THE STRUCTURE OF MOLECULES
AN EXPERIMENT USING MOLECULAR MODELS

In a footnot to a 1857 paper, Friedrich August Kekulé suggested that carbon was *tetratomic*, that is, carbon has a valence of 4. In 1858, Kelkulé stated

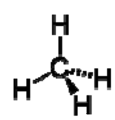
> "*When the simplest compounds of this element are considered (marsh gas, methyl chloride, chloride of carbon, chloroform, carbonic acid, phosgene, sulphide of carbon, hydrocyanic acid, etc.) it is seen that the quantity of carbon which chemists have recognized as the smallest possible, that is, as an atom, always unites with 4 atoms of a monoatomic or with 2 atoms of a diatomic element; that in general the sum of the chemical units of the elements united with one atom of carbon is 4. This leads us to the view that carbon is tetratomic or tetrabasic.*
>
> *In the cases of substances which contain several atoms of carbon, it must be assumed that at least some of that atoms are in the same way held in the compound by the affinity of carbon, and the carbon atoms attach themselves to one another,…*"

As early as 1870, graphic formulas of carbon compounds were drawn as shown:

$$\text{Methane}\quad \begin{array}{c} H \\ | \\ H{-}C{-}H \\ | \\ H \end{array} \qquad\qquad \text{ethylene}\quad \begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

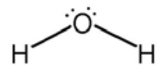
These drawings imply that the atom-atom linkages, indicated by valence strokes, lie in plane.

In 1874, Jacobus Henricus van 't Hoff and Joseph Achille LeBel, independently, proposed that the four bonds of carbon were arranged three dimensionally, pointed toward the corners of a tetrahedron. The tetrahedral carbon atom is sometimes referred to as the *Van't Hoff-Le Bel theory*. The three-dimensional structure of methane can be represented by a diagram known as a Fischer projection:



The physical significance of the chemical linkages between atoms, expressed by the lines or valence strokes in molecular structure diagrams, became evident soon after the discovery of the electron. In 1916 in a classic paper, G. N. Lewis suggested, on the basis of chemical evidence, that the single bonds in graphic formulas involve two electrons and that an atom tends to hold eight electrons in its outermost or valence shell.

Lewis' proposal that atoms generally have eight electrons in their outer shells is known as the *octet rule*. It can be applied to many atoms, but is particularly important in the treatment of covalent compounds of atoms in the second and third rows of the Periodic Table. For atoms such as carbon, oxygen, nitrogen, and fluorine, the eight valence electrons occur in pairs that occupy tetrahedral positions around the central atom core. Some of the electron pairs do not participate directly in chemical bonding and are called **unshared or nonbonding pairs**; however, the structures of compounds containing such unshared pairs reflect the tetrahedral arrangement of the four pairs of valence shell electrons. In the H_2O molecule, which obeys the octet rule, the four pairs of electrons around the central oxygen atom occupy essentially tetrahedral positions; there are two unshared nonbonding pairs and two bonding pairs that are shared by the O atom and the two H atoms. The H —O—H bond angle is nearly but not exactly tetrahedral since the properties of shared and unshared pairs of electrons are not exactly alike.



Essentially, all organic molecules obey the octet rule, and so do most inorganic molecules and ions. For species that obey the octet rule it is possible to draw electron-dot, or Lewis, structures. The drawing of the H_2O molecule, above, is an example of a Lewis structure.

In a Lewis structure there are eight electrons around each atom (except for H atoms, which always have two electrons) Group 2A atoms which form 2 bonds have 4 electrons and Group 3A atoms which form 3 bonds have 6 electrons.

There are two electrons in each bond (designated by a line).

When counting electrons in these structures, one considers the electrons in a bond between two atoms as belonging to the atom under consideration. Thus, electrons may be counted twice, once for each atom in the bond.

The bonding and nonbonding electrons in Lewis structures are all from the *outermost* shells of the atoms involved, and are the so-called valence electrons of those atoms.

For the main group elements, the number of valence electrons in an atom is equal to the group number of the element in the Periodic Table. Hydrogen in Group 1 has one valence electron, carbon, in Group 4, has four valence electrons, and chlorine, in Group 7, has seven valence electrons.

In an octet rule structure the valence electrons from all the atoms are arranged in such a way that each atom, except hydrogen and the Group 2 and Group 3 atoms, have eight electrons.

