Structure and Bonding

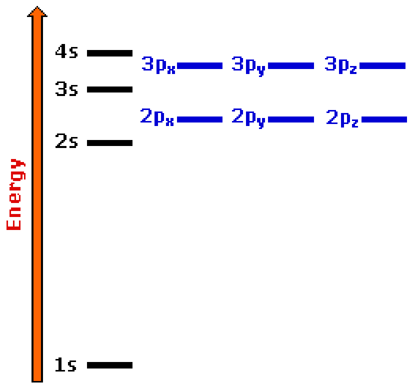
The study of organic chemistry must at some point extend to the molecular level, for the physical and chemical properties of a substance are ultimately explained in terms of the structure and bonding of molecules. This module introduces some basic facts and principles that are needed for a discussion of organic molecules.

Electronic Configurations

Electron Configurations in the Periodic Table

1A	2A	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$							2 **He** $1s^2$
3 **Li** $1s^2$ $2s^1$	4 **Be** $1s^2$ $2s^2$	5 **B** $1s^2$ $2s^22p^1$	6 **C** $1s^2$ $2s^22p^2$	7 **N** $1s^2$ $2s^22p^3$	8 **O** $1s^2$ $2s^22p^4$	9 **F** $1s^2$ $2s^22p^5$	10 **Ne** $1s^2$ $2s^22p^6$
11 **Na** [Ne] $3s^1$	12 **Mg** [Ne] $3s^2$	13 **Al** [Ne] $3s^23p^1$	14 **Si** [Ne] $3s^23p^2$	15 **P** [Ne] $3s^23p^3$	16 **S** [Ne] $3s^23p^4$	17 **Cl** [Ne] $3s^23p^5$	18 **Ar** [Ne] $3s^23p^6$

Four elements, hydrogen, carbon, oxygen and nitrogen, are the major components of most organic compounds. Consequently, our understanding of organic chemistry must have, as a foundation, an appreciation of the electronic structure and properties of these elements. The truncated periodic table shown above provides the orbital electronic structure for the first eighteen elements (hydrogen through argon). According to the **Aufbau principle**, the electrons of an atom occupy quantum levels or orbitals starting from the lowest energy level, and proceeding to the highest, with each orbital holding a maximum of two paired electrons (opposite spins).



Relative Energy of s and p Orbitals
(d orbitals are not shown)

Electron shell #1 has the lowest energy and its s-orbital is the first to be filled. Shell #2 has four higher energy orbitals, the 2s-orbital being lower in energy than the three 2p-orbitals. (x, y & z). As we progress from lithium (atomic number=3) to neon (atomic number=10) across the second row or period of the table, all these atoms start with a filled 1s-orbital, and the 2s-orbital is occupied with an electron pair before the 2p-orbitals are filled. In the third period of the table, the atoms all have a neon-like core of 10 electrons, and shell #3 is occupied progressively with eight electrons, starting with the 3s-orbital. The highest occupied electron shell is called the **valence shell**, and the electrons occupying this shell are called **valence electrons**.

The chemical properties of the elements reflect their electron configurations. For example, helium, neon and argon are exceptionally stable and unreactive monoatomic gases. Helium is unique since its valence shell consists of a single s-orbital. The other members of group 8 have a characteristic **valence shell electron octet** ($ns^2 + np_x^2 + np_y^2 + np_z^2$). This group of **inert (or noble) gases** also includes krypton (Kr: $4s^2$, $4p^6$), xenon (Xe: $5s^2$, $5p^6$) and radon (Rn: $6s^2$, $6p^6$). In the periodic table above these elements are colored beige.

The **halogens** (F, Cl, Br etc.) are one electron short of a valence shell octet, and are among the most reactive of the elements (they are colored red in this periodic table). In their chemical reactions halogen atoms achieve a valence shell octet by capturing or borrowing the eighth electron from another atom or molecule. The**alkali metals** Li, Na, K etc. (colored violet above) are also exceptionally reactive, but for the opposite reason. These atoms have only one electron in the valence shell, and on losing this electron arrive at the lower shell valence octet. As a consequence of this electron loss, these elements are commonly encountered as cations (positively charged atoms). The elements in groups 2 through 7 all exhibit characteristic reactivities and bonding patterns that can in large part be rationalized by their electron configurations. It should be noted that hydrogen is unique. Its location in the periodic table should not suggest a kinship to the chemistry of the alkali metals, and its role in the structure and properties of organic compounds is unlike that of any other element.

