

Chapter 8 General bonding

State the basic assumption of the Lewis theory.

Lewis theory assumes that in compounds an atom strives for as many paired electrons as possible, and then the electron configuration of the nearest noble gas. This second part is known as the octet rule since all noble gasses except helium have eight valence electrons. An octet may be obtained by losing, gaining, or sharing electrons. When electrons are lost, a cation is formed. When electrons are gained an anion is formed. When electrons are shared, a covalent bond is formed. When electrons are transferred, anionic attraction is formed.

The valence electron configurations of all elements in a representative family are identical except for the value of the principal quantum number. The Lewis symbol is the symbol of the element surrounded by dots—one dot for each valence electron. The number of valence electrons of a representative element equals the family number. There are four sides to a symbol. Each side can be thought of as representing one valence orbital. No given side represents any particular orbital. So all the electrons are equivalent in energy and bonding ability.

Write Lewis structures for simple ionic compounds

When electrons are gained or lost, cations and anions are formed. Anionic Lewis symbols are surrounded by square brackets to separate the electron dots from the ionic charge.

Define electronegativity and use its value to assess the relative metallic/nonmetallic character of an element.

Electronegativity is a combination of ionization potential and electron affinity—the former number expresses the ease at which an atom loses an outer electron, the latter expresses how strongly an atom attracts electrons. Thus, electronegativity is high for non-metallic elements and low for metallic ones. Electronegativities increase across a period and decrease down a family. These trends are a result of the trends in ionization energies and electron affinities. Generally speaking, metals have electronegativity values below 2.0 and nonmetals have values above 2.0. Metalloids have electronegativity values of about 2.0.

Describe the relationship between electronegativity differences and the percent ionic character of a bond.

The larger the electronegativity difference between two bonded atoms, the less covalent and the more ionic is the bond. An electronegativity difference of 0.5 produces about 6% ionic character. One of 1.0 is about 22% ionic, one of 1.5 is 43% ionic, one of 2.0 is 63% ionic, one of 2.5 is 79% ionic and one of 3.0 is 89% ionic. Often, in fact, it is possible to write both a covalent and an ionic Lewis structure for a molecule or an ion. The hydrogen halides (HF, HCl, HBr, and HI) are common examples. The larger the electronegativity differences between atoms, the greater the contribution of the ionic resonance structure. Resonance hybrids, in general, are more stable than a structure based on one resonance form. Hence, ionic resonance indicates a stronger bond, more difficult to break than a pure covalent bond.

Use the basic rules of Lewis theory to propose a plausible skeleton structure for a molecule and assign valence electrons to this structure.

Too often students believe that they must start with the Lewis symbols for the elements in order to draw Lewis structures—in this way lies madness. The guidelines that follow avoid that difficulty and embrace sanity.

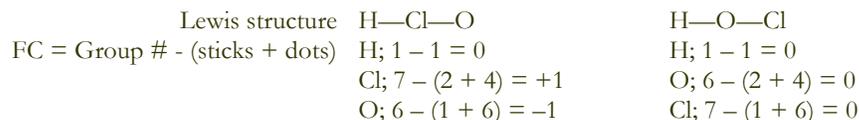
1. Count the total number of valence electrons in the species, remembering to add electrons for anions and subtract them for cations. (group numbers!!!)
2. Decide which atom in the molecule goes in the center. It will be either the most electro-positive element in the formula, or the largest of the atoms in the formula, or both. There are exceptions; F and H are **NEVER** in the center of a molecule.
3. Arrange the remaining atoms so that they are geometrically distributed around the central atom in a plane.
4. Connect each of the outer atoms to the center with a line. This line represents a bond using 2 electrons from your **Step 1** total per line (3 lines = 6 electrons)
5. The remaining electrons are used as lone pair electrons. They go on the outer electrons first (most electronegative) then the central electron.
6. Evaluate the structure based on the octet rule and formal charges to form multiply bonds and the best Lewis structure.

Compute formal charge on each atom in a Lewis structure; and use formal charges to determine which of several Lewis structures is the most plausible.

To determine the formal charge (FC) on an atom, use one of the formulas below. They give the same results.

1. $FC = \text{group number} - \text{number of unshared electrons} - \text{number of shared electrons}/2$
2. $FC = \text{group number} - (\text{sticks (bonds) and dots (lone pair electrons)})$

The most plausible structure is the one in which the formal charges are minimized, or the one in which the sum of the absolute values of the formal charges is the smallest. If formal charges remain in the species, the positive formal charges should be on the least electronegative atoms and the negative formal charges on the most electronegative atoms. Of course, there will always be some nonzero formal charges in an ion, since the sum of formal charges equals the charge on the ion (or zero for a molecule)



Notice that for the first structure the sum of the absolute values is 2, while on the other molecule, the sum is 0.

Recognize situations when resonance occurs and draw plausible resonance structures

Some compounds cannot be represented with a single Lewis structure. For these species, we write several equivalent structures, called resonance structures. These resonance structures have the following features that are true for all resonance structures: Often, the number of bonds of each type (single, double, triple) is the same in each resonance structure. The molecular skeleton is the same in each structure.