Construction of an octet rule structure for a molecule can be accomplished by counting the number of electrons. Using water as an example, an oxygen atom has six valence electrons (Group 6) and a hydrogen atom has one, the structure would need one O and two H atoms have a total of eight valence electrons; the octet rule structure for H_2O can be observed in the structure shown earlier. Structures like that of H_2O, which involve only single bonds and nonbonding electron pairs, are common. Sometimes, however, there is a "shortage" of electrons; that is, it is not possible to construct an octet rule structure in which all the electron pairs are either in single bonds or are nonbonding pairs. Ethene or ethylene, C_2H_4, is a typical example of such a species. In such cases, octet rule structures can often be made in which two atoms are bonded by two electron pairs, rather than one pair. The two pairs of electrons form a double bond. In the C_2H_4 molecule, shown below, the C atoms each get four of their electrons from the double bond. The assumption that electrons behave this way is supported by the fact that the C=C double bond is both shorter and stronger than the C—C single bond in the C_2H_6 molecule. Double bonds, and triple bonds, occur in many molecules, usually between C, O, N, and/or S atoms.

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                     H   H
                     |   |
Ethene or ethylene   C = C
                     |   |
                     H   H
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Lewis structures can be used to predict molecular and ionic geometries by assuming that the four pairs of electrons around each atom are arranged tetrahedrally. This is the method used to determine the geometry for H_2O. In the C_2H_4 molecule, the shape around each carbon atom is triangular (or trigonal) planar. (The two bonding pairs in the double bond are not lined up between the two nuclei, but are spread out in space above and below the plane of the molecule). In describing molecular geometry we indicate the positions of the atomic nuclei, not the electrons.

The idea of a correlation between molecular geometry and number of valence electrons (both shared and unshared) was first presented in 1940 by Sidgwick and Powell. In 1957, R. J. Gillespie and R. S. Nyholm refined this concept to build a more detailed theory capable of choosing between various alternative geometries. This theory is known as the Valence Shell Electron Repulsion Theory (VSEPR).

The VSEPR theory assumes

1. The electron pairs in the valence shell of a central atom repel each other.
2. The electron pairs occupy positions in space that minimize repulsions and maximize the distance of separation between them. (i.e., they are as far away from each other as possible)
3. The valence shell is treated as a sphere with electron pairs spread out on the spherical surface at maximum distance from one another.
4. A multiple bond is treated as if it is a single electron pair for determining the molecular geometry. There are some additional effects of the two or three electron pairs of a multiple bond on the actual bond angles.
5. Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.

Three types of repulsion take place between the electrons of a molecule:

1. The lone pair-lone pair repulsion
2. The lone pair-bonding pair repulsion
3. The bonding pair-bonding pair repulsion.

The VSEPR shapes for compounds formed from Group 2 to Group 6 atoms are given in Table 1

In addition to the common VSEPR shapes for the Group 5 and Group 6 elements, these elements may form structures that violate the octet rule by having 5 or 6 bonds to the central atom. Some examples of these molecules are given in Table 2.

It is also possible to predict polarity from Lewis structures. Polar molecules have their center of positive charge at a different point than their center of negative charge. This separation of charges produces a dipole moment in the molecule. Covalent bonds between different kinds of atoms are polar; all heteronuclear diatomic molecules are polar. In some symmetrical molecules the polarity from one bond may be canceled by that from others. Carbon dioxide, CO_2, which is linear, is a nonpolar molecule. Methane, CH_4, and carbon tetrachloride, CCl_4 which are tetrahedral, are also nonpolar. Non-symmetrial molecules such as CH_3Cl will be polar. Molecules with nonbonded electron pairs on the central atom are usually polar.

Although the conclusions we have drawn regarding molecular geometry and polarity can be determined from a combination of VSEPR shapes and Lewis structures , it is much easier to draw such conclusions by constructing models of molecules and ions. Models tend to be easier to construct than the drawings of Lewis structures on paper. In addition, the models are three-dimensional and are much more representative of the actual species. Using the models, it is relatively easy to see both geometry and polarity, as well as to deduce Lewis structures. In this experiment you will assemble models for a number of common chemical species and interpret them in the ways we have discussed.

Table 1. VSEPR shapes of molecules formed from Group 2 to Group 6 atoms

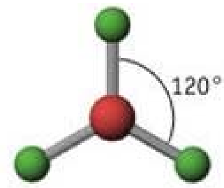
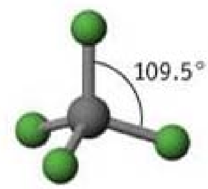
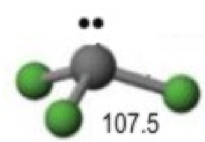
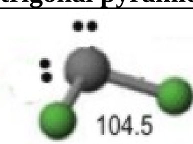
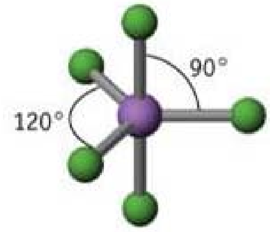
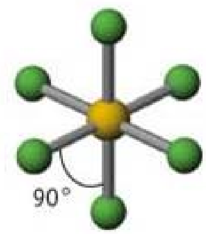
Periodic Group	Example	No. of bonded electron pairs	No. of nonbonded electron pairs	Shape	Other compounds with similar shapes
Group 2A	$BeCl_2$	2	0	 **linear**	$Mg\ Cl_2$ $CaBr_2$ SrI_2 $BaCl_2$
Group 3A	BCl_3	3	0	 **trigonal planar**	$AlCl_3$
Group 4A	CH_4	4	0	 **tetrahedral**	CCl_4 $SiCl_4$ $SnBr_4$ PbI_4
Group 5A	NH_3	3	1	 **trigonal pyramid**	PCl_3 $AsBr_3$ SbI_3
Group 6A	H_2O	2	2	 **bent**	H_2S H_2Te

