1.2: Bonding

Bonding Overview

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

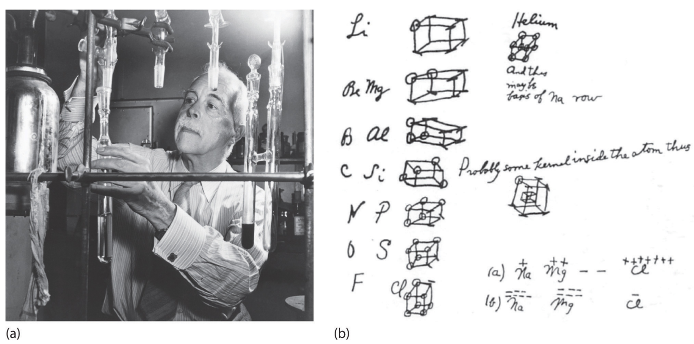


Figure 8.1.1 *G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.*

Lewis Symbols

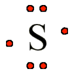
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Note

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

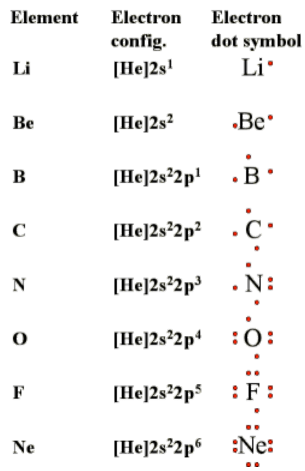
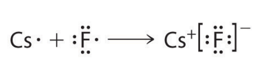


Figure 8.1.2: *Lewis Dot Symbols for the Elements in Period 2*

The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. An exception to the octet rule is helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

Note

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

Ionic bonding

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged.

Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 8.2.1a: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

For full video of making NaCl from sodium metal and chlorine gase, see https://www.youtube.com/watch?v=WVonuBjCrNo. These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):

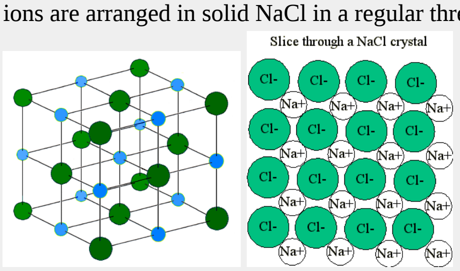
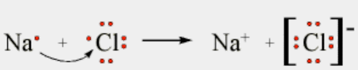


Figure: *NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.*

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using ***electron-dot symbols*** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- Na^{+}: $2s^2 2p^6$
- Cl^-: $3s^2 3p^6$

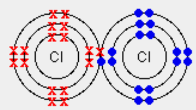
The importance of noble gas structures

At a simple level a lot of importance is attached to the electronic structures of noble gases like neon or argon which have eight electrons in their outer energy levels (or two in the case of helium). These noble gas structures are thought of as being in some way a "desirable" thing for an atom to have.
You may well have been left with the strong impression that when other atoms react, they try to achieve noble gas structures. As well as achieving noble gas structures by transferring electrons from one atom to another as in ionic bonding, it is also possible for atoms to reach these stable structures by sharing electrons to give covalent bonds.

Some very simple covalent molecules

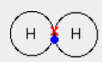
Chlorine

For example, two chlorine atoms could both achieve stable structures by sharing their single unpaired electron as in the diagram.



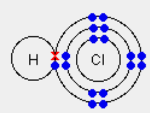
The fact that one chlorine has been drawn with electrons marked as crosses and the other as dots is simply to show where all the electrons come from. In reality there is no difference between them. The two chlorine atoms are said to be joined by a covalent bond. The reason that the two chlorine atoms stick together is that the shared pair of electrons is attracted to the nucleus of both chlorine atoms.

Hydrogen

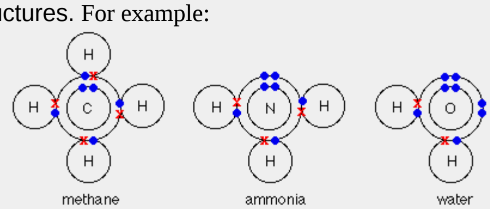


Hydrogen atoms only need two electrons in their outer level to reach the noble gas structure of helium. Once again, the covalent bond holds the two atoms together because the pair of electrons is attracted to both nuclei.

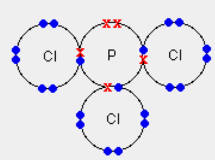
Hydrogen chloride



The hydrogen has a helium structure, and the chlorine an argon structure. Most of the simple molecules you draw do in fact have all their atoms with noble gas structures. For example:



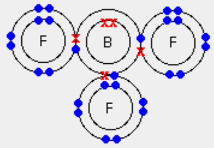
Even with a more complicated molecule like , there's no problem. In this case, only the outer electrons are shown for simplicity. Each atom in this structure has inner layers of electrons of 2, 8. Again, everything present has a noble gas structure.



