

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES

The formulas of many covalent compounds, especially those involving only the elements of the first few periods of the periodic table, were brought within the framework of the **octet rule**. The octet rule states that a total of eight **valence** electrons, either shared or unshared, should be in the region of each atom beyond the first period. For hydrogen the desired number is two. Electrons that are shared between two atoms are **bonding electrons** and are to be counted toward the octet of each of the bonding atoms. A single covalent bond consists of a pair of shared electrons, a double bond has two shared pairs, and a triple bond has three shared pairs. Bond distances are shorter and bond energies are greater for multiple bonds than for single bonds.

Structural formulas, such as shown in Fig. 1, represent the electron distributions in covalent molecules and ions. These structures are not meant to indicate actual bond angles in three-dimensional varieties; they merely show the number of bonds connecting the various atoms. In **Lewis formulas**, a single line between two atoms represents a **pair** of shared electrons and a **dot** represents an unshared electron.

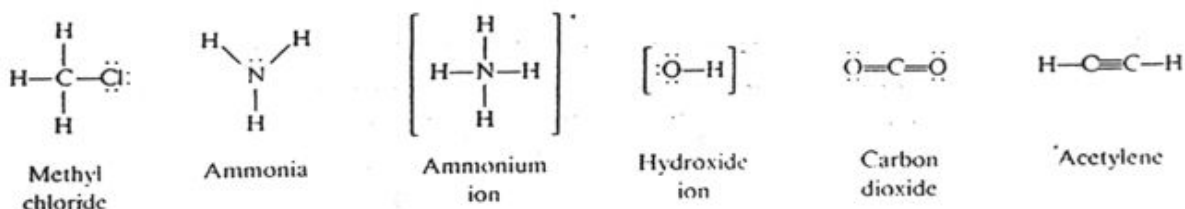
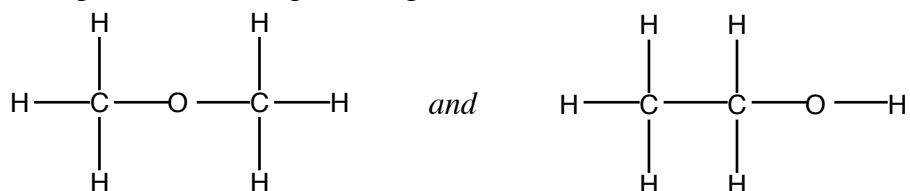


Figure 1

Two lines constitute a *double bond*, and three lines constitute a *triple bond*. The total number of electrons shown in such a molecular structure is equal to the sum of the numbers of valence (outer-shell) electrons in the free atoms: 1 for H, 4 for C, 5 for N, 6 for O, and 7 for Cl. For an ionic structure, one additional electron must be added to this sum for each unit of negative charge on the whole ion, as in OH^- , and one electron must be subtracted from the sum for each unit of positive charge on the ion, as in NH_4^+ . The number of pairs of electrons shared by an atom is called its **covalence**.

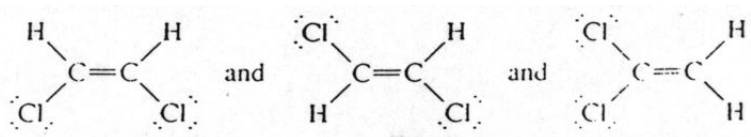
The covalence of hydrogen is always one. The covalence of oxygen is practically always one or two. The covalence of carbon is four in almost all its stable compounds. Thus each carbon is expected to form either four single bonds, a double bond and two single bonds, two double bonds, or a single and a triple bond. Although the octet rule is not a rigid rule of chemical bonding, it is obeyed for C, N, O, and F in almost all their compounds. The octet is exceeded commonly for elements in the third and higher periods of the periodic table.

Isomerism: For some molecules with a given molecular formula, it is possible to satisfy the octet rule with different atomic arrangements. A simple example would be



The two molecules are called **isomers** of each other, and the phenomenon is called **isomerism**. Although the molecular formulas of both substances are the same, $\text{C}_2\text{H}_6\text{O}$, their properties differ because of the different atomic arrangement. Since several different types of isomerism can exist especially in organic molecules, these are called **structural isomers**.

When **double bonds** are present, isomerism can occur in very small molecules. For example:



These isomers (called **geometric** isomers) result from the fact that there is no rotation around a double bond, as in single bonds.

Resonance: Sometimes more than one satisfactory structure can be written and there is no reason to select one over another. In such cases a single structural formula is inadequate to represent a substance correctly, and several such diagrams must be written. The true structure is then said to be a *resonance hybrid* of the several diagrams.

