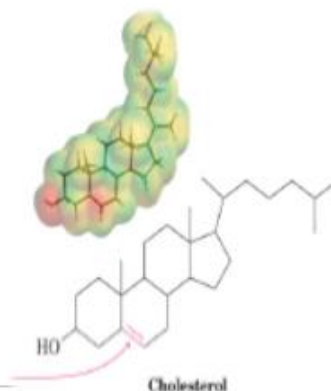


# Organic Chemistry

## 1<sup>st</sup> stage students

2<sup>nd</sup> COURSE

Dr. HUDA S. ABOOD



## References

Organic chemistry, Morrison & Boyd

Organic Chemistry, McMurry's /Chapter 3

### Syllabus of Org. Chemistry

1-introduction of structure and properties

2-alkanes

3-alkenes

4-alkyne

### Introduction of organic chemistry

#### Structure and properties

Explain where the term "organic chemistry" originally came from and what it currently means.

- **Organic chemistry** is the study of compounds that contain carbon and hydrogen atoms include the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, including hydrogen (most

compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, sulfur, halogens, ... .Organic compounds range from simple molecules to huge ones.

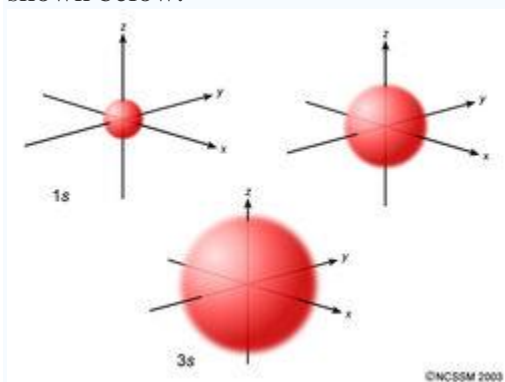
## Orbitals and Hybridization

1. Give atomic orbitals and electron configuration for isolated atoms.
2. Explain the difference between atomic and molecular orbitals.

### Atomic orbitals:

#### S Orbitals

An s orbital is spherically symmetric around the nucleus of the atom, like a hollow with the nucleus at its center. As the energy levels increase, the electrons are located further from the nucleus, so the orbitals get bigger. The order of size is  $1s < 2s < 3s < \dots$ , as shown below.

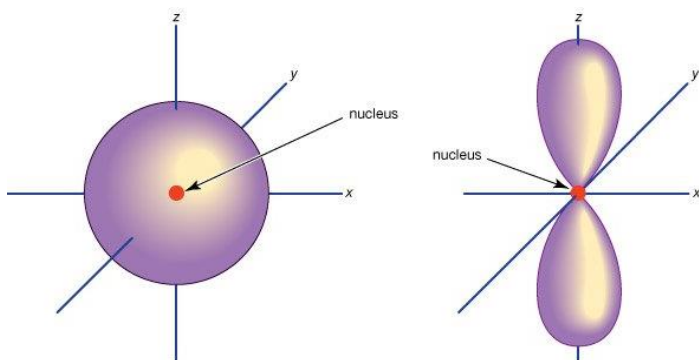


#### P-ORBITALS

Not all electrons inhabit s orbitals. At the first energy level, the only orbital available to electrons is the 1s orbital. However, at the second level, there are also orbitals called 2p orbitals in addition to the 2s orbital.

Unlike an s orbital, a p orbital points in a particular direction.

Each 2p orbital is dumbbell-shaped. It consists of two lobes with the atomic nucleus lying between them. The axis of each 2p orbital perpendicular to the axes of the other two. They are differentiated by the names 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub>, where the x, y, and z refer to the corresponding axes. Atomic orbitals: p orbitals. Axes mutually perpendicular.

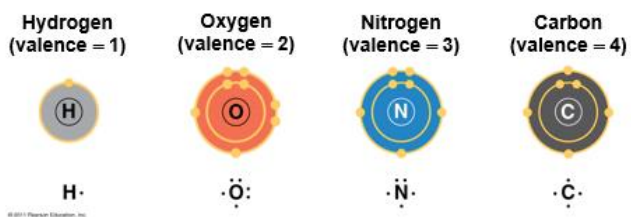
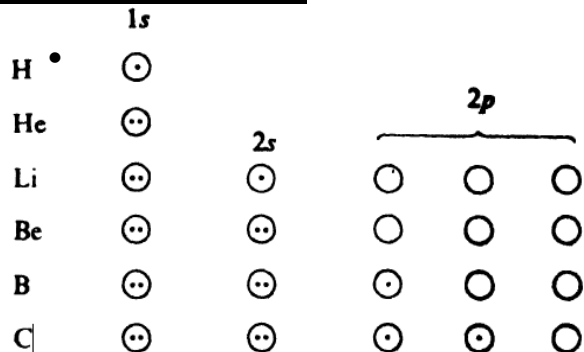


### Electronic configuration. Pauli Exclusion Principle

There are a number of "rules" that determine the way in which the electrons of an atom may be distributed, that is, that determine the electronic configuration of an atom.