Bonding & Valence

Chemical Bonding and Valence

As noted earlier, the inert gas elements of group 8 exist as monoatomic gases, and do not in general react with other elements. In contrast, other gaseous elements exist as diatomic molecules (H_2, N_2, O_2, F_2 & Cl_2), and all but nitrogen are quite reactive. Some dramatic examples of this reactivity are shown in the following equations.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

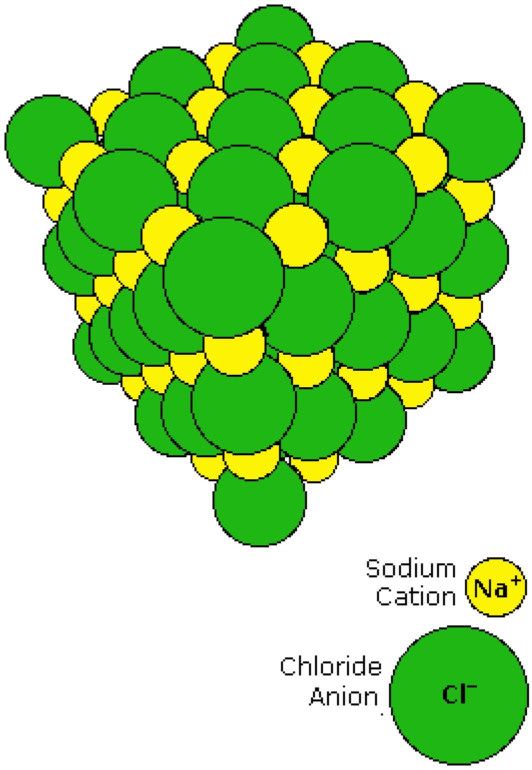
$$C + O_2 \longrightarrow CO_2$$

$$C + 2F_2 \longrightarrow CF_4$$

Why do the atoms of many elements interact with each other and with other elements to give stable molecules? In addressing this question it is instructive to begin with a very simple model for the attraction or bonding of atoms to each other, and then progress to more sophisticated explanations.

