CH101/105, GENERAL CHEMISTRY LABORATORY

LABORATORY LECTURE 5

EXPERIMENT 5: LEWIS STRUCTURES AND MOLECULAR SHAPES

Lecture topics

I. LEWIS STRUCTURES

a) calculation of the valence electron numbers;
b) choosing the central atom of the molecular structure;
c) how to arrange valence electrons in the octet around atoms;
d) hydrogen atoms in molecules;
e) calculation of the formal charges;
f) resonance structures;
g) Octet rule and the cases of exclusion.

II. MOLECULAR SHAPES

a) electron and molecular geometries;
b) 3-D modeling of the molecular shapes.

Report
Brief report. The report is due at the end of the lab section.Bring your molecular model kit and lab notebook: you need them to try different Lewis structures and molecular shapes for all assigned molecules.

In this lab you will investigate the Lewis structures of ten assigned molecules and construct their molecular shapes using the molecular model kit.

At this point of the course you should have all needed theoretical background on Lewis structures and 3-D molecular modeling from the lectures in CH101. Therefore, the goal of the lab lecture is to summarize all the information you already know in a short manual way, that shortly explains the "how's" and "why's" of this topic without detailed theoretical analysis.

I. HOW TO DRAW A LEWIS STRUCTURE

1. Determine the number of valence electrons for each atom in the molecule (it equals the atom's group number in the periodic table) and count the total number of valence electrons for the molecule.

2. For any molecular ion, count the additional (or subtracted) electrons. Put them on the central atom of the molecular structure.

3. Usually, the element with the largest oxidation number (+ or −) is the central atom of the molecular structure.

4. Fill the octets for all atoms, except hydrogen, boron and beryllium.

5. If several different structures are possible, choose one with the least formal charges.

6. Draw all acceptable resonance structures.

7. Check the exceptions to the octet rule in:

   a) Electron deficient compounds with B and Be atoms;

   b) Cases when atoms can exceed the octet rule (atoms from the 3-rd period or beyond).

Let's consider the applications of all these rules in examples.

I.A. Calculation of the valence electron numbers

1. H_2O

H (Group I, 1e); O (Group VI, 6e)

Total number of valence electrons = 2x1 + 6 = 8

2. CO_2

C (Group IV, 4e); O (Group VI, 6e)

Total number of valence electrons = 4 + 2x6 = 16

3. NO^+

N (Group V, 5e); O (Group 6, 6e); NO^+ is a positive ion with the charge +1, so we need to subtract one electron from the sum of all valence electrons:

Total number of valence electrons = 5 + 6 − 1 = 10

4. ICl_4^-

I (Group VII, 7e); Cl (Group VII, 7e); ICl_4^- is a negative ion with the charge -1, so we need to add one electron to the sum of all valence electrons:

Total number of valence electrons = 7 + 4x7 + 1= 36

5. XeF_5^+

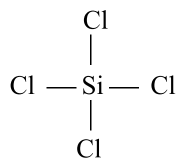
Xe (Group VIII, 8e); F (Group VII, 7e); Positive ion → subtract one electron:

Total number of valence electrons = 8 + 5x7 − 1 = 42

I.B. The problem of the central atom in the molecular structure

1. $SiCl_4$

Which atom is the central one? Should the structure of $SiCl_4$ have the form



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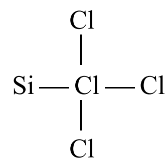

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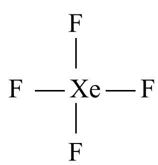
Let us check the oxidation numbers. The oxidation number for Cl is -1. Total charge of the molecule = 0 (it is neutral). So, the oxidation number of Si is : $0 - (-4) = +4$. It is larger than the oxidation number of Cl; therefore, it indicates that Si is the central atom of the molecular structure.

2. XeF_4. Which atom is the central atom of the molecular structure: Xe or F?



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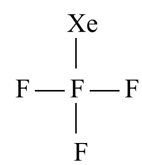

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Check the oxidation numbers. It is -1 for fluorine; XeF_4 is a neutral molecule, so the oxidation number for Xe: $0 - (-4) = +4$. It is larger for Xe, so Xe is the central atom in the molecular structure.