The most fundamental of these rules is the Pauli Exclusion Principle: only two electrons can occupy any atomic orbital, and to do so these two must have opposite spins. These electrons of opposite spins are said to be paired. Electrons of like spin tend to get as far from each other as possible. This tendency is the most important of all the factors that determine the shapes and properties of molecules.

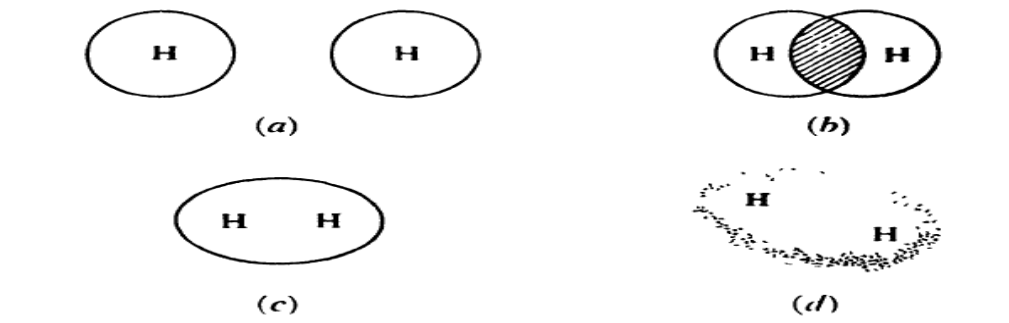
### Electronic configuration:



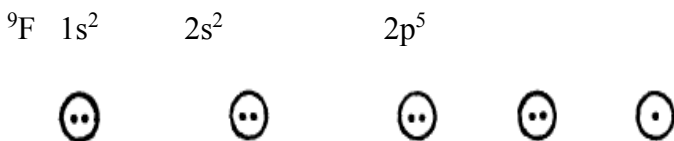
### Molecular orbitals

In molecules, as in isolated atoms, electrons occupy orbitals, and in accordance with much the same "rules." These molecular orbitals are considered to be centered about many nuclei, hydrogen molecule H<sub>2</sub>, from two hydrogen atoms.

### **H-H**

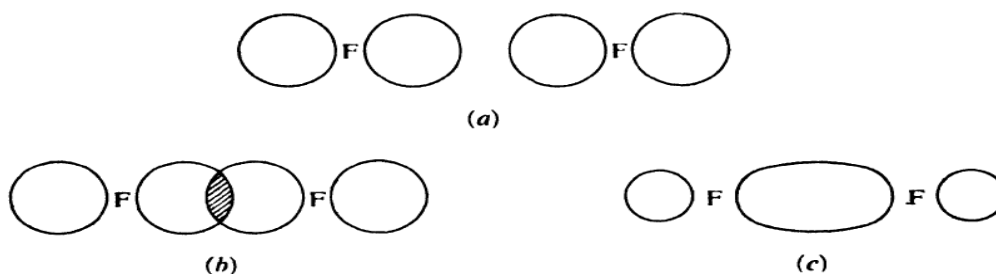


For hydrogen, the system is most stable when the distance between the nuclei is 0.74 Å; this distance is called the bond length. This bond orbital has cylindrical symmetry. Bond orbitals having this shape are called  $\sigma$  orbitals (sigma orbitals) and the bonds are called  $\sigma$  bonds or covalent bond.



In the third 2p orbital there is a single electron which is unpaired and available for bond formation.

The electronic charge is concentrated between the two nuclei, so that the back lobe of each of the overlapping orbitals shrinks to a small size.