For example, experiment has shown that the two terminal oxygens in ozone are equivalent; that is, they are equidistant from the central oxygen. If only one of the resonance diagrams in Fig.2(a) were written, it would appear that one of the terminal oxygens is bonded more strongly to the central oxygen by a double bond than is the other (by a single bond) and that the more strongly bonded atom should be closer to the central atom. The hybrid of the two ozone structures gives equal weight to the extra bonding of the two terminal oxygen atoms. Similarly, the three resonance structures of carbonate in Fig.2(b) are needed to account for the experimental fact that all three oxygens are equidistant from the central carbon.

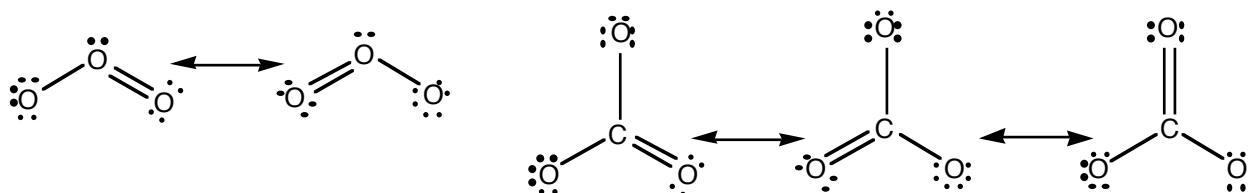
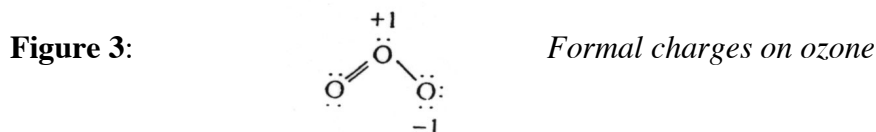


Figure 2: a) ozone (left) and b) carbonate (right)

The total bond energy of a substance for which resonance structures are written is greater than would be expected if there were only one formal Lewis structure. This additional stabilization is called **resonance energy**. It arises from the principle that is responsible for covalent bond energy, the **delocalization** of electrons about the atoms forming the bond. As a result of resonance in ozone, for example, the electrons constituting the second pair of the double bond are delocalized around the 3 oxygen atoms. The writing of two or more resonance structures is a way of overcoming the inability of a single valence-bond structure to show this delocalization.

Formal Charge: Although a molecule as a whole is electrically neutral, it is a matter of much current interest to know whether there are local charges which can be identified with particular parts of a molecule, the algebraic sum of which would equal zero. In an ion, the algebraic sum would equal the charge of the ion as a whole. In one approximate method of apportioning charges within a molecule or ion, the shared electrons in a covalent bond are arbitrarily divided equally between the two atoms forming the bond. Unshared valence electrons on an atom are assigned exclusively to that atom. Each atom is then assigned a **formal charge** which is equal to the number of valence electrons possessed by that atom in the neutral free state minus the number of valence electrons assigned to it in the structure. These charges may be written near the atoms on the structural diagrams.

Figure 3 shows a single resonance structure for ozone. The central oxygen is assigned just five electrons (two in the unshared pair plus half of the three pairs in the bonds); this atom, being one electron short of the complement of six in a free oxygen atom, is thus assigned a formal charge of **+1**. The terminal oxygen connected by a single bond is assigned 7 (6 in the unshared pairs plus half of one pair in the bond); having one electron more than a neutral oxygen atom, this atom is assigned a formal charge of **-1**. The other terminal oxygen has no formal charge because six electrons are assigned to it (four in the unshared pairs plus half of the two shared pairs).



A rule useful in choosing one Lewis structure over another is that **structures which minimize formal charge separation are favored**. Especially to be avoided are formal charges of magnitude greater than 1 and structures in which appreciable formal charges of the same sign are located on adjacent atoms.

Dipole moments and electronegativity: There are some experimental procedures that give information about the actual distribution of charges within a molecule (as distinct from the arbitrary assignment of formal charges). One such is the measurement of **dipole moment**. An electric dipole is a neutral object that has a positive charge of magnitude q and a separately located, equal but opposite negative charge. The rotation of a dipole by an electric field is dependent upon a measure of the dipole moment, defined as the product of q and the distance, d , separating the positive and negative charges.

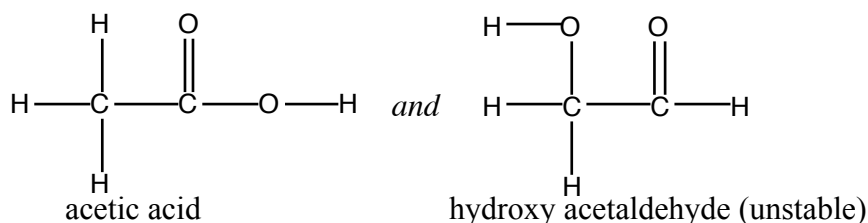
In a covalent diatomic molecule, the dipole moment would be expected to be zero if the bonding electrons were shared truly equally by the two atoms. This is indeed the case in molecules of the type XX where two identical atoms are bonded. In the more general type XY , two different kinds of atoms are bonded, and a dipole moment is usually observed. This is explained by hypothesizing that one of the atoms, say Y , has a greater attraction for the shared electrons in the bond than does X . Y is said to have a greater **electronegativity** than X . Electronegativity correlates with other atomic properties; in general, atoms with high ionization energies and/or high electron affinities tend to have high electronegativities. The most electronegative elements in order of decreasing electronegativity are **F > O > N = Cl**. C is more electronegative than H. Metals are less electronegative than nonmetals.

