

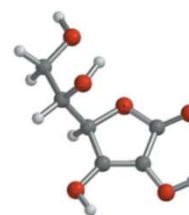
CHEM 244

PRINCIPLES OF ORGANIC CHEMISTRY I

FOR CHEMICAL ENGINEERING' STUDENTS, COLLEGE OF ENGINEERING

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)



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COURSE OBJECTIVES

Upon successful completion of this course, the student will be able to:

- **Name** organic compounds using IUPAC naming system, their occurrence in nature, physical properties.
- **Identify, classify and understand** physical and chemical properties of the major functional groups.
- **Understand** the basic organic reaction for preparation of common functional groups.
- **Understand** the reaction of functional groups and families of organic compounds.
- The practical uses of organic compounds as drugs, food additives, pesticides, plastics, and other products, as well as their occurrence in nature

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TOPICS TO BE COVERED

- **Introduction** (Lectures 3)
Introduction (Carbon Compounds, Chemical Bonds (ionic, Covalent), Atomic and Molecular orbitals, Hybridization, Polarity and Inductive effect).
- **Alkanes and Cycloalkanes** (Lectures 6)
(Alkyl groups, IUPAC nomenclature, Physical properties, Sources off, Synthesis. Reactions (Combustion, Halogenation, Ring opening). Configuration, cyclohexanes.
- **Alkenes and Alkynes** (Lectures 6)
(IUPAC nomenclature, Physical properties, Synthesis (Dehydrohalogenation, from vicinal dihalides, Dehydration of alcohols). Reactions (Acidity of terminal alkynes, Addition reactions (Reduction, Halogenation, Addition of HX – Markovnikov rule, Carbonium ions and their stability, Reaction mechanism), Addition in the presence of peroxides, Hydration, Halohydrin formation), Oxidation of Alkenes (KMnO₄, Peroxides and Ozonolysis).
- **Conjugated Dienes** (Lectures 3)
(Allyl radical and stability, Allyl cation, 1,3-Butadiene - electron delocalization, Resonance and the Stability of conjugated dienes, 1,4-Addition and 1,4-Cycloaddition reactions of diene).

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TOPICS TO BE COVERED

- **Aromatic Compound** (Lectures 5)
(Aromatic character, Hukel rule, Nomenclature, Electrophilic substitution reactions (Alkylation, Acylation, Halogenation, Sulphonation, Nitration; reaction mechanism), Side chain halogenation and oxidation, Reactivity and Orientation in substituted benzene, Polynuclear aromatics).
- **Stereochemistry** (Lectures 2)
(Structural isomers and Stereoisomerism, Enantiomers, Diastereomers and Chirality, D and L, The R-S system, Resolution, Molecules with more than one chiral carbon, Reactions of chiral molecules: Inversion, Racemization).
- **Alkyl halides** (Lectures 3)
(nomenclature, synthesis and reactions, optical isomerism (SN₁, SN₂ reactions)).

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SCHEDULE OF ASSESSMENT TASKS DURING THE SEMESTER

Assessment task	Week Due	Proportion of Total Assessment
1. Home work	All weeks	5 %
2. Quizzes	3, 5, 9	15 %
4. 1 st Midterm exam	7	20 %
5. 2 nd Midterm exam	13	20 %
6. Final exam		40 %

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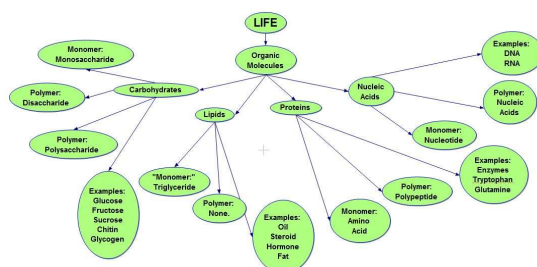
CHAPTER 1

INTRODUCTION

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ORGANIC CHEMISTRY: DEFINITION

- The term **organic** suggests that this branch of chemistry has something to do with *organisms*, or living things.
- Originally, organic chemistry did deal only with substances obtained from living matter.
- In particular, most compounds in living matter are made up of the same few elements: **carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur, phosphorus, and a few others.**



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ORGANIC CHEMISTRY: DEFINITION

What Is Organic Chemistry?



