

2. COVALENT BONDING, OCTET RULE, POLARITY, AND BASIC TYPES OF FORMULAS

LEARNING OBJECTIVES

To introduce the basic principles of covalent bonding, different types of molecular representations, bond polarity and its role in electronic density distributions, and physical properties of molecules.

VALENCE ELECTRONS

They are those found in the highest energy level of the atom, or outer shell. In the periodic table, the number of valence electrons is given by the group number. For example, in the second row, the nonmetals are:

BORON	Group III	3 valence electrons	$2s^2, 2p^1$
CARBON	Group IV	4 valence electrons	$2s^2, 2p^2$
NITROGEN	Group V	5 valence electrons	$2s^2, 2p^3$
OXYGEN	Group VI	6 valence electrons	$2s^2, 2p^4$
FLUORINE	Group VII	7 valence electrons	$2s^2, 2p^5$

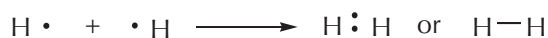
OCTET RULE

The atoms that participate in covalent bonding share electrons in a way that enables them to acquire a stable electronic configuration, or **full valence shell**. This means that **they want to acquire the electronic configuration of the noble gas of their row**. Obviously the name of this rule is a misnomer. Helium, the noble gas of the first row, has only two electrons. Hydrogen, the only element in the first row besides Helium, fulfills the "octet rule" by sharing two electrons only.

ELECTRON SHARING IN THE HYDROGEN MOLECULE



Orbital representation

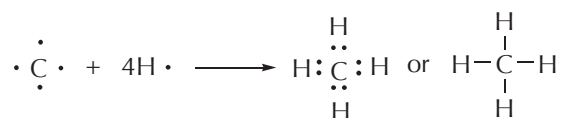


Lewis formula representation

Two hydrogen atoms form a covalent bond to make a hydrogen molecule. Each contributes one electron and forms a system that is much more stable than the isolated atoms. Although the orbital representation is more visually telling, the Lewis formula representation is easier to write, and therefore will be used from now on, unless there is reason to do otherwise.

The elements of the second row fulfill the octet rule by sharing eight electrons, thus acquiring the electronic configuration of **neon**, the noble gas of this row. Besides hydrogen, **most of the elements of interest in this course are the second row nonmetals: C, N, O, and the halogens**. As the building block of all organic molecules, **carbon** is of particular interest to us. Carbon (4 electrons in the valence shell) combines with four hydrogen atoms to form a stable covalent compound where it shares 8 electrons, while each hydrogen shares 2. Thus every atom in this stable molecule fulfills the octet rule.

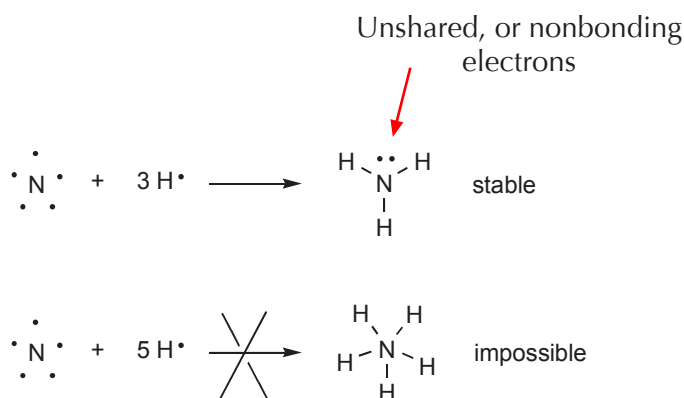
ELECTRON SHARING IN THE METHANE (CH₄) MOLECULE



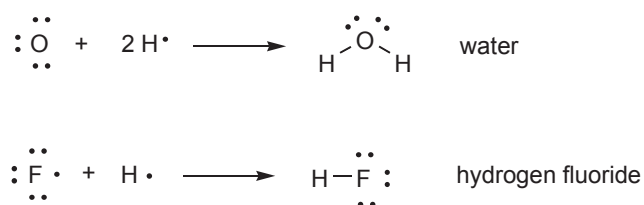
BUILDING SIMPLE MOLECULES

Among the simplest covalent compounds that the second row nonmetals can form are those that result from combination with hydrogen. Based on the number of electrons in their valence shells and the octet rule, we can predict how many hydrogen atoms will be needed to combine with each of those elements. Carbon, with 4 electrons in its valence shell, will need another four electrons to fulfill the octet rule. Thus it needs to combine with 4 hydrogen atoms to form a stable compound called **methane** (CH₄) as shown above.

