References:

1- Robert T. Morrison, Robert N. Boyd, Organic Chemistry, Sixth Edition, Prentice-Hall, Inc. U. S. A. (2000).

2-John McMurry " Organic Chemistry " 7th Edition Thomson Learning, Inc. U.S.A (2008).

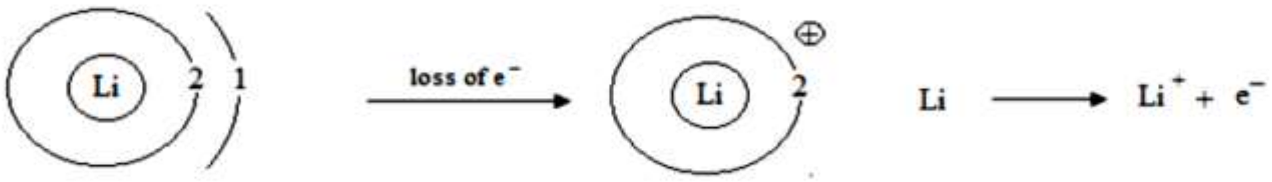
Introduction

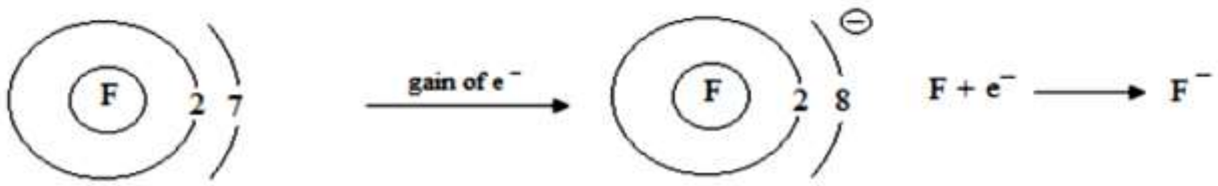
Organic Chemistry

Organic chemistry: is the chemistry of the compounds of carbon. Chemical compounds were divided into two classes, Inorganic compounds are those obtained from minerals, while organic compounds are those obtained from vegetable or animal sources, that is, from material produced by living organisms or synthesized in the laboratory.

The Bonds

A positively charged nucleus is surrounded by electrons arranged in shells or energy levels. There are a maximum number of electrons that can be accommodated in each shell: two in the first shell, eight in the second shell, eight or eighteen in the third shell, and so on. The greatest stability is reached when the outer shell is full, as in the noble gases. Both ionic and covalent bonds arise from the tendency of atoms to attain this stable configuration of electrons.





The ***ionic bond*** results from *transfer of electrons*, as for example, in the formation of lithium fluoride LiF. The ***covalent bond*** results from *sharing of electrons*, as for example, in formation of the hydrogen molecule H_2. And also, HF, H_2O, NH_3, CF_4, and CH_4.

$$H\cdot + \cdot H \longrightarrow H{:}H$$

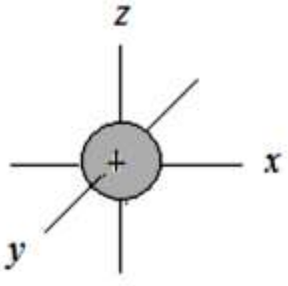
The covalent bond is typical of the compounds of carbon; it is the bond of importance in the study of organic chemistry.

Atomic Orbitals

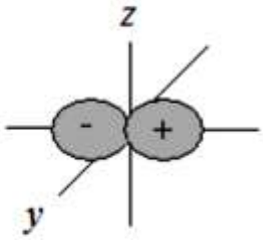
The region in space where an electron is likely to be found is called an orbital. There are different kind of orbitals, which have different sizes and different shapes. The particular kind of orbital that an electron occupies depends upon the energy of the electron.

The orbital at the lowest energy level is called the 1*s* orbital. It is a sphere with its center at the nucleus of the atom. The 2*s* orbital is naturally larger than 1*s*, and it is also a sphere with its center at the atomic nucleus.

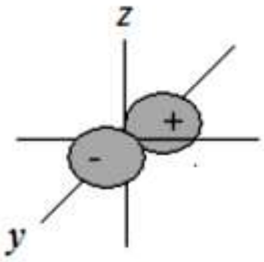
Next there are three orbitals of equal energy called 2*p* orbitals, each of them is dumbbell-shaped. It consists of two lobes with the atomic nucleus lying between them. The axis of each 2*p* orbital is perpendicular to the axes of the two others. They are differentiated by the names $2p_x$, $2p_y$, and $2p_z$ as shown in Figure 1-1.



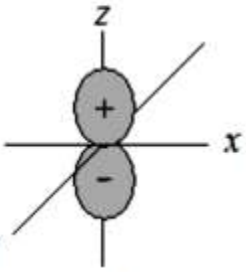
1s



$2p_x$



$2p_y$



$2p_z$

Figure 1-1 The Shapes of 1*s* and 2*p* orbitals

Molecular Orbitals

In molecule, as in isolated atoms, electrons occupy orbitals, and these molecular orbitals are considered to be centered about many nuclei, perhaps covering the entire molecule.