- **Organic chemistry** is the chemistry of carbon compounds.

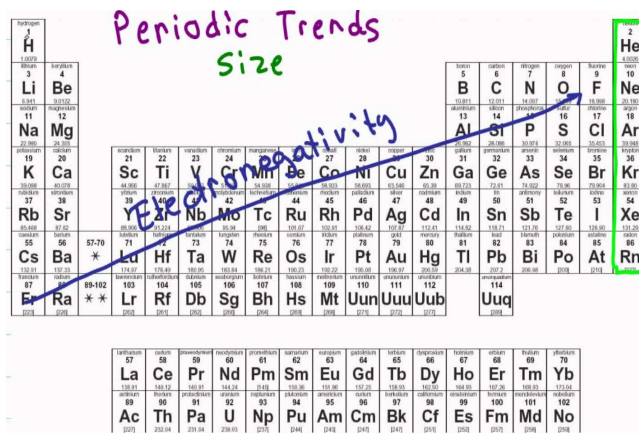
*This definition broadens the scope of the subject to include **not only compounds from nature but also synthetic compounds** - compounds invented by organic chemists and prepared in their laboratories.*

Examples:

The clothes, the petroleum products, the paper, rubber, wood, plastics, paint, cosmetics, insecticides and drugs.

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The Periodic Table:

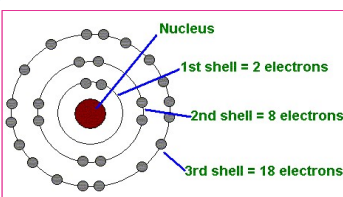


A diagram of an atom. At the center is the **Nucleus**, which contains **Protons** (red spheres with a '+' sign) and **Neutrons** (yellow spheres with a '0' sign). Surrounding the nucleus are two concentric circles representing electron shells. **Electrons** (blue spheres with a '-' sign) are located on these shells. Labels with arrows point to the Nucleus, Protons, Neutrons, and an Electron.

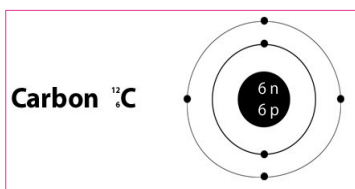
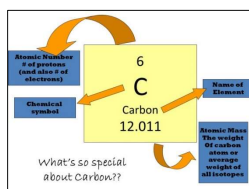
- The **atomic number** of an element is equal to *the number of protons in its nucleus* (and to *the number of electrons around the nucleus in a neutral atom*).
- The **atomic weight** is approximately equal to the *sum of the number of protons and the number of neutrons in the nucleus*.

ATOMIC STRUCTURE

- The **energy levels** are designated by capital letters (K, L, M, N, ..).
- The maximum capacity of a shell = $2n^2$ electrons.
 n = number of the energy level.



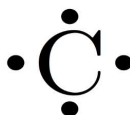
- **Example**, the element **carbon** (atomic number 6)



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ATOMIC STRUCTURE

- **Electron-dot structures**
 - The symbol of the element represents the core of the atom and the **valence electrons** are shown as dots around the symbol.



- **Valence Electrons** are those electrons located in the outermost energy level (the valence shell).

Valences of Common Elements						
Element	H·	·C·	·N·	·O·	·F·	·Cl·
Valence	1	4	3	2	1	1

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TYPES OF CHEMICAL BONDS

- In 1916 G.N. Lewis pointed out that:

The noble gases were stable elements and he ascribed their lack of reactivity to their having their valence shells filled with electrons.