Nitrogen, the next nonmetal, has 5 electrons in the valence shell, so it needs to combine with 3 hydrogen atoms to fulfill the octet rule and form a stable compound called **ammonia** (NH₃). This leaves two electrons that cannot be used for bonding (otherwise nitrogen would have to share more than 8 electrons, which is impossible). In the ammonia molecule, these electrons are paired and unshared, meaning that they are not engaged in bonding. Such electron pairs are referred to as **lone pairs, unshared electrons, or nonbonding electrons**.

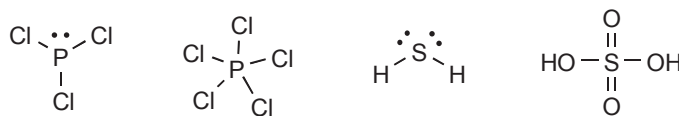


A similar process leads to the formation of stable hydrogen compounds for the next two nonmetals, oxygen and fluorine. We see that the water molecule contains two pairs of nonbonding electrons, and hydrogen fluoride contains three pairs.



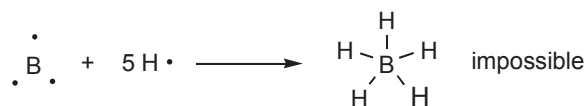
“EXCEPTIONS” TO THE OCTET RULE

The maximum number of electrons possible in the valence shell of the second row elements is eight. However, the elements of the **third row**, such as **phosphorus** and **sulfur**, can form stable systems by sharing eight or more electrons. The presence of **d-orbitals**, which can accommodate up to ten electrons, makes this possible.

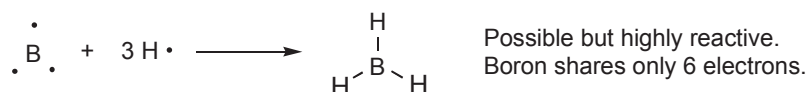


Some stable compounds of phosphorus and sulfur

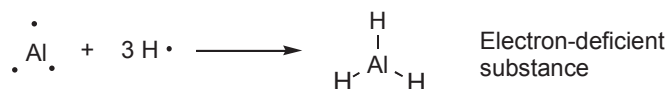
Now, back to the second row, what happens when the first nonmetal, boron ($Z=3$), combines with hydrogen? By repeating the process outlined before for carbon, nitrogen, oxygen, and fluorine, we conclude that boron needs to bond to 5 hydrogen atoms to fulfill the octet rule. The problem is that with only three electrons in the valence shell this is impossible:



The only possibility for boron is to bond to three hydrogen atoms, in which case it forms a compound (borane, BH₃) that does not fulfill the octet rule. The compound actually exists, but it is highly reactive, that is to say, unstable. Substances such as BH₃ are referred to as electron-deficient molecules, and are very reactive towards electron-rich substances.

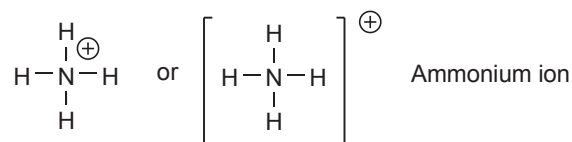


Aluminum, which is also in group III, exhibits similar behaviour.