Each pair of electrons is localized near just two nuclei, and the shapes of these localized molecular orbitals and their disposition with respect to each other are related in a simple way to the shapes and disposition of atomic orbital in the component atoms.

The covalent bond

Let us consider the formation of a molecule. For a covalent bond to form two atoms must be located so that an orbital of one *overlaps* an orbital of the other; each orbital must contain a single electron. When this happens, the two atomic orbitals merge to form a single *bond orbital* which is occupied by both electrons (of different spins). This arrangement of electrons and nuclei contains less energy, and it is more stable than the arrangement in the isolated atoms. As a result, formation of a bond is accompanied by evolution of energy.

The covalent bond is strong because of the increase in electrostatic attraction. In the isolated atoms, each electron is attracted by, and attracts, one positive nucleus. In the molecule, each electron is attracted by two positive nuclei.

It is the concept of *overlap* that provides the bridge between atomic orbitals and bond orbitals. Overlap of atomic orbitals means that the bond orbital occupies much of the same region in space that was occupied by both atomic orbitals. Figure 1-2 shows the formation of H_2 molecule by overlapping of two H atoms each contain one electron in 1*s* orbital, and formation of F_2 molecule by overlapping of two F atoms each contain five electrons in 2*p* orbital, one of these electrons is single electron which is unpaired and available for bond formation.

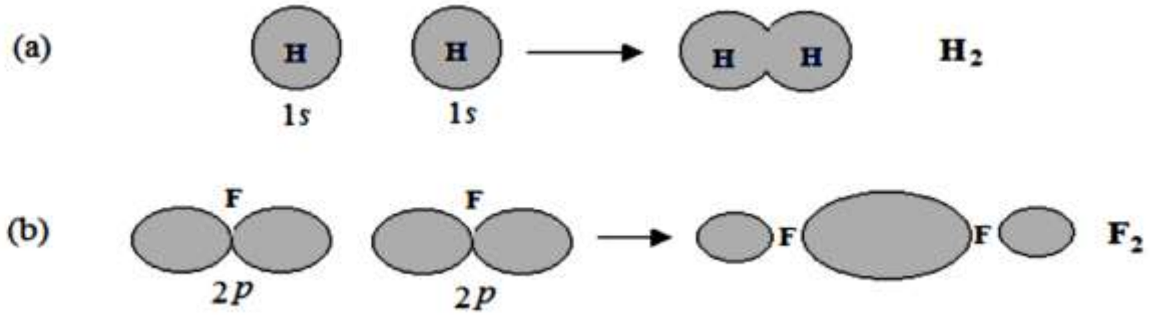
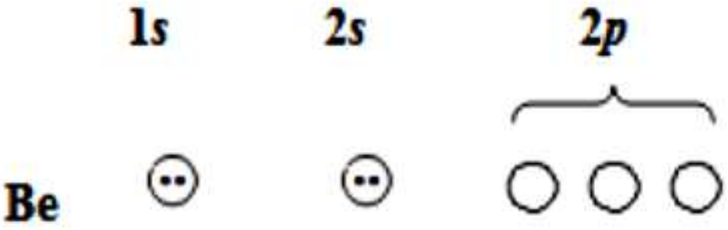


