more than one bond, *both shape and bond polarity determine whether or not the molecule is polar*. A molecule must contain polar bonds in order for the molecule to be polar, but if the polar bonds are aligned exactly opposite to each other, or if they are sufficiently symmetric, the bond polarities **cancel out**, making the molecule nonpolar. (Polarity is a vector quantity (think back to science 10), so both the magnitude and the *direction* must be taken into account.)

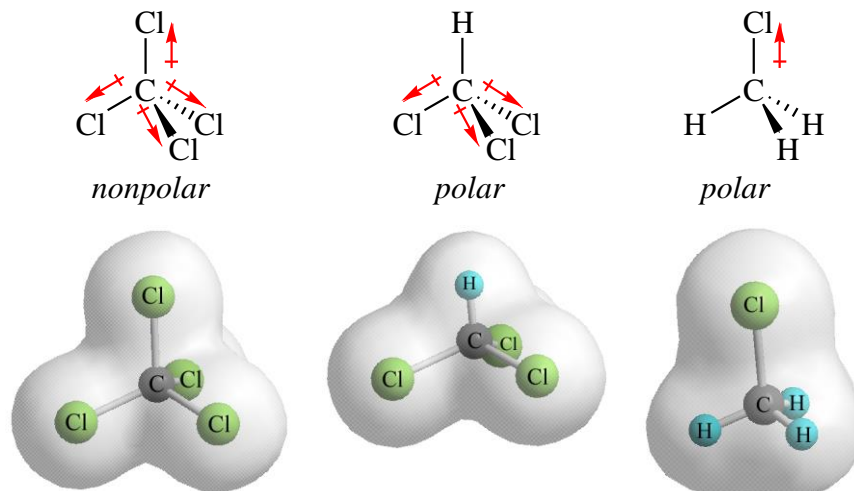
For example, consider the Lewis dot structure for carbon dioxide. This is a linear molecule, containing two polar carbon-oxygen double bonds. However, since the polar bonds are pointing exactly 180° away from each other, the bond polarities cancel out, and the molecule is nonpolar. (As an analogy, you can think of this is being like a game of tug of war between two teams that are pulling on a rope equally hard.)



The water molecule also contains polar bonds, but since it is a bent molecule, the bonds are at an angle to each other of about 105° . They do *not* cancel out because they are not pointing exactly towards each other, and there is an overall dipole going from the hydrogen end of the molecule towards the oxygen end of the molecule; water is therefore a polar molecule:



Molecules in which all of the atoms surrounding the central atom are the same tend to be nonpolar if there are no lone pairs on the central atom. If some of the atoms surrounding the central atom are different, however, the molecule may be polar. For example, carbon tetrachloride, CCl_4 , is nonpolar, but chloroform, CHCl_3 , and methyl chloride, CH_3Cl are polar:



The polarity of a molecule has a strong effect on its physical properties. Molecules which are more polar have stronger intermolecular forces between them (dipole-dipole and H-bonding), and have, in general, higher boiling points (as well as other different physical properties).

Examples

Methane (CH_4)

Carbon Dioxide (CO_2)

Putting it all Together

Examples

Phosgene (COCl_2)

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)


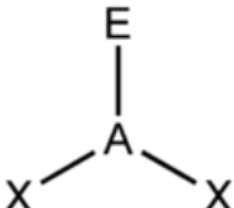
2.3 Assignment/Lab Activity

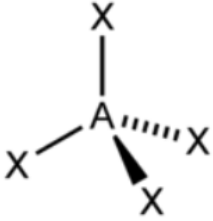

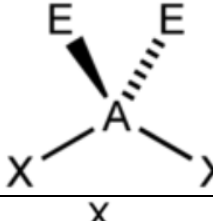

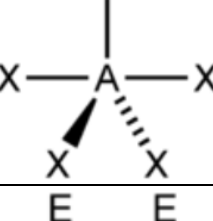
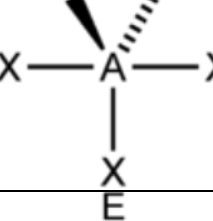
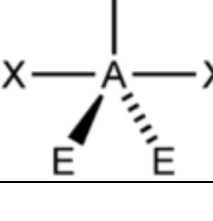
Grab your molecular model kit and build the following molecules to help you fill in the table below. You will have blank boxes as some molecular shapes are much more common than others.

H₂O
 BF₃
 XeF₄
 H₃O⁺
 HCN
 ClF₃
 NO

PCl₅
 SF₆
 N₂O
 XeF₂
 SF₄
 CH₃F
 O₃

Note, this table utilized the AXE method. “A” is the central atom. “X” are the bonded atoms (peripheral atoms). “E” if the unbound/lone pairs of electrons.

Shape	# Bonding Pair(s)	#Lone electron pairs	Molecular Geometry	Example **Specify whether your example is polar or nonpolar
A — X				
X — A — X				
				
				

Shape	# Bonding Pair(s)	#Lone electron pairs	Molecular Geometry	Example **Specify whether your example is polar or nonpolar
				
				
				
				
				
				
				

Shape	# Bonding Pair(s)	#Lone electron pairs	Molecular Geometry	Example **Specify whether your example is polar or nonpolar
