

Lewis Structures

Objectives:

- To learn how to use Lewis Structures of elements to predict formulas of simple binary molecular compounds.
- To learn the octet rule and how to apply it in drawing Lewis Structures for polyatomic ions and molecules.
- To learn about charge distribution in chemical bonds in terms of electronegativity differences of bonded atoms and formal charges.
- To learn how to use formal charges to predict the most stable Lewis Structure for a molecule or polyatomic ion.
- To understand what is meant by the terms "resonance hybrid" and "resonance stabilization".
- To learn about when the octet rule is violated and to be able to write Lewis Structures for such cases.
- To learn how to use the concepts of formal charges and expanded octets to explain experimentally observed bond lengths.

Background:

The properties of ionic, covalent (molecular) and metallic substances are remarkably different from each other. Ionic compounds have high melting points, making them solids at room temperature. In contrast, molecular compounds can be solids, liquids or gases at room temperature. Ionic compounds do not conduct electricity in the solid state, whereas metallic substances do. These are just a couple of the many differences between these three types of substances. The difference in their properties can be understood in terms of the type of bonding that occurs in each: ionic bonding, covalent bonding and metallic bonding. We will focus our attention mainly on covalent bonding in this exercise.

The chemical and physical properties of molecular substances depend upon which elements are bonded together and how the atoms and valence electrons are arranged in the molecule. For example, the bond between carbon and oxygen in CO requires more energy to break than the bond between carbon and oxygen in CO₂. Another example: CO₂, a gas at room temperature, consists of linear molecules (the three nuclei lie in a straight line), whereas H₂O, a liquid at room temperature, consists of v-shaped molecules. These differences can be explained by drawing the Lewis Structures of CO, CO₂ and H₂O. Chemists use Lewis Structures as a simple way to depict the bonding in molecules. Based upon the Lewis Structure, chemists can make reasonable predictions about the shape and properties of a molecule. A Lewis Structure shows the sequence in which the atoms are connected and the distribution of valence electrons around the atoms of a molecule or polyatomic ion. However, a Lewis Structure does not, by itself, depict the three dimensional arrangement (the geometry) of the atoms. We will focus our attention in this exercise on drawing Lewis Structures and will learn later how to use Lewis Structures to predict molecular geometries. It is important that you become skilled at drawing Lewis Structures so that you can successfully predict molecular geometries!

Exercise:

The questions in this worksheet up to the follow up questions should be completed with the guidance of your lab instructor as a discussion during lab lecture. The follow-up questions are then to be completed by you during the remainder of the lab time. As much of this exercise as possible should be completed during lab.

Part 1: Predicting formulas of binary molecular compounds

For the representative (main group) elements, the number of valence electrons an atom of the element possesses is given by its group number. (This is following the "A", "B" numbering system where the representative elements are in the eight columns labeled "A".) Atoms of these elements often lose, gain or share electrons to achieve the same number of outer electrons as the noble gas closest to them. All noble gases (except He) have eight valence electrons. These observations have resulted in the formulation of the octet rule: *atoms tend to lose, gain or share electrons until eight valence electrons surround them.* We understand this as only a rule, not a scientific law. Exceptions do occur. An octet of electrons corresponds to a full valence shell (s and p subshells) in an atom. For hydrogen, its valence shell consists of only an s subshell. Therefore, hydrogen can only accommodate two electrons in its valence shell and it follows its own rule rigorously, the duet rule. We also see cases where the octet rule cannot be satisfied due to an insufficient number of available valence electrons, cases where atoms acquire less than octet of valence electrons and cases where atoms acquire more than an octet. Even with these exceptions, the octet rule provides a useful framework for understanding many aspects of bonding.

When two atoms form a covalent bond, usually each atom provides one valence electron to share. (There are cases where both of the shared electrons come from one atom. In such a case the bond is called a coordinate covalent bond.) In either case, the shared electron pair is considered localized in the region between the nuclei of the two atoms. The attractive forces that hold two covalently bonded atoms together are thus electrostatic in nature; the positive nuclei of the two atoms are simultaneously attracted to the shared electrons within the bond. Formation of the bond lowers the potential energy of the system, making it an energetically favorable process.