Figure 1-2 Bond Formation of (a) H_2 molecule, (b) F_2 molecule

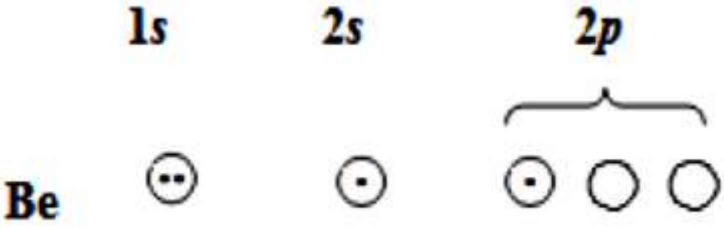
Hybrid Orbitals

sp Hybridization

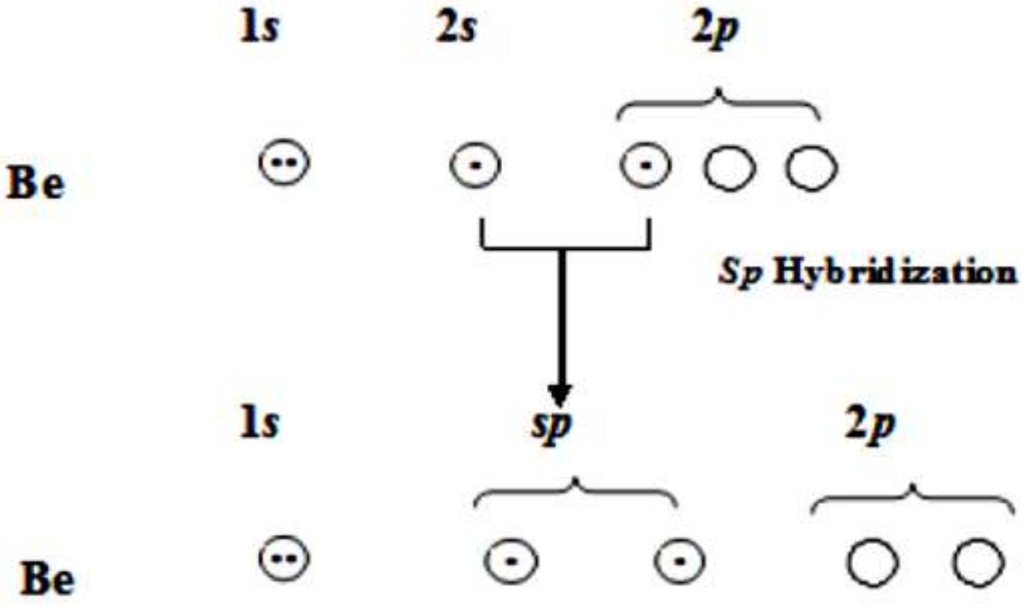
If we consider beryllium chloride, $BeCl_2$, the electronic configuration of Be is:



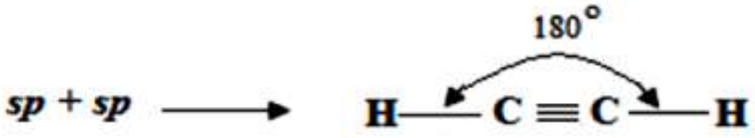
We promote one of the 2*s* electrons to an empty *p* orbital:



Next, we hybridize the orbitals:

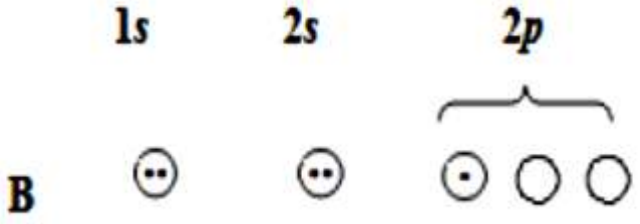


Acetylene (CH≡CH) is an example of *sp* hybridization. The two carbon atoms are joined by *sp*-*sp* sigma (σ) bond. Each carbon atom is also bonded to a hydrogen atom by an *sp*-*s* sigma bond. The two *p* orbitals of one carbon then overlap with the two *p* orbitals of the other carbon atom to form pi (π) bonds, one above and one below the line of the sigma bond. C≡C bond is shorter and stronger than C=C bond, which is shorter and stronger than C-C bond.

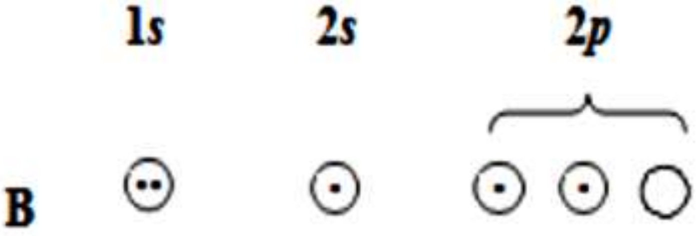


Sp2 Hybridization

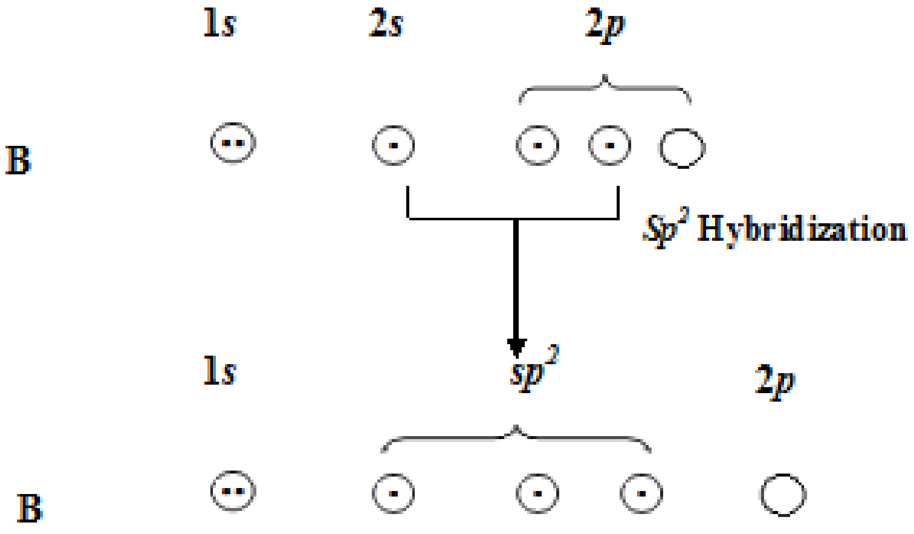
If we consider boron trifluoride, BF_3, boron has only one unpaired electron, which occupies a 2*p* orbital.