I.C. How to arrange valence electrons in the octet around atoms

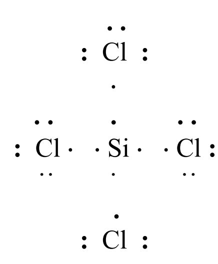
1. Lewis structure of $SiCl_4$.

We already know that Si is the central atom in the structure (see above). Let us try to arrange an octet of electrons around each atom in the molecule.

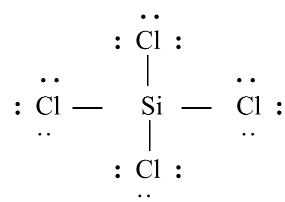
1-st step: Calculate the number of the valence electrons in each atom of the molecule.

Si (Group IV, 4e), Cl (Group VII, 7e).

2-nd step: Arrange all valence electrons of the atom around it.



3-rd step: Use one electron from Cl and one from Si to construct a single bond for each side of Si. All atoms will satisfy the octet rule.

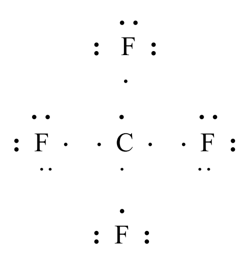


2. Lewis structure of CF_4.

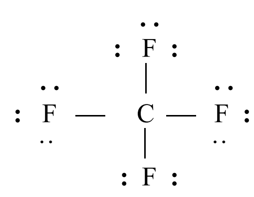
First, we need to decide which atom is the central one. Count the oxidation numbers of the atoms. For fluorine it is −1; CF_4 molecule is neutral, therefore, the oxidation state of carbon is + 4. It is larger for fluorine, so carbon is the central atom in the molecular structure.

1-st step: Count the number of the valence electrons in the atoms. C (Group IV, 4e); F(Group VII, 7e).

2-nd step: Arrange all these electrons around their atoms:



3-rd step: Use one electron from the F atom and one from the C atom to construct a single bond for each side of the carbon atom C. All atoms satisfy the octet rule.



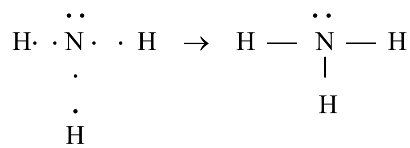
I.D. Hydrogen atoms in molecules

1. H_2 (hydrogen molecule)

H (Group 1, 1e). Lewis structure: H· · H or H — H; No octet rule (hydrogen does not have enough electrons to satisfy the octet rule).

2. NH_3 (ammonia)

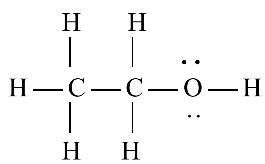
N(Group V, 5e), H(Group 1, 1e). Oxidation numbers: H : +1, N : –3. So, nitrogen is the central atom in the molecular structure.



Octet for the nitrogen atom. No octet for the hydrogen atoms.

3. C_2H_5 0H (ethanol).

In complex molecules hydrogen atoms are usually the terminal atoms.



As you can see from the Lewis structure of ethanol, there are octets around carbon and oxygen atoms, but no octets for hydrogen atoms.

I. E. Formal charges.

When drawing Lewis structures, it is possible to come up with more than one arrangement of atoms, bonds and lone pairs of electrons that satisfy the octet rule. How can you check which one is the preferred Lewis structure?

Usually it helps to assign formal charges to the atoms using the following formula:

$$\begin{array}{l}\text{Formal charge}\\ \text{of the atom}\end{array} = \left(\begin{array}{l}\text{Number of valence}\\ \text{electrons in}\\ \text{the free atom}\end{array}\right) - \left(\begin{array}{c}\text{Total number of}\\ \text{lone-pair electrons}\end{array}\right) - (1/2)\cdot\left(\begin{array}{c}\text{Total number of}\\ \text{shared electrons}\end{array}\right)$$

Formal charge assignment is an electron bookkeeping system. The formal charges do not necessarily represent the actual charges on the atoms. But they are very helpful when you need to choose between two probable Lewis structures of the same molecule.

THE PREFERABLE LEWIS STRUCTURE WILL BE THE ONE WITH THE LEAST FORMAL CHARGES.