We can predict formulas of binary molecular compounds by first considering the Lewis Symbol of the atoms involved. In writing the Lewis Symbol for an atom, the chemical symbol for the element is used to represent the core (the inner, non-valence electrons plus the nucleus) and the valence electrons are represented by dots arranged around the core. The dots are placed arbitrarily, one at a time, around the symbol. If there are more than four valence electrons, we continue around the symbol, pairing the dots until all the valence electrons are represented by dots.

The Lewis Symbol for hydrogen is: $\text{H} \cdot$

The Lewis Symbol for sulfur is:



Since hydrogen needs one more electron to satisfy its duet rule and sulfur needs two more electrons to satisfy the octet rule, we can predict that the formula for a binary compound containing hydrogen and sulfur will be H_2S , sulfur forming two bonds and hydrogen forming one bond. In writing the Lewis Structure for the molecule, the valence electrons are arranged to satisfy the octet and duet rules as shown below:



In this structure, the line (—) between each hydrogen atom and the sulfur atom represents a shared pair of electrons (a bonding pair) and the unshared (non-bonding or lone pair) electrons on the sulfur are represented by dots. Note that the hydrogen atoms have attained a duet of electrons and the sulfur has attained an octet by sharing of electrons.

Practice:

1. Write the Lewis Symbols for all of the elements in the second period of the periodic table.
2. Based on the Lewis Symbols for nitrogen and fluorine, predict the formula of a stable binary compound of nitrogen and fluorine and draw its Lewis Structure. Also, give the name of this compound.

Part 2: Simple Lewis Structures

The following steps outline general guidelines for writing **SIMPLE** Lewis Structures (Octet and Duet Rules Obeyed):

- Step 1.** Determine the total number of valence electrons available. This exact number of electrons must be included in the Lewis Structure.
- Add up the valence electrons of all the atoms present.
 - Add extra electrons for (-) ions, subtract electrons for (+) ions.
- Step 2.** Decide the sequence of atoms, i.e. the skeleton arrangement of the atoms.
- For some compounds, the formula gives the order in which the atoms are attached in the molecule. Two examples are HCN and condensed structural formulas such as CH_3OCH_3 .
 - When there is a central atom surrounded by other atoms bonded to it, the central atom is usually written first in the formula. For example, nitrogen is the central atom in NO_3^- .
 - The central atom is usually the least electronegative atom.
 - Oxygen is rarely the central atom.
 - Hydrogen is NEVER the central atom.
 - Exceptions to (b) (c) and (d) do exist. For example, in H_2O and NH_3 where the highly electronegative O and N are the central atoms. Note, however, that in these two examples guideline (e) is followed.
- Step 3.** Draw a single bond (a line) between each atom in the skeleton arrangement.
- All atoms must have at least one bond.
 - Subtract two electrons for each bond from the total available electrons.
- Step 4.** Distribute the remaining electrons in pairs so each atom acquires eight electrons (two for H).
- Place lone pairs on the surrounding (terminal) atoms first to complete an octet on each.
 - If any electrons remain add them as lone pairs on the central atom(s).
- Step 5.** If, after step 4, a central atom still does not have an octet, change a lone pair from one of the terminal atoms into a bonding pair to the central atom to make a multiple bond. In this way, sufficient multiple bonds should be made in order to complete an octet for the central atom(s).
- When forming bonds follow these general guidelines:**
- H atoms ALWAYS make only one bond.
 - O atoms usually make a total of either one or two bonds: When an oxygen atom makes only one bond, it is a coordinate covalent bond with the other atom providing both electrons for the bond. In the case of two bonds, oxygen can make either two single bonds or one double bond.
 - C atoms usually make a total of four bonds: four single, two double, a double with two single or a triple with one single.
 - For oxyacids, the acidic hydrogen atoms are bonded to oxygen atoms, which in turn are bonded to the central atom. For example, in H_2CO_3 the carbon is the central atom, the oxygen atoms are all bonded to the carbon atom and the hydrogen atoms are bonded to two separate oxygen atoms.

A common exception to (b) and (c) that we will explore later in this exercise is found with carbon monoxide.

Practice (Lewis Structures containing only single bonds):

1) Draw Lewis structures for the following molecules or polyatomic ions.



