Molecular Models: Lewis Dot Formulas, VSEPR Theory, and Valence Bond Theory

OBJECTIVES To use Lewis Dot formulas and the Valence Shell Electron Pair Repulsion (VSEPR) Theory to predict shapes and polarity of small molecules and polyatomic ions.

CONCEPTS TO BE TESTED Macro models such as molecular stick models and Lewis Dot formulas can be used to predict or explain properties of particles that are too small to be seen.

Text References: (1) Whitten, K. W., Gailey, K. D., and Davis, R. E., *General Chemistry*, 3rd ed., Saunders College Publishing, Philadelphia, 1988, Chapters 6 and 7. (2) Kotz, J. C., and Purcell, K. F., *Chemistry and Chemical Reactivity*, Saunders College Publishing, Philadelphia, 1987, Chapters 9 and 10.

INTRODUCTION

Because atoms are too small to see with the human eye, chemists use models to visualize the physical arrangements of atoms in molecules and polyatomic ions. These three dimensional models aid in understanding the polarity of some molecules. The reactivity and interaction of atoms in molecules can also be better understood.

Lewis Dot formulas give basic information in two dimensional representations that can be used to predict the three dimensional shapes of molecules and polyatomic ions. Molecular models can then be constructed from ball and stick sets. (Candy gum drops and toothpicks can also be used. Each color can represent a different element.)

A basic concept of the atomic theory is that the chemical and physical properties of a substance are determined by the distribution of outer shell (highest n value) electrons in its atoms and by the arrangements of these atoms.

Experimentally, the relative positions of atoms in molecules or polyatomic ions can be deduced by techniques such as x-ray or neutron defraction in crystals; infra-red, Raman and microwave spectroscopy; and dipole moment measurements. Experimental measurements agree very closely with models for simple molecules and ions.

The following rules and procedures are given as a guide in drawing Lewis Dot Formulas.

A. *Arrangement of molecular skeleton structure*

Rule 1. For small molecules and polyatomic ions, place the element with the lowest electronegativity in the center and arrange the more electronegative atoms around it. Hydrogen is never the central atom.

CS_2 [S C S]⁰ CO_3^{2-} $\left[\begin{matrix} & O & \\ O & C & O \end{matrix}\right]^{2-}$

Rule 2. For oxyacids, the hydrogen atoms are usually bonded to oxygen atoms which are bonded to the less electronegative central atom.

HNO_3 $\left[\begin{matrix} & & O & \\ H & O & N & \\ & & O & \end{matrix}\right]^{0}$ H_2SO_4 $\left[\begin{matrix} & & O & & \\ H & O & S & O & H \\ & & O & & \end{matrix}\right]^{0}$

B. *Arrangement of electron dots**

Step 1. Determine the number of electrons that will be needed (N) to satisfy each atom. Usually all atoms need 8 electrons each except hydrogen which needs 2 electrons.

CS_2 $N = 8 + 2(8) = 24e^-$

CO_3^{2-} $N = 8 + 3(8) = 32\ e^-$

Step 2. Determine the number of electrons available (A) from each atom. For polyatomic ions, *subtract* one electron for each *positive* charge and *add* one electron for each negative charge.

CS_2 $A = 4 + 2(6) = 16\ e^-$

CO_3^{2-} $A = 4 + 3(6) + 2 = 24\ e^-$

Step 3. Calculate the number of electrons shared (S) in the molecule. $S = N - A$

CS_2 $S = 24 - 16 = 8\ e^-$

CO_3^{2-} $S = 32 - 24 = 8\ e^-$

Step 4. Place two dots (one bond) between the central atom and each bonded atom. If all the shared electrons (Step 3) have not been used, insert pairs to make double bonds. Do not exceed the number of covalent bonds that the *outer* atom can form. (H and Gp VII = 1, Gp VI = 2, Gp V = 3, Gp IV = 4)

