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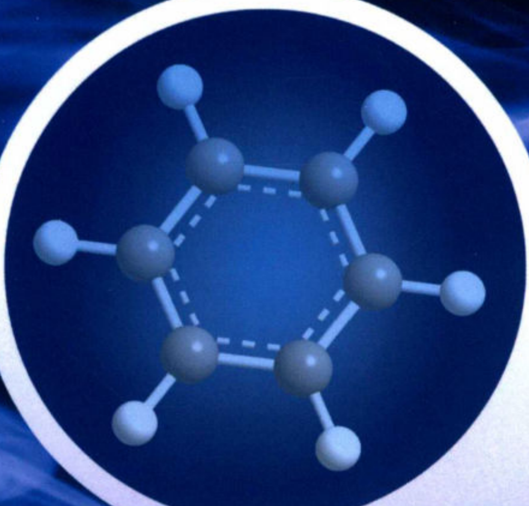
# ORGANIC CHEMISTRY



# 有机化学

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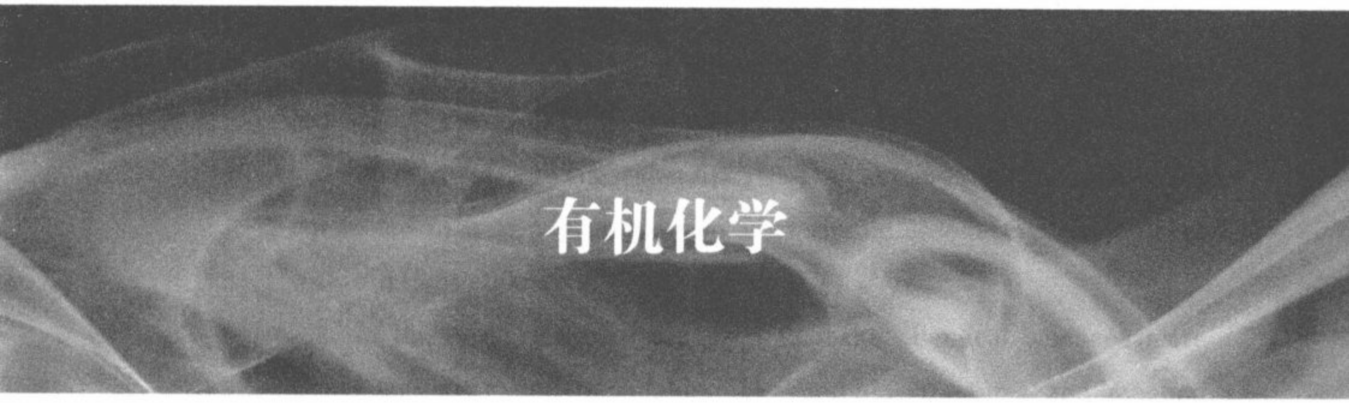

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**有机化学**
Organic Chemistry

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# PREFACE

Organic Chemistry has been designed to meet the needs of the inspired-teaching and self-discovery study in the undergraduate organic chemistry course. The main theme is that organic chemistry is an interesting and logical subject. This text reveals the relevant of organic chemistry and common life from natural organic compounds to other important compounds, combined basic knowledge and current development of organic chemistry. The organic compounds were connected in a steady progression from simple structures to complexes with different structures.

In this text, graphics are used to make chemical sciences more visual and more understandable. The graphic structures and reaction types will assist students to think and discover the mechanisms of organic chemistry. Selected thinking questions and exercises make students more easily in self-study.

This text with rigorous structure, clear logic, abundant content, well designed and good connection, is organized according to five parts, basic concepts units (chapters 1 to 3), reaction types (chapters 4 to 7), reaction mechanisms (chapters 8 to 10), natural organic compounds (chapters 11 to 13) and important compounds (chapter 14). This organization of the content helps most students in different majors to study step by step. It's applicable for teaching in majors of chemical engineering, materials, food science and medicine.

Any comment is welcomed for future improvement.

