Chemical Bonding: General Concepts

Lewis Dot Symbols

Lewis explanation, is that atoms combine to achieve a more stable electron configuration. When atoms interact to form a chemical bond, only their outer regions are in contact. For this reason, it is concerned with the valence electrons of the atoms while forming chemical bonding.

A Lewis dot symbol consists of the symbol of an element and one dot for each valence electron in an atom of the element. Note that, except for helium, the number of valence electrons each atom has is the same as the group number of the element. For example, Li is a Group 1A element and has one dot for one valence electron; Be, a Group 2A element, has two valence electrons (two dots); and so on.

Elements in the same group have similar outer electron configurations and hence similar Lewis dot symbols.

Writing Lewis Structures

Although the octet rule and Lewis structures do not present a complete picture of covalent bonding, they do help to explain the bonding scheme in many compounds and account for the properties and reactions of molecules.

For this reason, you should practice writing Lewis structures of compounds. The basic steps are as follows:

1. Write the skeletal structure of the compound, using chemical symbols and placing bonded atoms next to one another.

2. Count the total number of valence electrons present referred. For polyatomic anions, add the number of negative charges to that total.

3. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. Electrons belonging to the central or surrounding atoms must be shown as lone pairs if they are not involved in bonding.

4. If the central atom has fewer than eight electrons, try adding double or triple bonds between the surrounding atoms and the central atom, using lone pairs from the surrounding atoms to complete the octet of the central atom.

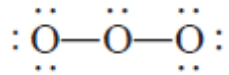
Formal Charge and Lewis Structure

By comparing the number of electrons in an isolated atom with the number of electrons that are associated with the same atom in a Lewis structure, it can be determined the distribution of electrons in the molecule and draw Lewis structure.
In an isolated atom, the number of electrons associated with the atom is simply the number of valence electrons.

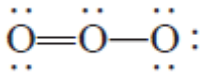
In a molecule, electrons associated with the atom are the nonbonding electrons plus the electrons in the bonding pair(s) between the atom and other atom(s).

An atom's ***formal charge*** is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

Formal charge using the ozone molecule (O_3) is shown. It is drawn the skeletal structure of O_3 and then add bonds and electrons to satisfy the octet rule for the two end atoms:



To remedy this, we convert a lone pair on one of the end atoms to a second bond between that end atom and the central atom, as follows:



1. For molecules, the sum of the formal charges must add up to zero because molecules are electrically neutral species.

2. For cations, the sum of the formal charges must equal the positive charge.

3. For anions, the sum of the formal charges must equal the negative charge. In the O_3 molecule, there is no evidence that the central atom bears a net +1 charge or that one of the end atoms bears a -1 charge. Writing these charges on the atoms in the Lewis structure merely helps us keep track of the valence electrons in the molecule.

• For molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.

• Lewis structures with large formal charges are less plausible than those with small formal charges.

• Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

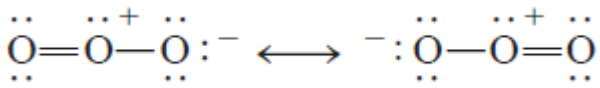
The Concept of Resonance

Our drawing of the Lewis structure for ozone (O3) satisfied the octet rule for the central atom because we placed a double bond between it and one of the two end O atoms. In fact, we can put the double bond at either end of the molecule, as shown by these two equivalent Lewis structures:

However, neither one of these two Lewis structures accounts for the known bond lengths in O3.

We would expect the O¬O bond in O3 to be longer than the O“O bond because double bonds are known to be shorter than single bonds. Yet experimental evidence shows that both oxygen-to-oxygen bonds are equal in length.

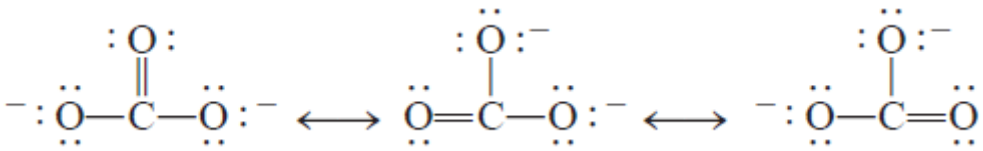
We resolve this discrepancy by using *both* Lewis structures to represent the ozone molecule:



Each of these structures is called a resonance structure.

A ***resonance structure,*** then, is *one* of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure. The double-headed arrow indicates that the structures shown are resonance structures. The term ***resonance*** itself means *the use of two or more Lewis structures to represent a particular molecule.* Like the medieval European traveler to Africa who described a rhinoceros as a cross between a griffin and a unicorn, two familiar but imaginary animals, we describe ozone, a real molecule, in terms of two familiar but nonexistent structures.