All that is involved in creating one resonance structure from another is shifting a few pairs of electrons. Many students have the mistaken impression that the resonance hybrid (the molecule) hops back and forth between its various resonance forms. This is no truer than believing a tangelo is sometimes a grapefruit or other times a tangerine, or that a mule is sometimes a horse or sometimes a donkey. The difficulty in picturing hybrids is the Lewis theory itself. A single structure is not enough since it implies set bond lengths in a molecule. The double bond in a hybrid is longer than a regular double bond but shorter than a single bond.

State which elements can have expanded octets and draw Lewis structures with expanded octets.

For elements of the first and second periods, it is very difficult to place more than an octet around the atom mainly because it requires too much energy, but also because the central atom is very small, leaving little room for more than four pairs of electrons. To add an extra electron we must go to a new quantum shell. This is not the case for elements of the third period and higher. The d orbitals begin here and they are empty, waiting for electrons. These elements can have expanded octets (emphasis on can, it means that they obey the octet rule but can also expand). COFN (coffin) must obey the octet rule.

Use bond distances to help writing Lewis structures and bond energies to compute the enthalpy change of a reaction.

Bond order (single, double, triple) lets us predict relative bond length and strength. Bond strength from weakest to strongest is: single < double < triple. Bond length from longest to shortest is: Single > double > triple. This information can help us decide between various Lewis structures. For example, B—F bond length is somewhat shorter than the average B—F bond in BF_3 . Therefore, the bond should have some double bond character and resonance structures.

Bond energies can be used to calculate and approximate ΔH° value for a reaction involving reactants and products that are all gases. $\Delta H^\circ = \text{bonds broken} - \text{bonds formed}$.

Predict the electron pair geometry and the molecular shape of a molecule or ion with VSEPR theory. Know that single bonds act similarly to multiple bonds in determining molecular shape.

Lewis theory does not predict molecular shape. The VSEPR theory accounts for molecular shape. The basis of the theory is that pairs of electrons in the valence shell of an atom try to get as far apart as they can and still remain attached to the atom. A general molecular formula is AX_mE_n , where A represents the central atom; X represents each of the atoms or groups of atoms bound to the central atom. E represents each of the lone pairs on the central atom. n is the number of lone pairs and m is the number of bonding pairs. $m + n$ is the total number of electron pairs. A double or triple bond is counted as one bonding pair. This total determines the electron pair geometry of the molecule or ion. We use dashes to indicate atoms in a plane away from you and wedges to indicate atoms pointing toward you.

Although the total number of electron pairs determines the electron pair geometry, we only can see the ligands. We see only the effect of the lone pairs. Size electron pairs decrease in the following manner: lone pair > lone electron > triple bond > double bond > single bond. Repulsions between different types of electron pairs decrease as follows: lone pair–lone pair > lone pair–bond pair > bond pair–bond pair. Since there is more room around the equator of a trigonal bipyramidal than

its axes, the lone pair occupies the equatorial position. (We count only 90° repulsions.) First you draw a good Lewis structure. Then count the number of ligands and lone pairs. From this information, you can get the electron pair geometry and the molecular geometry.

Use electronegativities to determine if a bond is polar and use bond polarities and molecular shape to predict whether a molecule has a dipole moment.

In a pure covalent bond, the bonding pair of electrons is shared equally between the two atoms. In a polar bond, the bonding pair is shifted toward the more electronegative atom. Thus, carbon dioxide and water both have polar bonds. The dipole points away from the more electron positive atom. Having polar bonds in a molecule does not mean the molecule will necessarily be polar.

VSEPR predicts that carbon dioxide is linear and water is bent. Since the two bond dipoles in carbon dioxide are equal and point in opposite directions, they cancel. Carbon dioxide has no net dipole moment. The molecular shape of water (bent) is based on the VSEPR shape of tetrahedral. In the water molecule, the bond dipoles do not point in exactly opposite directions and therefore they do not cancel. Water has a dipole moment.

This is an important point to remember: Whether a molecule is polar or non-polar does not depend on the internal bonds. Often, the molecular bonds are non-polar, yet structural features lead to a polar molecule.

There are three main factors in predicting polarity. They are shape, presences or absence of lone pairs, and symmetry (or lack there of). Symmetry means that the molecule is completely symmetrical; all of the dipoles in the molecule cancel; the atoms attached to the central atom are the same; there are no lone pairs on the central atom. Of course, in chemistry, there are exceptions to this observation. For two shapes, trigonal bipyramidal, and octahedral, the molecule can have lone pairs and still be non polar. The polarity of molecules with this VSEPR shape would be determined by the symmetry of the lone pairs. In general, though, lone pairs present on the central atom mean the molecule is polar. Molecular geometries that indicate the presences of lone pairs (such as bent, trigonal pyramidal, seesaw, T-shaped, and square planar) are always polar. Molecular geometries that are the same as VSEPR, or that depend on lone-pairs canceling due to placement around the central atom are usually not polar.