Editors
June, 2018

# Contents

# Chapter 1 Introduction

## 1.1 Organic Chemistry and Organic Compounds

**What is organic chemistry?**

Organic chemistry, previously known as the chemistry of carbon compounds, is the study of the composition, structure, properties, methods of preparation and application of organic compounds, which is an important branch of chemistry. Carbon compounds were known as organic compounds because chemists believed that carbonaceous substances must be made from organisms; however, in 1828, the German chemist Friedrich Weiler, for the first time reported the synthesis of urea (a biomolecule) in the laboratory, since then organic chemistry has been out of the scope of the traditional definition, and expanded into carbon-containing chemicals.

**What are organic compounds?**

Organic matter is the material basis of life, and all living organisms contain organic compounds. Fat, amino acids, protein, sugar, heme, chlorophyll, enzymes, hormones and so on. Biological metabolism and biological genetic phenomena are related to the transformation of organic compounds. In addition, many substances are closely related to human life, such as oil, natural gas, cotton, dyes, chemical fiber, plastic, plexiglass, natural and synthetic drugs, are closely linked with organic compounds. The organic compounds are mainly composed of carbon and hydrogen, and are carbon-containing compounds, but do not include carbon oxides (carbon monoxide, carbon dioxide), carbonates, cyanides, thiocyanates, cyanic acid salts, metal carbides, some simple carbon compounds (such as SiC) and other substances.

In addition to carbon, organic compouds may contain hydrogen, oxygen, nitrogen, chlorine, phosphorus, sulfur or other elements. In summary, organic compounds are carbon-containing compounds, but carbon-containing compounds are not necessarily organic compounds.

**The origin of organic chemistry**

**(1) Early budding period**

The term "Organic Chemistry" was first proposed by Besheusius (father of organic chemistry) in 1806. Organic chemistry was named after opposite of "inorganic chemistry". Because of the scientific conditions at that time, the object of organic chemistry research can only be extracted from the natural animal and plant organisms.

In 1824, Ville, a German chemist, produced oxalic acid by hydrolysis of cyanide. In 1828, he inadvertently converted ammonium cyanate into urea by heating.

$$NH_4OCN \xrightarrow{\triangle} CO(NH_2)_2$$

Cyanide and ammonium cyanate are inorganic compounds, but oxalic acid and urea are organic compounds. Ville's experimental results gave the "vitality" theory the first impact. Since the report of acetic acid and other organic compounds , the "vitality" theory gradually faded in the minds of chemists. From the beginning of the 19th century to 1858 was the embryonic period of organic chemistry. During this period, many organic compounds were isolated, some derivatives were prepared, and their properties have been described qualitatively, recognizing the properties of some organic compounds.

### (2) Classic organic chemistry

From the establishment of valence bond theory in 1858 to the introduction of valence bond electron theory in 1916 is the period of classical organic chemistry.

In 1858, German chemist Kekul and British chemist Cooper put forward the concept of valence key. They believed that molecules of organic compounds are made up of bonds of their constituent atoms. The valence of an element is the number of hydrogen atoms that this element combines with. Kekule also proposed the important concept that carbon atoms can combine with each other in a molecule.

In 1848, Pasteur separated two tartaric acid crystals, a half facing to the left and a half facing to the right. The former can make the plane polarized light rotate to the left, while the latter makes it rotate to the right with the same angle. Similar phenomena have also been encountered in the study of lactic acid. To this end, in 1874, French chemist Lebel and Holland chemist Vantov put forward a new concept, isomer, satisfactorily explained this isomerism. They believed the molecule is a three-dimensional entity and the carbon price of the four keys in space is symmetrical respectively pointing to a tetrahedron of the four vertices, carbon atoms are located in the center of the tetrahedron. When a carbon atom is attached by four different atoms or groups, a pair of isomers are generated, which are either optical isomers or enantiomers. This is called **enantiomeric phenomena.** These two molecules are inlaid with the mirror, but can not completely coincide with the molecules known as **chiral molecules.** The doctrine of Lubel and Van Tuo Fu is the basis of stereochemistry in organic chemistry.

In 1900 the first free radical, trityl free radical was found, which is a long life free radical. The presence of unstable free radicals was also confirmed in 1929. During this period, organic Chemistry has made significant progress in structural assays and reactions and classifications. But the valence was only a concept that the chemist got from the practical experience, the nature of the price key was not yet then resolved.