- 2 electrons in case of helium.
- 8 electrons for the other noble gases.

- Types of Chemical Bonds

A) Ionic Bonding

B) Covalent Bonding

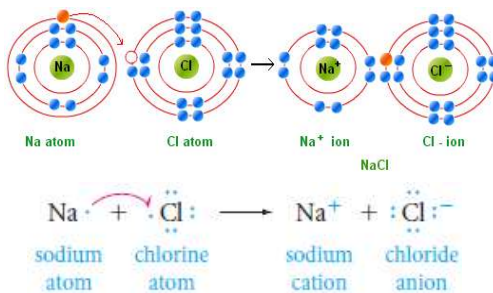
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TYPES OF CHEMICAL BONDS

A) IONIC BOND

- Ionic bonds are formed by the transfer of one or more valence electrons from one atom to another.

- The atom that gives up electrons becomes positively charged, a cation.
- The atom that receives electrons becomes negatively charged, an anion.



Ionic Bond is the electrostatic force of attraction between oppositely charged ions.

- The majority of ionic compounds are **inorganic substances**.

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TYPES OF CHEMICAL BONDS

B) COVALENT BOND

- A **covalent bond** is formed when two atoms share one or more electron pairs.

Elements that are neither strongly electronegative nor strongly electropositive, or that have similar electronegativities, tend to form bonds by sharing electron pairs rather than completely transferring electrons.

- A **molecule** consists of two or more atoms joined by covalent bonds.
- When the **two atoms are identical or have equal electronegativities**, the electron pairs are shared **equally**.

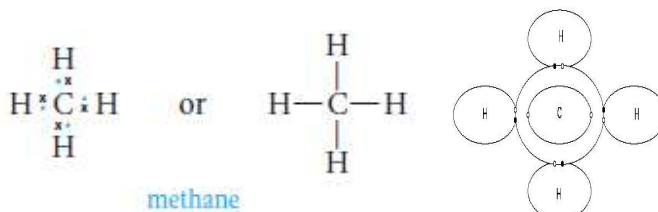


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TYPES OF CHEMICAL BONDS

B) COVALENT BOND

- **For example**, carbon combines with four hydrogen atoms (each of which supplies one valence electron) by sharing four electron pairs. The substance formed is known as **methane**.



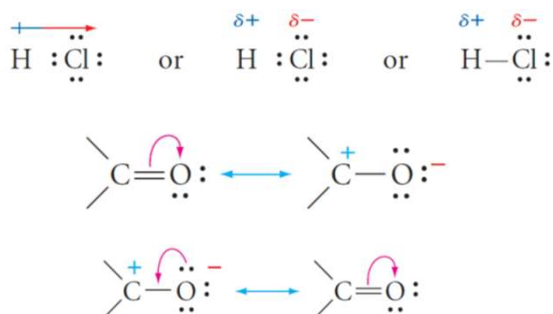
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TYPES OF CHEMICAL BONDS

C) POLAR COVALENT BONDS

- A **polar covalent bond** is a covalent bond in which the electron pair is not shared equally between the two atoms.

The more electronegative atom assumes a partial negative charge and the less electronegative atom assumes a partial positive charge.



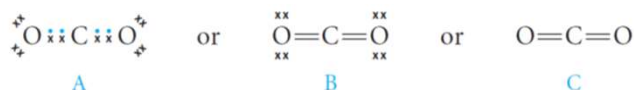
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TYPES OF CHEMICAL BONDS

MULTIPLE COVALENT BONDS

- In a **double bond**, two electron pairs are shared between two atoms.

Example; Carbon dioxide, CO_2

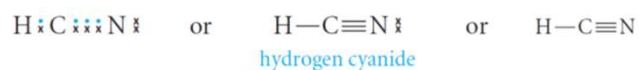


Structure A, the dots represent the electrons from carbon, and the x's are the electrons from the oxygens.

Structure B shows the bonds' and oxygens' unshared electrons (nonbonding electrons).

Structure C shows only the covalent bonds.

- In a **triple bond**, three electron pairs are shared between two atoms.



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QUIZZES

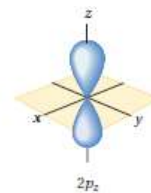
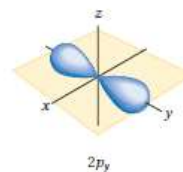
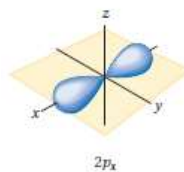
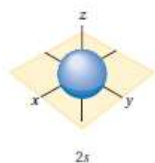
TYPES OF CHEMICAL BONDS

- PROBLEM 1.1** Write an equation for the reaction of sodium atoms (Na) with chlorine atoms (Cl).
- PROBLEM 1.2** Write an equation for the formation of a fluorine molecule from two fluorine atoms.
- PROBLEM 1.3** Draw the structures for dichloromethane (also called methylene chloride), CH_2Cl_2 , and trichloromethane (chloroform), CHCl_3 .
- PROBLEM 1.4** Draw the structure of the refrigerant dichlorodifluoromethane, CCl_2F_2 (CFC-12), and indicate the polarity of the bonds. (The C atom is the central atom.)
- PROBLEM 1.5** Draw the formula for methanol, CH_3OH , and (where appropriate) indicate the bond polarity with an arrow, \rightarrow . (The C atom is bonded to three H atoms and the O atom.)
- PROBLEM 1.6** Draw an electron-dot structure for carbon monoxide, CO.
- PROBLEM 1.7** Draw three different structures that have the formula C_4H_8 and have one carbon-carbon double bond.

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ATOMIC ORBITALS

- An **atomic orbital** represents a specific region in space in which an electron is most likely to be found.
- Atomic orbitals** are designated in the order in which they are filled by the letters **s**, **p**, **d**, and **f**.
 - An **s orbital** is **spherically shaped** electron cloud with the atom's nucleus and its center.
 - A **p orbital** is a **dumbbell-shaped** electron cloud with the nucleus between the two lobes.



- Examples:

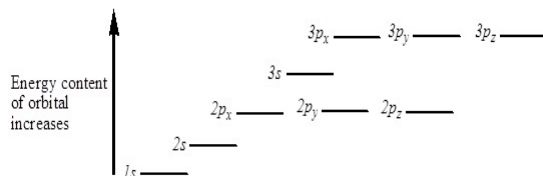
K shell has only **one 1s** orbital.

L shell has **one 2s** and **three 2p** (**2p_x**, **2p_y** and **2p_z**).

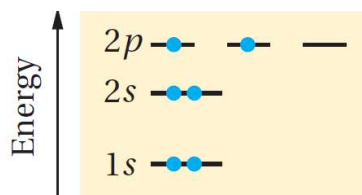
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ATOMIC ORBITALS

- An **energy level diagram** of atomic orbitals.



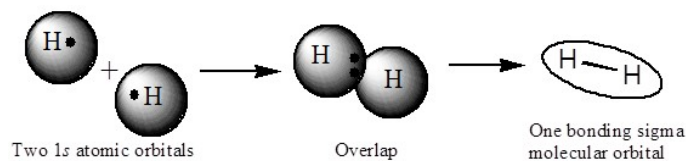
- The electronic configuration of **carbon (atomic number 6)** can be represented as



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MOLECULAR ORBITALS

- A covalent bond consists of the overlap between two atomic orbitals to form a **molecular orbital**.
- Example:** Molecular orbital of H_2

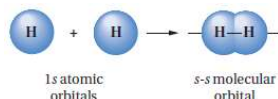


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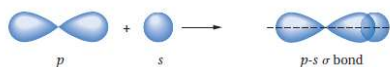
SIGMA (σ) AND pi (π) BONDS

○ **Sigma bonds (σ bonds)** can be formed from

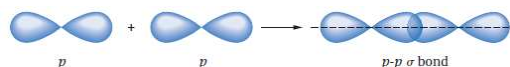
- The overlap of **two s** atomic orbitals.



- The overlap of two an **s** atomic orbital with a **p** atomic orbital.

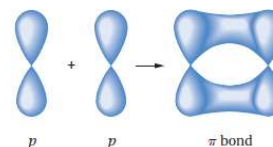


- The **end-on overlap** of two **p** atomic orbitals.



○ **pi bonds (π bonds)** can be formed from

- The **side-side overlap** between two **p** atomic orbitals.

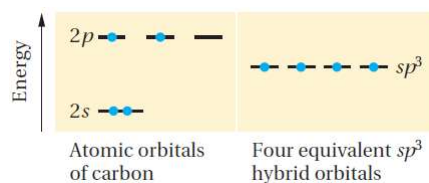


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HYBRIDIZATION

CARBON sp^3 HYBRID ORBITALS

○ The electronic configuration of the isolated or ground-state carbon



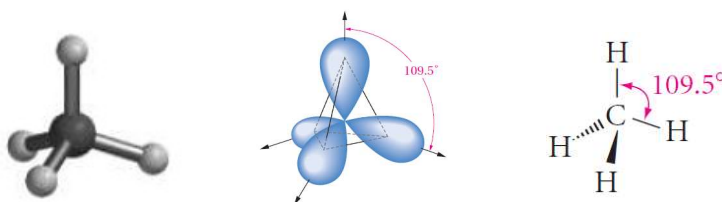
- Mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron. In this model, the hybrid orbitals are called **sp^3 hybrid orbitals** because each one has one part s character and three parts *p* character
- Each sp^3 orbital has the same energy: less than that of the 2*p* orbitals but greater than that of the 2*s* orbital.

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HYBRIDIZATION

CARBON sp^3 HYBRID ORBITALS

- The angle between any two of the four bonds formed from sp^3 orbitals is approximately 109.5° .
- Regular tetrahedral geometry
- The tetrahedral is a pyramid-like structure with the carbon atom at the center and the four attached atoms located at a corner.

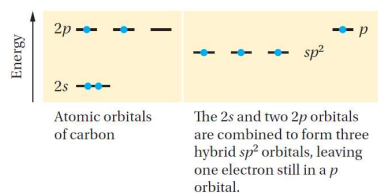


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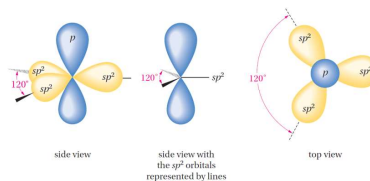
HYBRIDIZATION

CARBON sp^2 HYBRID ORBITALS

- Combine only three of the orbitals, to make three equivalent sp^2 -hybridized orbitals (called sp^2 because they are formed by combining one s and two p orbitals)



- Three valence electrons are placed in the three sp^2 orbitals. The fourth valence electron is placed in the remaining $2p$ orbital, whose axis is perpendicular to the plane formed by the three sp^2 hybrid orbitals
- The angle between them is 120° .
- A trigonal carbon

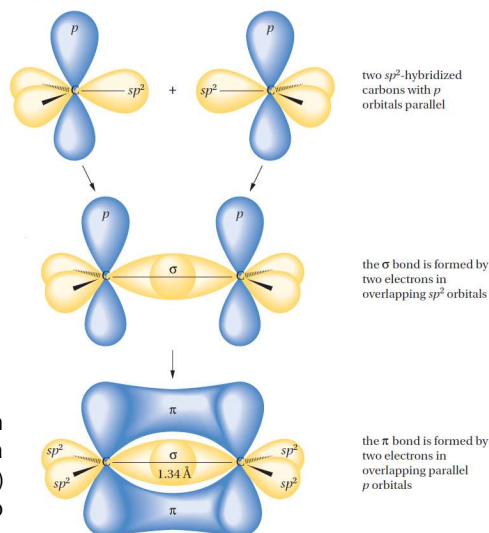


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HYBRIDIZATION

CARBON sp^2 HYBRID ORBITALS

Schematic formation of a carbon-carbon double bond. Two sp^2 carbons form a sigma (σ) bond (end-on overlap of two sp^2 orbitals) and a pi (π) bond (lateral overlap of two properly aligned p orbitals).

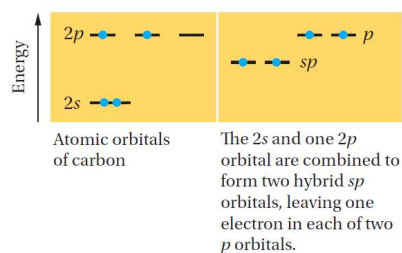


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HYBRIDIZATION

CARBON sp HYBRID ORBITALS

- The carbon atom of an acetylene is connected to only two other atoms. Therefore, we combine the 2s orbital with only one 2p orbital to make two sp -hybrid orbitals

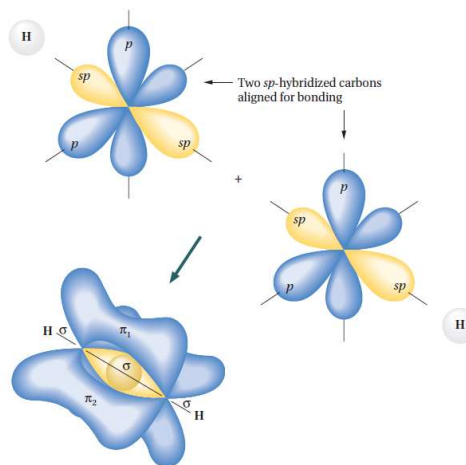


- The angle between the two hybrid orbitals is 180°
- Linear



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HYBRIDIZATION

CARBON *sp* HYBRID ORBITALS

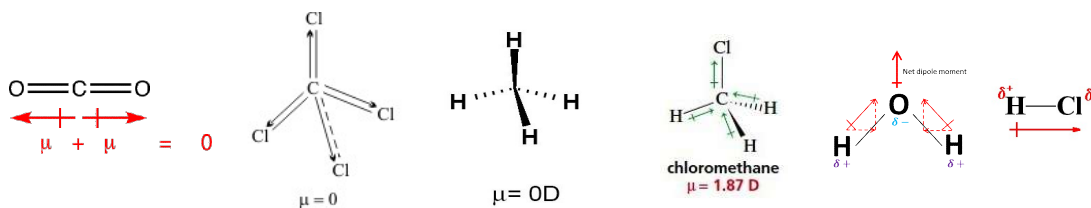
A triple bond consists of the end-on overlap of two *sp*-hybrid orbitals to form a σ bond and the lateral overlap of two sets of parallel-oriented *p* orbitals to form two mutually perpendicular π bonds.

The resulting carbon-carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

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BOND POLARITY AND DIPOLE MOMENT (μ)

- A **polar bond** is a covalent bond between two atoms where the electrons forming the bond are **unequally** distributed.
- A **nonpolar bond** is a covalent bond between two atoms where the electrons forming the bond are **equally** distributed.
- A **dipole moment** is a measurement of the separation of two oppositely charged.
- Dipole moments are a **vector** quantity.
- The **magnitude** is equal to the charge multiplied by the distance between the charges and the direction is from negative charge to positive charge.



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INDUCTIVE EFFECT

- An **inductive effect** is an electronic effect due to the polarization of σ bonds within a molecule or ion.
- This is typically due to an electronegativity difference between the atoms at either end of the bond.
 - This is the electron-withdrawing inductive effect, also known as the **-I effect**
 - This is electron releasing character and is indicated by the **+I effect**



$-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{NH}_2, -\text{OH}, -\text{OCH}_3, \dots$ (+I) electron-donating substituent

$-\text{NO}_2, -\text{CN}, -\text{SO}_3\text{H}, \text{C}(=\text{O})\text{R}, \dots$ (-I) electron-withdrawing substituent

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ACID-BASE CONCEPT

- In the Brønsted–Lowry definitions (1923),
An acid is a species that donates a proton, and a base is a species that accepts a proton (or any compound possessing a lone pair).
- **Example:**
Hydrogen chloride (HCl) meets the Brønsted–Lowry definition of an acid because it donates a proton to water.
Water (H₂O) meets the definition of a base because it accepts a proton from HCl.



Acid-Base reactions are often called proton-transfer reactions.

In the reverse reaction, H₃O⁺ is an acid because it donates a proton to Cl⁻, and Cl⁻ is a base because it accepts a proton from H₃O⁺.

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ACID-BASE CONCEPT

- When a compound loses a proton, the resulting species is called its conjugate base.

Thus, Cl^- is the conjugate base of HCl , and H_2O is the conjugate base of H_3O^+

Thus, HCl is the conjugate acid of Cl^- and H_3O^+ is the conjugate acid of H_2O

- **Acidity** is a measure of the tendency of a compound to give up a proton.
- **Basicity** is a measure of a compound's affinity for a proton.

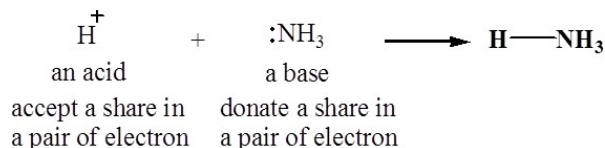
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ACID-BASE CONCEPT

- In 1923, G. N. Lewis offered new definitions for the terms “acid” and “base.”

An acid as a species that accepts a share in an electron pair.

A base as a species that donates a share in an electron pair.



- **Lewis acid** such as aluminum chloride (AlCl_3) boron trifluoride (BF_3) and borane (BH_3).

The term “acid” is used to mean a proton-donating acid, and the term “Lewis acid” is used to refer to non-proton-donating acids such as AlCl_3 or BF_3 .

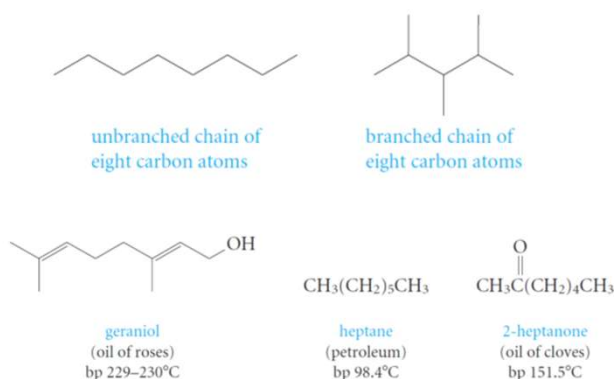
- All bases are **Lewis bases** because they have a pair of electrons that they can share, either with an atom such as aluminum or boron or with a proton.

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CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

a) Acyclic Compounds

Acyclic organic molecules have chains of carbon atoms but no rings.



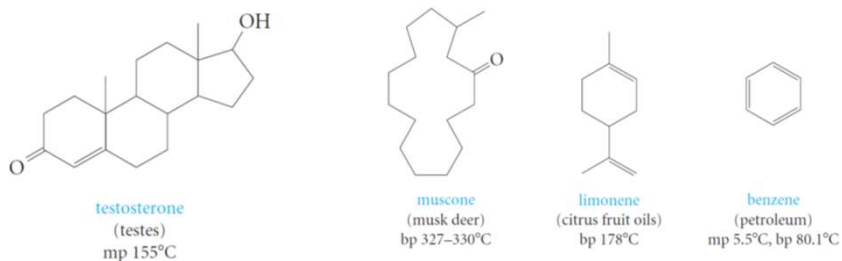
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CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

b) Carbocyclic Compounds

Carbocyclic compounds contain rings of carbon atoms.

- The **smallest** possible carbocyclic ring has **three carbon atoms**.
- **Five- and six-membered rings** are most common, but smaller and larger rings are also found.
- Many compounds with more than one carbocyclic ring are known.

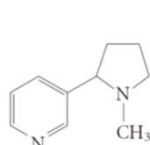


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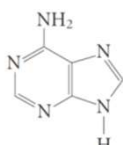
CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

c) Heterocyclic Compounds

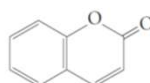
- **Heterocyclic compounds** make up the third and largest class of molecular frameworks for organic compounds.
- In heterocyclic compounds, at least one atom in the ring must be a heteroatom, an atom that is not carbon.
- The most common heteroatoms are **oxygen**, **nitrogen**, and **sulfur**, but heterocyclics with other elements are also known.



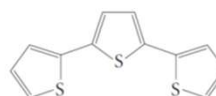
nicotine
bp 246°C



adenine
mp 360–365°C
(decomposes)



coumarin
mp 71°C



α -terthienyl
mp 92–93°C

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CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

The Main Functional Groups				
	Structure	Class of compound	Specific example	Common name of the specific example
A. Functional groups that are a part of the molecular framework		alkane	CH ₃ —CH ₃	ethane, a component of natural gas
		alkene	CH ₂ =CH ₂	ethylene, used to make polyethylene
		alkyne	HC≡CH	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds		alcohol	CH ₃ CH ₂ OH	ethyl alcohol, found in beer, wines, and liquors
		ether	CH ₃ CH ₂ OCH ₂ CH ₃	diethyl ether, once a common anesthetic

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CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

continued				
	Structure	Class of compound	Specific example	Common name of the specific example
2. With carbon-oxygen double bonds*		aldehyde	$\text{CH}_2=\text{O}$	formaldehyde, used to preserve biological specimens
		ketone	$\text{CH}_3\text{C}(=\text{O})\text{CH}_3$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon-oxygen bonds		carboxylic acid	$\text{CH}_3\text{C}(=\text{O})\text{OH}$	acetic acid, a component of vinegar
		ester	$\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$	ethyl acetate, a solvent for nail polish and model airplane glue
C. Functional groups containing nitrogen**		primary amine	$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine, smells like ammonia
		nitrile	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	acrylonitrile, raw material for making Orlon

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CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

continued				
	Structure	Class of compound	Specific example	Common name of the specific example
D. Functional group with oxygen and nitrogen		primary amide	$\text{H}-\text{C}(=\text{O})\text{NH}_2$	formamide, a softener for paper
E. Functional group with halogen		alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur†		thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
		thioether (also called sulfide)	$(\text{CH}_2=\text{CHCH}_2)_2\text{S}$	diallyl sulfide, has the odor of garlic

*The $\text{C}=\text{O}$ group, present in several functional groups, is called a **carbonyl group**. The $\text{C}=\text{O}$ group of acids is called a **carboxyl group** (a contraction of carbonyl and hydroxyl).

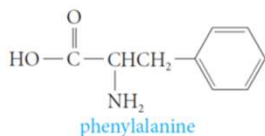
The $-\text{NH}_2$ group is called an **amino group.

†Thiols and thioethers are the sulfur analogs of alcohols and ethers.

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QUIZZES

PROBLEM 1.1 Many organic compounds contain more than one functional group. An example is phenylalanine (shown below),



- What functional groups are present in phenylalanine?
- Redraw the structure, adding all unshared electron pairs.
- What is the molecular formula of phenylalanine?