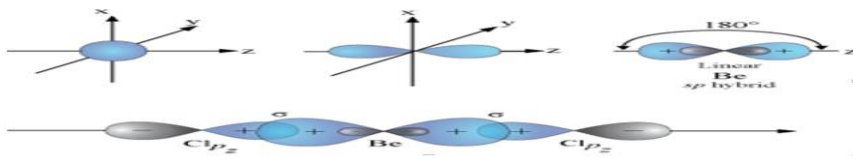
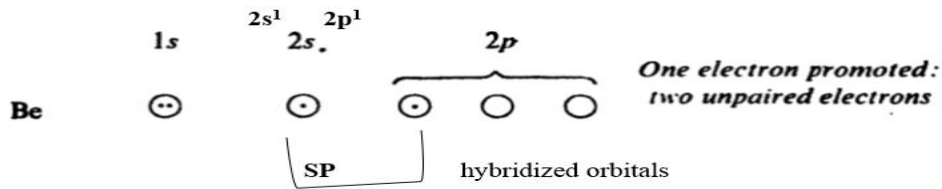


**Hybrid orbitals: SP**

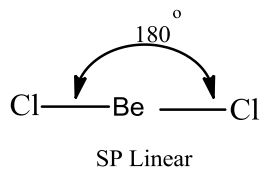
Beryllium chloride,  $\text{BeCl}_2$ ,

Be has no unpaired electrons



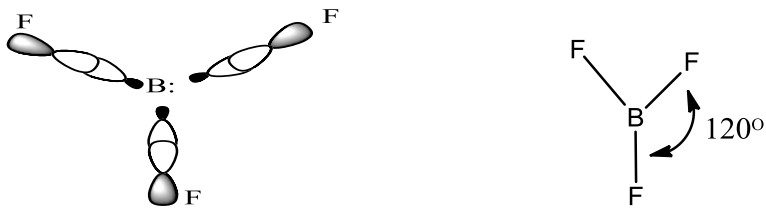
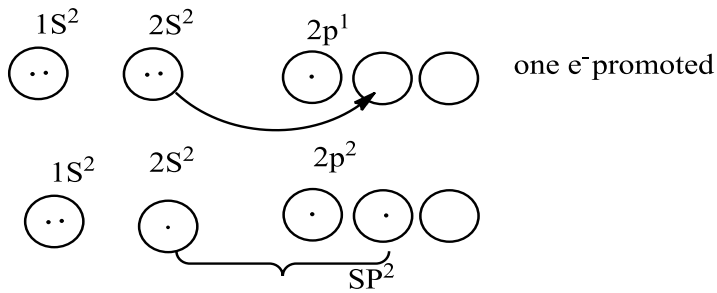


Atomic orbitals (hybridized orbital) 2SP

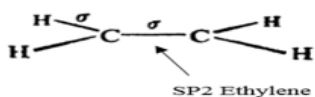


Atomic orbitals (hybridized orbital) 2SP

**Hybrid orbitals:  $SP^2$**

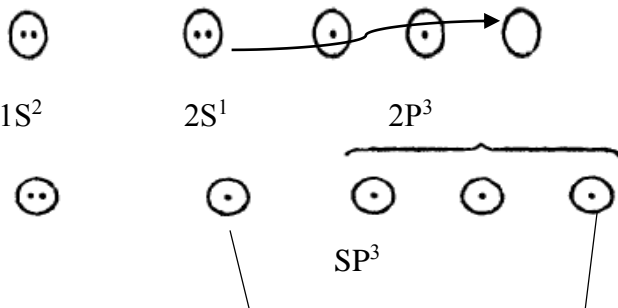


$SP^2$  Triangle

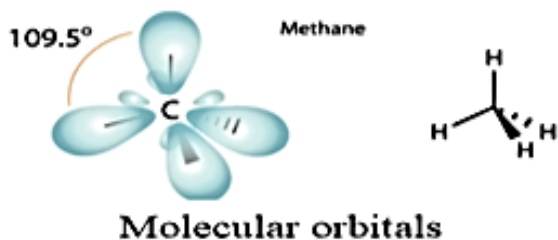
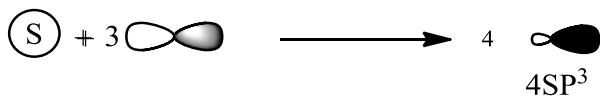


**Hybrid orbitals:  $SP^3$   $CH_4$**

${}^6C$   $1S^2$        $2S^2$        $2P^2$       one  $e^-$  promoted



Four unpaired electrons  
(Hybridization)



