

LEWIS STRUCTURES

The purpose of this experiment is to gain practical experience of drawing lewis structures and to use molecular models to represent the three-dimensional shapes of molecules, which will lead to a better understanding of the concepts of covalent bonding and molecular structure. With the molecular model kits provided, you will build several models of small molecules and ions.

Lewis Structures

A Lewis structure is a representation of covalent bonding where shared electron pairs are shown as lines and lone electron pairs are shown as dots.

When drawing a Lewis structure, the octet rule is followed to attain the most stable electron configuration and achieve a complete octet of electrons for each atom in the molecule. All the valence electrons of the atoms in a Lewis structure must appear in the structure.

General Guidelines

1. For the A-group elements, the number of valence electrons of an atom is equal to the group number.

For example, carbon, in Group 4A, has 4 valence electrons.

2. The number of unpaired electrons on an atom of Groups 4A through 8A is 8 minus the group number. For example, oxygen in Group 6A has $8 - 6 = 2$ unpaired electrons and forms 2 bonds. Carbon in Group 4A has $8 - 4 = 4$ unpaired electrons and forms 4 bonds. (The number of unpaired electrons is equal to the group number for Groups 1A to 3A).
3. Hydrogen always forms one bond.
4. Oxygen usually doesn't bond with another oxygen atom. Exceptions: peroxides, superoxides, molecular oxygen, O_2 , and ozone, O_3 .
5. In general, only C, N, O, and S form multiple (double and triple) bonds.
6. Usually, all the electrons in a Lewis structure are paired.

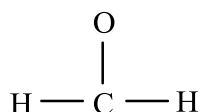
Writing Lewis Structures

1. Count the total number of valence electrons in the molecule or ion. For anions, add an electron for every negative charge. For cations, subtract an electron for every positive charge.
2. Write the skeletal structure of the compound. Generally, the least electronegative atom occupies the central position. Hydrogen atoms are always terminal atoms. (A central atom is bonded to two or more atoms. A terminal atom is bonded to just one other atom).
3. Join the atoms in the structure by single bonds. For each single bond formed, subtract two electrons from the total number of valence electrons.
4. With the valence electrons remaining, complete the octets of the terminal atoms (except H). Then complete the octets of the central atom(s).
 - a) If pairs are still left at this point, assign them to the central atom. If the central atom is from the third or higher period, it can accommodate more than 4 electron pairs.
 - b) If there are "too few electrons to go around", convert single bonds to multiple bonds. A double bond compensates for a deficiency of two electrons; a triple bond compensates for a deficiency of four electrons.

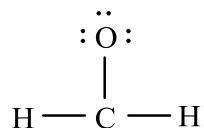
Example: Draw the Lewis structure for CH₂O

There are a total of 12 valence electrons:
 2 (1 for each H) + 4 (for C) + 6 (for O) = 12

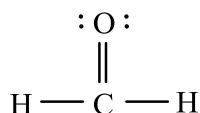
Carbon is the central atom:



The 6 remaining electrons are placed around the O atom as lone pairs.



The C atom is deficient by one pair; therefore a double bond is used.



5. Assign Formal Charges.

When drawing Lewis structures, sometimes only one arrangement of atoms is possible. In other cases, there may be two or more alternative structures.

Formal charges are used in selecting the more plausible Lewis structures for a given compound.

Formal charges do not indicate actual charge separation within the molecule; they merely help keep track of the valence electrons in the molecule. The formal charge on an atom in a Lewis structure is calculated as follows:

$$FC = VE - NBE - 1/2 BE(\# \text{ of bonds})$$

FC = formal charge

VE = valence electrons

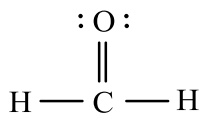
NBE = nonbonding electrons

BE = bonding electrons

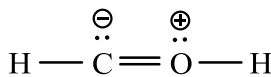
Guidelines:

- a) The most likely Lewis structure is the one with the fewest formal charges and the one with the formal charges of the smallest charge. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.

For example, CH₂O



This is the correct Lewis structure.



This is not a valid Lewis structure.