Table 2. VSEPR shapes of molecules formed from Group 5 and Group 6 atoms which violate the octet rule. Note: Only the main shapes are shown.

Periodic Group	Example	No. of bonded electron pairs	No. of nonbonded electron pairs	Shape	Other compounds with similar shapes
Group 5A	PCl_5	5	0	 **trigonal bipyramid**	$SbCl_5$ AsI_5
Group 6A	SF_6	6	0	 **octahedral**	$Te(OH)_6$

Construction of Molecular Models

Materials Needed

Molecular model kit

Safety

There are no safety precautions needed for this experiment

Disposal

There are no disposal of materials in this experiment

Experimental Procedure

The models used in this experiment consist of pre-drilled wooden balls, two different length wood sticks, and springs. The balls represent atoms and the sticks and springs represent electron pairs or chemical bonds and fit in the holes in the wooden balls. Together, a model (molecule or ion) consists of wooden balls (atoms) connected by sticks or springs (chemical bonds). Some sticks may be connected to only one atom (nonbonding pairs).

Although the wood balls may be used to represent a number of different atoms, common atoms are depicted by the colors as listed in Table 3.

Table 3. Molecular Models and Color Coding		
Atom	**Color**	**No. of Valence Electrons**
Hydrogen	Yellow or White	1
Carbon	Black	4
Nitrogen	Blue	5
Oxygen	Red	6
Chlorine	Green	7
Bromine	Orange or Brown	7
Iodine	Purple	7

In this experiment we will deal with atoms that obey the octet rule: such atoms have four electron pairs around the central core and will be represented by balls with four tetrahedral holes in which there are four sticks or springs. The only exception will be hydrogen atoms, which share two electrons in covalent compounds, and which are represented by balls with a single hole in which there is a single stick.

In assembling a molecular model of the kind we are considering, we will proceed in a systematic manner. We will illustrate the recommended procedure by developing a model for a molecule with the formula CH_2O.

1. Determine the total number of valence electrons in the species:

   The number of valence electrons on an atom is equal to the number of the group to which the atom belongs in the Periodic Table. For CH_2O,

   C Group 4 H Group I O Group 6

   Therefore each carbon atom in a molecule or ion contributes four electrons, each hydrogen atom one electron, and each oxygen atom six electrons.

   The total number of valence electrons equals the sum of the valence electrons on all of the atoms in the species being studied. For CH_2O this total would be

   $4 + (2 \times 1) + 6$, or 12 valence electrons.

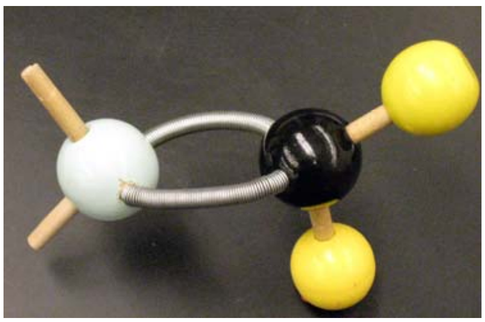
   If we are working with an ion, we **add one electron for each negative charge** or **subtract one electron for each positive charge** on the ion.

2. Select wooden balls and sticks to represent the atoms and electron pairs in the molecule. You should use four-holed balls for the carbon atom and the oxygen atom, and one-holed balls to represent the hydrogen atoms. Since there are 12 valence electrons in the molecule and electrons occur in pairs, you will need six sticks to represent the six electron pairs. The sticks will serve both as bonds between atoms and as nonbonding electron pairs.

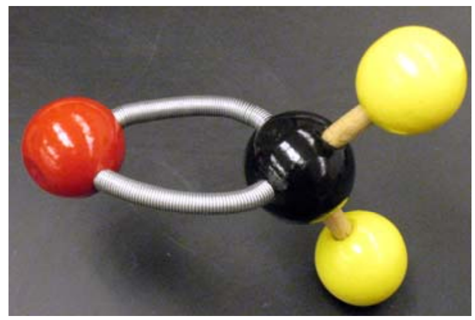
3. The central atom in the molecule is the one with the lowest electronegativity, that is, the one located farthest to the left on the periodic table. Look at the VSEPR structures in Table 1 to see the shape of bonds around the central atom.