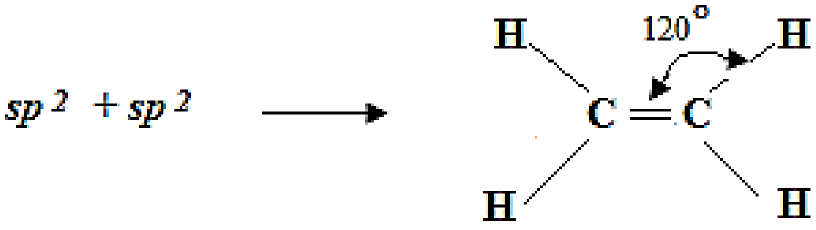
For three bonds we need three unpaired electrons, and so we promote one of the 2*s* electrons to a 2*p* orbital:



Next, we hybridize the orbitals:

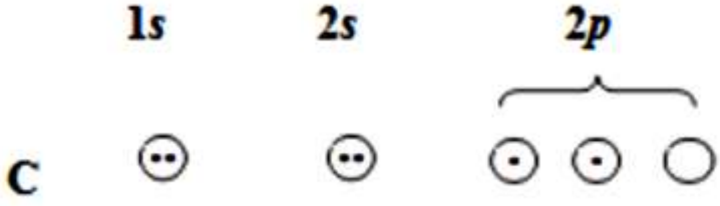


In ethylene $CH_2=CH_2$, two *sp*2 carbons are joined by a sigma bond formed by the overlap of the *sp*2 orbital from each carbon atom. Each carbon atom still has two *sp*2 orbitals left four bonding with hydrogen. Also, each carbon atom has a *p* orbital with one electron, the two *p* orbitals overlap their sides, the result is pi bond. A *sp*2 carbon atom is said to be a trigonal (triangular) carbon.



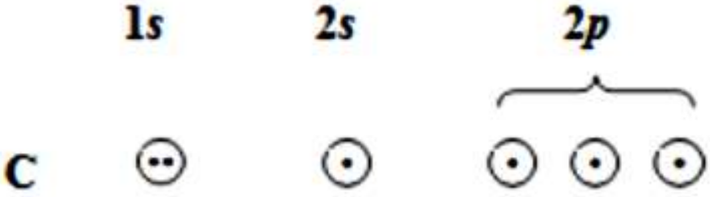
Sp3 Hybridization

Carbon has an unpaired electron in each of the two *p* orbitals, and on this basis might be expected to form a compound CH_2.

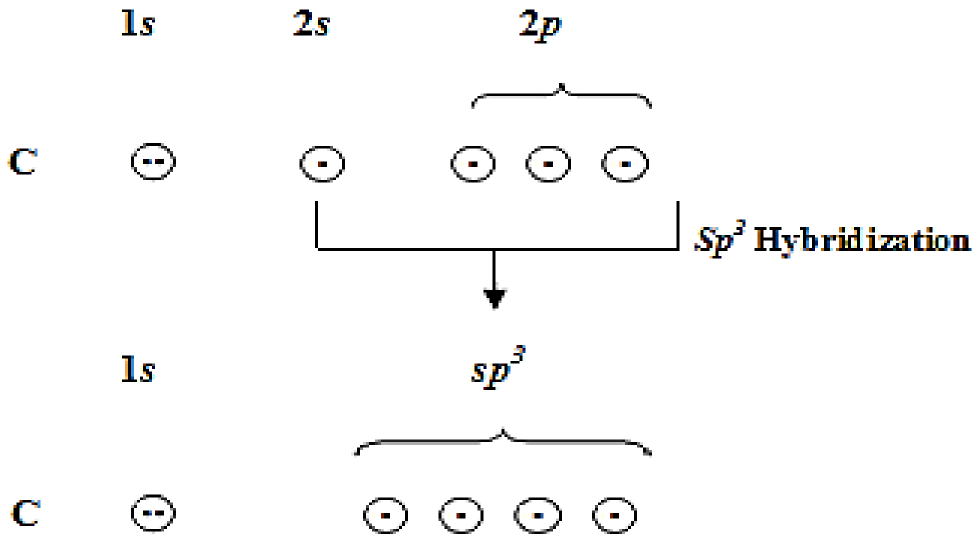


It does, but CH_2 is a highly reactive molecule whose properties center about the need to provide carbon with two more bonds. Again, we see the tendency to form as many bonds as possible: in this case, to combine with four hydrogen atoms.