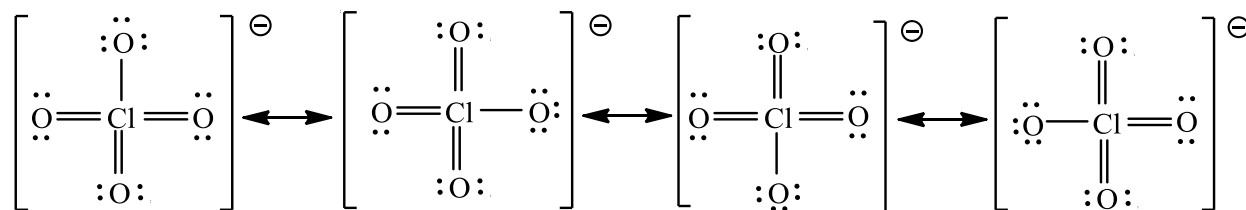
- b) Lewis structures with large formal charges are less plausible than those with small formal charges.
- c) In choosing among Lewis structures having similar distributions of formal charges, the most plausible Lewis structure is the one in which negative formal charges are placed on the more electronegative atoms and positive formal charges are placed on the more electropositive atoms.

- d) For neutral molecules, the sum of the formal charges must add up to zero. For cations, the sum of the formal charges must equal the positive charge. For anions, the sum of the formal charges must equal the negative charge.
- e) Avoid the same formal charge on adjacent atoms.

Resonance

Resonance structures are used when a single Lewis structure doesn't adequately describe the bonding in the molecule. Resonance structures differ only in the position of the electrons.

For example, the resonance structures for ClO_4^- are:



One Lewis structure doesn't accurately portray the bonding in ClO_4^- . The true structure of ClO_4^- is a "hybrid" of the four resonance structures. The central chlorine atom is identically bonded to all the terminal oxygen atoms. The bonds are intermediate between a single and three double bonds.

Resonance forms do not imply different molecules. The molecule has a single structure; it does not oscillate back and forth between the Lewis structures. The true structure has an electron distribution that is a hybrid of all possible resonance structures.

Exceptions to the Octet Rule

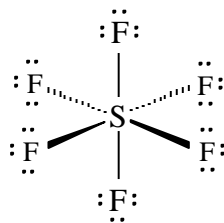
1. Incomplete Octets: In some compounds the number of electrons surrounding the central atom is fewer than eight.

For example: BeH_2 and BF_3



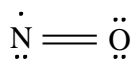
2. Expanded Octets: In some compounds there are more than eight electrons surrounding the central atom. Expanded octets occur for atoms in and beyond the third period of the periodic table.

For example: SF₆



3. Odd-electron molecules: Some molecules contain an odd number of electrons. Since we need an even number of electrons for complete pairing, the octet rule cannot be satisfied for all of the atoms in any of these molecules.

For example: nitric oxide, NO



The VSEPR Model

The VSEPR (valence shell electron pair repulsion) model can be used for predicting molecular geometries.

The VSEPR model accounts for the geometric arrangements of electron pairs around a central atom in terms of repulsions between electron pairs. Because the pairs try to avoid one another, they move as far apart as possible, and, since all the pairs are "tied" to the same central atom, they orient themselves so as to make the angles between themselves as large as possible.

Guidelines for Predicting Molecular Geometries by VSEPR

1. Write the Lewis structure of the molecule or ion.
2. Count the number of bonding pairs and lone pairs around the central atom. Treat double and triple bonds as though they were single bonds.
3. Use Table 1 to predict the geometry of the molecule. For the molecular type, AB_xE_y ,

A = the central atom

B = a surrounding atom

E = a lone pair on A

x = the number of surrounding atoms

y = the number of lone pairs on the central atom

TABLE 1 Molecular Geometry as a Function of Electron Group Geometry: VSEPR


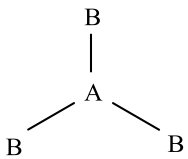
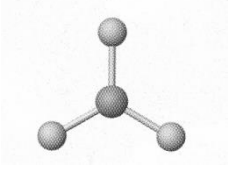
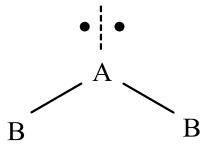
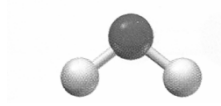
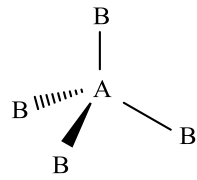
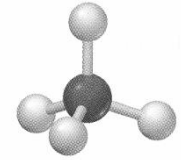
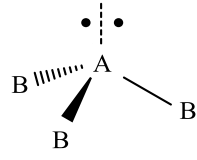

