

Chemistry

Unit 4

Bonding

POLYATOMIC IONS YOU MUST MEMORIZE

NAME	FORMULA
acetate	$\text{C}_2\text{H}_3\text{O}_2^{-1}$
ammonium	NH_4^{+1}
carbonate	CO_3^{-2}
bicarbonate or hydrogen carbonate	HCO_3^{-1}
chromate	CrO_4^{-2}
chlorate	ClO_3^{-1}
cyanide	CN^{-1}
hydroxide	OH^{-1}
nitrate	NO_3^{-1}
permanganate	MnO_4^{-1}
phosphate	PO_4^{-3}
peroxide	O_2^{-2}
sulfate	SO_4^{-2}

Chemical Bonding and Intermolecular Forces

Drawing Lewis Structures to Determine Molecular Geometry, Hybridization, and Molecular Polarity

Have you ever wondered why some substances at room temperature exist as solids, others as liquids and still others as gases? The *intramolecular* and *intermolecular* forces of attraction can explain almost every observable property of a substance. The prefix “*intra*” means “within”, thus *intramolecular* forces of attraction are otherwise known as chemical bonds which are the attractive forces between atoms within a compound. The prefix “*inter*” means “between”, thus *intermolecular* forces of attraction are those occurring between molecules and are ultimately responsible for properties such as boiling point, freezing point, and physical state.

PURPOSE

In Part I of this lesson you will study the main types of binding forces that exist within a molecule. These forces bind atoms together. You will also learn to draw Lewis structures which allow you to predict the molecular geometry, hybridization and polarity of molecules. In Part II of this lesson you will be introduced to the types of *intermolecular* forces of attraction that occur between neighboring molecules.

MATERIALS

- periodic table
- molecular models

PART I: CLASS NOTES ON BONDING

What is a chemical bond?

Chemical bonds are forces of attraction that hold atoms or groups of atoms together and allow them to function as one unit. The type of attractive force or bond formed between atoms within a molecule is directly related to the molecule's physical properties such as melting point, hardness, electrical and thermal conductivity, as well as solubility characteristics. If you think about it, most of the chemical substances you can name or identify are *not* elements. They are compounds. Matter tends to favor systems that have positions of lowest energy. That means being bonded requires less energy than existing in the elemental form. It also means that energy *was released* from the system when the atoms joined together. This is a *huge* misconception that most students have—it takes energy to break a bond, not make a bond! Energy is *released* when a bond is formed (an exothermic process); therefore, it *requires* energy to break a bond (an endothermic process). Just remember “breaking up is hard to do”.

Types of Chemical Bonds and Identifying Characteristics

Ionic

Characteristics of ionic substances usually include:

- electrons that are transferred between atoms having large differences in electronegativity (greater than 1.67)
- compounds containing a metal and a nonmetal (Remember that metals are located on the left side of the periodic table and nonmetals are to the right of the “stairs.”)
- strong electrostatic attractions between positive and negative ions
- formulas given in the simplest ratio of elements (empirical formula; NaCl)
- crystalline structures that are solids at room temperature
- ions that form a crystal lattice structure as pictured in Figure 1
- compounds that melt at high temperatures
- substances that are good conductors of electricity in the molten or dissolved state

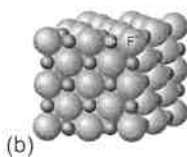
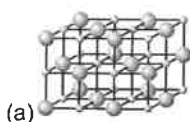


Figure 1

Covalent

Characteristics of covalent substances usually include:

- the sharing of electrons between atoms having small differences in electronegativities (less than 1.67)
- nonmetals attracted to other nonmetals
- formulas that are given in the true ratios of atoms (molecular formulas; $C_6H_{12}O_6$)
- substances that may exist in any state of matter at room temperature (solid, liquid, or gas)
- compounds that melt at low temperatures
- substances that are nonconductors of electricity

Metallic

Characteristics of metallic substances usually include:

- substances that are metals
- a “sea” of mobile or delocalized electrons surrounding a positively charged metal center
- an attraction between metal ions and surrounding electrons
- formulas written as a neutral atom (Mg, Pb)
- solids with a crystalline structure at room temperature
- a range of melting points—usually depending on the number of valence electrons
- substances that are excellent conductors of electricity since the electrons in the “sea” are free to move

Most chemical bonds are in fact somewhere between purely ionic and purely covalent.