Tetrahedral  $SP^3$  orbitals

**Unshared pairs of electrons:**

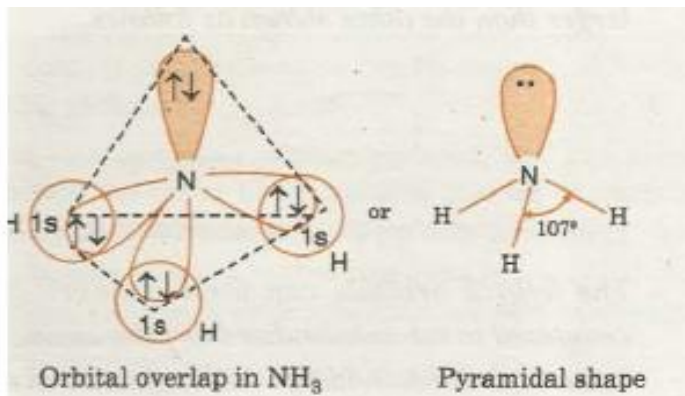
**$NH_3$  and  $H_2O$**

1)  $NH_3$

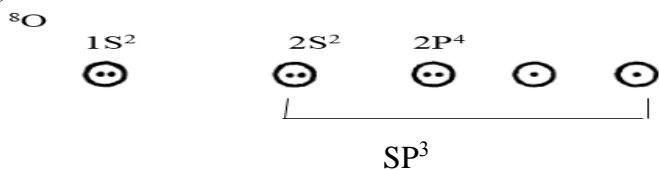


One of  $\text{SP}^3$  orbital of nitrogen a pair of electrons

3  $\text{SP}^3$  orbitals bonding with H atoms.

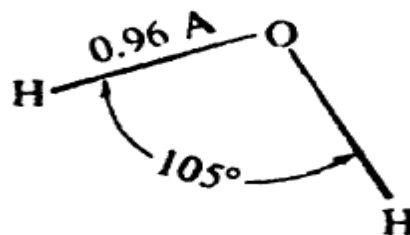
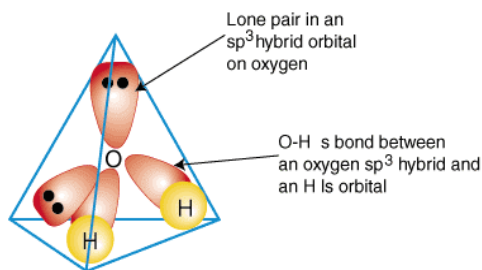


2)  $\text{H}_2\text{O}$



Two hydrogen atoms, which occupy two corners of a tetrahedron

Unshared pairs of electrons are occupied the other corners of a tetrahedron



H.W.

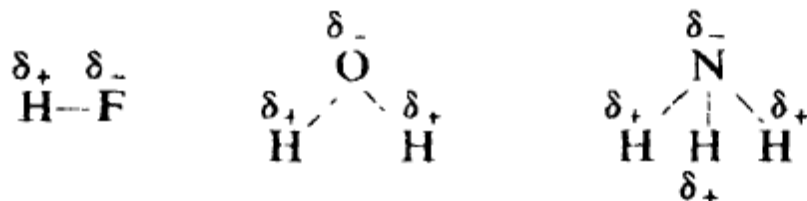
$\text{H}_2\text{CO}$

$\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$

**Polarity of bonds**

Two atoms joined by a covalent bond share electrons; their nuclei are held by the same electron cloud. The electron cloud is denser about one atom than the other. We can indicate

polarity by using the symbols  $\delta^+$  and  $\delta^-$ , which indicate partial + and - charges. For example:



We can expect a covalent bond to be polar if it joins atoms that differ in their tendency to attract electrons that is, atoms that differ in electronegativity.

### Electronegativity

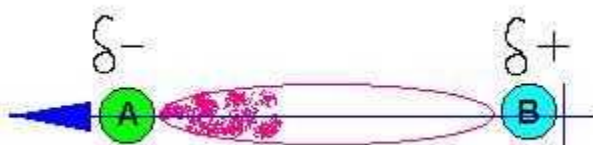
•• > F > O > Cl, N > Br > C, H

### Polarity of molecules

Polarity depending on:

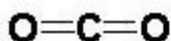
- 1) Electronegativity of atoms
- 2) Asymmetry of molecules

**Polarity** is a separation of [electric charge](#). Polar molecules must contain polar [bonds](#) due to a difference in [electronegativity](#) between the bonded atoms.