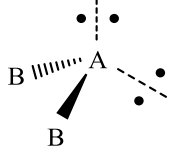

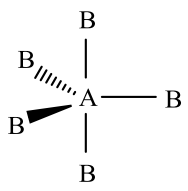
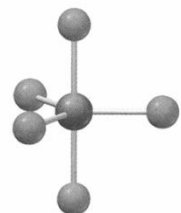
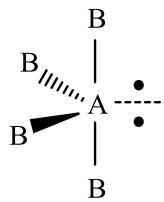
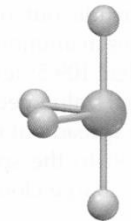
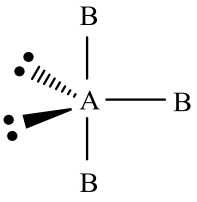
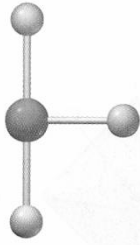
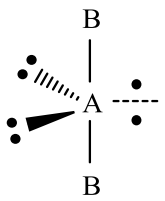

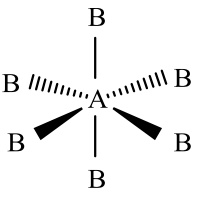
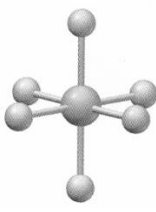
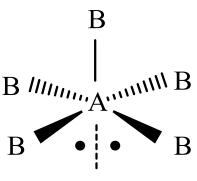
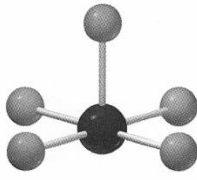
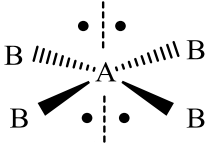
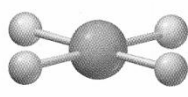
Molecule type	# Electron pairs on central atom	# Bonding pairs	# Lone pairs	Arrangement of electron pairs	Molecular shape	Description
AB_2	2	2	0	B — A — B		linear
AB_3	3	3	0			trigonal planar
AB_2E	3	2	1			bent
AB_4	4	4	0			tetrahedral
AB_3E	4	3	1			trigonal pyramidal
AB_2E_2	4	2	2			bent
AB_5	5	5	0			trigonal bipyramidal

TABLE 1 (continued)

Molecular Geometry as a Function of Electron Group Geometry: VSEPR

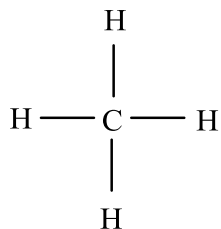
Molecule type	# Electron pairs on central atom	# Bonding pairs	# Lone pairs	Arrangement of electron pairs	Molecular shape	Description
AB_4E	5	4	1			unsymmetrical tetrahedron (seesaw)
AB_3E_2	5	3	2			T-shaped
AB_2E_3	5	2	3			linear
AB_6	6	6	0			octahedral
AB_5E	6	5	1			square pyramidal
AB_4E_2	6	4	2			square planar

Perspective Drawings of Molecular Shape

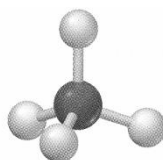
Three-dimensionality may be represented in a structural drawing using a solid wedge to depict a bond projecting from the plane of the paper toward you, a dashed wedge to depict a bond receding from the plane of the paper away from you, and a simple line to depict a bond in the plane of paper.

Example: methane, CH₄

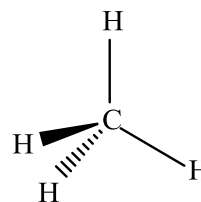
Lewis Structure



Molecular Model



Perspective Drawing



Hybrid Atomic Orbitals

Hybridization is the mixing of atomic orbitals in an atom to generate a set of new atomic orbitals, called hybrid orbitals. For example, two sp hybrid orbitals are formed from one s and one p orbital; three sp^2 hybrid orbitals are formed from one s and two p orbitals; four sp^3 hybrid orbitals are formed from one s and three p orbitals.

One of the main purposes of hybridizing orbitals is to describe molecular geometries. We generally apply hybridization schemes only to central atoms, not to terminal atoms. Each hybrid orbital in the bonded central atom acquires an electron pair. The electron pair is a bonding pair for hybrid orbitals that overlap with the orbitals of other atoms, or it is a lone pair if the hybrid orbital is not involved in bonding.

In order to decide the hybridization of the central atom in a molecule, we must have some idea about the geometry of the molecule. We can start by drawing the Lewis structure of the molecule and predict the overall arrangement of electron pairs using the VSEPR model.

We can then predict the type of hybridization of the central atom by choosing the hybridization scheme that produces the same number of hybrid orbitals, and in the same orientation as found for the electron pairs of the central atom. Table 2 summarizes the common hybridization schemes.