The carbonate ion provides another example of resonance:



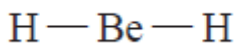
Exceptions to the Octet Rule

As mentioned earlier, the octet rule applies mainly to the second-period elements. Exceptions to the octet rule fall into three categories characterized by an incomplete octet, an odd number of electrons, or more than eight valence electrons around the central atom.

The Incomplete Octet

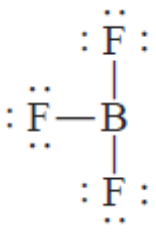
In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Consider, for example, beryllium, which is a Group 2A and a second-period element.

In the gas phase, beryllium hydride (BeH2) exists as discrete molecules. The Lewis structure of BeH2 is

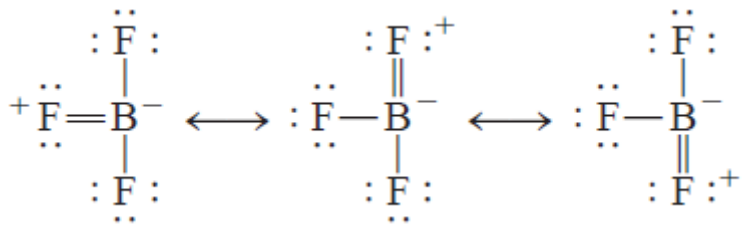


Elements in Group 3A, particularly boron and aluminum, also tend to form compounds in which they are surrounded by fewer than eight electrons. Take boron as an example. Because its electron configuration is $1s^2 2s^2 2p^1$, it has a total of three valence electrons. Boron reacts with the halogens to form a class of compounds having the general formula BX_3, where X is a halogen atom.

Thus, in boron trifluoride there are only six electrons around the boron atom:

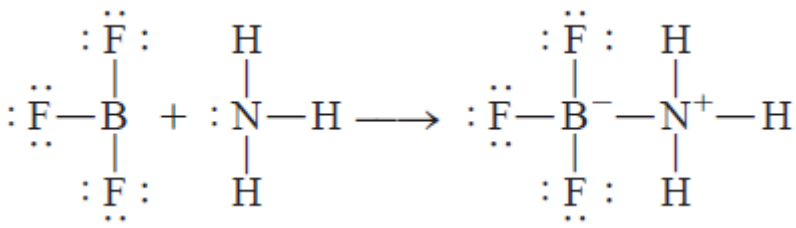


The following resonance structures all contain a double bond between B and F and satisfy the octet rule for boron:



The fact that the BOF bond length in BF3 is shorter than a single bond lends support to the resonance structures even though in each case the negative formal charge is placed on the B atom and the positive formal charge on the F atom.

Although boron trifluoride is stable, it readily reacts with ammonia. This reaction is better represented by using the Lewis structure in which boron has only six valence electrons around it:



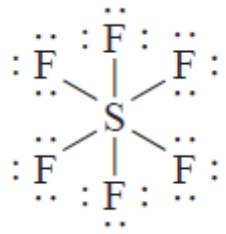
It seems that the properties of the BF3 molecule are best explained by all four resonance structures.

This type of bond is called a **coordinate covalent bond** defined as a covalent bond in which one of the atoms donates both electrons. Although the properties of a coordinate covalent bond do not differ from those of a normal covalent bond, the distinction is useful for keeping track of valence electrons and assigning formal charges.

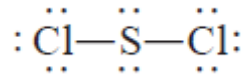
The Expanded Octet

Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom. In addition to the 3*s* and 3*p* orbitals, elements in the third period also have 3*d* orbitals that can be used in bonding. These orbitals enable an atom to form an *expanded octet.* One compound in which there is an expanded octet is sulfur hexafluoride, a very stable compound.

The electron configuration of sulfur is [Ne]3*s*23*p*4. In SF6, each of sulfur's six valence electrons forms a covalent bond with a fluorine atom, so there are twelve electrons around the central sulfur atom:



In sulfur dichloride, for instance, S is surrounded by only eight electrons:



A final note about the expanded octet: In drawing Lewis structures of compounds containing a central atom from the third period and beyond, sometimes we find that the octet rule is satisfied for all the atoms but there are

still valence electrons left to place. In such cases, the extra electrons should be placed as lone pairs on the central atom.