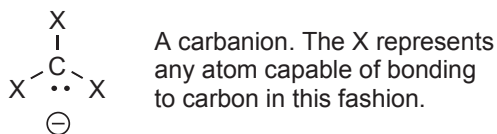


FORMAL CHARGE

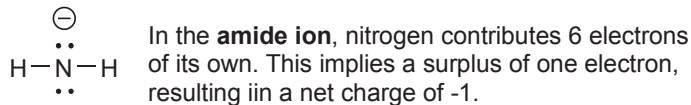
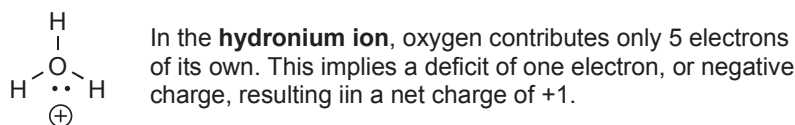
Sometimes atoms engage in covalent bonding by contributing more or less electrons than they have in their valence shell (we'll examine the processes that lead to the loss or gain of electrons later). For example nitrogen can actually combine with four hydrogen atoms to form a stable species called **ammonium ion** (NH₄). In this species, nitrogen still shares eight electrons, but contributes only four **of its own**. Since electrons are negative charges and this nitrogen is missing one, it acquires a **net** charge of +1 (in other words, there is a proton in the nucleus that is not matched by an electron outside the nucleus). This net charge is referred to as **formal charge**, and it must be indicated as part of the notation for the NH₄ formula, as shown.



In another species known as a carbanion, carbon forms only three bonds and carries a pair of unshared electrons. In this species, carbon shares eight electrons, but it is **contributing five of its own**. Since it has a surplus of one electron (a negative charge), **it carries a net charge of -1**.



Obviously the concept of formal charge refers to a specific atom. Formulas should show these charges on the atoms where they belong. Other examples of covalent species with charged atoms are the hydronium ion and the amide ion.



CONNECTIVITY OR BONDING SEQUENCE

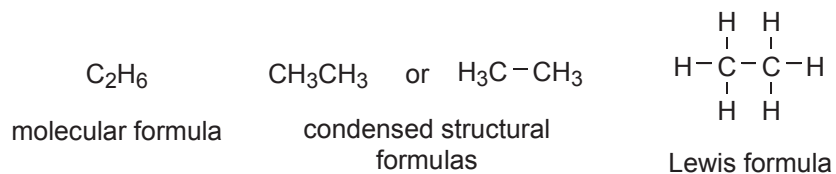
The term **connectivity**, or **bonding sequence**, describes the way atoms are connected together, or their bonding relationships to one another, in covalent compounds. For example, in the methane molecule one carbon is connected to four hydrogen atoms simultaneously, while each hydrogen atom is connected to only one carbon. No hydrogen atoms are connected together. In complex molecules the complete connectivity map is given by **structural formulas** (see below).

TYPES OF FORMULAS

The simplest type of formula for a compound indicates the types of atoms that make it up and their numbers. This is called a **molecular formula**. Examples of molecular formulas are BH_3 , C_6H_6 , or $\text{C}_3\text{H}_5\text{ClO}$. Chemical catalogs such as the *Aldrich catalog*, scientific manuals, and databases such as *Chemical Abstracts* typically contain molecular formula indices to help locate substances whose elemental makeup is known.

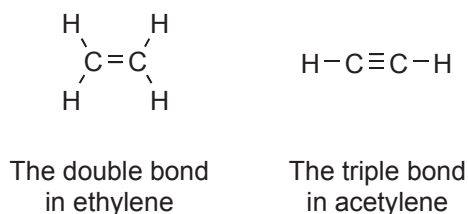
Condensed structural formulas give some idea of the connectivity, but are still largely abbreviated. For example the ethane molecule, which has molecular formula C_2H_6 can be represented by the condensed formula CH_3CH_3 . This at least tells us that each carbon is connected to three hydrogen atoms, and that two carbon atoms are connected together.

Lewis formulas are a second type of structural formulas. They give the most complete representation of the connectivity that is possible in two dimensions. The three types of formulas mentioned so far are shown below for the ethane molecule.



