

## Experiment 14 - Lewis Dot Structures & Geometry by VSEPR Theory

### I. PURPOSE

In this exercise we will learn and practice the determination of Lewis dot structures of covalently bonded molecules (and ions) as a tool for predicting or explaining the number of bonds present, the number and location of bonding and non-bonding electrons pairs, and the formal charge distribution within the chemical species. We will then combine the Lewis dot information with the Valence Shell Electron Pair Repulsion (VSEPR) theory of Gillespie to predict the electron and molecular geometry of the molecule or ion.

### II. INTRODUCTION AND THEORY

The shape of the molecules which make up a chemical substance often has a significant impact on the chemical and physical properties exhibited by the substance. Solubility, density, boiling and melting point, dipole moment, and reactivity are all influenced to a greater or lesser extent by the molecular shape. In living systems biochemists and molecular biologists are discovering that odor, taste, selectivity of enzymatic catalysts, drug activities, and even the genetic coding which directs all organisms usually depend on a match between geometry and polarity of a receptor site and that of a reactant molecule. As a result, chemists have long sought simple means of predicting the shapes of molecules and ions.

A theory of covalent bonding first proposed by G.N. Lewis in 1916 provides a means of predicting the number of bonds formed between a central atom and the outer atoms which surround it (often called *ligand* atoms). The theory of electron repulsion between outer shell electron pairs first espoused by R.J. Gillespie and others in the late 1950's and early 1960's allows semi-quantitative prediction of molecular geometries without complexity of hybridization or molecular orbital theory.

#### A. Lewis Theory

Covalent molecules are held together by the simultaneous attraction of outer (valence) electrons for the positive charges on two or more adjacent nuclei, a situation called "sharing" of electron pairs between the atoms involved. Lewis proposed that atoms will strive to form enough shared electron bonds to get access to enough electrons to fill their outer (valence) orbitals, and so to mimic the electron configuration of the noble gases. Since the outer s and p orbitals can hold a total of 8 electrons, this gives rise to the octet rule, or "rule of eight". Simply stated, Lewis's theory predicts that each atom will gain access to eight electrons through electron transfer (in ionic compounds) or through electron sharing (in covalent compounds), with shared electrons being counted toward the octet requirements of each partner in the bond. This means that in covalent molecules each atom will form one bond for each electron by which it is short of an octet. Thus C will form 4 bonds; N, 3; O, 2; and F, 1.

We now know that stable molecules may have *more* than eight electrons in the outermost shell of the central atom if it has low-lying d orbitals available to accommodate the extra electrons, and that certain stable compounds form with *fewer* than eight valence electrons on the central atom, notably compounds of boron and some metals. Lewis theory does not effectively address bonding involving transition metals.

## B. Rules for Writing Lewis Structures

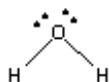
Lewis structures can be fairly easily written by application of the following rules:

1. Write the chemical formula of the molecule or ion and determine the total number of valence electrons available, including any ionic charge.
2. Draw the skeletal arrangement of the molecule, generally with the unique, most metallic, or first element in the formula in the center and all the others connected to it by single, two-electron bonds. Subtract the electrons used to form these bonds from the total available.
3. Distribute the remaining electrons to satisfy the octet rule, starting first with the outer atoms and then with the central atom until all atoms have an octet.
4. If electrons are left over after step three, the extra ones are placed on the central atom.
5. If there are not enough electrons to satisfy the octet rule for atoms, form multiple bonds to the central atom by moving unshared electron pairs to form double or triple bonds (except in boron and certain covalent metal compounds).

The most difficult step for most students (and many teachers) is determining the arrangement of atoms in Step 2. Often the most symmetric structure is correct. Sometimes at this point we need to keep in mind the number of bonds an atom must form to satisfy the octet rule. Thus H can only form one bond, so it must be an outer atom. Oxygen will usually form two bonds, so it cannot be put where it needs to form more, etc. Carbon is often the central atom in its compounds, and many organic compounds with more than one C atom will have a string of carbons linked together as a backbone. Although formation of small rings of atoms (3 or 4) may seem reasonable, such structures are rare and usually unstable.

Examples:

H<sub>2</sub>O Step 1: No of electrons: 2(1) + 6 = 8  
 Step 2: H-O-H e<sup>-</sup> left = 8 - 4 = 4  
 Step 3: put 4 e<sup>-</sup> on O, since H needs only 2, all octets are satisfied, O extra

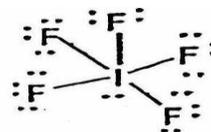
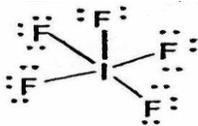
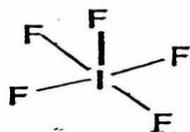


No steps 4 and 5.

NO<sub>2</sub><sup>1-</sup> Step 1: 5 + 2(6) + 1 = 18  
 Step 2: O-N-O e<sup>-</sup> used, N short 2 e<sup>-</sup>  
 Step 3: all 14 e<sup>-</sup> used, N short 2 e<sup>-</sup> Step 5: (one of 2 resonance forms)



IF<sub>5</sub> Step 1: 6(7) = 42  
 Step 2: Step 3: 42-10=32 Step 4: 32-30=2 extra put 2 extras on I



### C. Formal Charges

It is often useful to consider charge distributions within a molecule, not only to determine negative and positive charge centers but also to decide which of several alternative Lewis structures might be more stable. The formal charge is the ionic charge on each atom assuming that all bonded electrons are equally shared. It can be calculated by subtracting from the group number of a given atom the number of all its lone pair electrons, and one-half of all the bond pairs it shares with other atoms (which is the number of bonds formed to it):

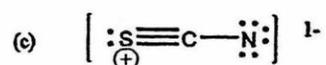
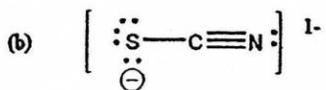
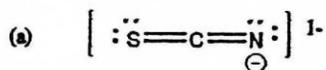
$$\text{Formal Charge} = \text{group no.} - \text{no. of unshared } e^- \text{'s} - \text{no. of bonds}$$

Note that the formal charges may be meaningless as far as reality is concerned, since electrons shared between atoms with radically different electro negativities are far from equally shared.

Lewis structures with the lowest formal charges are usually the most important. If several satisfy this criterion, then structures with negative charges are usually the most important. If several satisfy this criterion, then structures with negative charge on the more electronegative atoms will be favored. Especially unfavorable are structures in which positive or negative charges are assigned to adjacent atoms.

Consider the following example:

Thiocyanate ion  $\text{SCN}^-$  could have the following structures:



Structures (a) and (b) have the same total charge but (a) is favored because the negative charge rests on N, the more electronegative atom.

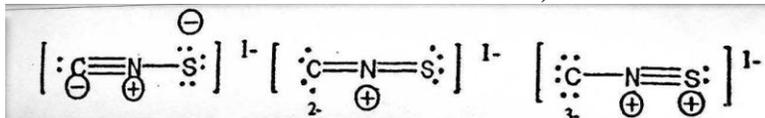
Higher charges make this the least likely form.

### D. Resonance

Whenever more than one Lewis structure can be drawn for a molecule which satisfy the octet rule and keep the atoms in the same positions, the different structures are said to be resonance forms (or resonance isomers), and the actual molecule is a mixture, or resonance hybrid, of the various forms. If the individual resonance forms are equally stable (such as nitrate ion,  $\text{NO}_2^-$ , given as an example on the previous page) the actual molecule is a single form which is an equal mix of the resonance forms. In the case above, structures (b) and (c) simply average out to (a), so it will be the only important structure.

It is important to realize that resonance *does not* mean that some molecules are in form and some in another. *Nor* does it mean that the molecule rapidly switches back and forth among the possible resonance forms. In fact the problem is that we are using a localized bonding model to describe a bonding system which is *intrinsically not localized*. Only a bonding model which involves all the bonding orbitals on all atoms of the molecule, a so-called molecular orbital system, can effectively describe delocalized "resonance" type bonding.

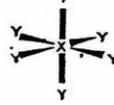
Resonance is an approximation to what the molecule actually is, and represents a failure of the model. It is also worth noting that resonance structures cannot involve atomic rearrangements. Thus the isothiocyanate ion,  $\text{CNS}^-$ , with the resonance forms shown is *NOT* a resonance form of the thiocyanate ion listed above, because the atoms have been moved. It is a geometric isomer of thiocyanate. (Which resonance form of this ion would be more stable??)



### E. VSEPR Theory

Dr. R.J. Gillespie has been, and continues to be, a champion of the cause of simplification of the General Chemistry curriculum. In the late 50's and early 60's he published a series of papers on the geometry of simple molecules in which he asserted that the geometry of most molecules could be predicted on the basis of electron repulsions. Specifically he stated that the gross geometry of most molecules results from placing regions of high electron density on the central atom of a molecule as far apart as possible, so as to minimize electron-electron repulsive effects. Regions of high electron density include single and multiple bonds and lone pairs of electrons in the valence shell of the central atom. If more than one central atom is present in a molecule, each will be treated successively as a central atom. To a first approximation, the geometry assumed about a central atom is a function only of the total number of regions of electron density (usually stated as electron pairs). Distortions from the idealized geometries are expected where necessary to minimize repulsions involving the proportionately larger unshared or lone pairs, and electron clouds associated with double or triple bonds. Multiple bonds, however, are to be considered as only a single "electron pair" for determination of geometry. The basic geometries can be shown to be as listed in the table below.

**TABLE 1 –GEOMETRIES ASSOCIATED WITH NUMBERS OF ELECTRON PAIRS**

# Electron Pairs on Central Atom	Geometry	Sketch of Shape
2	Linear	
3	Trigonal Planar	
4	Tetrahedral	
5	Trigonal Bipyramidal	
6	Octahedral	

Because of the size of non-bonded electron pairs, called lone pairs, their repulsions must be considered first, and they must be placed as far apart as possible. Their best locations are usually obvious except in 5-pair systems, in which they always go into the triangular planar

(equatorial) portion of the molecule because of the  $120^\circ$  bond angles there. In general we will expect to see minor deviations in the molecular geometry caused by repulsions involving the oversized lone pairs and multiple bond pairs. Nearby bonds will tend to move away from the larger lone or multiple bond pairs like a folding umbrella. This is especially obvious in the series of molecules:  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , in which the H-X-H bond angle closes down from  $109.5^\circ$  in the regular tetrahedral molecule to  $107^\circ$  in  $\text{NH}_3$  (1 lone pair), and  $104.5^\circ$  in  $\text{H}_2\text{O}$  (2 lone pairs). The same thing happens in phosgene,  $\text{C}_1\text{C}=\text{O}$ , a molecule predicted to be planar triangular because of its 3 pairs, in which the C1-C-C1 bond angle closes down from the ideal  $120^\circ$  to  $111.4^\circ$  and the C1-C-O angle expands to  $124.3^\circ$ . These deviations are not unexpected, and, in fact, are predictable, although not necessarily quantitatively.

The table below shows the electron pair geometry for various numbers of electron pairs with and without lone pairs. Note that the electron pair geometry for various numbers of electron pairs with and without lone pairs. Note that the *molecular geometry* names the atom arrangement, which will not be the same as the electron pair geometry if lone pairs are present.

**Table 2 --- Electron Pair and Molecular Geometries for 3-6 Electron Pairs**

No. e <sup>-</sup> Prs.	No. Lone Prs.	Electron Pr. Geom.	Name of Mol. Geom.	Example
3	0		trigonal planar	$\text{BF}_3$
	1		angular (bent)	$\text{SO}_2$
4	0		tetrahedral	$\text{CH}_4$
	1		trigonal pyramidal	$\text{PCl}_3$
	2		angular (bent)	$\text{H}_2\text{O}$
5	0		Trigonal bipyramidal	$\text{PF}_5$
	1		Distorted tetrahedral (see saw)	$\text{SF}_4$
	2		T-shaped	$\text{ICl}_3$
	3		Linear	$\text{XeF}_2$
6	0		Octahedral	$\text{SF}_6$
	1		Square pyramidal	$\text{IF}_5$
	2		Square planar	$\text{KrF}_4$

## F. Cheating Method of Electron Counting

There is a quick-and-dirty method of counting electrons around the central atom which can be used in certain cases to rapidly determine the number of electron pairs, and thus geometry of the molecule, as well as to check the Lewis dot structure. It will not show the presence of multiple bonds, but will give the number of "Gillespie" pairs of electrons. It is based on the fact that ligand atoms which are short only one electron, like H or the halogens, will contribute one electron to the central atom to form a single bond and get the one they need. Group six elements, like O, S, and Se, need two electrons and either accept a pair from the central atom (a coordinate covalent bond), or form a double bond. In either case, because of the way electron pairs are counted in VESPR, no net electrons are donated to the central atom when a group six non metal bonds. The short story is: The number of electrons around the central atom is its group number, corrected for any ionic charge, plus 1 e<sup>-</sup> for each H, OH, or halogen that is bonded, plus 0 for any group VIA ligand. That is:

Valence e<sup>-</sup> = grp no. - ionic charge + 1x (no. of H's, OH's and halogens) + 0x (no. of group VI atoms)

For example: BF<sub>3</sub> = 3 + 3 (1) = 6 = 3 pairs, all bonding

SO<sub>2</sub> = 6 + 2 (0) = 8 = 4 pairs, 2 bond, one lone (each ligand needs a bond pair)  
(double bond to one O counted once)

SO<sub>4</sub><sup>2-</sup> = 6 + 2 = 8 (0) = 8 = 4 pairs, all bonding

IF<sub>5</sub> = 7 + 5 (1) = 12 = 6 pairs, 5 bond, one lone

H<sub>2</sub>CO = 4 + 2 (1) + 1 (0) = 6 = 3 prs, all bonding (double bond to O counted once)

If you check these with Lewis dots, you'll get the same number of pairs for VESPR. This method just can't identify multiple bonding. It's *very* fast, however.

## III. EXPERIMENTAL PROCEDURE

Obtain a molecular model set and construct models of the geometries expected for 3 through 6 electron pairs. The two pair systems are just linear and easy to visualize. Then, working with a partner if it is permitted, go through the problems on the worksheet in the following sequence. Each student must hand in an individual report sheet, with the name(s) of your team member(s) included:

1. Write Lewis dot structures for each molecule or molecular ion. Identify those for which resonance structures are required, and write them as well.
2. Assign formal charges to each atom. Write any non-zero formal charge near each atom to which it is assigned. Check that the charges add up to the molecular charge, if any.
3. List the total number of bonding and non-bonding electron pairs for each species, counting multiple bond pairs only once.
4. Determine and record the electron pair and the molecular geometry for the number of pairs obtained; sketch the molecule showing the location of lone pairs, using the drawings in Tables 1 and 2 for guidance; and make a model by modifying your stock by removal of atoms to indicate lone pairs.

If you have questions, ask other lab members and the instructor for help. By the end of the period you should have total comprehension of the topics covered on subsequent exams and quizzes. If allowed, take your model kit home for reference.

## MOLECULAR GEOMETRY REPORT PAGE

Name: \_\_\_\_\_

Lab Section: \_\_\_\_\_

Formula	Lewis Dot	Resonance (Y/N)	Electron Groups on Central Total / Bonding / Lone prs.	----- Geometry -----		
				Electronic	Molecular	Sketch
NO <sub>3</sub> <sup>1-</sup>		_____	_____ _____ _____	_____	_____	
<hr/>						
NF <sub>3</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						
ICl <sub>3</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						
IF <sub>5</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						

## MOLECULAR GEOMETRY REPORT PAGE

Name: \_\_\_\_\_

Lab Section: \_\_\_\_\_

Formula	Lewis Dot	Resonance (Y/N)	Electron Groups on Central Total / Bonding / Lone prs.	----- Geometry -----		
				Electronic	Molecular	Sketch
SCl <sub>6</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						
PO <sub>4</sub> <sup>3-</sup>		_____	_____ _____ _____	_____	_____	
<hr/>						
OF <sub>2</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						
CO <sub>2</sub>		_____	_____ _____ _____	_____	_____	
<hr/>						

## MOLECULAR GEOMETRY REPORT PAGE

Name: \_\_\_\_\_

Lab Section: \_\_\_\_\_

Formula	Lewis Dot	Resonance (Y/N)	Electron Groups on Central Total / Bonding / Lone prs.	----- Geometry -----		
				Electronic	Molecular	Sketch
XeF <sub>2</sub>		_____	_____ _ ____	_____	_____	
XeCl <sub>4</sub>		_____	_____ _ ____	_____	_____	
H <sub>2</sub> CO		_____	_____ _ ____	_____	_____	
SiF <sub>5</sub> <sup>1-</sup>		_____	_____ _ ____	_____	_____	

## MOLECULAR GEOMETRY REPORT PAGE

Name: \_\_\_\_\_

Lab Section: \_\_\_\_\_

Formula	Lewis Dot	Resonance (Y/N)	Electron Groups on Central Total / Bonding / Lone prs.	----- Geometry -----		
				Electronic	Molecular	Sketch
SeO <sub>2</sub>		_____	_____ _ ____	_____	_____	
SO <sub>3</sub>		_____	_____ _ ____	_____	_____	
CH <sub>3</sub> CHO (treat each C separately) (acetaldehyde)		_____	C <sub>1</sub> _____ _ ____	_____	_____	
			C <sub>2</sub> _____ _ ____	_____	_____	
SeBr <sub>4</sub>		_____	_____ _ ____	_____	_____	

**Post-Lab Assignment – Experiment 14**

Name \_\_\_\_\_

1. How do you calculate the formal charge on an atom?

2. Nitrous oxide ( $\text{N}_2\text{O}$ ) has two possible arrangements: (i) NON or (ii) NNO.

a. Complete their Lewis structures shown below.



b. Calculate the formal charge on Each Atom in Each Structure. Show all your work.

c. Which structure is the most stable? Explain clearly and specifically.

**Pre-Lab Assignment – Experiment 14**

Name \_\_\_\_\_

1. Draw the Lewis Structure for ozone, O<sub>3</sub>. Show all work including any resonance forms of ozone.

a. Electronic Geometry =

b. Molecular Geometry =

2. Draw the Lewis Structures for (a) C<sub>2</sub>H<sub>6</sub>, (b) C<sub>2</sub>H<sub>4</sub>O, and (c) CH<sub>5</sub>N. Carbon atoms are always central. Then label the electronic & molecular geometries about each of the central atoms.

(a)

(b)

(c)

C1: Electronic Geometry =

C1: Electronic Geometry =

C: Electronic Geometry =

Molecular Geometry =

Molecular Geometry =

Molecular Geometry =

C2: Electronic Geometry =

C2: Electronic Geometry =

N: Electronic Geometry =

Molecular Geometry =

Molecular Geometry =

Molecular Geometry =