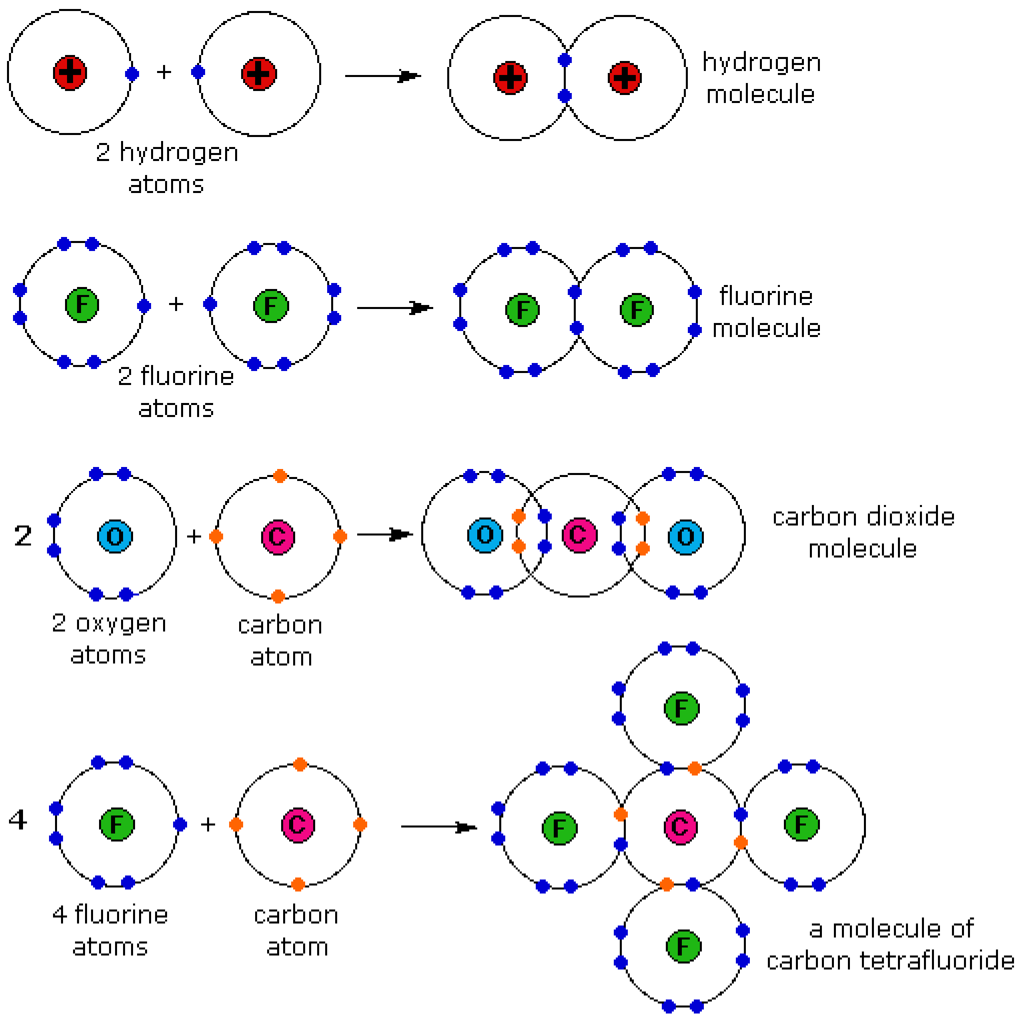
Ionic Bonding

When sodium is burned in a chlorine atmosphere, it produces the compound sodium chloride. This has a high melting point (800 ºC) and dissolves in water to to give a conducting solution. Sodium chloride is an ionic compound, and the crystalline solid has the structure shown on the right. Transfer of the lone 3s electron of a sodium atom to the half-filled 3p orbital of a chlorine atom generates a sodium cation (neon valence shell) and a chloride anion (argon valence shell). Electrostatic attraction results in these oppositely charged ions packing together in a lattice. The attractive forces holding the ions in place can be referred to as ionic bonds. By clicking on the NaCl diagram, a model of this crystal will be displayed and may be manipulated.

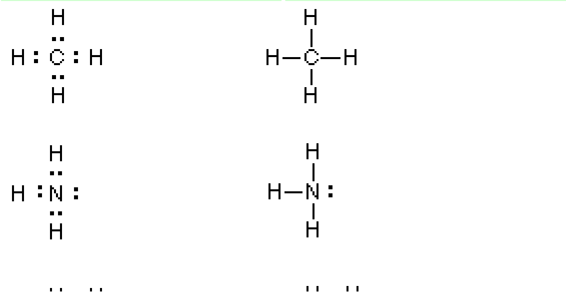


Covalent Bonding

The other three reactions shown above give products that are very different from sodium chloride. Water is a liquid at room temperature; carbon dioxide and carbon tetrafluoride are gases. None of these compounds is composed of ions. A different attractive interaction between atoms, called covalent bonding, is involved here. Covalent bonding occurs by a sharing of valence electrons, rather than an outright electron transfer. Similarities in physical properties (they are all gases) suggest that the diatomic elements H_2, N_2, O_2, F_2 & Cl_2 also have covalent bonds. Examples of covalent bonding shown below include hydrogen, fluorine, carbon dioxide and carbon tetrafluoride. These illustrations use a simple Bohr notation, with valence electrons designated by colored dots. Note that in the first case both hydrogen atoms achieve a helium-like pair of 1s-electrons by sharing. In the other examples carbon, oxygen and fluorine achieve neon-like valence octets by a similar sharing of electron pairs. Carbon dioxide is notable because it is a case in which two pairs of electrons (four in all) are shared by the same two atoms. This is an example of a double covalent bond.



These electron sharing diagrams (Lewis formulas) are a useful first step in understanding covalent bonding, but it is quicker and easier to draw Couper-Kekulé formulas in which each shared electron pair is represented by a line between the atom symbols. Non-bonding valence electrons are shown as dots. These formulas are derived from the graphic notations suggested by A. Couper and A. Kekulé, and are not identical to their original drawings. Some examples of such **structural formulas** are given in the following table.

Common Name	Molecular Formula	Lewis Formula	Kekulé Formula
Methane	CH_4		
Ammonia	NH_3		
Ethane	C_2H_6		
Methyl Alcohol	CH_4O		
Ethylene	C_2H_4		
Formaldehyde	CH_2O		
Acetylene	C_2H_2		

Hydrogen Cyanide	CHN

Multiple bonding, the sharing of two or more electron pairs, is illustrated by ethylene and formaldehyde (each has a double bond), and acetylene and hydrogen cyanide (each with a triple bond). Boron compounds such as BH_3 and BF_3 are exceptional in that conventional covalent bonding does not expand the valence shell occupancy of boron to an octet. Consequently, these compounds have an affinity for electrons, and they exhibit exceptional reactivity when compared with the compounds shown above.

Valence

The number of valence shell electrons an atom must gain or lose to achieve a valence octet is called valence. In covalent compounds the number of bonds which are characteristically formed by a given atom is equal to that atom's valence. From the formulas written above, we arrive at the following general valence assignments:

Atom	H	C	N	O	F	Cl	Br	I
Valence	1	4	3	2	1	1	1	1

The valences noted here represent the most common form these elements assume in organic compounds. Many elements, such as chlorine, bromine and iodine, are known to exist in several valence states in different inorganic compounds.

Source : http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro1.htm