### (3) Modern organic chemistry

As the discovery of electrons by physicists and the elaboration of atomic structures, American physicist Luis et al. proposed the electronic theory of valence in 1916. They argue that the interaction of the outer electrons of the atoms is the reason why the atoms are joined together. The interaction of the outer electrons, such as from one atom to another atom, forms an ionic bond; the two atoms form a covalent bond if the outer electrons are shared. By electron transfer or sharing, the electrons of the atoms interacting with each other obtain an inert gas electronic configuration. After 1927, Heitler, London and others used quantum mechanics to deal with molecular structure problems, established a valence bond theory and proposed a mathematical model for the chemical bond.

## 1.2 Chemical Bond

### (1) Ionic bond

There is an electrostatic interaction between the oppositely charged ions, and when the two oppositely charged ions are near, they are attracted to each other, while there is an electrostatic repulsion between electron and electron or nuclei and nuclei. When the electrostatic attraction and electrostatic repulsion achieve balance, it forms an ionic bond(see Figure 1.1). Thus, **the ionic bond refers to the chemical bond formed by the electrostatic interaction between the anion and the cation.**

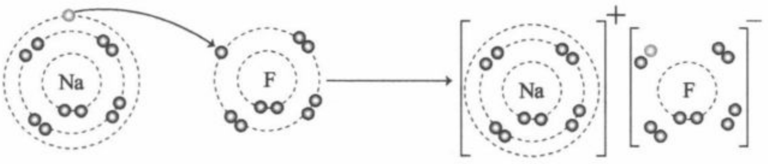


**Figure 1.1 A diagram of the formation of ionic bonds in sodium fluoride in solution**

### (2) Covalent bond

When two or more atoms together use their outer electrons, in the ideal case to achieve the state of electronic saturation, it results in a relatively stable chemical structure, the bord formed is covalent bond. The covalent bond is the interaction between the atoms through the common electron pair. Its essence is the electrical effect between the electrons and the two nuleus when the atomic orbit overlap.

In 1919, chemist Owen Langmuer used "covaluation" for the first time to describe the bonding process between atoms, he said "we shall denote by the term covalence the number of pairs of electrons which a given atom shares with its neighbors". In 1923, American chemist Gilbert Louis (G. N. Lewis) developed the theory of Korsel, proposing covalent bond electronic theory. Lewis hypothesis indicated that in molecules, an electron from one atom and another electron form the chemical bond in the form of an electron pair. This hypothesis was contrary to orthodox theory, because Coulomb's law shows that the two electrons are mutually exclusive, but Louis's idea is soon accepted by the chemical industry. Louis theory, also known as "octagonal rule" and "electronic pairing theory" is the first proposed. The formation process of hydrogen molecular covalent bond is shown in Figure 1.2.

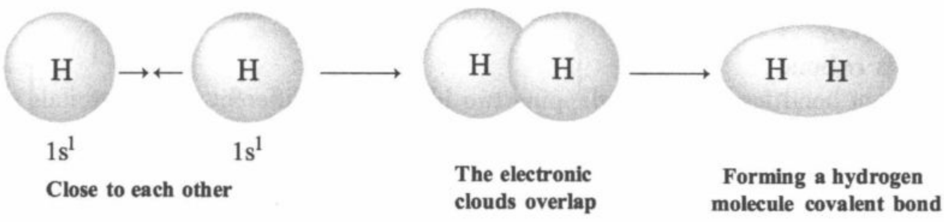


**Figure 1.2 Hydrogen molecular covalent bond formation diagram**

## 1.2.1 Carbon-carbon single bond

A single bond refers to a covalent bond between two atoms in a compound molecule that share a pair of electrons, usually represented by " – ". In ionic compounds (such as sodium chloride), the combination of ions is not by covalent single bond, but by electrostatic force. Many organic compounds carry a carbon-carbon single bond such as methane ($CH_4$) and ethane ($CH_3CH_3$) molecules. Before we explore the single bond, we must understand the carbon $sp^3$ hybrid orbitals.

