

7.1: Prelude to Covalent Bonding

While other sections concentrate on [the octet rule](#) and Lewis diagrams for simple covalent molecules, there are numerous examples of molecules which are quite stable, but contain one or more atoms which do not have a noble-gas electron configuration. Furthermore, structural formulas like those from sections under "[Chemical Bonding - Electron Pairs and Octets](#)" only show which atoms are connected to which. They do not tell us how the atoms are arranged in three-dimensional space. In other words a Lewis diagram does not show the shape of a molecule. It may actually be misleading because most molecules don't have the 90° or 180° bond angles that are conventionally used in the Lewis Diagram.

In the following sections, we will develop a more detailed picture of molecules—including some which do not obey the octet rule. You will learn how both the shapes and bonding of molecules may be described in terms of orbitals. In addition it will become apparent that the distinction between covalent and ionic bonding is not so sharp as it may have seemed. You will find that many covalent molecules are electrically unbalanced, causing their properties to tend toward those of ion pairs. Rules will be developed so that you can predict which combinations of atoms will exhibit this kind of behavior.

[Lewis diagrams](#) are used as the first step in predicting the structures for covalently bonded molecules. We will see what supplemental information is required to describe covalent molecules. We will describe some molecules which [do not obey the octet rule](#) and some which contain [multiple bonds](#), as well as simple molecules. The structure of a molecule is determined by the positions of atomic nuclei in three-dimensional space, but it is repulsions among electron pairs—bonding pairs and lone pairs—which determine molecular geometry.

When dealing with molecular shapes, it is often convenient to think in terms of sp , sp^2 , sp^3 , or other [hybrid orbitals](#). These correspond to the same overall electron density and to the same physical reality as do the s and p atomic orbitals considered earlier, but hybrid orbitals emphasize the directions in which electron density is concentrated. Hybrid orbitals may also be used to describe multiple bonding, in which case bonds must be bent so that two or three of them can link the same pair of atoms. A second equivalent approach to multiple bonding involves sigma and pi bonds. Electron density in a sigma bond is concentrated directly between the bonded nuclei, while that of the pi bond is divided in two—half on one side and half on the other side of the sigma bond.

No chemical bond can be 100 percent ionic, and, except for those between identical atoms, 100 percent covalent bonds do not exist either. Electron clouds—especially large, diffuse ones—are easily polarized, affecting the electrical balance of atoms, ions, or molecules. Large negative ions are readily polarized by small positive ions, increasing the covalent character of the bond between them. Electron density in covalent bonds shifts toward the more electronegative atom, producing partial charges on each atom and hence a dipole. In a polyatomic molecule, bond dipoles must be added as vectors to obtain a resultant which indicates molecular polarity. In the case of symmetric molecules, the effects of individual bond dipoles cancel and a nonpolar molecule results.

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such [intermolecular forces](#) may be of three types. All molecules are attracted together by weak [London forces](#). These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, [dipole forces](#) occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the [hydrogen bond](#), occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the [properties of water](#). This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

Oxidation numbers are used by chemists to keep track of electrons during the course of a chemical reaction. They may be obtained by arbitrarily assigning valence electrons to the more electronegative of two bonded atoms and calculating the resulting charge as if the bond were 100 percent ionic. Alternatively, some simple rules are available to predict the oxidation number of each atom in a formula. Oxidation numbers are used in the names of compounds and are often helpful in predicting formulas and writing Lewis diagrams.

In addition to deficiency of electrons and expansion of the valence shell, the octet rule is violated by species which have one or more unpaired electrons. Such free radicals are usually quite reactive. A difficulty of another sort occurs in benzene and other

molecules for which more than one Lewis diagram can be drawn. Rearranging electrons (but not atomic nuclei) results in several structures which are referred to collectively as a resonance hybrid. Like an sp hybrid, a resonance hybrid is a combination of the contributing structures and has properties intermediate between them.

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