<u>EXAMPLES.</u>

1. H_2O_2 (Hydrogen peroxide).

H (Group 1, 1e); O (Group VI, 6e). Total number of electrons = 2x1 + 2x6= 14

Lewis structure:

a) 1-st variant H — O — O — H 14e; Octet for all oxygen atoms.

b) 2-nd variant (H)(H) > O — O : 14e; Octet for all oxygen atoms.

Question: Which variant is the real molecular structure of hydrogen peroxide? To find the answer, let us calculate the formal charges for each molecular structure variant.

<u>1-st variant</u> H — O — O — H

$Z_H = 1 – 1/2x2 =0$ $Z_O = 6 – 4 –1/2x4 = 0$ $Z_H = 1 – 1/2x2= 0$

All formal charges are zero in this molecular structure.

<u>2-nd variant</u> (H)(H) > O — O : Two oxygen atoms have formal charges.

$Z_H= 1–1/2x2 = 0$ $Z_O = 6 – 2 – 1/2x6 = + 1$ $Z_H = 6 – 6 –1/2x2 = –1$

Now we can see that the first variant is the preferred molecular structure because the formal charges are zero for all atoms. Experiments confirm this conclusion: the real molecular structure of hydrogen peroxide is the first one.

I.F. Resonance molecular structures.

For many molecules and ions, we can draw two or more satisfactory Lewis structures with no difference between them from the point of view of formal charge. How should we choose the right structure in this case? Let us discuss it with the following example: NO_2^- ion.

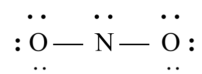
<u>Total number of valence electrons in neutral NO_2 molecule:</u>

N: (Group V, 5e); O: (Group VI, 6e). 5e + 2x6e +1e (it is a negative ion) =18e

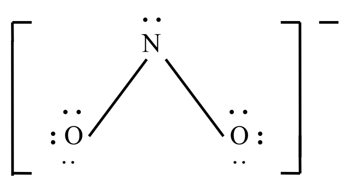
<u>Oxidation numbers</u>. First consider the neutral molecule NO_2. It has an oxidation number of –2 for oxygen atoms; the total charge of NO_2 is zero, so the oxidation number for the nitrogen atom is +4.

| +4 | > | –1|, so the nitrogen atom is the central atom of the NO_2 molecular structure.

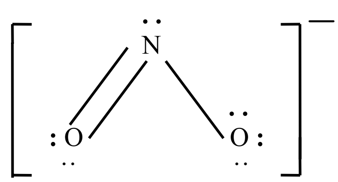
<u>Octet assignment</u>. Put the additional electron (NO_2^- is a negative ion!) on the central atom.



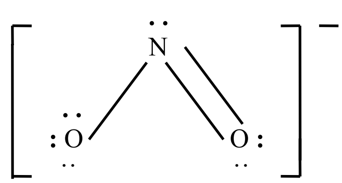
<u>Draw the molecular structure</u> using the concept of VSEPR theory about electron-electron repulsion.
For example, as a beginning structure to consider, we can draw



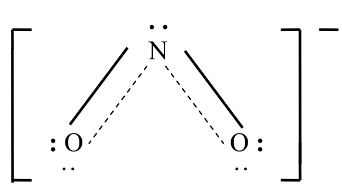
It is not the best possible structure because we don't have an octet of electrons around nitrogen atom. So, let us take two electrons from the oxygen atom and use them to construct a double bond between the oxygen and nitrogen atoms.



As you can see, the last structure is much better because it has an octet around all atoms. Nevertheless, there is a real problem with it: why should this double bond be mandatory at the left side of the structure? Can it be at the right side? Of course: there is nothing special about left or right sides. Let us do it:



Actually, we can not choose between these two structures: there is no preference between them. So, in reality, both of them can exist simultaneously. That is why the real molecular structure of the NO_2^- ion has the features of both of these structures and is represented as:



Thus, in reality the molecular structure of the NO_2^- ion does not have double or single bonds between the oxygen and nitrogen atoms. It has two bonds that are averaged between single and double bonds (dotted lines in the last structure). These kind of structural effects are called **resonance molecular structures**.