TYPES OF COVALENT BONDS

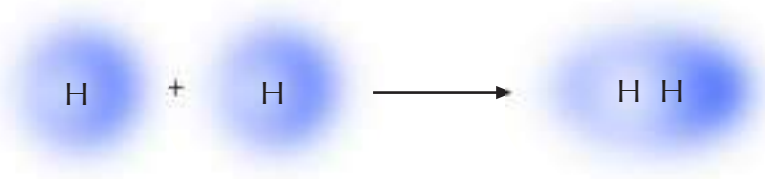
In the ethane Lewis formula shown above all bonds are represented as single lines called **single bonds**. Each **single bond is made up of two electrons, called bonding electrons**. It is also possible for two atoms bonded together to share 4 electrons. This bonding pattern is represented by two lines, each representing two electrons, and is called a **double bond**. The ethylene molecule shown below is an example. Finally, sharing of 6 electrons between two atoms is also possible. In such case, the representation uses three single lines, an arrangement called a **triple bond**. The acetylene molecule provides an example of a triple bond.



This terminology (single, double, or triple bond) is very loose and informal. The formulas shown above do not do justice to the actual nature of the bonds. All they do is show how many electrons are being shared between the two atoms (2, 4, or 6) but they say nothing about the electronic distribution, or the relative energies of the bonds, or the types of orbitals involved. They are, however, very useful in many situations.

ELECTRONIC DISTRIBUTION AND BOND POLARITY

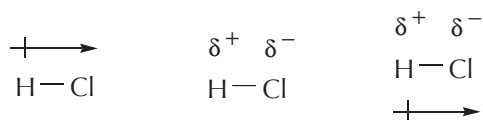
As we already learned, the atoms engaged in covalent bonding share electrons in order to fulfill the octet rule. However, this electron sharing can take place on an equal or unequal basis. If the atoms involved in covalent bonding are of equal electronegativities (which occurs only if they are the same atoms), then sharing takes place on an equal basis and there is no bias in the amount of time the bonding electrons spend around each atom. The hydrogen molecule (H_2) shown below is an example of this. The electronic cloud surrounding the two atoms is highly symmetrical, and the H-H bond is said to be **nonpolar**.



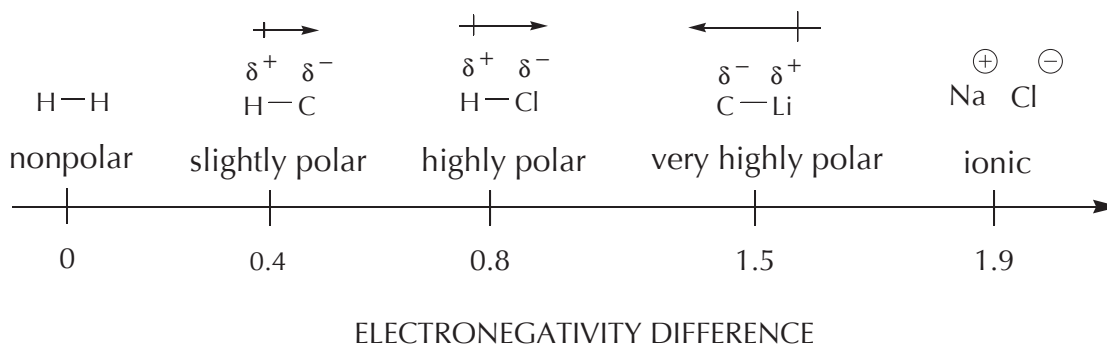
Now consider the case of hydrogen chloride, H-Cl. Hydrogen and chlorine are engaged in covalent bonding, but the electronegativity of chlorine is higher than that of hydrogen. The greater tendency of chlorine to attract electrons results in unequal sharing between the two atoms. The bonding electrons spend more time around chlorine than around hydrogen. They are still being shared, but chlorine behaves as if it carried a negative charge, and hydrogen behaves as if it carried a positive charge. **These charges are not full charges** as is the case in ionic molecules. In covalent molecules they are referred to as **partial charges**, or poles, because they are analogous of the poles of a magnet. The positive pole is indicated by δ^+ , and the negative pole by δ^- . The two together constitute a **dipole**, and the bond in question is said to be **polar**.



A polar bond is sometimes represented as a vector, with an arrow pointing in the direction of the more electronegative atom. The following are valid representations for polar bonds.