HOW TO COMPLETE THIS LAB:

In this experiment you will be constructing models of molecules and ions containing atoms covalently bonded. The model kit you will be using consists of plastic colored balls. Each type of ball represents a certain species of atoms; see the front cover of the model box to determine each atom type.

In assembling a molecular model of a molecule you should use a systematic approach keeping in mind the valence of the atoms in the molecule. Let us illustrate the recommended procedure with the following molecule, $C_2H_4O_2$:

1. Draw a correct Lewis structure, remembering that carbon will always have four bonds and oxygen two. Unless otherwise informed assume the carbon atoms form a carbon - carbon bond. Count up the total number of valence electrons ($24 e^-$). Those that are not bonding are nonbonding electrons. This leads to the following two isomers (other isomers exist as well):



2. Connect the balls and sticks to according to the Lewis structure. Use two bonds to represent the carbon-oxygen double bond.
3. Determine the shape of the molecule from the molecular model. For acetic acid we say that the molecule is tetrahedral at one carbon, trigonal planar at the other carbon and bent at the oxygen.
4. Determine whether any isomers exist by changing the location of the atoms; however you must maintain the correct valence of each atom.
5. Resonance will most often exist when the central atom forms a double bond to one atom and a single bond to another atom of the same element.

PROCEDURE:

1. Use the procedure outlined above to construct and report on models of the molecules and ions listed below using the attached worksheet. Neatness counts! Be sure to **include all lone pair electrons** on your drawings. In addition, get **two unknowns** from your instructor and report them likewise. For *each* molecule:

- i) Draw the Lewis structure.
- ii) Describe the electron pair geometry and molecular geometry.
- iii) Determine if the molecule is polar or nonpolar.
- iv) Draw the Lewis structures of isomers and resonance forms, if any.

1. CH ₄	6. NH ₄ OH	11. C ₂ H ₂	16. SCN ⁻	21. AsCl ₃ Br ₂
2. CH ₂ Cl ₂	7. CH ₂ O	12. SO ₂	17. NO ₃ ⁻	22. PCl ₅
3. CH ₄ O	8. NH ₃	13. C ₂ H ₄	18. SO ₄ ²⁻	23. SiF ₆ ²⁻
4. H ₂ O	9. H ₂ O ₂	14. C ₂ H ₂ Cl ₂	19. CO ₂	24. SiF ₄ Cl ₂ ²⁻
5. P ₄	10. HNO ₃	15. C ₂ H ₄ Br ₂	20. SeF ₄	25. SiF ₃ Cl ₃ ²⁻

2. Also, construct six possible isomers of C₆H₁₂O₂.

Name: _____

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET

Molecule/ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
CH₄		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
CH₂Cl₂		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
CH₄O		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
H₂O		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
P₄		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET - *Continued*

Molecule/ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
NH₄OH		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
CH₂O		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
NH₃		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
H₂O₂		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
HNO₃		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET - *Continued*

Molecule/Ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
C_2H_2		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
SO_2		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
C_2H_4		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
$C_2H_2Cl_2$		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
$C_2H_4Br_2$		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET - *Continued*

Molecule/ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
SCN^{-1} <i>C in middle</i>		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
NO_3^{-1}		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
SO_4^{-2}		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
CO_2		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
SeF_4		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET - *Continued*

Molecule/ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
AsCl_3Br_2		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
PCl_5		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
SiF_6^{2-}		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
$\text{SiF}_4\text{Cl}_2^{2-}$		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
$\text{SiF}_3\text{Cl}_3^{2-}$		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

THE GEOMETRICAL STRUCTURE OF COVALENT MOLECULES WORKSHEET - *Continued*

Ask your instructor for two unknowns.

Molecule/Ion	Lewis Structure	Geometry and Polarity	Resonance/Isomers (if any)
<i>Unknown 1:</i> <hr/>		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	
<i>Unknown 2:</i> <hr/>		<i>Electron Pair Geometry:</i> <i>Molecular Geometry:</i> <i>Polar or Nonpolar:</i>	

Finally, construct six possible isomers of $\text{C}_6\text{H}_{12}\text{O}_2$ in the space provided below.