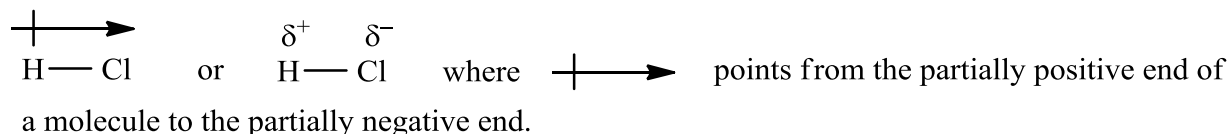
TABLE 2 Hybrid Orbitals and their Geometric Orientation

PURE ATOMIC ORBITALS OF THE CENTRAL ATOM	HYBRIDIZATION OF THE CENTRAL ATOM	NUMBER OF HYBRID ORBITALS (# OF ELECTRON PAIRS ON CENTRAL ATOM)	GEOMETRIC ORIENTATION OF ELECTRON PAIRS
s,p	sp	2	linear
s,p,p	sp ²	3	trigonal planar
s,p,p,p	sp ³	4	tetrahedral
s,p,p,p,d	sp ³ d	5	trigonal bipyramidal
s,p,p,p,d,d	sp ³ d ²	6	octahedral

Polarity

A nonpolar bond is one in which the electron pair is shared equally between atoms of identical electronegativities. (For example, H – H and Br - Br).

A polar bond is one in which there is an unequal sharing of the electron pair between atoms of different electronegativities. The electrons are attracted to the more electronegative atom and a separation of charge occurs which generates a bond dipole (+ pole and - pole). The charge separation can be represented as:



δ^+ (partial positive charge)

δ^- (partial negative charge)

Any molecule that has a net separation of charge has a dipole moment. The dipole moment μ , is a measure of the magnitude of the separated charges and the distance between them.

$$\mu = Q \times r \quad \text{where } Q \text{ is the charge and } r \text{ is the distance between charges.}$$

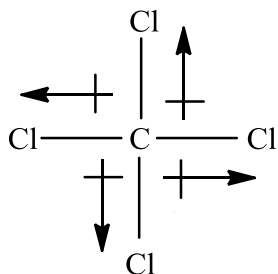
A molecule that possesses a dipole moment is a polar molecule. A molecule that does not possess a dipole moment is a nonpolar molecule. The molecular dipole moment is the vector sum of all the individual dipoles in the molecule. Depending upon the molecular shape, the bond dipoles may add together (reinforce one another) to give a polar molecule, or they may cancel one another resulting in a nonpolar molecule. Therefore, the two criteria for determining the polarity of a molecule are bond polarity and molecular geometry.

Molecules having all nonpolar bonds are nonpolar molecules, there are no dipoles present.

Polar bonds in a molecule usually cause the molecule to be polar. However, polar bonds of equal magnitude can cancel one another if they are arranged symmetrically around the central atom, resulting in no net dipole moment.

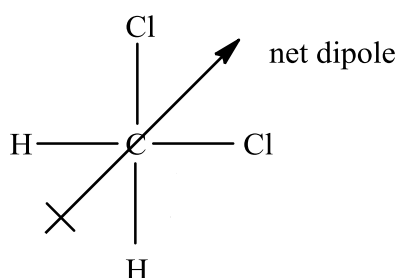
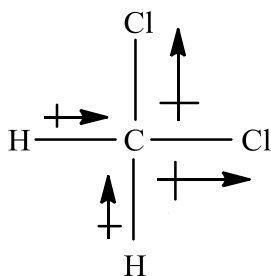
Examples:

a) carbon tetrachloride



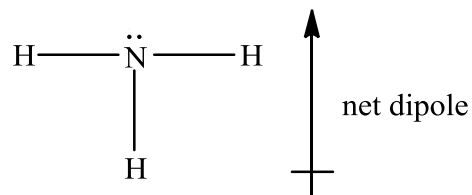
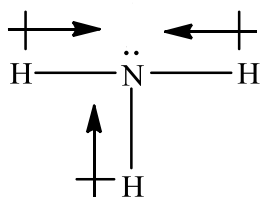
All the polar bonds of carbon tetrachloride are equal in magnitude, and, because the bonds are directed symmetrically about the central carbon atom, the bond dipoles cancel to give a net dipole moment of zero. The molecule is nonpolar.

b) dichloromethane



Because not all the polar bonds in dichloromethane are identical, the bond moments do not cancel and the molecule is a polar molecule.

c) ammonia



The arrangement of bond dipoles within the ammonia molecule is not symmetrical. The bond dipoles do not cancel each other. Instead, they add to give the molecule a net dipole resulting in a polar molecule.