Part 3: Advanced Lewis Structures

3.A Resonance Structures

For molecules and polyatomic ions with multiple bonds adjacent to single bonds it is often possible to write more than one Lewis structure for the same sequence of atoms that satisfies the octet rule and general rules of bonding. Consider the following Lewis structures for ozone, O_3 .



Notice how the double bond can be written in two different positions. We call these structures **resonance forms** of each other. Which of the above two resonance forms is the correct representation of bonding in the O_3 molecule? The answer is neither of them! **Resonance structures are not real bonding descriptions: the bonding arrangement does not shift back and forth between the different forms.** The correct representation of bonding in O_3 is a combination of the two resonance forms to create a **resonance hybrid**, a blend of the two structures. To describe the bonding in O_3 properly, we write both resonance hybrids and use a double-arrow to indicate that the real molecule is a blend of the two. Be careful not to misinterpret the double arrow as meaning that the molecule flips back and forth between two forms; it does NOT! In terms of bond length and bond energy, the O_3 molecule has two equivalent oxygen-oxygen bonds with bond lengths and energies between those of a single and double bond. The bond order for both of the oxygen-oxygen bonds in ozone is described as being "one-and-one-half" (one bond plus half of the second bond). In other words, one of the bonds is spread out (delocalized) over all three atoms.

It is important to remember that resonance forms of the same molecule differ in only the location of the bonding and lone pair electrons, but not in the sequence of atoms. Resonance forms are common in many molecules and polyatomic ions; in these cases some of the bonding electrons are **delocalized**, that is they are shared between more than two atoms. This results in greater stability (lower overall energy) of the molecule or ion and we say that the structure is **resonance stabilized**.

In Summary: *Resonance is the blending of two or more Lewis Structures with the same arrangement of atoms but different arrangements of electrons. It spreads multiple bond character out over three or more atoms giving a more stable (lower energy) structure (resonance stabilization).*

Questions:

1. Draw all possible resonance structures for the nitrate ion, NO_3^- .

Bond Polarity and Electronegativity:

When two identical atoms bond, as in H_2 or Cl_2 , the electron pairs are shared equally since both atoms exert the same force of attraction for electrons. When electrons are shared equally, the bond is described as being **nonpolar covalent**. In contrast, for ionic compounds, such as KCl , there is essentially no sharing of electrons. Instead, electrons are viewed as being transferred from one atom to another resulting in the formation of oppositely charged ions that are held together by strong electrostatic forces of attraction. In between these two extremes, as is the case for bonding in the HCl molecule, there exists **polar covalent bonds** where the electrons are not equally shared between the two atoms. These differences in bonding arise due to differences in electronegativities of the bonded atoms.

Electronegativity is defined as the ability of an atom in a molecule to attract electrons to itself. (A common misconception students tend to have is that molecules have electronegativity values. This is not true; electronegativity is a property of atoms, not molecules.) Electronegativity values are listed in your textbook. Electronegativity is not a measured property, the values are calculated and you will find that they vary slightly depending on the reference source. Generally, electronegativity increases from bottom to top within a group of the periodic table and from left to right across a period. Thus, fluorine (in the upper right-hand corner of the periodic table) has the greatest electronegativity and cesium (in the lower

(left-hand corner) has the lowest electronegativity. A chlorine atom has a greater electronegativity compared to a hydrogen atom, therefore in HCl the electron distribution is uneven; the hydrogen atom having a partial positive charge and the chlorine a partial negative charge. We can illustrate the charge distribution in a polar covalent bond like that in HCl in one of two ways as illustrated below:



The $\delta+$ and $\delta-$ symbols indicate the partial positive and partial negative charges on the H and Cl atoms. The arrow is used to show the shift in electron density from H towards Cl.

A separation of charge between two bonded atoms is called a **bond dipole**. The greater the difference in electronegativity values between two bonded atoms the more polar the bond, and the greater the magnitude of the bond dipole. When the difference becomes large enough, electron transfer occurs instead of sharing, and an ionic compound results. There thus exists a graduation in bond types. Generally, if the difference in electronegativities between two bonded atoms is about 0.3 or less the bond is considered to be nonpolar. If the difference is between 0.3 and 0.5, the bond is slightly polar. If the difference is between about 0.5 and 2.0 the bond is considered to be polar covalent. For electronegativity differences of 2.0 or greater the bond is considered to be ionic.