### What is carbon $sp^3$ hybrid orbital?

The hybrid orbital theory states that when the carbon atoms are combined with other atoms, the arrangement of the electrons outside the nuclei changes in both the orbital and the shape. First, a 2s electron of the carbon atom is excited and transitions to the 2p orbital, so that the carbon atom has four unpaired electrons ($2s^1$, $sp_x^1$, $2p_y^1$, $2p_z^1$). And then by a 2s orbital, and three 2p orbitals recombine and forms four new hybrid orbitals of the same energy, as $sp^3$ hybrid orbitals (see Figure 1.3).

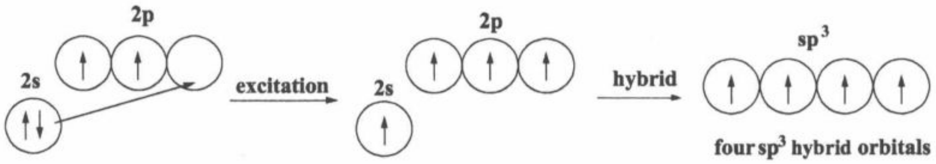


Figure 1.3 The formation process of $sp^3$ hybrid orbitals

The following is an example of methane to introduce how its hybrid orbital is formed. It is well known that the spatial structure of methane is a regular tetrahedron configuration( Figure 1.4) because it has four identical covalent bonds. The carbon atoms on the methane are $sp^3$ hybrid, and their hybrid orbitals correspond to the four vertices of the tetrahedron.

Each $sp^3$ hybrid orbital has an unpaired electron, the 1s orbital electron of the hydrogen atom overlap with the hybrid orbitals along the axis of symmetry to form four equivalent C—H covalent bonds( see Figure 1.4) in methane molecule.

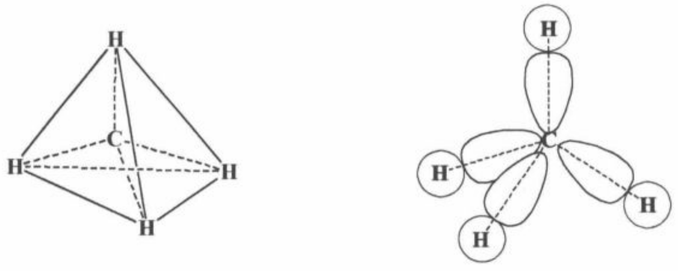


Figure 1.4 The tetrahedron configuration of methane

### What is σ bond?

A covalent bond formed by overlapping two identical or different atomic orbitals along the axis of the orbital symmetry is called σ bond ( see Figure 1.5). The σ bond is formed by overlapping of the atomic orbitals in the axial direction, with a large degree of overlap, so the σ bond is relatively stable. The σ bond is able to rotate the axis of symmetry without affecting the bond strength and the angle between the bond and the bond ( bond angle). According to the molecular orbital theory, after two atomic orbitals are sufficiently close, they form two molecular orbitals through the linear combination of atomic orbitals. Energy is lower than the original atomic orbital of the molecular orbital called the bond orbit, the energy is higher than the original atomic orbital of the molecular orbital called the backtracking orbital. The bond between the core axis as the axis of symmetry is called σ orbital and the corresponding bond is σ bond. The inter-axis as the axis of symmetry of the anti-key track is called σ ∗ track and the corresponding key is $\sigma^*$ bond. When the molecule is in the ground state, the electrons that make up the chemical bonds are usually in the bonding orbitals, leaving the anti — bonding orbitals empty.