To provide four unpaired electrons, we promote one of the 2*s* electrons, to the empty *p* orbital:

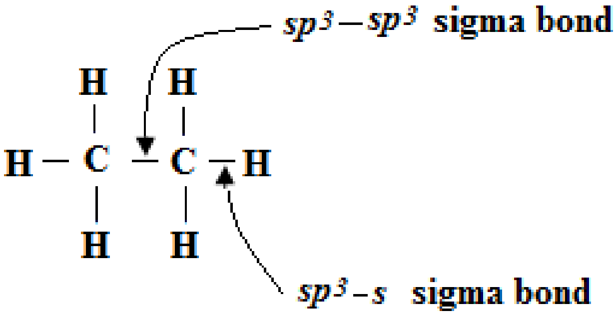


Once more the most strongly directed orbitals are hybrid orbitals: this time, sp^3 orbitals, from the mixing of one *s* orbital and three *p* orbitals.



Overlap of each of the sp^3 orbitals of carbon with an *s* orbital of hydrogen result in methane: carbon at the center of a regular tetrahedron, and the four hydrogens at the corners.

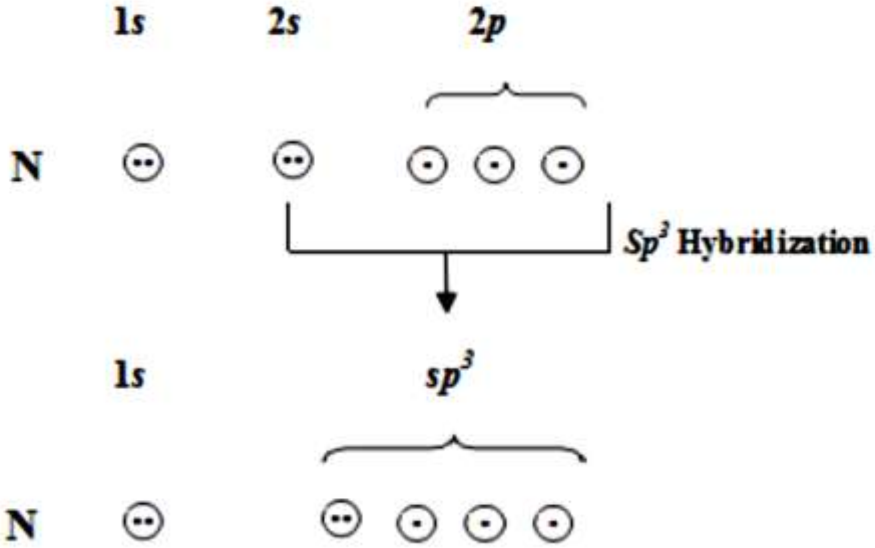
Ethane CH_3CH_3 contains two sp^3 carbon atoms. These two carbon atoms form a C-C sigma bond by the overlap of one sp^3 orbital from each carbon (sp^3-sp^3 sigma bond). Each carbon atom has three remaining sp^3 orbitals, and each of these overlap with a 1*s*orbital of a hydrogen atom to form a C-H sigma bond. Each carbon atom in ethane is tetrahedral.



Unshared pairs of electrons

Two compounds, ammonia (NH_3) and water (H_2O), show how *unshared pairs of electrons* can affect molecular structure.

In ammonia, nitrogen is *sp*$_3$ hybridized, but has only three unpaired electrons; they occupy three of the *sp*$_3$ orbitals. Overlap of each of these orbitals with the *s* orbital of a hydrogen atom results in ammonia. The fourth *sp*$_3$orbital of nitrogen contains a pair of electrons.



In order to get maximum overlap, the hydrogen nuclei must be located at three corners of a tetrahedral, the fourth corner is occupied by an unshared pair of electrons. Considering only atomic nuclei, we would expect ammonia to be shaped like a pyramid with nitrogen at the apex and hydrogen at the corners of a triangular base. Each bond angle should be the tetrahedral angle 109.5_o. Experimentally, ammonia is found to have the pyramidal shape (Figure 1-3). The bond angles are 107_o, slightly smaller than the predicted value. The unshared pair of electrons occupies more space than any of the hydrogen atoms, and hence tends to compress the bond angles slightly. The nitrogen-hydrogen bond length is 1.01 Å. The *sp*$_3$ orbital occupied by the unshared pair of electrons is a region of high electron density. This region is a source of electrons for electron-seeking atoms and molecules, and thus gives ammonia its basic properties.

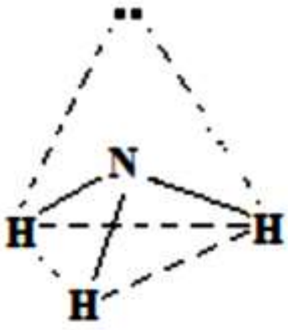
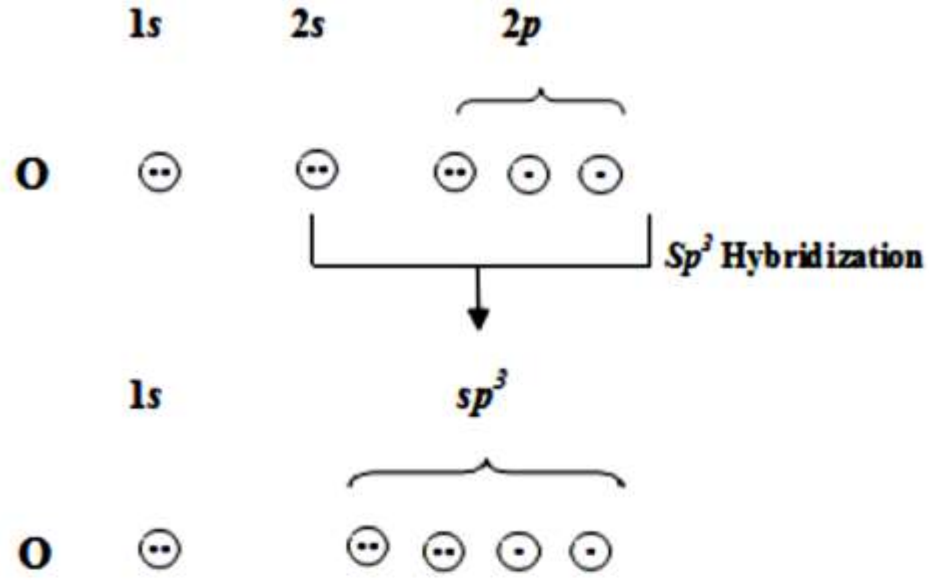


Figure 1-3 Bond formation of NH_3 pyramidal molecule

In water, oxygen has only two unpaired electrons, and hence it bonds with only two hydrogen atoms, which occupy two corners of a tetrahedron. The other two corners of the tetrahedron are occupied by unshared pairs of electrons.



The H-O-H angle is 105°, smaller than the calculated tetrahedral angle, and even smaller than the angle in ammonia. The two unshared pairs of electrons compressing the bond angles. The oxygen-hydrogen length is 0.96 A° (Figure 1-4).

Because of the unshared pairs of electrons on oxygen, water is basic, although less strongly so than ammonia.

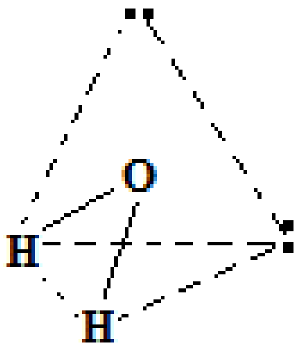
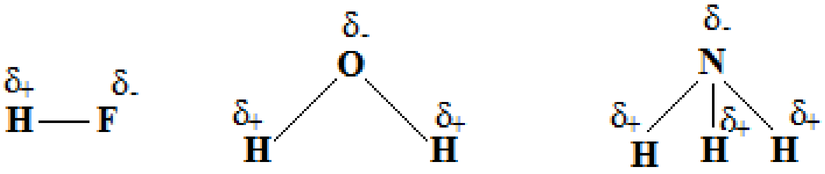


Figure 1-4 Bond formation of H_2O non-linear molecule

Polarity of Bonds

Certain covalent bonds have a property of polarity. Two atoms joined by a covalent bond share electron; their nuclei are held by same electron cloud. But in most cases the two nuclei do not share the electrons equally; the electron cloud is denser about one atom than the other. One end of the bond is thus relatively negative and the other end is relatively positive; that is, there is a negative pole and a positive pole. Such a bond is said to be a polar bond, or to possess polarity.

We can indicate polarity by using the symbols δ_+ and δ_-, which indicate partial + and – charges. For example:



Polar Bonds

We can expect a covalent bond to be polar if it joins atoms differ in their tendency to attract electrons, that is, atoms that differ in *electronegativity*. Furthermore, the greater the difference in electronegativity, the more polar the bond will be.

The most electronegative elements are those located in the upper right-hand corner of the Periodic Table. Of the elements we are likely to encounter in organic chemistry, fluorine has the highest electronegativity, then oxygen, then nitrogen and chlorine, then bromine, and finally carbon. Hydrogen does not differ very much from carbon in electronegativity; it is not certain whether it is more or less electronegative.

$$F > O > Cl, N > Br > C, H$$

Bond polarities are intimately concerned with both physical and chemical properties. The polarity of bond can lead to polarity of molecules, and thus profoundly affect melting point, boiling point and solubility. The polarity of a bond determines the kind of reaction that can take place at that bond, and even affects reactivity at nearby bonds.

Polarity of Molecules

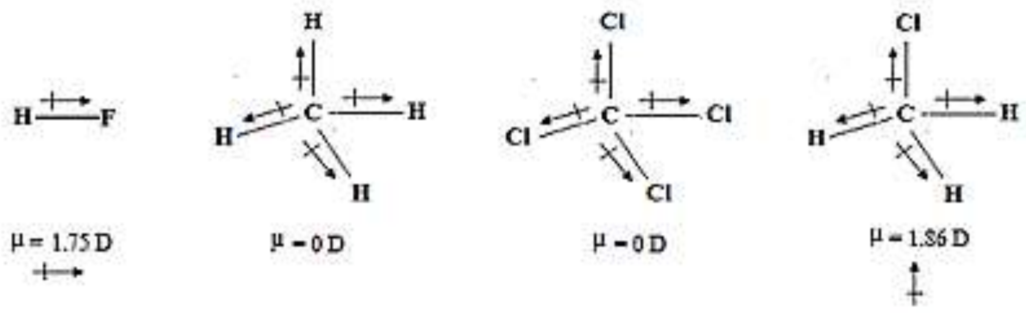
A molecule is polar if the center of negative charge does not coincide with the center of positive charge. Such a molecule constitutes a dipole: two equal and opposite charge separated in space. A dipole is often symbolized by $+\!\!\!\longrightarrow$, where the arrow points from positive to negative. The molecule possesses a dipole moment, μ, which is equal to the magnitude of the charge, *e*, multiplied by the distance, *d*, between the centers of the charge:

$$\mu = e \times d$$

The polarity of a molecule is a composite of the polarities of the individual bonds. Molecules like H_2, O_2, N_2, Cl_2, and Br_2 have zero dipole moments, that is are non-polar. The two identical atoms of each of these molecules have, of course, the same electronegativity and share electrons equally; *e* is zero and hence μ is zero, too.

A molecule like hydrogen fluoride has the large dipole moment of 1.75 Debye (D). Although hydrogen fluoride is a small molecule, the very high electronegative fluorine pulls the electrons strongly; although *d* is small, *e* is large, and hence μ is large, too.
Methane and carbon tetrachloride, CCl_4, have zero dipole moments. We certainly would expect the individual bonds of carbon tetrachloride at least to be polar; because of the very symmetrical tetrahedral arrangement, however, they exactly cancel each other.

In methyl chloride, CH_3Cl, the polarity of the carbon-chlorine bond is not cancelled, however, and methyl chloride has a dipole moment of 1.86 D. Thus, the polarity of a molecule depends not only upon the polarity of its individual bonds but also upon the way the bonds are directed, that is, upon the shape of the molecule.



Hydrogen Fluoride

Methane

Carbon tetrachloride

Methyl chloride

Structure and physical properties

Melting Point

In a crystalline solid the particles acting as structural units, ions or molecules, are arranged in some very regular, symmetrical way; there is a geometric pattern repeated over and over within a crystal.

Melting is the change from the highly ordered arrangement of particles in the crystalline lattice to the more random arrangement that characterizes a liquid. Melting occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the intra crystalline forces that hold them in position.

An ionic compound forms crystal in which the structural units are ions. Solid sodium chloride, for example, is made up of positive sodium ions and negative chloride ions alternating in a very regular way. Surrounding each positive

To melt sodium chloride, we must supply enough energy to break ionic bonds between Na^+ and Cl^- where sodium chloride has a melting point of 801° C. To melt methane, CH_4, we do not need to supply enough energy to break covalent bonds between carbon and hydrogen; we need only supply enough energy to break CH_4 molecules away from each other. In contrast to sodium chloride, methane melts at -183°C.

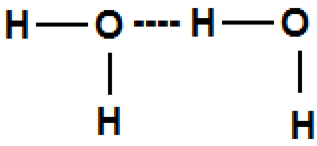
hydrogen bonding

In which a hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic force. When hydrogen is attached to a highly electronegative atom, the electron cloud is greatly distorted toward the electronegative atom, exposing the hydrogen nucleus.

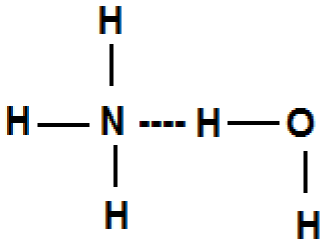
The strong positive charge of the thinly shielded hydrogen nucleus is strongly attracted by the negative charge of the electronegative atom of a second molecule. This attraction has a strength of about 5 kcal/mole, and is thus much weaker than the covalent bond, about 50-100 kcal/mole, that holds it to the first electronegative atom. It is however, much stronger than other dipole-dipole attractions.

Hydrogen bonding is generally indicated in formulas by broken line:

$\mathrm{H{-}F\text{----}H{-}F}$



$$\mathrm{H{-}\underset{\underset{H}{|}}{O}\text{----}H{-}\underset{\underset{H}{|}}{O}}$$



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\text{----}H{-}\underset{\underset{H}{|}}{O}}$$

For hydrogen bonding to be important, both electronegative atoms must be come from the group: F, O, N. Only hydrogen bonded to one of these three elements is positive enough, and only these three elements are negative enough, for the necessary attraction to exist. These three elements owe their special effectiveness to the concentrated negative charge on their small atoms.

Boiling Point

In the liquid state the unit of an ionic compound is again the ion. Each ion is still held strongly by a number of oppositely charged ions. Again, there is nothing we could properly call a molecule. A great deal of energy is required for a pair of oppositely charged ions to break away from the liquid; boiling occurs only at a very high temperature. The boiling point of sodium chloride, for example, is 1413$_{o}$C. In the gaseous state we have an ion pair, which can be considered a sodium chloride molecule.

In the liquid state the unit of a non-ionic compound is again the molecule. The weak intermolecular forces here, dipole-dipole interactions and van der Waals forces, are more readily overcome than the strong interionic forces of ionic compounds, and boiling occurs at a very much lower temperature. Non-polar methane boils at -161.5$_{o}$C, and even polar hydrogen chloride boils at -85$_{o}$C.

Liquids whose molecules are held together by hydrogen bonds are called associated liquids. Breaking these hydrogen bonds takes considerable energy, and so an associated liquid has a boiling point that is abnormally high for a compound of its molecular weight and dipole moment. Hydrogen fluoride, for example, boils 100 degree.

The bigger the molecule, the stronger the van der Waals forces. Other things being equal, polarity, hydrogen bonding, boiling point rises with increasing molecular size.

Solubility

A polar molecule has a positive end and a negative end. Consequently, there is electrostatic attraction between a positive ion and the negative end of the solvent molecule, and between a negative ion and the positive end of the solvent molecule. These attractions are called ion-dipole bonds. Each ion-dipole bond is relatively weak, but in the aggregate, they supply enough energy to overcome the interionic forces in the crystal. In solution each ion is surrounded by a cluster of solvent molecules, and is said to be solvated; if the solvent happens to be water, the ion is said to be hydrated. In solution, as in the solid and liquid states, the unit of a substance like sodium chloride is the ion, although in this case it is a solvated ion, as shown in Figure 1.5.

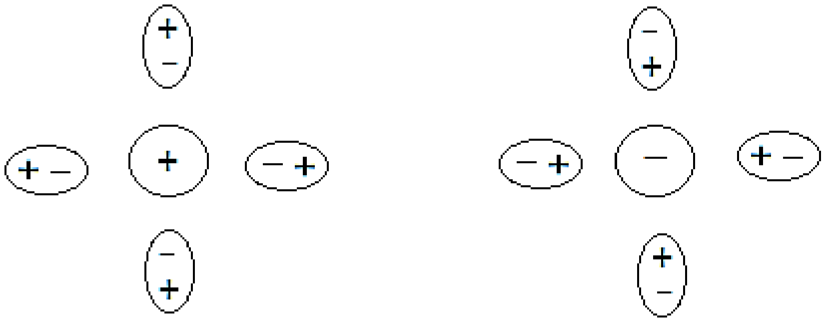


Figure 1.5 Ion-dipole interactions: solvated cation and anion

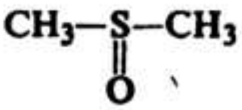
To dissolve ionic compounds a solvent must also have a high dielectric constant, that is, have high insulating properties to lower the attraction between oppositely charged ions once they are solvated.

The solubility characteristics of non-ionic compounds are determined chiefly by their polarity. Non-polar or weakly polar compounds dissolve in non-polar or weakly polar solvents; highly polar compounds dissolve in highly polar solvents. "Like dissolves like" is an extremely useful rule of thumb. Methane dissolves in carbon tetrachloride because the force holding methane molecules to each other and carbon tetrachloride molecules to each other are replaced by very similar forces holding methane molecules to carbon tetrachloride molecules.

Neither methane nor carbon tetrachloride is readily soluble in water. The highly polar water molecules are held to each other by very strong dipole-dipole interactions hydrogen bonds; there could be only very weak attraction forces between water molecules on the one hand and the non-polar methane or carbon tetrachloride molecules on the other hand.

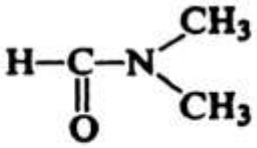
In contrast, the highly polar organic compound methanol, CH_3OH, is quite soluble in water. Hydrogen bonds between water and methanol can readily replace the very similar hydrogen bonds between different methanol molecules and different water molecules.

Solvents like water or methanol are called protic solvents: solvents containing hydrogen that is attached to oxygen or nitrogen, and hence is appreciably acidic. Aprotic solvents: polar solvents of moderately high dielectric constants, which do not contain acidic hydrogen. For example:

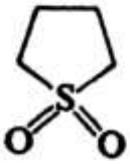


$$CH_3-\underset{\underset{O}{\|}}{S}-CH_3$$

Dimethyl sulfoxide
DMSO



N,N-Dimethylformamide
DMF



Sulfolane