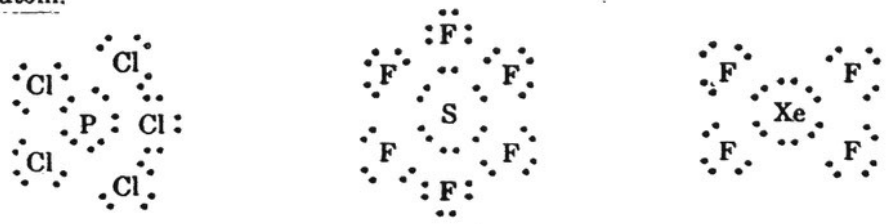
Step 5. Calculate the number of the available electrons which are not shared (*NS*) in the molecule (*NS*) = A – S.

CS_2 $(NS) = 16 - 8 = 8\ e^-$

CO_3^{2-} $(NS) = 24 - 8 = 16\ e^-$

Step 6. Use the nonshared electrons (Step 5) to complete the number of electrons each atom *needs*.

* There are compounds that can not be represented by these rules for Lewis Dot Formulas. The central atom may have less than 8 electrons (BF_3) or more than 8 electrons (PCl_5, SF_6, XeF_4, etc). For most of these compounds, the central atom and each outer atom are bonded by single bonds consisting of one electron from the central atom and one electron from the outer atom. If there are any extra electrons on the central atom, they are grouped as unshared pairs on the central atom.



C. *Electronic Geometry*

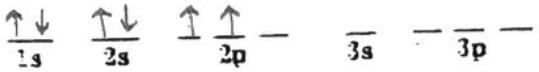
1. The VSEPR theory states that regions of high electron density will arrange themselves as far apart as possible around the central atom. One region of high electron density is counted for each single, double, or triple bond, or for each unshared pair of

electrons (lone pair) on the central atom. In the examples shown above, CS_2 has two regions, CO_3^{2-} has three regions, PCl_5 has five regions, SF_4 and XeF_4 have six regions. The following electronic geometries are expected for these numbers of regions of high electron density.

regions	2	3	4	5	6
geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral

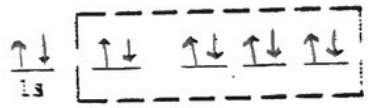
2. The Valence Bond Theory proposes that the higher energy atomic orbitals on the central atom hybridize (mix) when atoms approach for bonding. Electrons in orbitals on the central atom are "promoted" to higher orbitals which were not used in the ground state. These orbitals can accept electrons from other atoms. The atomic orbitals that are hybridized give new shapes that are different from the original atomic orbitals. When atoms bond through the new hybridized orbitals, the molecule will have a characteristic shape that depends on the atomic orbitals used in hybridization.

In methane, CH_4, carbon is the "central atom" and hydrogen is the "other atoms."

For C ground state 

promoted state 

(1 – s, 3 – p orbitals)

bonded state 

four sp^3 hybrid orbitals (tetrahedral)

The shapes of common kinds of hybrid orbitals follow:

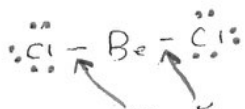
sp	linear
sp^2	trigonal planar
sp^3*	tetrahedral
sp^3d or dsp^3	trigonal bipyramidal
sp^3d^2 or d^2sp^3	octahedral

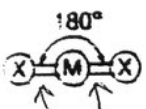
* This hybridization is not used for elements in Gp V and Gp VI except in period 2. For these elements in higher periods, atomic "p" orbitals are used in bonding. These are at right angles to each other. This still accounts for the molecular shapes of trigonal pyramidal Gp V and bent (angular) Gp IV molecules.

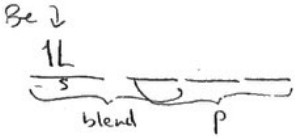
D. *Molecular Geometry (shape)*

Attach the other atoms to the regions of electron density so that these other atoms are as far apart as possible. The relative positions of the central atom and the other atoms can be described as the molecular geometry. Some examples follow.