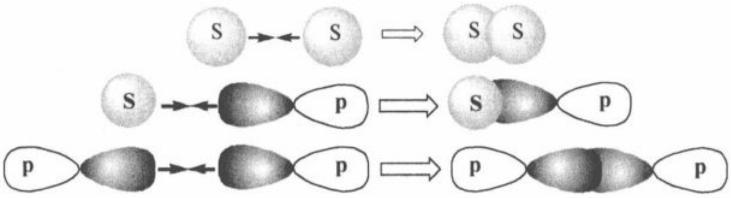
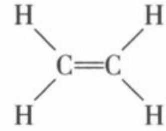


Figure 1.5 σ bond schematic

Atomic orbital, in addition to the s orbital is spherical symmetry, p and d orbital have certain spatial orientation. They bond only along a certain direction to reach maximum overlap, in order to form a stable covalent bond, which is the direction of covalent bond

### 1.2.2 Carbon-carbon double bond

The carbon-carbon double bond ( C=C ) refers to the 2s sub-layer of carbon and two 2p sub-layers hybridized to three $sp^2$ hybrid orbitals. The three $sp^2$ hybrid orbitals are distributed on the same plane. The key can be greater than a single key. Ethylene is the simplest organic compound with carbon-carbon double bond structure. Here is the ethylene as an example to illustrate carbon-carbon double bond. Each of the carbon atoms in ethene ( also called ethylene) forms four bonds, but each carbon is bonded to only three atoms.



Ethene

**What is carbon $sp^2$ hybrid orbital?**

To bond to three atoms, each carbon hybridizes three atomic orbitals: an s orbital and two of the p orbitals. Because three orbitals are hybridized, three hybrid orbitals are formed. These are called $sp^2$ orbitals. After hybridization, each carbon atom has three degenerate $sp^2$ orbitals and one unhybridized p orbital( see Figure 1.6).

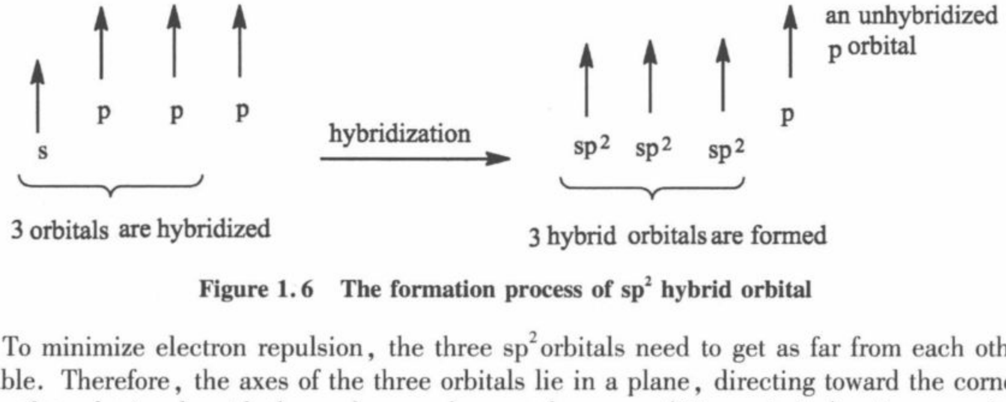
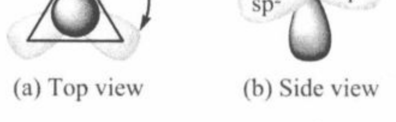


**Figure 1.6 The formation process of $sp^2$ hybrid orbital**

To minimize electron repulsion, the three $sp^2$orbitals need to get as far from each other as possible. Therefore, the axes of the three orbitals lie in a plane, directing toward the corners of an equilateral triangle with the carbon nucleus at the center( Figure 1.7a). As a result, the bond angles are all close to 120°. Because an $sp^2$ carbon is bonded to three atoms that define a plane, it is called a trigonal planar carbon. The unhybridized p orbital is perpendicular to the plane defined by the axes of the $sp^2$ orbitals( Figure 1.7b).



(a) Top view (b) Side view

**Figure 1.7 The spatial position of $sp^2$ hybrid orbitals**

### What is π bond?

The carbons in ethene form two bonds with each other. Two bonds connecting two atoms are called a double bond. The two carbon-carbon bonds in the double bond are not identical. As shown in Figure 1. 8, one of them results from the overlap of an $sp^2$ orbital of one carbon with an $sp^2$ orbital of the other carbon; this is a sigma (σ) bond because it is cylindrically symmetrical. Each carbon uses its other two $sp^2$ orbitals to overlap the s orbital of a hydrogen to form the C—H bonds. The other carbon carbon bond results from side-to-side overlap of the two unhybridized p orbitals. Side-to-side overlap of p orbitals forms a pi (π) bond. Thus, one of the bonds in a double bond is a σ bond, and the other is a pi (π) bond. All the C—H bonds are σ bonds (Remember that all single bonds in organic compounds are σ bonds). In order to maximumly overlap, the two p orbitals that overlap to form the π bond must be parallel to each other. This forces the triangle formed by one carbon and two hydrogens to lie in the same plane as the triangle formed by the other carbon and two hydrogens.