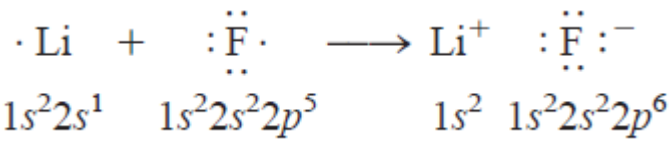
Types of Chemical Bonds

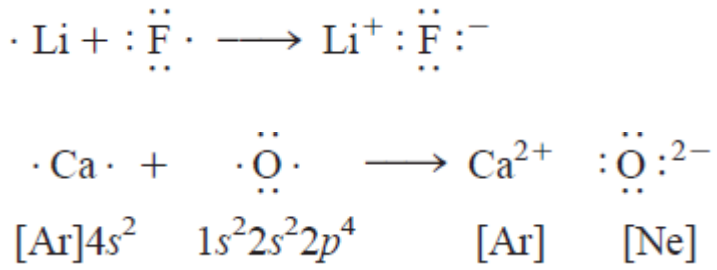
The Ionic Bond

Atoms of elements with low ionization energies tend to form cations, while those with high electron affinities tend to form anions. As a rule, the elements most likely to form cations in ionic compounds are the alkali metals and alkaline earth metals, and the elements most likely to form anions are the halogens and oxygen.

Consequently, a wide variety of ionic compounds combine a Group 1A or Group 2A metal with a halogen or oxygen.

An **ionic bond** is the electrostatic force that holds ions together in an ionic compound. Consider, for example, the reaction between lithium and fluorine to form lithium fluoride, a poisonous white powder used in lowering the melting point of solders and in manufacturing ceramics. The electron configuration of lithium is $1s^2 2s^1$, and that of fluorine is $1s^2 2s^2 2p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s1$ valence electron of lithium is transferred to the fluorine atom. Using Lewis dot symbols, we represent the reaction like this:





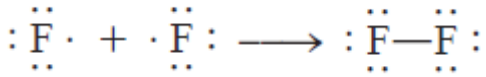
The Covalent Bond

The first major breakthrough was Gilbert Lewis's suggestion that a chemical bond involves electron sharing by atoms. He depicted the formation of a chemical bond in H_2 as This type of electron pairing is an example of a **covalent bond,** a bond in which two electrons are shared by two atoms. **Covalent compounds** are compounds that contain only covalent bonds. For the sake of simplicity, the shared pair of electrons is often represented by a single line.

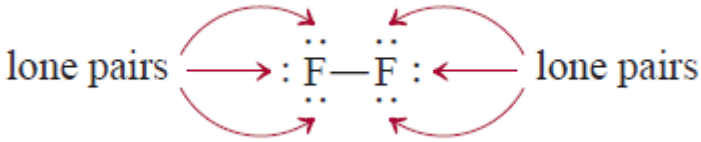
Thus, the covalent bond in the hydrogen molecule can be written as HOH. In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in H2 together and is responsible for the formation of covalent bonds in other molecules.

Covalent bonding between many-electron atoms involves only the valence electrons. Consider the fluorine molecule, F_2. The electron configuration of F is $1s^2 2s^2 2p^5$. The 1*s* electrons are low in energy and stay near the nucleus most of the time. For this reason they do not participate in bond formation. Thus, each

F atom has seven valence electrons. There is only one unpaired electron on F, so the formation of the F2 molecule can be represented
as follows:



Note that only two valence electrons participate in the formation of F2. The other, nonbonding electrons, are called **lone pairs**. Thus, each F in F2 has three lone pairs of electrons:



The structures we use to represent covalent compounds, such as H2 and F2, are called Lewis structures. A **Lewis structure** is a representation of covalent bonding in which shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms.

Because hydrogen has only one electron, it can form only one covalent bond. Thus, the Lewis structure for water is In this case, the O atom has two lone pairs. The hydrogen atom has no lone pairs because its only electron is used to form a covalent bond.

In the F2 and H2O molecules, the F and O atoms achieve the stable noble gas configuration by sharing electrons:

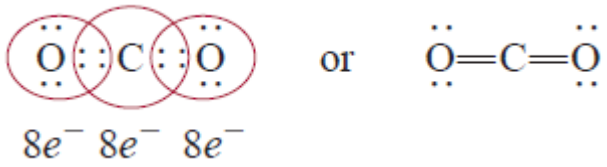
The formation of these molecules illustrates the ***octet rule,*** formulated by Lewis:

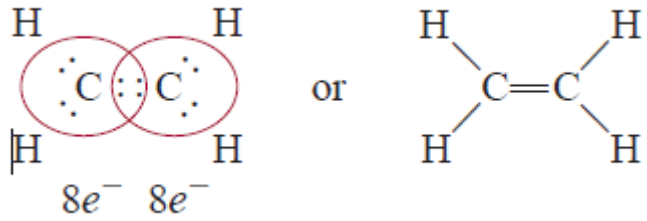
An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons. In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electron configuration of helium, or a total of two electrons.