4. Connect the balls with some of the sticks. (Assemble a skeleton structure for the molecule, joining atoms by single bonds.) In some cases this can only be done in one way. Usually, however, there may be more than one possibility, some of which are more reasonable than others. In CH_2O, the model can be assembled by connecting the two H atom balls to the C atom ball with two of the available sticks, and then using a third stick to connect the C atom and O atom balls.

5. The next step is to use the sticks that are left over in such a way as to fill all the remaining holes in the balls. (Distribute the electron pairs so as to give each atom eight electrons and to satisfy the octet rule.) In the model we have assembled, there is one unfilled hole in the C atom ball, three unfilled holes in the O atom ball, and three available sticks. A way to meet the required condition is to use two sticks to fill two of the holes in the O atom ball and the open hole in carbon. To do this, you will need to use two springs instead of two sticks to connect the C atom and O atom balls. The model, as completed, is shown below:

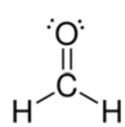


This model uses a blue wood ball to represent the oxygen atom. The two sticks represent nonbonded electron pairs



This model uses a red ball to represent the oxygen atom. There are only two holes in the red ball, so the nonbonded electron pairs are not represented

6. Interpret the model in terms of the atoms and bonds represented. The sticks and spatial arrangement of the balls will closely correspond to the electronic and atomic arrangement in the molecule. Given our model, we would describe the CH_2O molecule as being planar with single bonds between carbon and hydrogen atoms and a double bond between the C and O atoms. The H—C—H angle is approximately tetrahedral. There are two nonbonding electron pairs on the O atom. Since all bonds are polar and the molecular symmetry does not cancel the polarity in CH_2O, the molecule is polar. The Lewis structure of the molecule is given below:



This compound is called formaldehyde or methanal.

7. Investigate the possibility of the existence of isomers or resonance structures. It turns out that in the case of CH_2O one can easily construct an isomeric form that obeys the octet rule, in which the central atom is oxygen rather than carbon. It is found that this isomeric form of CH_2O does not exist in nature. As a general rule, carbon atoms almost always form a total of four bonds; put another way, nonbonding electron pairs on carbon atoms are very rare. Another useful rule of a similar nature is that if a species contains several atoms of one kind and one of another, the atoms of the same kind will assume equivalent positions in the species. In SO_4^{2-}, for example, the four O atoms are all equivalent, and are bonded to the S atom and not to one another.

8. Resonance structures are reasonably common. For resonance to occur, however, the atomic arrangement must remain fixed for two or more possible electronic structures. For CH_2O there are no resonance structures.

Using the procedure outlined, construct and report on models of the molecules in the table on the following pages. Draw the complete Lewis structure for each molecule, showing nonbonding as well as bonding electrons. Given the structure, describe the geometry of the molecule or ion, and state whether the species is polar. Finally, draw the Lewis structures of any likely isomers or resonance forms.

Name ____ **Date** _______________

Report: Structure of Molecules Using Molecular Models

Molecule	**Lewis Structure (Draw the structure)**	**Molecular Geometry: (Tell shape)**	**Is this molecule polar? EXPLAIN**	**Does this molecule have any isomers or resonance structures? If yes, draw them**
Methane CH_4				
Dichloro methane CH_2Cl_2				
Nitrogen N_2				
Oxygen O_2				
Water H_2O				
Hydronium ion H_3O^+				

Molecule	Lewis Structure (Draw the structure)	Molecular Geometry: (Tell shape)	Is this molecule polar? EXPLAIN	Does this molecule have any isomers or resonance structures? If yes, draw them
Hydrogen peroxide H_2O_2				
Carbon dioxide CO_2				
Hydrofluoric acid HF				
Ammonia NH_3				
Phosphorus P_4				
Ethene C_2H_4				
1,2-dibromo ethane $C_2H_4Br_2$				

Molecule	**Lewis Structure (Draw the structure)**	**Molecular Geometry: (Tell shape)**	**Is this molecule polar? EXPLAIN**	**Does this molecule have any isomers or resonance structures? If yes, draw them**
Ethyne C_2H_2				
Sulfate ion SO_4^{2-}				
Thiocyanate ion SCN^-				
Nitrate ion NO_3^-				
Nitric acid HNO_3				
Carbon monoxide CO				
Sulfur dioxide SO_2				

Molecule	Lewis Structure (Draw the structure)	Molecular Geometry: (Tell shape)	Is this molecule polar? EXPLAIN	Does this molecule have any isomers or resonance structures? If yes, draw them
Sulfur trioxide SO_3				
CH_4O				