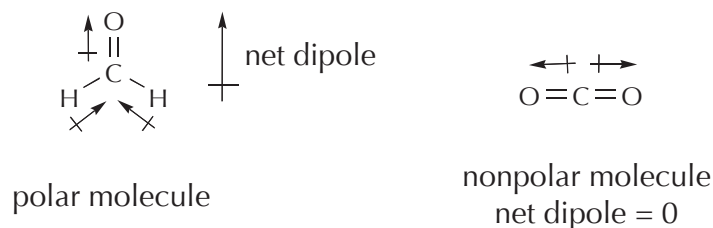
Electronegativity is the tendency of an atom to attract bonding electrons. Since the difference in electronegativity between two bonding atoms can be zero or very large, there is a **polarity continuum**, ranging from nonpolar to highly polar bonds. In an extreme case where the difference in electronegativity is very large, the bond ceases to be covalent and becomes ionic.



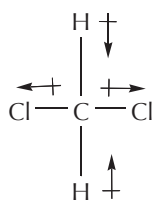
Bond polarity is measured by the **dipole moment**. This parameter is reported in *Debye* units (D). General Chemistry textbooks typically contain tables of dipole moments for different types of bonds. For example, the dipole moment for the C-H bond is 0.3 D, whereas that for the H-Cl bond is 1.09 D.

POLARITY IN ORGANIC MOLECULES

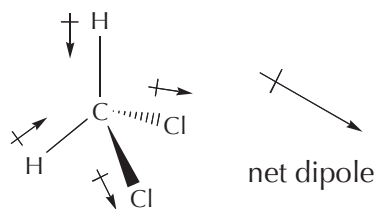
Every covalent bond is either polar or nonpolar. When all the dipoles for all the covalent bonds that make up a molecule are added together as vectors, the result is the **net dipole moment** of the entire molecule. **When its value is zero, the molecule is said to be nonpolar, otherwise it's said to be polar.** Obviously, it is possible to have nonpolar molecules made up of polar bonds, as long as the corresponding dipoles add up to zero. Some examples are shown below. Refer to chapter 2 in your textbook for a more comprehensive discussion of polarity and dipoles.



One must be careful in deciding whether a molecule is polar or nonpolar based purely on a two-dimensional representation. Molecules are three-dimensional, and direction is as important as magnitude when it comes to adding vectors. For example, a two-dimensional representation of the methylene chloride molecule (CH_2Cl_2) shown below might lead to the erroneous conclusion that it is nonpolar when in fact it is polar.

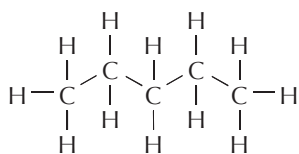


The dipoles appear to cancel out in this 2D representation

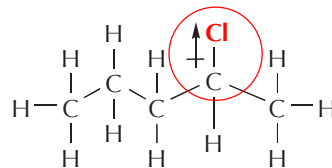


The pyramidal shape of the molecule makes it apparent that the dipoles do not cancel out, and that the molecule is polar

Many organic molecules are made up of long hydrocarbon chains with many C-H bonds. Since the difference in electronegativity between carbon and hydrogen is very small, the C-H bond has a very small dipole moment, and hydrocarbons are for the most part considered nonpolar molecules. However, the introduction of a relatively polar bond in such structures dominates the entire molecule, rendering it polar.



Hydrocarbons are relatively nonpolar molecules



The introduction of a relatively polar bond dictates the polarity of the entire molecule

POLARITY AND PHYSICAL PROPERTIES

The polarity of molecules affects their physical properties. As a rule of thumb and other factors being similar, the higher the polarity of the molecule, the higher the value of properties such as melting and boiling point. The solubility of molecules in solvents is also largely determined by polarity. The rule "*like dissolves like*" makes reference to the fact that polar molecules dissolve better in polar solvents, and nonpolar molecules dissolve better in nonpolar solvents. Water and oil don't mix because water is highly polar and oil is largely made up of hydrocarbon chains, which are nonpolar. Conversely, water and alcohol do mix because they are both of very similar polarities. For a more comprehensive discussion refer to chapter 2 of your textbook.