Electronegativities of selected elements																		He —				
1	H 2.1																	Ne —				
2	Li 1.0	Be 1.5															B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ar —
3	Na 0.9	Mg 1.2															Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Kr —
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Xe —				
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5					
6	Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Ra —				
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf —	Db —	Sg —	Bh —	Hs —	Mt —													

General rules for bond types and electronegativity difference (ΔEN):

Bond Type	$ \Delta EN $
Nonpolar	≤ 0.3
Weakly Polar	Between 0.3 to 0.5
Polar	Between 0.5 to 2
Ionic	≥ 2

Practice:

- 1) Use electronegativity values to determine if each of the following bonds are nonpolar, weakly polar, polar, or ionic.

- | | | |
|--------|---------|---------|
| a) C-H | e) N-S | i) H-I |
| b) C-O | f) C-S | j) H-Br |
| c) O=O | g) F-Cl | k) K-Cl |
| d) H-O | h) O-P | |

Some Common Bonding Arrangements by Group
(all have no formal charge unless indicated)

Group 3 (no l.p. never terminal)	Group 4 (usually no l.p. never terminal)	Group 5 (usually 1 l.p. rarely terminal)	Group 6 (usually 2 l.p. can be terminal)	Group 7 (usually 3 l.p. usually terminal)
$\begin{array}{c} \\ \text{---B---} \end{array}$	$\begin{array}{c} \\ \text{---C---} \\ \\ \text{=C} \diagup \\ \text{=C=} \\ \text{=C=} \\ \text{=C---} \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{---}\ddot{\text{N}}\text{---} \\ \\ \text{=}\ddot{\text{N}}\text{---} \\ \text{=}\ddot{\text{N}}\text{:} \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{---}\ddot{\text{O}}\text{---} \\ \cdot\cdot \\ \text{=}\ddot{\text{O}}\text{:} \\ \cdot\cdot \\ \text{:}\ddot{\text{O}}\text{:}^{-1} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \text{:}\ddot{\text{F}}\text{:} \\ \end{array}$

l.p. is abbreviation for "lone pair"

3.C Exceptions to the Octet Rule

The octet rule is very simple and useful for determining the structures of many molecules and polyatomic ions of the main group elements. Carbon, nitrogen, oxygen, and fluorine obey the octet rule rigorously, provided that there are enough electrons. However, in some cases there are insufficient electrons to form a complete octet to all atoms. In addition, a number of atoms of the main-group elements do not always follow the octet rule, either acquiring less than or more than an octet of valence electrons. The three exceptions to the octet rule are discussed in more detail below.

- 1. Odd number of electrons:** A few molecules have an odd number of total valence electrons. They cannot possibly have all their electrons in pairs. These molecules contain a lone (unpaired) electron and are called **free radicals**. Free radicals tend to be reactive. Two examples of single atom free radicals are H and Cl. When drawing Lewis Structures for free radicals, one atom will have less than an octet. Formal charges can be used to determine the most stable arrangement of the electrons.

- 2. Less than an octet of valence electrons:** This situation is relatively rare, Be and B tend to be the most common elements to form structures with an incomplete octet.

Example: Draw two Lewis Structures for BCl_3 . One where the boron atom has an incomplete octet of only six electrons and one where the octet rule is satisfied for all atoms in the structure.

- 3. More than an octet of valence electrons:** Many molecules and polyatomic ions exist where the central atom has acquired more than eight valence electrons; we call this an **"expanded octet"**. Atoms that exceed an octet do so by using empty outer d orbitals for bonding in addition to valence s and p orbitals. Thus, only atoms from period 3 or higher are capable of expanding beyond an octet. (Remember that the valence shell must have a principle quantum number of 3 or higher for it to contain a d subshell.) The "extra" electrons in an expanded valence shell may be present as lone pairs, usually on the central atom, or they may be the result of the central atom forming multiple bonds. The minimization of formal charges to form a more stable structure is considered to be a factor in cases where an octet is exceeded due to the formation of multiple bonds. Beginning with silicon, Group 4A and 5A atoms will usually expand to 10 electrons, group 6A atoms to 10 or 12 electrons and group 7A atoms to 10, 12 or 14 electrons.