Electronic geometry	Compound	Molecular geometry
Linear	$BeCl_2$	linear (sym)

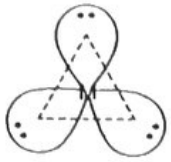


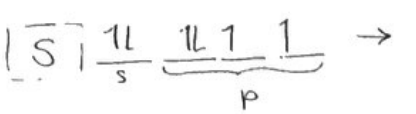




Two areas of e^- density = linear = sp hybrid

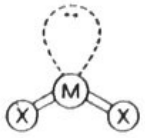
sp^2 **Trigonal planar**





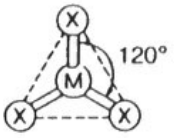
SO_2

bent (unsym)



SO_3

trigonal planar (sym)



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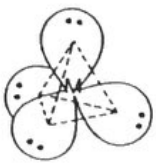
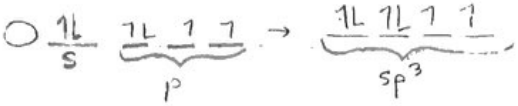
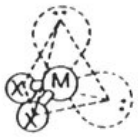
sp^3 **Tetrahedral**



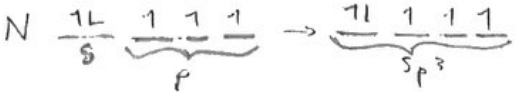
H_2O



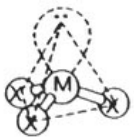
bent (unsym)



NH_3

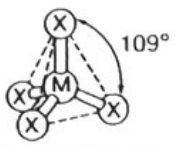


trigonal pyramidal (unsym)



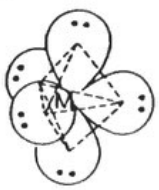
CH_4

tetrahedral (sym)



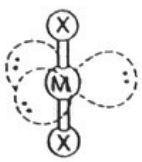
Trigonal bipyramidal

dsp^3



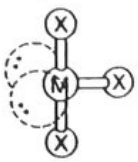
XeF_2

linear (sym)



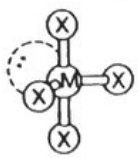
ClF_3

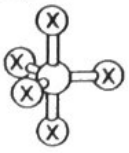
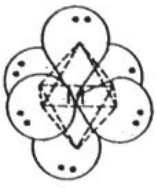
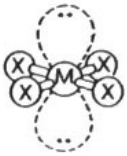
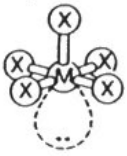
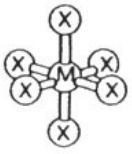
t-shaped (unsym)



SCl_4

seesaw (unsym)



	PCl_5	trigonal bipyramidal (sym) 
Octahedral  d^2sp^3	XeF_4	square planar (sym) 
	IF_5	square pyramidal (unsym) 
	SCl_6	octahedral (sym) 

E. Molecular Polarity (Dipole moment)

If its molecular geometry is *completely* symmetrical, a molecule is nonpolar. If the molecular geometry is unsymmetrical, the molecule will be polar because of lone pairs of electrons on the central atom. Polar bonds (due to differences in the electronegativities) may re-enforce or oppose the effect of the lone pairs of electrons.

PROCEDURE

In this experiment you will predict the polarity of a series of molecules and polyatomic ions by the following process:

Lewis Dot Formula → Electronic Geometry → Stick model → Molecular Geometry → Stick model → Symmetry → Polarity

Step 1. Calculate the number of electrons needed (N), available (A), shared (S), and not shared (*NS*) (1).

Step 2. Draw the Lewis Dot Formula for the molecule or polyatomic ion on the REPORT FORM (2).

Step 3. Count the number of regions of high electron density. Sketch (3a) and describe the electronic geometry on the REPORT FORM (3b).

Step 4. Draw the ground state electronic configuration of the central atom for the electrons beyond the noble gas core on the REPORT FORM (4a). Predict the atomic obritals that hybridize to account for the electronic geometry in Step 3 (4b).