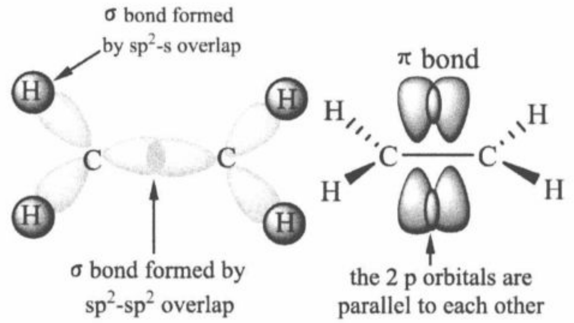


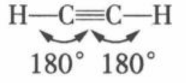
Figure 1.8 The molecular structure of ethene

Four electrons hold the carbons together in a carbon-carbon double bond but only two electrons hold the carbons together in a carbon-carbon single bond. Since more electrons hold the carbons together, a carbon-carbon double bond is stronger (174 kcal/mol or 728 kJ/mol) and shorter (1. 33Å) than a carbon-carbon single bond (90 kcal/mol or 377 kJ/mol, and 1. 54Å).

## 1.2.3 Multiple covalent bond

The above explained the $sp^3$ hybridization of methane and the $sp^2$ hybridization of ethylene. The following will describe in the case of acetylene as an example to show the acetylene sp hybridization pathway. Hydrocarbons bonded by a triple bond, are called alkynes. The two simplest alkynes are ethyne and propyne.

Ethyne, a compound that is also called acetylene, consists of a linear arrangement of atoms. The H—C≡C bond angles of ethyne molecules are 180°.



Ethyne

As shown in Figure 1. 9, in order for sp bybridization in alkyne, each carbon hybridizes two atomic orbitals, an s and a p, which result in two degenerate sp orbitals.

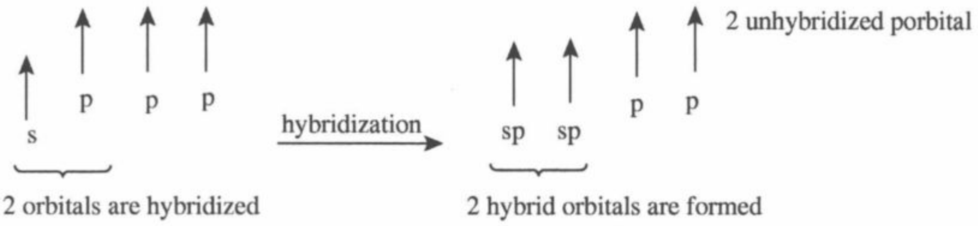


**Figure 1.9 The formation process of sp hybrid orbital**

Each carbon atom in ethyne, therefore, has two sp orbitals and two unhybridized p orbitals. To minimize electron repulsion, the two sp orbitals point in opposite directions. As shown in Figure 1.10, the two unhybridized p orbitals are perpendicular to each other and to the sp orbitals. The two carbons in ethyne are held together by three bonds. Three bonds connecting two atoms is called a triple bond. One of the sp orbitals of one carbon in ethyne overlaps an sp orbital of the other carbon to form a carbon-carbon σ bond. The other sp orbital of each carbon overlaps the s orbital of a hydrogen to form a C—H σ bond. Each of the unhybridized p orbitals engages in side-to-side overlap with a parallel p orbital on the other carbon, resulting in the formation of two π bonds

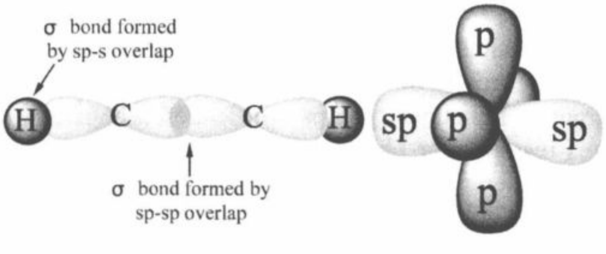


**Figure 1.10 The molecular structure of acetylene**

Thus, a triple bond consists of one σ bond and two π bonds. Because the two unhybridized π orbitals on each carbon are perpendicular to each other, they create regions of high electron density above and below and in front of and back of the internuclear axis of the molecule.