A polar molecule with two or more polar bonds must have a [geometry](#) which is asymmetric in at least one direction, so that the [bond dipoles](#) do not cancel each other. If the two atoms are identical, the magnitude of the vector is zero, hence we have a nonpolar bond.

In  $\text{CO}_2$  molecule the electronegativities of carbon and oxygen are 2.55 and 3.44. The 0.89 difference in electronegativity indicates that the C-O bonds are polar, but the symmetrical arrangement of these bonds makes the molecule nonpolar.



Vector  
cancellation  
nonpolar

The molecule possesses a dipole moment,  $\mu$ , which is equal to the magnitude of the charge,  $e$ , multiplied by the distance,  $d$ , between the centers of charge:



$$\mu = e \times d$$

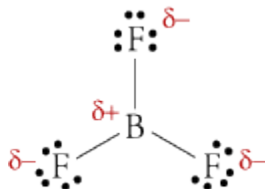
$\mu$  in Debye units, D      =       $e$  in e.s.u.       $\times$        $d$  in Angstroms

H-F	$\mu = 1.75$ D
H-Cl	1.08
H-Br	0.82
H-I	0.44

H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, and Br<sub>2</sub>  $\mu = 0 \rightarrow$  non-polar.

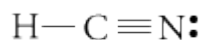
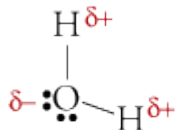
### BF<sub>3</sub>

The three bonds in a molecule of BF<sub>3</sub> (boron trifluoride) are considerably polar, but they are symmetrically arranged around the central boron atom. No side of the molecule has more negative or positive charge than another side, and so the molecule is nonpolar:



### Water

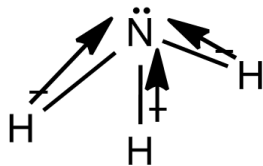
A water molecule is polar because (1) its O-H bonds are significantly polar, and (2) its bent geometry makes the distribution of those polar bonds asymmetrical. The side of the water molecule containing the more electronegative oxygen atom is partially negative, and the side of the molecule containing the less electronegative hydrogen atoms is partially positive.



The electronegativities of hydrogen, carbon, and nitrogen are 2.20, 2.55, and 3.04. The 0.35 difference in electronegativity for the H-C bond shows that it is essentially nonpolar. The 0.49 difference in electronegativity for the C-N bond tells us that it is polar. Molecules with one polar bond are always polar.

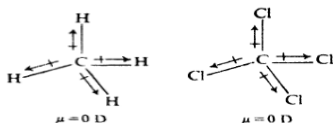
### NF<sub>3</sub>

### Ammonia NH<sub>3</sub>



Ammonia has a dipole moment of 1.46 D. This could be accounted for as a net dipole moment (a vector sum) resulting from the three individual bond moments.

### Methane & Carbene tetrachloride



The molecular geometry of  $\text{CCl}_4$  and  $\text{CH}_4$  are tetrahedral. Even though the C-Cl and C-H bonds are polar, their symmetrical arrangement makes the molecule nonpolar.

Methane and carbon tetrachloride,  $\text{CCl}_4$ , 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 out.

### H.W.

$\text{CHCl}_3$ ,  $\text{SO}_2$ ,  $\text{NF}_3$

### Structure and physical properties

We have just discussed one physical property of compounds: dipole moment.

Other physical properties like melting point, boiling point, or solubility in a particular solvent are also of concern to us.

The physical properties of a new compound give valuable hints about its structure. Conversely, the structure of a compound often tells us what physical properties to expect of it.

Usually the isolation and purification of a product take much more time and effort than the actual making of it.

The possibility of isolating the product by distillation depends upon its boiling point and the boiling points of the contaminants; isolation by recrystallization depends upon its solubility in various solvents and the solubility of the contaminants.

**1) Melting point:** 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 crystals in which the structural units are ions.

These powerful interionic forces are overcome only at a very high temperature; sodium chloride has a melting point of 801°C.

Crystals of other ionic compounds resemble crystals of sodium chloride in having an ionic lattice, although the exact geometric arrangement may be different. As a result, these other ionic compounds, too, have high melting points. Many molecules contain both ionic and covalent bonds. Potassium nitrate,  $\text{KNO}_3$ , for example, is made up of  $\text{K}^+$  ions and  $\text{NO}_3^-$  ions; the oxygen and nitrogen atoms of the  $\text{NO}_3^-$  ion are held to each other by covalent bonds. The physical properties of compounds like these are largely determined by the ionic bonds; potassium nitrate has very much the same sort of physical properties as sodium chloride.