The octet rule works mainly for elements in the second period of the periodic table. These elements have only 2*s* and 2*p* subshells, which can hold a total of eight electrons. When an atom of one of these elements forms a covalent compound, it can attain the noble gas electron configuration [Ne] by sharing electrons with other atoms in the same compound. Later, we will discuss a number of important exceptions to the octet rule that give us further insight into the nature of chemical bonding.

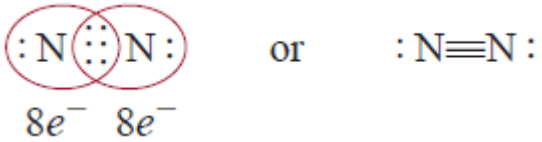
Atoms can form different types of covalent bonds. In a **single bond,** two atoms are held together by one electron pair. Many compounds are held together by **multiple bonds,** that is, bonds formed when two atoms share two or more pairs of electrons.

If *two atoms share two pairs of electrons,* the covalent bond is called a ***double bond.*** Double bonds are found in molecules of carbon dioxide (CO2) and ethylene (C2H4):

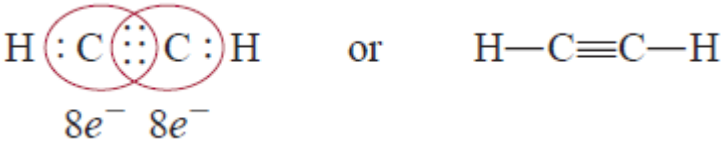




A **triple bond** arises when two atoms share three pairs of electrons, as in the nitrogen molecule (N2):



The acetylene molecule (C_2H_2) also contains a triple bond, in this case between two carbon atoms:



Note that in ethylene and acetylene all the valence electrons are used in bonding; there are no lone pairs on the carbon atoms. In fact, with the exception of carbon monoxide, the vast majority of stable molecules containing carbon do not have lone pairs on the carbon atoms.

Electronegativity

A covalent bond is the sharing of an electron pair by two atoms. In a molecule like H_2, in which the atoms are identical, we expect the electrons to be equally shared that is, the electrons spend the same amount of time in the vicinity of each atom. However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms: The bond in HF is called a polar covalent bond, or simply a polar bond, because the electrons spend more time in the vicinity of one atom than the other.

In the HF molecule the electrons spend more time near the F atom. This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. To distinguish a nonpolar covalent bond from a polar covalent bond is electronegativity, the ability of an atom to attract toward itself the electrons in a chemical bond. Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity.

Electronegativity is related to electron affinity and ionization energy. Thus, an atom such as fluorine, which has a high electron affinity and a high ionization energy, has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character.

Atoms of elements with widely different electronegativities tend to form ionic bonds such as NaCl and CaO compounds with each other because the atom of the less electronegative element gives up its electron(s) to the atom of the more electronegative element.

An ionic bond generally joins an atom of a metallic element and an atom of a nonmetallic element. Atoms of elements with comparable electronegativities tend to form polar covalent bonds with each other because the shift in electron density is usually small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same element, which have the same electronegativity, can be joined by a pure covalent bond.

An ionic bond forms when the electronegativity difference between the two bonding atoms is 2.0 or more. This rule applies to most but not all ionic compounds. A polar covalent bond forms when the electronegativity difference between the atoms is in the range of 0.5–1.6. If the electronegativity difference is below 0.3, the bond is normally classified as a covalent bond, with little or no polarity.

Electronegativity and electron affinity are related but different concepts. Both indicate the tendency of an atom to attract electrons. However, electron affinity refers to an isolated atom’s attraction for an additional electron, Furthermore, electron affinity is an experimentally measurable quantity, whereas electronegativity is an estimated number that cannot be measured.

Electronegativity and Oxidation Number

It was introduced the rules for assigning oxidation numbers of elements in their compounds. The concept of electronegativity is the basis for these rules. In essence, oxidation number refers to the number of charges an atom would have if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Consider the NH_3 molecule, in which the N atom forms three single bonds with the H atoms. Because N is more electronegative than H, electron density will be shifted from H to N. If the transfer were complete, each H would donate an electron to N, which would have a total charge of -3 while each H would have a charge of +1. Thus, we assign an oxidation number of -3 to N and an oxidation number of +1 to H in NH_3.

Oxygen usually has an oxidation number of -2 in its compounds, except in hydrogen peroxide (H_2O_2), whose Lewis structure is

A bond between identical atoms makes no contribution to the oxidation number of those atoms because the electron pair of that bond is equally shared. Because H has an oxidation number of +1, each O atom has an oxidation number of -2. Can you see now why fluorine always has an oxidation number of -1? It is the most electronegative element known, and it usually forms a single bond in its compounds.