Complete Self-Check #1 on your student answer page.

What part of the atom is involved in chemical bonding?

The valence electrons, the outermost electrons, are the only subatomic particle involved in bonding. The electron configuration for each element allows us to predict the number of valence electrons that element has available for bonding. Since the periodic table is arranged by electron configurations, it serves as an essential tool when drawing proper Lewis structures.

Complete Self-Check #2 on your student answer page.

Drawing Lewis Structures

Lewis structures allow us to predict the arrangement of atoms within a molecule, determine its molecular geometry, and help us understand how molecules interact with each other. Lewis structures are only drawn for covalently bonded molecules. Ionically bonded substances do not share electrons. They are the result of strong electrostatic attractions between + and - ions and usually form very large 3-dimensional crystalline structures. Metals are also not represented by Lewis structures. There is no true sharing of electrons because the delocalized electrons are available for any positive metal center.

Types of Covalent Bonds

- **Single bond**—one pair of electrons shared; represented by a single line drawn connecting the two atoms. Example: C—C
- **Double bond**—two pairs of electrons shared; represented by two lines drawn connecting the two atoms. Example: C=C
- **Triple bond**—three pairs of electrons shared; represented by three lines drawn connecting the two atoms. Example: C≡C
- **Multiple bonds**
 - are commonly formed by carbon, nitrogen, oxygen, phosphorous and sulfur. The acronym “C-NOPS” will help you remember the symbols of those elements that can form multiple bonds with themselves and with each other.
 - are stronger than single bonds. Consequently, it takes more energy to break a double bond than a single bond and still more energy to break a triple bond.
 - increase the electron density between two nuclei. As the electron density increases, the repulsion between the two nuclei decreases. Also, as the electron density increases, the attraction *each* nucleus has for the additional bonding electron pairs increases. Both of these effects draw the nuclei closer together, shortening the bond length. This means that the distance between the two nuclei is shortest for a triple bond.

Rules for Drawing Lewis Structures

1. Determine the total number of valence electrons in the molecule or polyatomic ion. Use a periodic table that has the representative elements numbered as groups IA–VIIIA. For example, C has 4 valence electrons since it is in group IVA and F has 7 valence electrons since it is group VIIA. If the structure is a polyatomic ion add the number of electrons equal to the charge for negative ions and subtract the number of electrons equal to the charge for positive ions.
2. Divide the total number of electrons by 2 to get the number of electron pairs available.
3. The element with the lowest electronegativity is the central atom in the molecule or polyatomic ion.

4. Hydrogen is always a terminal atom. It may only connect to one other atom since it can only form one bond.
5. Place one pair of electrons, as a dash representing a single bond, between each pair of bonded atoms.
6. Subtract the number of pairs used from the total the number of pairs you had available.
7. Place lone pairs around each terminal atom (except for H) to satisfy the octet rule. Left over pairs are assigned to the central atom. (If the central atom is from periods 3–7, it can accommodate more than four electron pairs due to the presence of d-orbitals.)
8. If the central atom is not yet surrounded by four electron pairs, convert one or more terminal atom lone pairs into double or triple bonds. Remember, not all elements form multiple bonds; only C, N, O, P, and S.

Exceptions to the Octet Rule

A few elements will have fewer than eight electrons.

- Hydrogen, as mentioned above, has only two electrons.
- Beryllium has a maximum of four valence electrons.
- Boron compounds are stable with only six valence electrons.

Also mentioned above, elements in periods 3 through 7 are often able to expand their octet and may have five or six electron pairs around the central atom. This is due to the availability of d-orbitals that begins with the third energy level. Even if the original atom has no electrons occupying d-orbitals before bonding, these empty d-orbitals can be drawn into the hybridization process.