Cases where the simple view throws up problems

Boron trifluoride, BF_3

A boron atom only has 3 electrons in its outer level, and there is no possibility of it reaching a noble gas structure by simple sharing of electrons. Is this a problem? No. The boron has formed the maximum number of bonds that it can in the circumstances, and this is a perfectly valid structure.

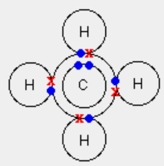


Energy is released whenever a covalent bond is formed. Because energy is being lost from the system, it becomes more stable after every covalent bond is made. It follows, therefore, that an atom will tend to make as many covalent bonds as possible. In the case of boron in BF_3, three bonds is the maximum possible because boron only has 3 electrons to share.
Note: You might perhaps wonder why boron doesn't form ionic bonds with fluorine instead. Boron doesn't form ions because the total energy needed to remove three electrons to form a B^{3+} ion is simply too great to be recoverable when attractions are set up between the boron and fluoride ions.

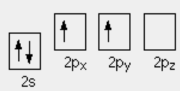
A more sophisticated view of covalent bonding

The bonding in methane, CH_4

What is wrong with the dots-and-crosses picture of bonding in methane?
We are starting with methane because it is the simplest case which illustrates the sort of processes involved. You will remember that the dots-and-crossed picture of methane looks like this.



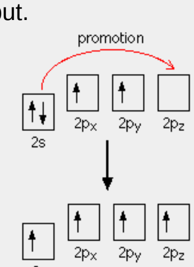
There is a serious mis-match between this structure and the modern electronic structure of carbon, $1s^22s^22p_x^{\,1}2p_y^{\,1}$. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 which the simple view requires.



You can see this more readily using the electrons-in-boxes notation. Only the 2-level electrons are shown. The $1s^2$ electrons are too deep inside the atom to be involved in bonding. The only electrons directly available for sharing are the 2p electrons. Why then isn't methane CH_2?

Promotion of an electron

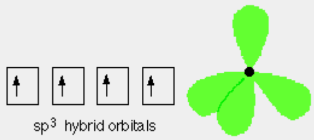
When bonds are formed, energy is released and the system becomes more stable. If carbon forms 4 bonds rather than 2, twice as much energy is released and so the resulting molecule becomes even more stable.
There is only a small energy gap between the 2s and 2p orbitals, and so it pays the carbon to provide a small amount of energy to promote an electron from the 2s to the empty 2p to give 4 unpaired electrons. The extra energy released when the bonds form more than compensates for the initial input.



The carbon atom is now said to be in an excited state. Now that we've got 4 unpaired electrons ready for bonding, another problem arises. In methane all the carbon-hydrogen bonds are identical, but our electrons are in two different kinds of orbitals. You aren't going to get four identical bonds unless you start from four identical orbitals.

Hybridization

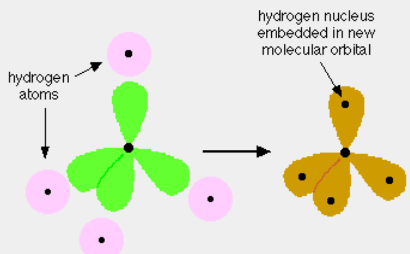
The electrons rearrange themselves again in a process called hybridization. This reorganizes the electrons into four identical hybrid orbitals called sp^3 hybrids (because they are made from one s orbital and three p orbitals). You should read "sp^3" as "s p three" - not as "s p cubed".



sp^3 hybrid orbitals look a bit like half a p orbital, and they arrange themselves in space so that they are as far apart as possible. You can picture the nucleus as being at the center of a tetrahedron (a triangularly based pyramid) with the orbitals pointing to the corners. For clarity, the nucleus is drawn far larger than it really is.

What happens when the bonds are formed?

Remember that hydrogen's electron is in a 1s orbital - a spherically symmetric region of space surrounding the nucleus where there is some fixed chance (say 95%) of finding the electron. When a covalent bond is formed, the atomic orbitals (the orbitals in the individual atoms) merge to produce a new molecular orbital which contains the electron pair which creates the bond.



Four molecular orbitals are formed, looking rather like the original sp^3 hybrids, but with a hydrogen nucleus embedded in each lobe. Each orbital holds the 2 electrons that we've previously drawn as a dot and a cross.
The principles involved - promotion of electrons if necessary, then hybridisation, followed by the formation of molecular orbitals - can be applied to any covalently-bound molecule.

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