## 1.3 Polarity of Bonds and Molecules

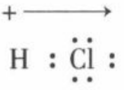
**What is polarity of bonds?**

In the molecule, the covalent bonds formed by different atoms, due to the inability of the two atoms to attract electrons equally, the common electron pair is inevitably biased towards the atoms with strong electron attracting capabilities, thus other atoms with less attracting for electrons are weak. Hence, the atom with weak attraction to electron is shown to be positively charged. This covalent bond is called the polar covalent bond and is referred to as the polar bond. The atoms that share the bonding electrons in the F—F and H—H covalent bonds are identical. Therefore, they share the electrons equally. Such a bond is called a nonpolar covalent bond.

An example of such polar covalent bond is the one in hydrogen chloride. The chlorine atom, with its greater electronegativity, pulls the bonding electrons closer to it. This makes the hydrogen atom somewhat electron deficient and gives it a partial positive charge ($\delta^+$). The chlorine atom becomes somewhat electron rich and bears a partial negative charge ($\delta^-$).

$$\overset{\delta^+}{\mathrm{H}} : \overset{\delta^-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}} :$$

The direction of bond polarity can be indicated with an arrow. By convention, chemists draw the arrow so that it points out the direction in which the electrons are pulled. Thus, the head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond (Physicists draw the arrow in the opposite direction).



$$\overset{+\!\longrightarrow}{\mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} :}$$

A polar bond has a dipole: it has a negative end and a positive end. The size of the dipole is indicated by the dipole moment, symbolized by the Greek letter $\mu$.

$$\mu = \text{size of the charge} \times \text{the distance between the charges}$$

The charges are typically on the order of $10^{-10}$ esu and the distances are on the order of $10^{-8}$ cm. Dipole moments, therefore, are typically on the order of $10^{-18}$ esu cm. For convenience, this unit, $1 \times 10^{-18}$ esu cm, is defined as one debye and is abbreviated D (The unit is named after Peter J. W. Debye, a chemist born in the Netherlands and who taught at Cornell University from 1936 to 1966. Debye won the Nobel Prize in Chemistry in 1936). In SI units, $1\ \mathrm{D} = 3.336 \times 10^{-30}$ coulomb meter (C · m). Polar covalent bonds strongly influence the physical properties and reactivity of molecules. In many cases, these polar covalent bonds are part of functional groups. Functional groups are defined groups of atoms in a molecule that give rise to the function (reactivity or physical properties) of the molecule. Functional groups often contain atoms having different electronegativity values and unshared electron pairs. Atoms such as oxygen, nitrogen, and sulfur that form covalent bonds and have unshared electron pairs are called heteroatoms.

### What is polarity of molecules?

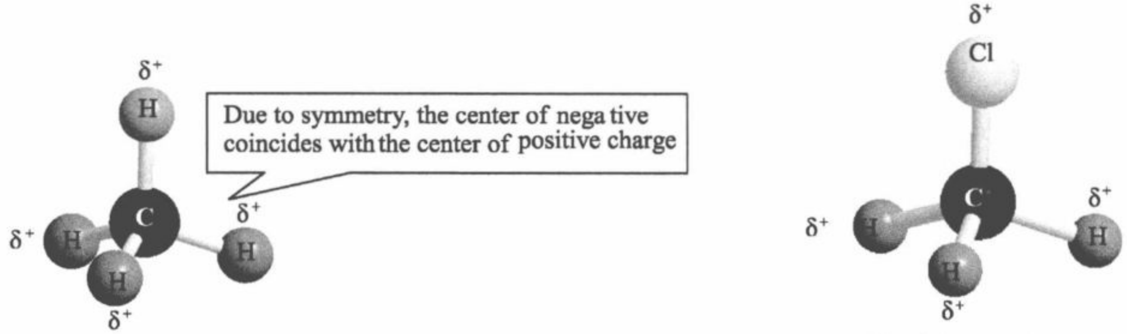
Any diatomic molecule in which the two atoms are different (and thus have different electronegativity) will of necessity have a dipole moment. In general, a molecule with a dipole moment is a polar molecule. From Table 1.1, we find that a number of molecules (e.g., $CCl_4$, $CO_2$) consisting of more than two atoms, have polar bonds, but have no dipole moment.