Electron Dot Structures/Lewis Structures

Part I. Electron Dot Structures

Draw the electron dot structure for the following atoms:

1. Hydrogen

2. Helium

3. Boron

4. Nitrogen

5. Carbon

6. Neon

7. Fluorine

8. Xenon

9. Phosphorus

Part II. Lewis Structures: Single Bonds

Draw the Lewis Structure for the following molecules

1. CCl_4

2. H_2O

3. NH_3

4. CH_4

5. BrO_3^{-1}

6. SO_2^{-2}

7. PCl_3

8. NH_4^{+1}

9. H_2S

Part III. Lewis Structures: Multiple Bonds

Draw the Lewis Structure for the following molecules



Draw the Resonance structures for #4 and #5 below:



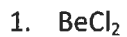
Part IV. Lewis Structures: Expanded Octets

Draw the Lewis Structures for the following molecules



Part V. Lewis Structures: Exceptions

Draw the Lewis Structures for the following molecules



Name _____

Period _____

Lewis Structure Worksheet #1

Read the Instructions for Drawing Lewis Structures worksheet carefully and draw Lewis structures for each of the following molecules:

Group A: Simple Molecules

CH ₄	NH ₃	H ₂ O	SiF ₄	NCl ₃
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Group B: Polyatomic Ions

PO ₄ ³⁻	ClO ₃ ⁻	ClO ₄ ⁻	SO ₃ ²⁻
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Group C: Multiple Bonds

H ₂ CO	HCN	CO	CO ₂
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Group D: Incomplete Octets

BCl_3	BeF_2
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Group E: Expanded Octets

SF_6	PCl_5	BrF_5	XeF_4	ClF_3
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Group F: Random

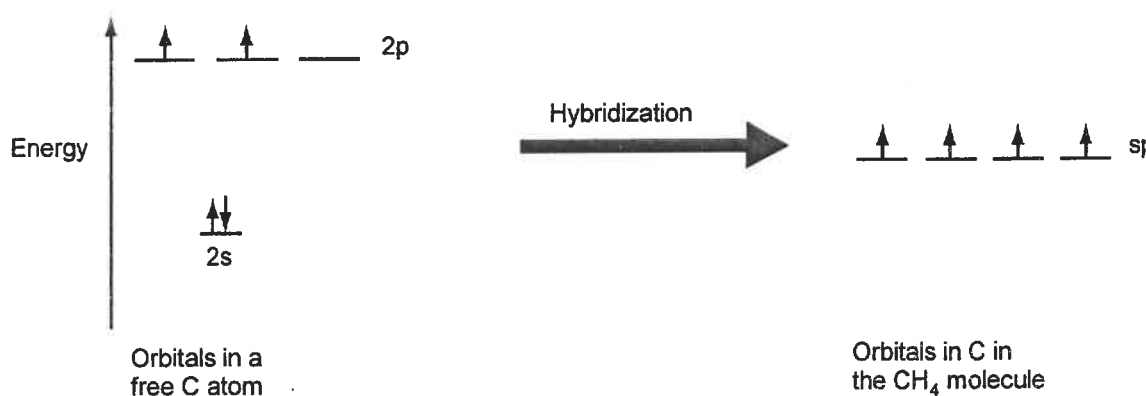
H_2CS	PS_3^-	CHO_2^-	ICl_3	ClF_5
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Valence Bond Theory

A second bonding theory which attempts to describe *how* the bonding occurs is known as the **valence bond theory**. The VB theory focuses on the atomic orbitals that must have overlapped and blended in order to obtain a particular molecular geometry. The two theories compliment each other to better explain molecular geometry.

Consider a molecule of methane, CH_4 . Examine the electron configuration for the central carbon atom, $1s^2 2s^2 2p^2$. It is clear that the valence electrons are the 2s and 2p electrons. However, the 2s orbital is full, two of the p-orbitals are half-full, and the third p-orbital remains empty. How can the central C atom be using its four valence electrons to participate in four bonds? And more importantly, how can we explain the experimental evidence that shows that all four bonds have identical characteristics? The valence bond theory explains just this—the second energy level has two types of orbitals available for bonding, s and p. By blending the one s-orbital and the three p-orbitals we can create four “spaces” for each valence electron of the central C to singly occupy. The idea is similar to mixing pigments. When red and white pigments are mixed, the result is a mixture of pigments we have named “pink” which is a hybrid, or blend, of the two original pigments. The new orbitals are not s and not p; they are four hybrid orbitals, each known as sp^3 . The new name for *each* of the four newly-formed orbitals of equal energy is taken from the name

of the atomic orbitals that formed it, sp^3 or sp^3 for short. These sp^3 orbitals are all equal in energy.



Since boron can violate the octet rule by having only three bonds surrounding it as the central atom (due to the fact that it only has 5 protons and is extremely small), it forms three orbitals of equal energy by blending one s-orbital with two of its p-orbitals. These three orbitals are named sp^2 for short.

The same pattern occurs when expanding the octet to form trigonal bipyramidal and octahedral molecular geometries. Once the one s-orbital is blended with the three p-orbitals, the d-orbital is brought into the mix to yield five sp^3d orbitals and six sp^3d^2 orbitals, respectively. An easy way to determine the hybridization an atom is exhibiting is to count the regions of electron density around the central atom and then use that number of orbitals to build your hybrid. A multiple bond counts as *one* region of electron density as does a lone, unshared pair of electrons. Use Table 10.1 as a guide to predict the molecular geometry and hybridization of various molecules.

Using Lewis Structures to Predict Molecular Geometry

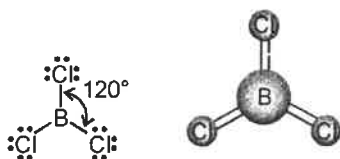
The atoms involved in bonding will arrange themselves to minimize electron pair repulsions. This is known as the **VSEPR Theory**—Valence Shell Electron Pair Repulsion Theory. Molecular geometry is determined by the areas of electron density surrounding the central atom. If the central atom is surrounded by four bonding pairs of electrons, the molecular geometry is tetrahedral with a 109.5° bond angle. The molecular geometry is altered when one or more of the areas of electron density surrounding the central atom are occupied by an unshared electron pair (also called a lone pair). Unshared electron pairs have greater repulsive force than shared electron pairs and thus occupy more space. The increased repulsion causes the shared pairs of electrons to be “pushed” closer together. The presence of one lone pair reduces the bond angle to approximately 107° , while the presence of two lone pairs reduces it to approximately 104.5° .

The Basic Shapes with No Unshared Electron Pairs

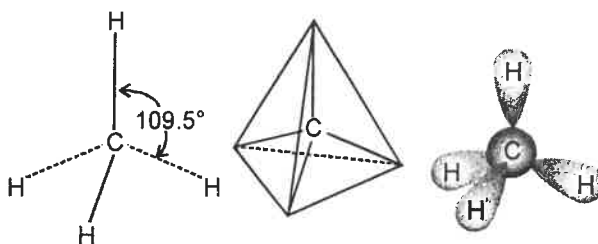
Linear



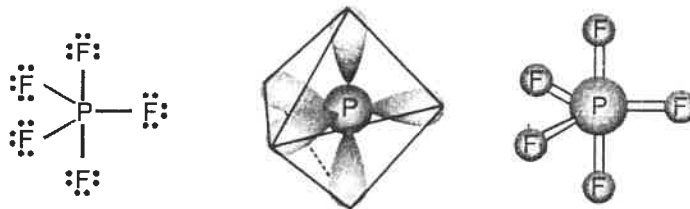
Trigonal Planar



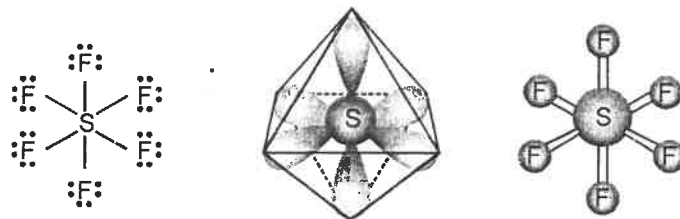
Tetrahedral



Trigonal bipyramidal

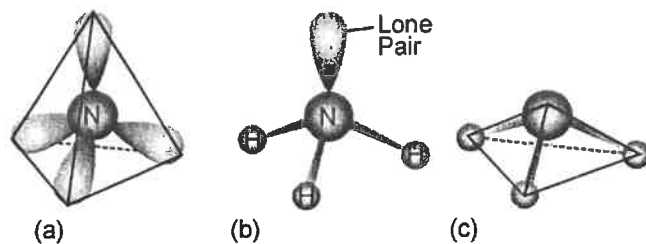


Octahedral

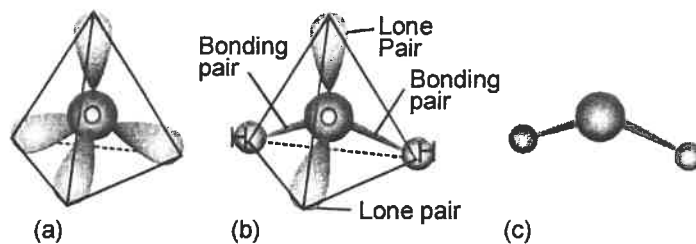


Variations in Molecular Geometry as a Result of Lone Pair Electrons

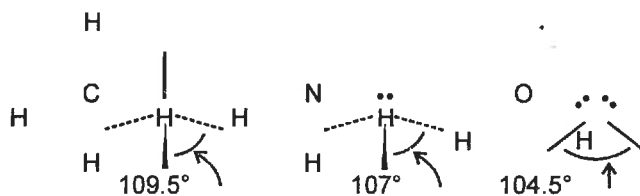
Ammonia, NH_3 , is predicted to have a tetrahedral shape based solely on the positions of the electron pairs surrounding the central atom. Since only three of these regions contain *shared* electron pairs, with the fourth site being occupied by a *lone pair*, its molecular geometry is in fact trigonal pyramidal. The lone pair on nitrogen causes the H—N—H bond angle, to decrease from 109.5° to 107° .



Water, H_2O , is also predicted to have a tetrahedral shape since it has four sites of electron density around the central atom. However, it exhibits a molecular geometry variation known as V-shape or bent. The two lone pairs “gang up” on the shared pairs and decrease the H—O—H bond angle from 109.5° to 104.5° .



In summary, lone pairs have greater repulsive force than shared pairs and cause distortion of the remaining bond angles. The molecular geometry is determined by the positions of the *atoms* surrounding the central atom. The presence of a lone pair with its increased repulsion determines the positions of the other electron pairs and thus the attached atoms. Because they are not attracted to another atom they appear “invisible” when naming the shape.



The same type of phenomenon occurs when unshared pairs occupy positions around the central atom in the trigonal bipyramidal and octahedral molecular geometries. The names of the resulting molecular geometry variations are shown in Table 10.1.

TABLE 10.1			
Areas of Electron Density on Central Atom	Number of Lone Pairs on Central Atom	Predicted Geometry of the Molecule	Hybridization
2	0	Linear	sp
3	0	Trigonal planar	sp^2
4	0	Tetrahedral	sp^3
4	1	Trigonal pyramidal	sp^3
4	2	V-shape (or bent or angular)	sp^3
5	0	Trigonal bipyramidal	sp^3d
5	1	See-saw	sp^3d
5	2	T-shape	sp^3d
5	3	Linear	sp^3d
6	0	Octahedral	sp^3d^2
6	1	Square pyramidal	sp^3d^2
6	2	Square planar	sp^3d^2

Complete Self-Check #3 on your student answer page

PART II: CLASS NOTES ON INTERMOLECULAR FORCES AND POLARITY

Molecular Polarity

Covalent chemical bonds between atoms are considered *polar* if the electronegativity difference between the two atoms is greater than 0.4, but less than 1.67. The term polarity refers to a separation of charge.

A **molecule** is considered polar if there are uneven electron forces acting on the central atom. Uneven forces (called dipole moments) are generally caused by the presence of a lone pair on central atom or different kinds of atoms being bonded to the central atom. A molecule can obey the octet rule, have four polar bonds and be a *nonpolar* molecule since all four bonds exert an equivalent dipole moment on the central atom, canceling each other out.

Intermolecular Attractive Forces (IMF's)

Intermolecular forces are those forces that exist *between* molecules. As stated earlier, the prefix "inter-" means between. You are most likely familiar with the term "interstate" which describes the highways that connect one state to another; they are highways that allow travel between states. Intermolecular attractive forces are *not* chemical bonds. They are simply forces of attraction between neighboring molecules.

Physical properties such as melting points and boiling points can be attributed to the strength of intermolecular attractions present between molecules. It works like this: the lower the boiling point, the weaker the intermolecular attractions; the higher the boiling point, the stronger the intermolecular attractions. For example, gasoline evaporates much more quickly than water.

Therefore, the intermolecular attractive forces that hold one gasoline molecule to another are weaker than the forces of attraction that hold one water molecule to another water molecule. In fact, water molecules are held together by the strongest of the intermolecular attractive forces, hydrogen bonds. Hydrogen bonds are not true bonds—they are just forces of attraction that exist between a hydrogen atom on one molecule and the unshared electron pair on fluorine, oxygen, or nitrogen atoms of a neighboring molecule. The strands of DNA that make up our genetic code are held together by this type of intermolecular attraction.

THE TYPES OF INTERMOLECULAR FORCES IN DECREASING ORDER

- **Dipole-dipole**—the force of attraction that enables two polar molecules to attract one another. Compounds exhibiting this type of IMF have higher melting and boiling points than those exhibiting weaker IMFs.
 - **Hydrogen bonding**—the force of attraction between the hydrogen atom of one molecule and an unshared electron pair on F, O, or N of a neighboring molecule (a special case of dipole-dipole). Never confuse hydrogen bonding with a bonded hydrogen. The unique physical properties of water are due to the fact that it exhibits hydrogen bonding.
- **Dipole-induced dipole**—the force of attraction between a polar molecule and a nonpolar molecule. The polar molecule induces a temporary dipole in the nonpolar molecule. Large molecules are more polarizable than smaller molecules since they contain more electrons. Larger molecules are more likely to form induced dipoles.
- **Induced dipole-induced dipole or London dispersion forces**—the only force of attraction between two nonpolar molecules due to the fact that they can form temporary dipoles. Nonpolar molecules have no natural attraction for each other. This IMF is known by both names. All molecules have this type of IMF and it is often the predominant force.

Lewis Dot Structures

1. CHCl_3

Name: _____

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

2. CS_2

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

3. BrO_3^-

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

4. NH_4^+

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

5. SCl_4

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

6. BrF_5

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

7. BF_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

8. SCl_6

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

9. PH_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

10. NF_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

11. SO_4^{-2}

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

12. CO_3^{-2}

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

13. SiCl_4

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

14. H_2S

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

Study Guide

15. BrF_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

16. NO_3^-

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

17. H_3O^+

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

18. CCl_4

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

19. AlH_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

20. SO_2

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

21. SO_3

Valence e^- pairs: _____

Hybridization: _____

Shape: _____

Polarity: _____

Test Review

1. What are the general properties of an ionic bond, a covalent bond, and a metallic bond. List the types in order of increasing strength. Are these intra or inter-molecular forces?
2. How is an ion different from its parent atom?
3. What does a metal atom need to do in order to form a cation?
4. What does a nonmetal atom need to do in order to form an anion?
5. Explain why the PROPERTIES of an ion differ from its parent atom.
6. Explain the difference between a shared pair and a unshared pair (lone pair) of electrons.
7. What term is used to describe the situation when two or more correct Lewis structures represent a molecule?
8. Why is the electronegativity of an element important?
9. Contrast a polar covalent bond and a nonpolar covalent bond.

10. How does a covalent bond differ from an ionic bond?
11. What is Valence Bond Theory (VBT)
12. Why does hybridization occur?
13. VSEPR. What does the acronym stand for? How do atoms arrange themselves? What does this mean for bond angles?
14. List the exceptions we have used for Lewis Structures and why they are exceptions.
15. Why can elements in periods 3-7 have expanded octets?
16. What are the steps we used to determine polarity?
17. List the types of intermolecular forces in increasing order. List the properties of each.

STUDY YOUR BONDING PACKET.

PRACTICE DRAWING LEWIS STRUCTURES.