A non-ionic compound, one whose atoms are held to each other entirely by covalent bonds, forms crystals in which the structural units are molecules. It is the forces holding these molecules to each other that must be overcome for melting to occur. In general, these intermolecular forces are very weak compared with the forces holding ions to each other. To melt sodium chloride we must supply enough energy to break ionic bonds between  $\text{Na}^+$  and  $\text{Cl}^-$ . To melt methane,  $\text{CH}_4$ , we do not need to supply enough energy to break covalent bonds between carbon and hydrogen; we need only supply enough energy to break  $\text{CH}_4$  molecule away from each other. In contrast to sodium chloride, methane melts at -183°C.

### Intramolecular forces

Tetrahedral ( $\text{sp}^3$ -hybridized), trigonal ( $\text{sp}^2$ -hybridized), and digonal ( $\text{sp}$ -hybridized). By use of this result of a combination of repulsive and attractive forces, which are related to charge and electron spin.

- (a) Repulsive forces. Electrons tend to stay as far apart as possible because they have the same charge.
- (b) Attractive forces. Electrons are attracted by atomic nuclei of the nuclei by the electrons-because of their opposite charge.

### Intermolecular forces

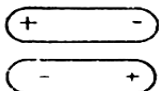
Attractive forces. Electrons are attracted by atomic nuclei-as are the nuclei by the electrons-because of their opposite charge, and

What kind of forces hold neutral molecules to each other? Like interionic forces, these forces seem to be electrostatic in nature, involving attraction of positive charge for negative charge. There are two kinds of intermolecular forces:

- 1) dipole-dipole interactions
- 2) Van der Waals forces.

Dipole-dipole interaction is the attraction of the positive end of one polar molecule for the negative end of another polar molecule. In hydrogen chloride, for example, the relatively positive hydrogen of one molecule is attracted to the relatively negative chlorine of another:





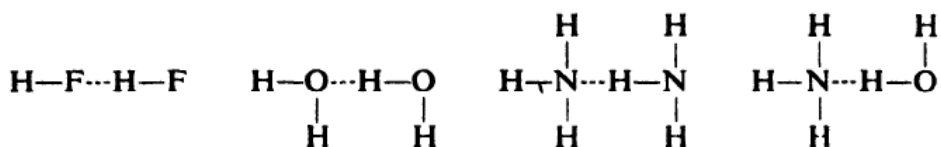
As a result of dipole- dipole interaction, polar molecules are generally held to each other more strongly than are non-polar molecules of comparable molecular weight; this difference in strength of intermolecular forces is reflected in the physical properties of the compounds concerned.

### Hydrogen bonding (H- bonding)

An especially strong kind of dipole- dipole attraction is 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 forces. 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 a broken line:



When the distance between the nuclei is equal to the sum of the van der Waals radii. Now, if the atoms are forced still closer together, van der Waals attraction is very rapidly replaced by van der Waals repulsion. Thus, non-bonded atoms welcome each other's touch, but strongly resist crowding.

### Boiling point

#### **Ionic compound**

Boiling occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the cohesive forces that hold them in the liquid.

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.

Boiling occurs only at a very high temperature. The boiling point of sodium chloride, for example, is 1413.

#### **Nonionic compound**

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, and even polar hydrogen chloride boils at only -85.

#### **Associated liquids**

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 degrees higher than the heavier, non-associated hydrogen chloride.

Tiny, non-polar methane, but we seldom encounter boiling points much above 350; at higher temperatures, covalent bonds within the molecules start to break, and decomposition competes with boiling. It is to lower the boiling point and thus minimize decomposition that distillation of organic compounds is often carried out under reduced pressure.

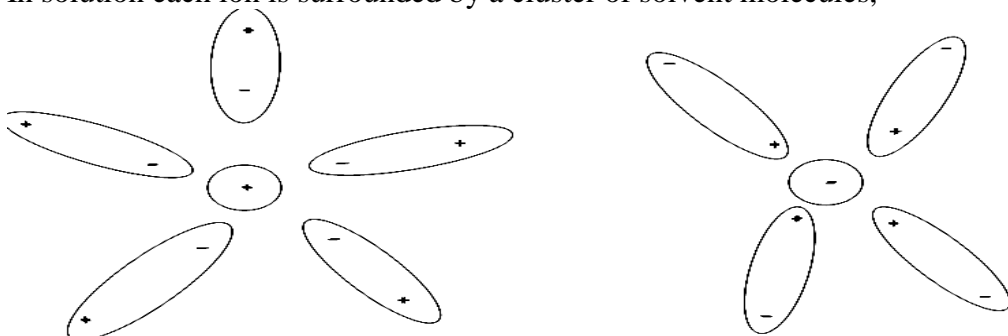
### Solubility

When a solid or liquid dissolves, the structural units ions or molecules become separated from each other, and the spaces in between become occupied by solvent molecules.