**Table 1.1 Dipole moments of some simple molecules**

| Formula | $\mu$ (D) | Formula | $\mu$ (D) |
|---|---|---|---|
| $H_2$ | 0 | $CH_4$ | 0 |
| $Cl_2$ | 0 | $CH_3Cl$ | 1.87 |
| HF | 1.83 | $CH_2Cl_2$ | 1.55 |
| HCl | 1.08 | $CHCl_3$ | 1.02 |
| HBr | 0.8 | $CCl_4$ | 0 |
| HI | 0.42 | $NH_3$ | 1.47 |
| $BF_3$ | 0 | $NF_3$ | 0.24 |
| $CO_2$ | 0 | $H_2O$ | 1.85 |

Because the electronegativity of carbon is greater than that of hydrogen, each of the C—H bonds in $CH_4$ is polar. Each hydrogen atom has a partial positive charge, and the carbon atom is considerably negative (see Figure 1.11). Because a molecule of methane is tetrahedral, however, the center of negative charge and the center of positive charge coincide, and the molecule has no net dipole moment.

The chloromethane molecule ($CH_3Cl$) has a net dipole moment of 1.87 D. Since carbon and hydrogen have electronegativity that are nearly the same, the contribution of three C—H bonds to the net dipole is negligible. The electronegativity difference between carbon and chlorine is large, however, highly polar C—Cl bond accounts for most of the dipole moment of $CH_3Cl$.



Due to symmetry, the center of nega tive coincides with the center of positive charge

(a) Methane

(b) Chloromethane

**Figure 1.11 Ball and stick model of molecule**

## 1.4 Intermolecular Forces

Intermolecular forces (IMFs) are the forces which mediate interaction between molecules, including forces of attraction or repulsion which act between molecules and other types of neighboring particles, e. g., atoms or ions. Inter-molecular forces are weak relative to intramolecular forces. For example, the covalent bond, involving sharing electron pairs between atoms, is much stronger than the forces present between neighboring molecules. Both sets of forces are essential parts of force fields frequently used in molecular mechanics. We will focus our attention on three types: ① Dipole dipole forces, ② Hydrogen bonds, ③ Dispersion forces.

### 1.4.1 Dipole dipole forces

Dipole-dipole interactions are electrostatic interactions between molecules which have permanent dipole. These interactions tend to align the molecules to increase attraction (reducing potential energy). An example of a dipole-dipole interaction can be seen in hydrogen chloride (HCl), the positive end of a polar molecule will attract the negative end of the other molecule and influence its position. Polar molecules have a net attraction between them. Examples of polar molecules include hydrogen chloride (HCl) and chloroform ($CHCl_3$).

$$\overset{\delta^+}{\mathrm{H}}—\overset{\delta^-}{\mathrm{Cl}}{}^-—\overset{\delta^+}{\mathrm{H}}—\overset{\delta^-}{\mathrm{Cl}}$$

Often molecules contain dipolar groups, but have no overall dipole moment. This occurs if there is symmetry within the molecule that causes the dipoles to cancel each other out. This occurs in molecules such as tetrachloromethane and carbon dioxide.

### 1.4.2 Hydrogen bond

Very strong dipole-dipole attractions occur between hydrogen atoms bonded to small but strongly electronegative atoms (O, N, or F) and nonbonding electron with other such electronegative atoms. This type of intermolecular force is called a hydrogen bond. Hydrogen