I.G. Atoms that exceed the octet rule

Exceeding of the octet rule is observed only for the elements in period 3 and beyond. These elements will usually be the central atoms of the molecular structure, with the number of valence electrons more than eight. All "extra" electrons can be arranged as lone pairs around these elements. This sort of valence electrons arrangement is called an **expanded electron shell.** Let us consider this effect in examples.

Examples.

1. $RnCl_2$.

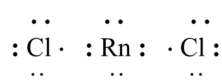
Number of valence electrons.

Rn (Group VIII, 8e), Cl (Group VII, 7e). So, the total number of valence electrons is: 8e + 2x7e=22e.

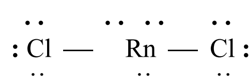
Oxidation numbers

Cl: always −1; the $RnCl_2$ molecule is neutral, so the oxidation number of Rn is 0 − (−2) = + 2. It is larger than for the chlorine atom, so radon is the central atom in the molecular structure.

Lewis structure

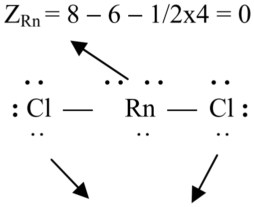


Let us use one electron from the chlorine atom and one from the radon atom to arrange single bonds between them:



Formal charges

$Z_{Rn} = 8 - 6 - 1/2x4 = 0$



$Z_{Cl} = 7 - 6 - 1/2x2 = 0$

Therefore, all formal charges are zero: the molecular structure is quite good. But notice: there is no octet rule around the radon atom. We can do it with radon because this is an element of the sixth period; it can have an expanded valence shell.

WHEN YOU NEED TO EXCEED THE OCTET RULE, PLACE THE EXTRA ELECTRONS ON THE CENTRAL ATOM OF THE MOLECULAR STRUCTURE

II. MOLECULAR SHAPES

II. A. Electron and molecular geometries

The basic mechanism behind the forming of molecular shapes is the electron pairs' repulsion that happens because all electron pairs in atoms have the same (negative) charge. Shared and lone electron pairs in molecules repel each other and try to find such a configuration in space that allows them to be as much apart as they can. Nuclei of atoms (which are charged positively) also repel each other, but attract all electron pairs back. As a result of this repulsion/attraction process, all atoms along with shared and lone electron pairs in the molecules arrange themselves in several very stable geometrical structures with minimal repulsion, called **molecular shapes**. These molecular shapes may have relatively simple geometry and be in a plane (as linear, angular, triangle or square planar molecular shapes are) or they may have much more complicated forms (as, for example, tetra- or octahedron or square bipyramid).

It is very important to mention that there are two kinds of geometry in molecules. One is the electron pairs' geometry. It depends on the number of all electron pairs (shared and lone) in the molecule. Each lone electron pair, and each single, double or triple bond in the molecule can be considered as one "stick" in the frame of the electron geometry. Using this idea, we can transform the Lewis structure of bonds around each central atom into the 3-dimensional construction of sticks attached to this atom. This kind of molecular construction can be called the **electron pairs' geometry of the molecule**.

The form of the molecular shape depends on the situation at the distant ends of these "sticks". If the molecule has atoms on all these ends, molecular shape around the central atom will be just the same as determined by electron geometry. But in cases when some distant ends of the sticks are empty (which means a lone electron pair), the molecular shape will be different. It will be simpler, because we don't need to consider these empty sticks with lone electron pairs as part of the molecular shape. So we can say that molecular shape is based on the same frame as electron pairs' geometry, but can be the same or simpler than the later because of the presence or absence of lone electron pairs around the central atom of the structure.

To illustrate this idea, let us consider a central atom with three electron pairs around it. Because of the central symmetry, it is obvious that all electron pairs repel each other in such a way that they will arrange themselves in the trigonal planar form (if we connect all distant ends of the bonds):

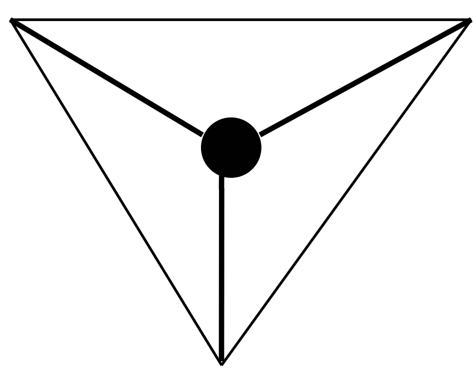


Fig.1. The spatial geometry of three electron pairs bonded to the central atom in the molecular structure.

What will be the molecular shape of this Lewis structure? To answer this question we need to consider three different variants.

A)

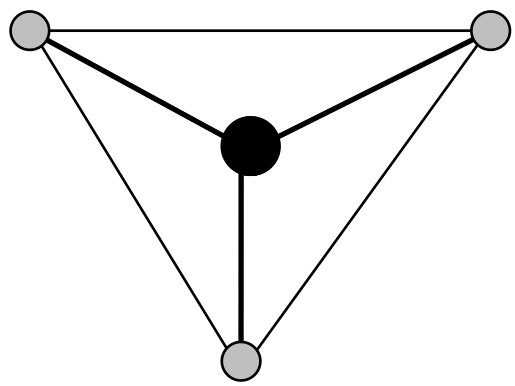


Fig. 2. All electron pairs in the molecular structure are bonded to atoms.

As you can see from Fig. 2, the molecular shape of the given structure has the same form as the electron geometry: it is also trigonal planar.

B)

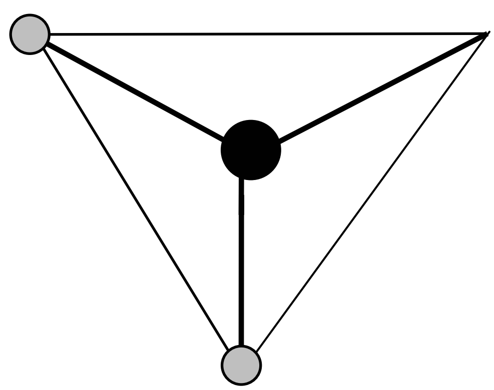


Fig. 3. Only two electron pairs attached to the central atom in the molecule are bonded to atoms. One additional "stick" is a lone electron pair.

As it follows from Fig.3, the molecular structure around the central atom now has a different (and simpler) **bent** form. The electron geometry is still the same - trigonal planar.

C)

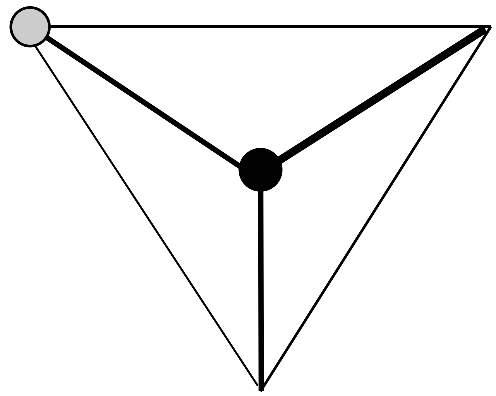


Fig. 4 Only one electron pair attached to the central atom in the molecule is bonded to the atom. Two additional "sticks" are the lone electron pairs.

As it follows from the Fig. 4, the molecular structure around the central atom now has the simplest form: it is **linear**. **Notice that the electron geometry is still the same: it is trigonal planar.**

As you can see from this simple example, the electron pairs' geometry represents the "frame" of the molecular shape. The form of this "frame" depends on the so called **steric number** of the central atom, which is the total number of electron pairs "connected" to the central atom in the molecular structure:

Steric number, S = The number of atoms bonded to the central atom, N_A + The number of lone pairs on the central atom, LP

Below in Table 1 and Fig.5 you will find the list of all possible molecular shapes and their 3-dimensional drawings that correspond to the given combination of the steric number and the given number of atoms bonded to the central atom in the molecular structure.

II.B. 3-D modeling of the molecular structures

Let's formulate a short manual way how to use Lewis structures for the molecular shape determination.

1. Draw the Lewis structure of the molecule.
2. For each central atom count the steric number S and the number of atoms N_A bonded to it.
3. Use the steric number S to find the **electron's geometry** around the given central atom from Table 1.
3. Use the combination of S and N_A numbers to find the **molecular shape** around the given central atom (see **Table 1 of molecular shapes** and its **3-D drawing** in Fig.5 below).

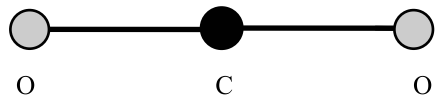
Let's do several examples of 3-D modeling for different molecular structures.

1. Carbon dioxide, CO_2

Lewis structure: $\ddot{\underset{..}{O}} = C = \ddot{\underset{..}{O}}$

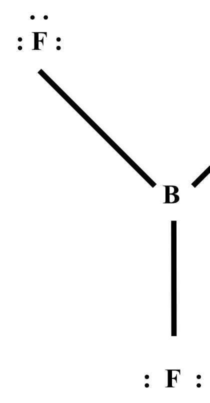
For the central atom C: Steric number: S= 2; The number of atoms bonded to the central atom, N_A = 2;
The molecular shape based on the combination of S=2; N_A =2 (see table 1): **Linear.**

3-D drawing of the molecular shape (see Fig 5):



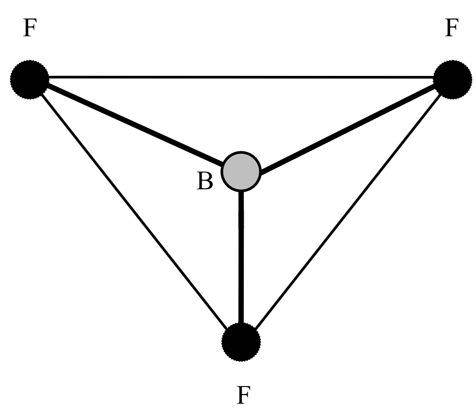
2. Boron trifluoride, BF_3.

Lewis structure:



Steric number: S=3; The number of atoms bonded to the central atom: N_A = 3. The molecular shape based on the combination of S=3, N_A =3 (see table 1): **Trigonal planar.**.

3-D drawing of the molecular shape (see Fig 5):



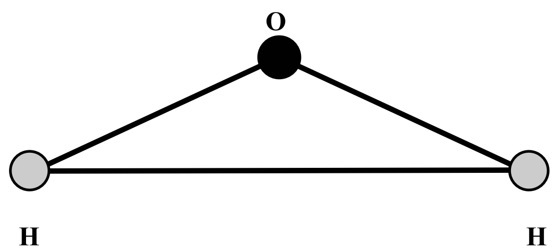
3. Water, H_2O.

Lewis structure:

.. ..
H — O — H

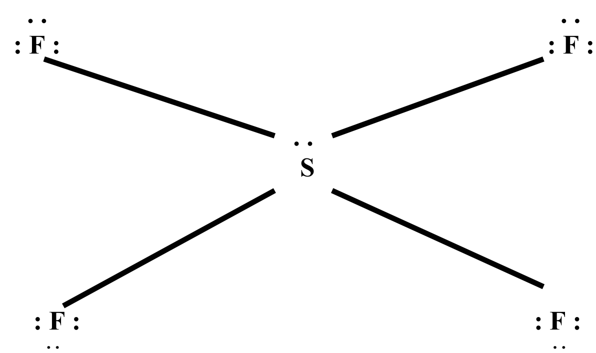
Steric number: S = 4; The number of atoms bonded to the central atom: N_A = 2. The molecular shape based on the combination of S=4; N_A =2 (see table 1): **Angular (bent)**

<u>3-D drawing of the molecular shape</u> (see Fig 5):



4. Sulfur tetrafluoride, **SF_4.**

Lewis structure:



Steric number: S = 5; The number of atoms bonded to the central atom: N_A = 4. The molecular shape based on the combination of S=5; N_A =4 (see table 1): **See-saw**.

<u>3-D drawing of the molecular shape (see Fig 5)</u>:

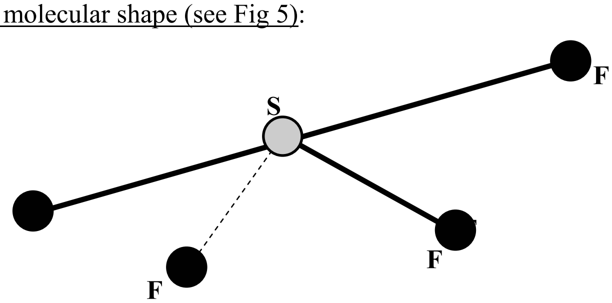
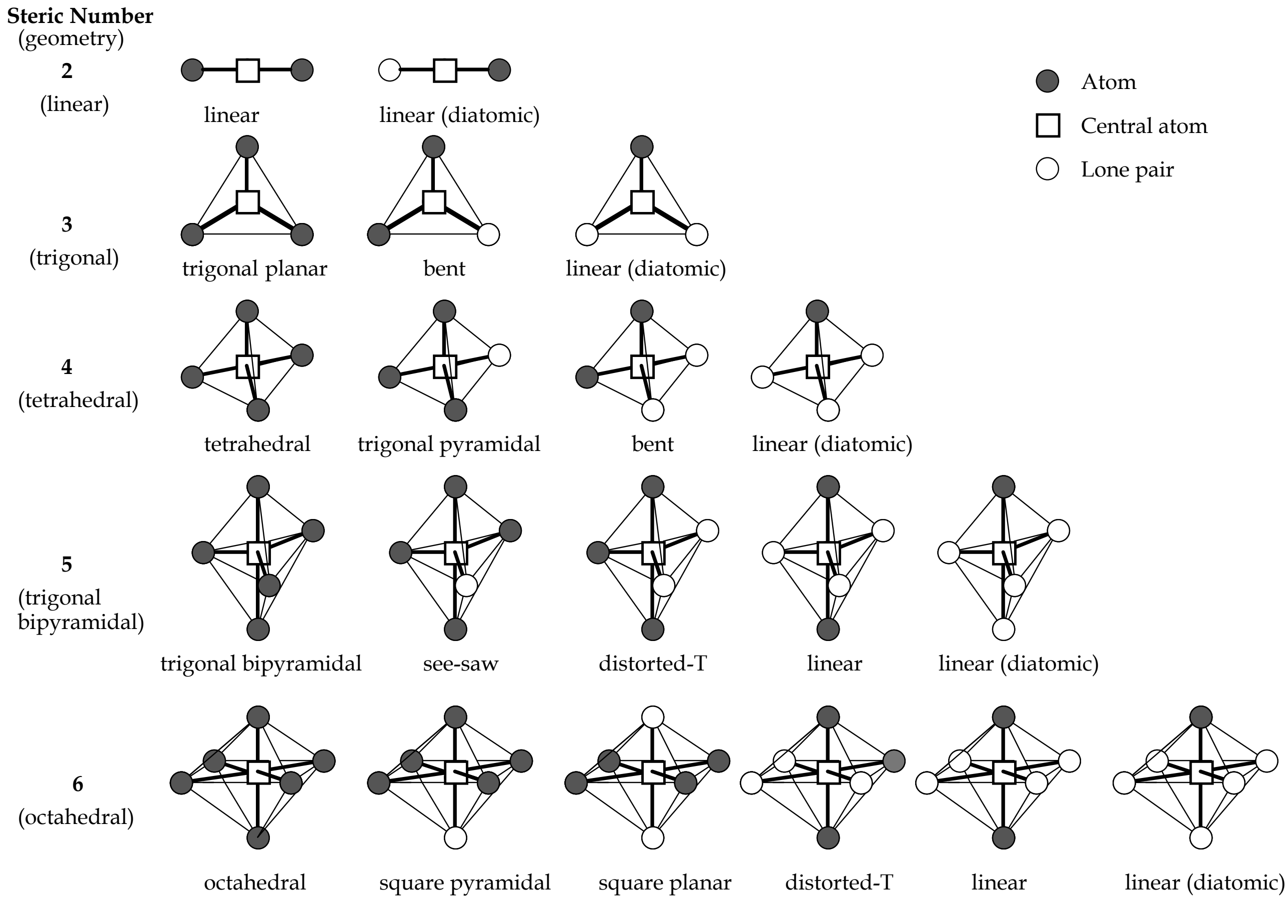


TABLE 1. LIST OF MOLECULAR SHAPES

Steric Number S (Electron's geometry)	The number of atoms bonded to the central atom, N_A	The combination S/N_A	SHAPE OF MOLECULE
2 (LINEAR)	1	2/1	LINEAR (DIATOMIC)
	2	2/2	LINEAR
3 (TRIGONAL PLANAR)	3	3/3	TRIGONAL PLANAR
	2	3/2	ANGULAR (BENT)
	1	3/1	LINEAR (DIATOMIC)
4 (TETRAHEDRAL)	4	4/4	TETRAHEDRAL
	3	4/3	TRIANGULAR PYRAMIDAL
	2	4/2	ANGULAR (BENT)
	1	4/1	LINEAR (DIATOMIC)
5 (TRIGONAL BIPYRAMIDAL)	5	5/5	TRIANGULAR BIPYRAMIDAL
	4	5/4	SEE-SAW
	3	5/3	DISTORTED T-SHAPE
	2	5/2	LINEAR
	1	5/1	LINEAR (DIATOMIC)
6 (OCTAHEDRAL)	6	6/6	OCTAHEDRAL
	5	6/5	SQUARE PYRAMIDAL
	4	6;4	SQUARE PLANAR
	3	6/3	DISTORTED T-SHAPE
	2	6/2	LINEAR
	1	6/1	LINEAR (DIATOMIC)



Steric Numbers, Geometries and the Shapes of Molecules

Fig.5. 3-D drawing of molecular shapes

CH 101/105, GENERAL CHEMISTRY LABORATORY

LABORATORY EXPERIMENT #5:

LEWIS STRUCTURES AND MOLECULAR SHAPES

Name:____

ID#:____

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SECTION/Day/ Time:__________________________________

BOSTON UNIVERSITY

III. DETAILS OF THE LABORATORY

You will be asked to determine the Lewis structures of **any ten** molecular particles from the list of molecular species (see below), the molecular shapes around each central atom of the molecular structure, and construct 3-dimensional models of the structures using the molecular model kit, Table of molecular shapes, and Fig 5 with 3-D drawings of all possible molecular shapes. You will also be asked to draw 3-D schemes of these molecular structures. All this work has to be done in the worksheets provided below. **The lab report is due at the end of the laboratory period.**

NOTICE FOR YOUR LAB REPORT:

a) In case the molecular structure has several central atoms, indicate the molecular shapes around each of them.

b) For the molecules marked **bold** in the table answer the question about their permanent dipole moment. Write your answer in the worksheet's table as **$D \neq 0$** (if you think the molecule has nonzero dipole moment) or **$D=0$** (for the molecule with zero dipole moment).

LIST OF MOLECULAR SPECIES									
SiO_4^{4-}	NO_3^-	HNO_3	**SF_6**	**BrF_5**	$SiCl_4$	**H_2CO**	C_4H_8O	$CHCl_3$	C_5H_{10}
I_3^-	ICl_2^+	NO_2^-	**BeF_2**	XeF_5^+	$SbCl_5$	**ClF_3**	**D_2O**	$CH_3CH_2CO_2^-$	C_6H_{12}
O_3	NH_4^+	ClF_5	**NOF**	C_3H_5Cl	**PCl_3**	SbF_5	XeF_2	CCl_4	**C_2H_6**
PCl_6^-	**SF_2**	**NO_2F**	**SO_2**	H_3O^+	**BCl_3**	$TeCl_4$	C_3H_8O	**OF_2**	C_6H_6
$AlCl_3$	**BF_2^+**	**SF_5Cl**	CH_3NH_2	$HCOOH$	CCl_2F_2	CH_4O	C_2H_4	**$BFCl_2$**	**NH_3**

LEWIS STRUCTURES AND MOLECULAR SHAPES: WORKSHEETS

1.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

2.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

3.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

4.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

5.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

6.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

7.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

8.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or $=0$?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

9.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or =0 ?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom

10.

Lewis structure:

Central atom	Steric number, S	# of atoms bonded to the central atom, N_A	**Molecular shape**	Dipole moment, D ($\neq 0$ or =0 ?) (only for molecules marked bold)

3-D drawing of the molecular shape around each central atom