In dissolution, as in melting and boiling, energy must be supplied to overcome the interionic or intermolecular forces.

By definition, 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 rather 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,



Ion-dipole interactions: solvated cation and anion (association cluster)

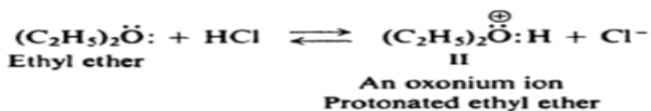
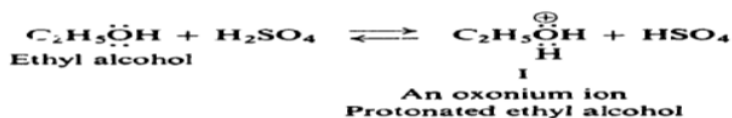
Non-polar or weakly polar compounds dissolve in non-polar or weakly polar solvents; highly polar compounds dissolve in highly polar solvents. "Like dissolves like" is a very useful rule.

Methane dissolves in carbon tetrachloride because the forces holding very similar forces holding methane molecules. Neither methane nor carbon tetrachloride is readily soluble in water.

\*CCl<sub>4</sub> dissolve CH<sub>4</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>

In contrast, the highly polar organic compound methanol, CH<sub>3</sub>OH, is quite soluble in water. Hydrogen bonds between water and methanol molecules can readily replace the very similar hydrogen bonds between different methanol molecules and different water molecules (solvation H<sub>2</sub>O hydration).

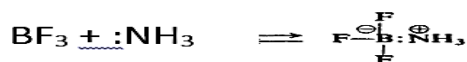




**Lewis definition**, a base is a substance that give an electron pair



Acid is a substance that can take up an electron pair.



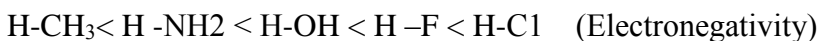
\*Thus an acid is an electron-pair acceptor.

a base is an electron-pair donor.

The strength of acid is depended on: (a) the atom's electronegativity, and (b) its size.

Thus, within a given row of the Periodic Table,

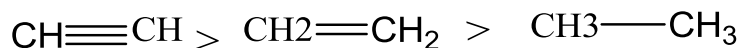
acidity increases as electronegativity increases:



And within a given family, acidity increases as the size increases:



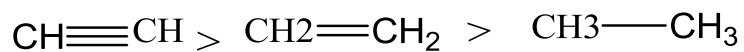
\* Strength of acidity depend of electronegativity and hybridize of atoms:



In ethane, ethene and ethyne, the C atoms are  $\text{Sp}^3$ ,  $\text{sp}^2$  and  $\text{Sp}$  hybridized. In ethyne, as the C atoms are  $\text{Sp}$  hybridized, it has greater S character (50%) as compared to 33% in case of ethene C atoms and 25% in case of ethane C atoms.

Greater the S character, greater is the electronegativity of that C atom. Thus ethyne C atoms are most electronegative due to which they pull the electron density of the bonded hydrogen more towards itself, thereby making the release of  $\text{H}^+$  easier. Hence, ethyne is most acidic.

\*Strength of acidity depend of electronegativity and hybridize of atoms:



In ethane, ethene and ethyne, the C atoms are  $sp^3$ ,  $sp^2$  and  $sp$  hybridized. In ethyne, as the C atoms are  $sp$  hybridized, it has greater S character (50%) as compared to 33% in case of ethene C atoms and 25% in case of ethane C atoms.

Greater the S character, greater is the electronegativity of that C atom. Thus ethyne C atoms are most electronegative due to which they pull the electron density of the bonded hydrogen more towards itself, thereby making the release of  $H^+$  easier. Hence, ethyne is most acidic.

However, acidity actually corresponds to the heterolytic dissociation of the bond, with both electrons in the bond going to X:

