

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department



Organic Chemistry: Definition

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- The word **Organic** can be a biological or chemical term, in biology it means anything that is living or has lived. The opposite is Non-Organic.
- **Organic Chemistry** is unique in that it deals with vast numbers of substances, both natural and synthetic.

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

- But, from the chemical makeup of organic compounds, it was recognized that one constituent common to all was **the element carbon**.
- **Organic chemistry** is defined as *the study of carbon/hydrogen-containing compounds and their derivatives*.

The Uniqueness of Carbon

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- What is unique about the element **carbon**?
- Why does it form so many compounds?
 - **The answers lie in**
 - The **structure** of the *carbon* atom.
 - The **position** of *carbon* in the periodic table.
- **These factors enable it to form strong bonds with**
 - other carbon atoms
 - and with other elements (hydrogen, oxygen, nitrogen, halogens,...etc).
- Each **organic compound** has its own characteristic set of physical and chemical properties which depend on the *structure of the molecule*.

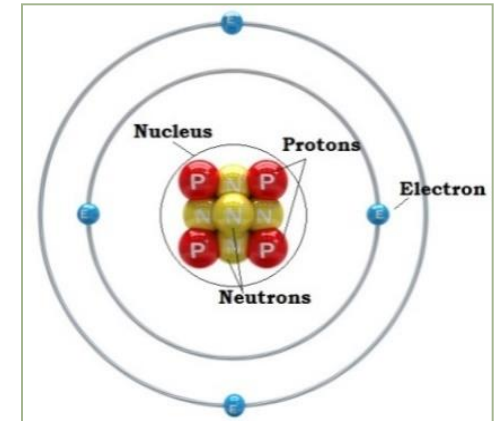
IA	IIA							III A	IV A	V A	VIA	VII A	Zero
H								B	C	N	O	F	He
Li	Be							Al	Si	P	S	Cl	Ar
Na	Mg	Transition Elements						Ga	Ge	As	Se	Br	Kr
K	Ca							In	Sn	Sb	Te	I	Xe
Rb	Sr							Tl	Pb	Bi	Po	At	Rn
Cs	Ba												
Fr	Ra												

Atomic Structure

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- **Atoms** consist of three main particles: **neutrons** (have no charge), **protons** (positively charged) and **electrons** (negatively charged).
 - Neutrons and protons are found in the nucleus.
 - Electrons are found outside the nucleus.

Electrons are distributed around the nucleus in successive *shells* (principal energy levels).

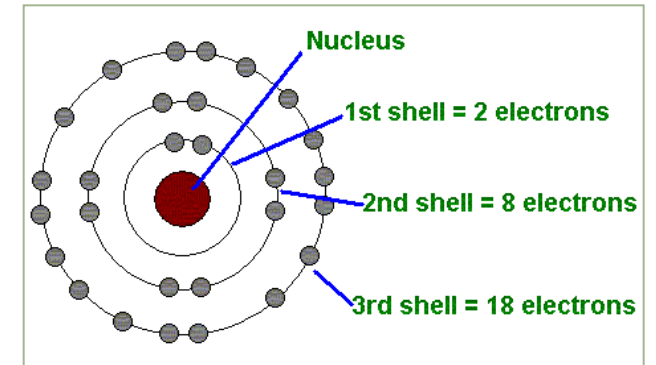


- **Atom** is electrically neutral.
 - i.e. Number of electrons = Number of protons
- **Atomic number** of an element is the number of protons.
- The **atomic weight** is approximately equal to the sum of the number of protons and the number of neutrons in the nucleus

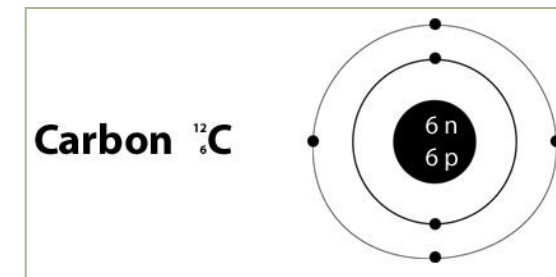
Atomic Structure

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- **The energy levels** are designated by capital letters (K, L, M, N, ..) or whole numbers (n).
- **The maximum capacity of a shell = $2n^2$ electrons.**
 n = number of the energy level.
- **For example,** the element carbon (atomic number 6)
6 electrons are distributed about the nucleus as



Shell	K	L	M	N
Number of electrons	2	4	0	0

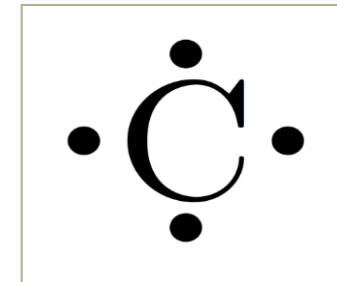


Atomic Structure

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Electron-dot structures

- **Valance Electrons** are those electrons located in the *outermost energy level (the valance shell)*.
- **Electron-dot structures**
 - The symbol of the element represents the core of the atom.
 - The valance electrons are shown as dots around the symbol.



Valance Electrons are those electrons located in the *outermost energy level (the valance shell)*.

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

Chemical Bonding



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

The noble gases were stable elements and he described 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.

- **According to Lewis,**

in interacting with one another atoms can achieve a greater degree of stability

by rearrangement of the valence electrons

to acquire the outer-shell structure of the closest noble gas in the periodic table.

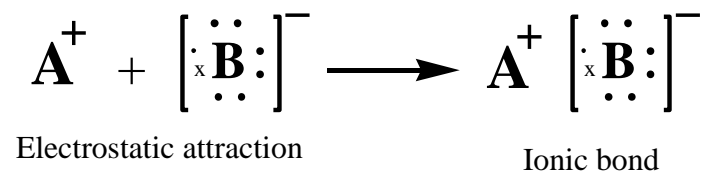
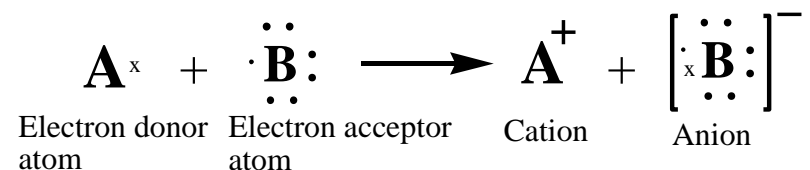
A) Ionic Bonds

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- Elements at the left of the periodic table give up their valance electrons and become +ve charged ions (**cations**).
- Elements at the right of the periodic table gain the electrons and become -ve charged ions (**anions**).

- **Ionic bond**

The electrostatic force of attraction between oppositely charged ions.



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

Chemical Bonding

A) Ionic Bonds

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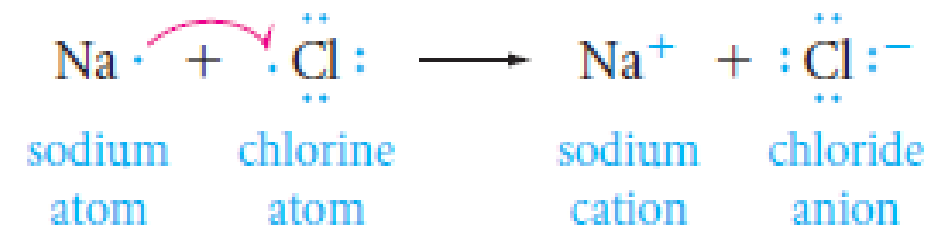
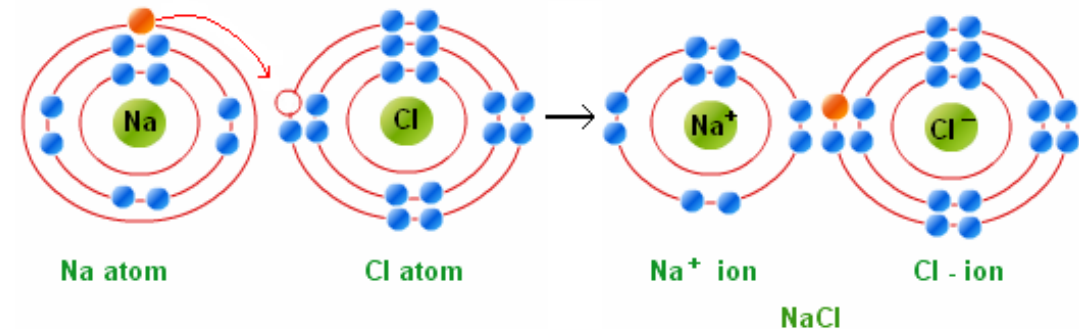
Electronegativity Measures The Ability
of An Atom To Attract Electrons

Increasing Electronegativity

H							
2.1							
Li	Be		B	C	N	O	F
1	1.5		2	2.5	3	3.5	4
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3
K							Br
0.8							2.8

Increasing Electronegativity

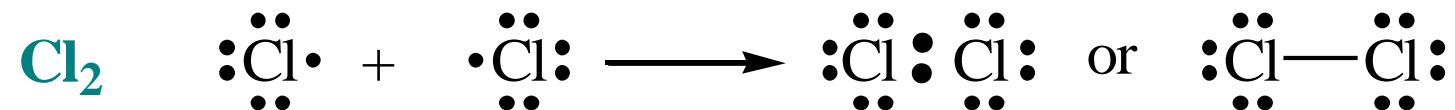
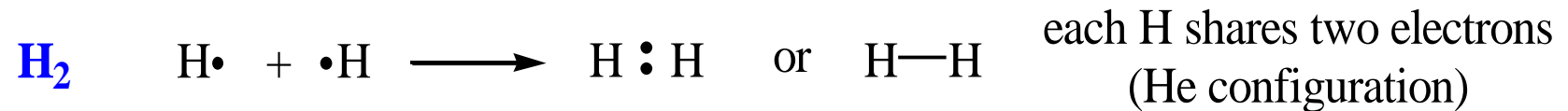
Example



B) Covalent Bonds

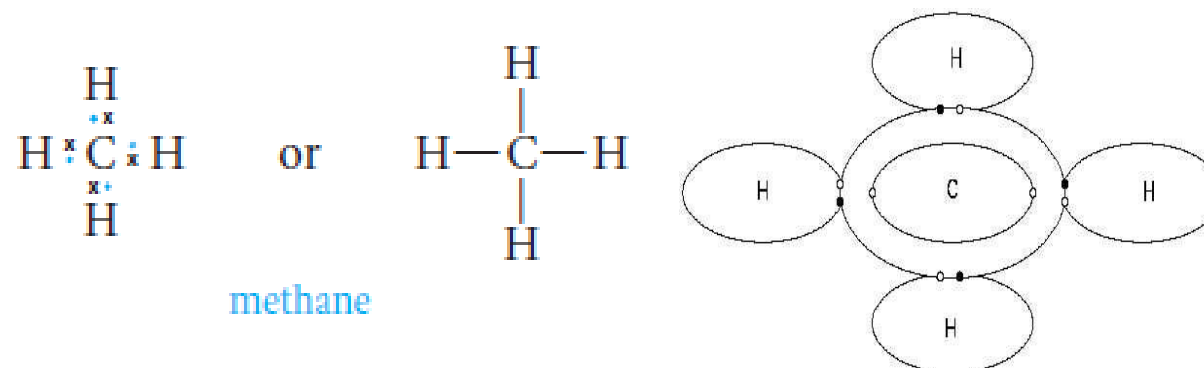
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- Elements that are close to each other in the periodic table attain the stable noble gas configuration by sharing valence electrons between them.
 - A shared electron pair between two atoms or single covalent bond, will be represented by a dash (-).
 - **A covalent bond** involves the mutual sharing of one or more electron pairs between atoms.
- ❖ When the two atoms are identical or have equal electronegativities, the electron pairs are shared equally



B) Covalent Bonds

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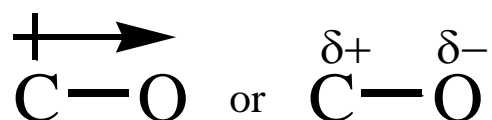
❖ When **two unlike atoms**;

the bonding electrons are no longer shared equally (shared unequally).

1) A Polar Covalent Bond

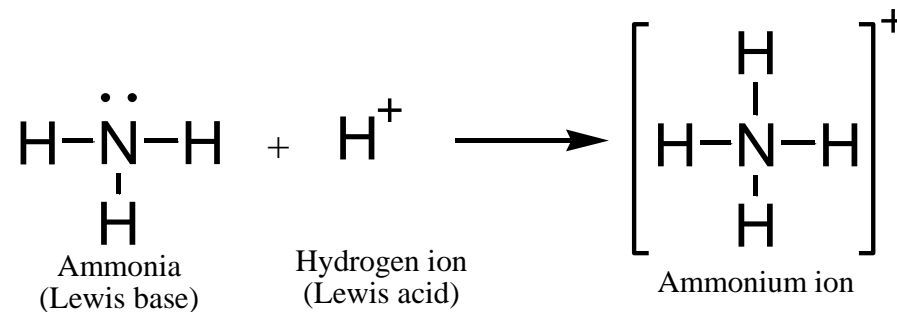
A bond, in which an electron pair is shared unequally.

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



2) Coordinate Covalent Bonds

- There are molecules in which one atom supplies both electrons to another atom in the formation of a covalent bond.
- **For example;**



- **Lewis base**

The species that furnishes the electron pair to form a coordinate covalent bond.

- **Lewis acid**

The species that accepts the electron pair to complete its valance shell.

Chemical Bonding



How Many Bonds to an Atom?

Covalence Number

The number of covalent bonds that an atom can form with other atoms.

i.e. **the covalence number** is equal to the number of electrons needed to fill its valance shell.

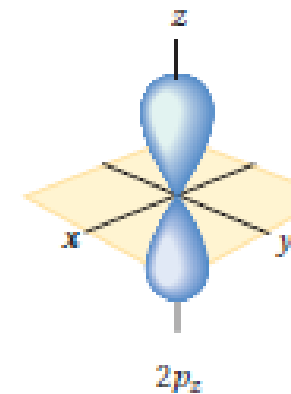
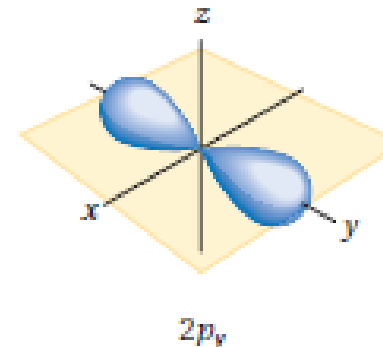
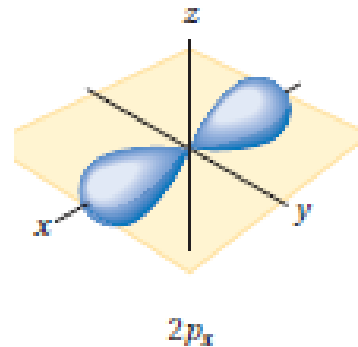
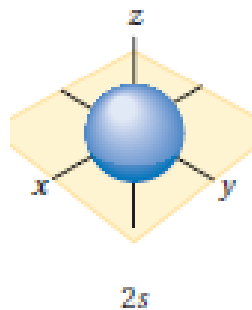
Element	Number of valence electrons	Number of electrons in filled valence shell	Covalence number
H	1	2	1
C	4	8	4
N	5	8	3
O	6	8	2
F, Cl, Br, I	7	8	1

Shapes of Organic Molecules: Orbital Picture of Covalent Bonds

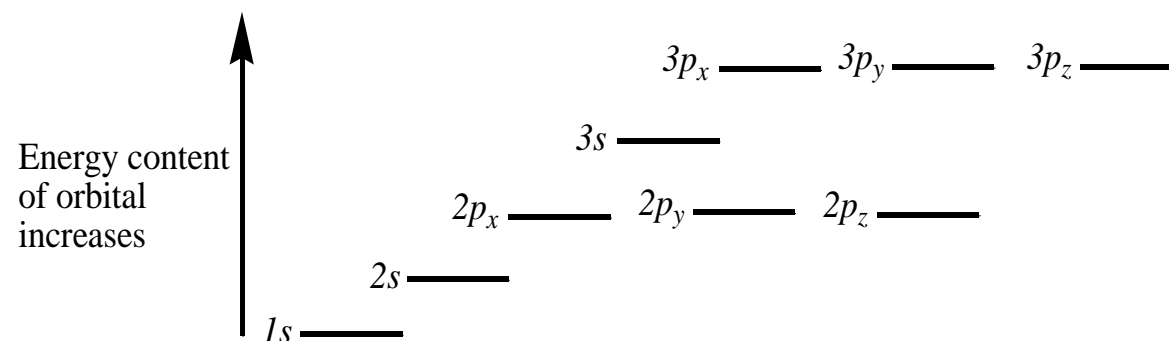
Atomic Orbitals

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- 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*.
- Examples: *K shell* has only **one 1s** orbital.
L shell has **one 2s** and **three 2p** ($2p_x$, $2p_y$ and $2p_z$).
- 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.



- An energy level diagram of atomic orbitals.



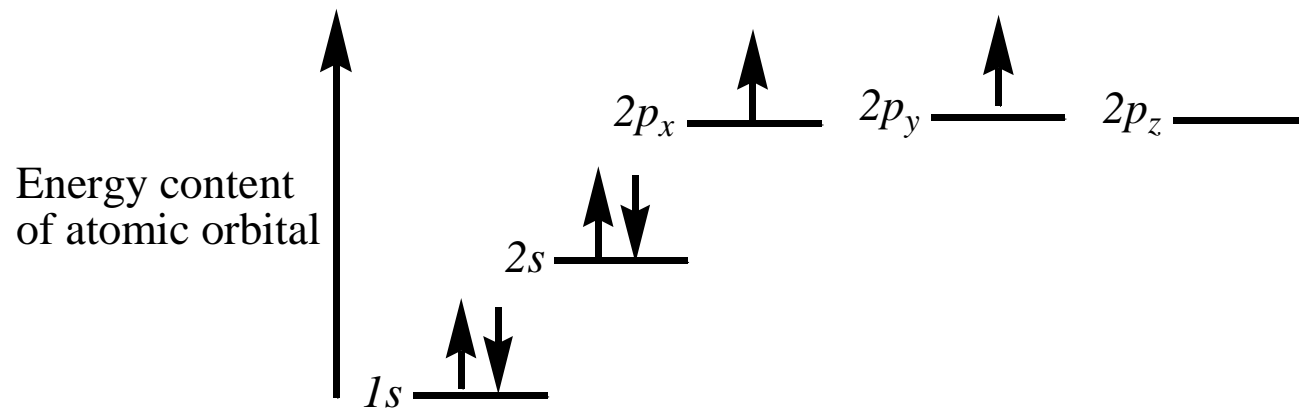
- **When filling the atomic orbitals, keep in mind that**
 - (1) An atomic orbital contain no more 2 electrons.
 - (2) Electrons fill orbitals of lower energy first.
 - (3) No orbital is filled by 2 electrons until all the orbitals of equal energy have at least one electron.

Shapes of Organic Molecules: Orbital Picture of Covalent Bonds

Atomic Orbitals

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



Energy level diagram for carbon.

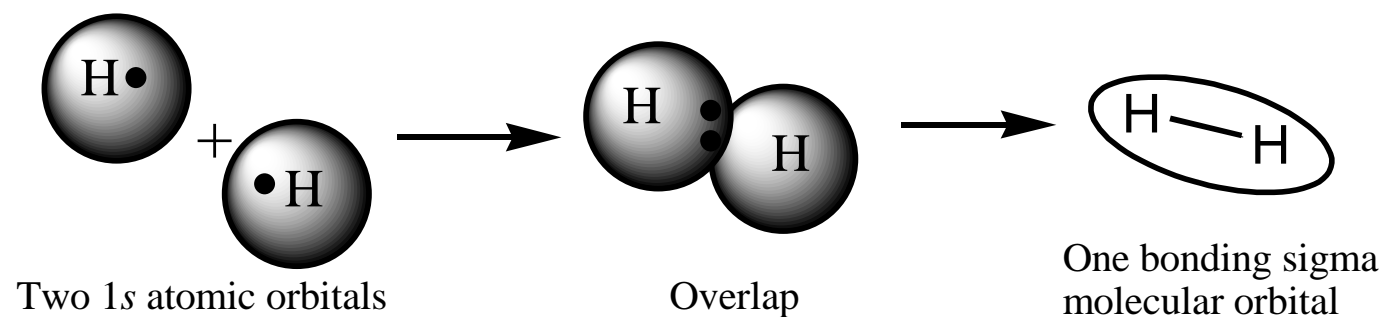
Molecular Orbitals

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

- **Example:**

Molecular orbital of H_2



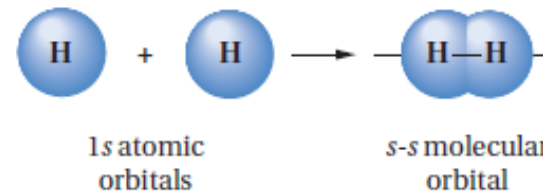
Shapes of Organic Molecules: Orbital Picture of Covalent Bonds

Molecular Orbitals

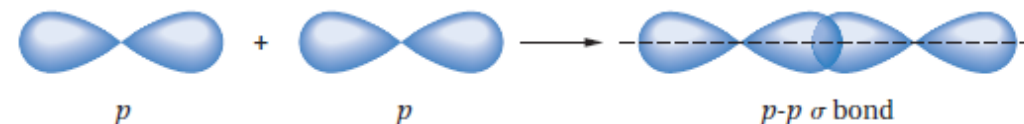
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○ **Sigma bonds (σ bonds)** can be formed from

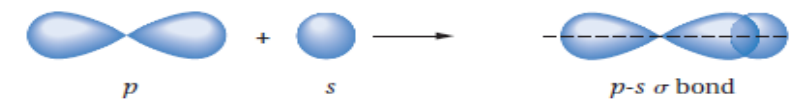
➤ The overlap of **two s** atomic orbitals.



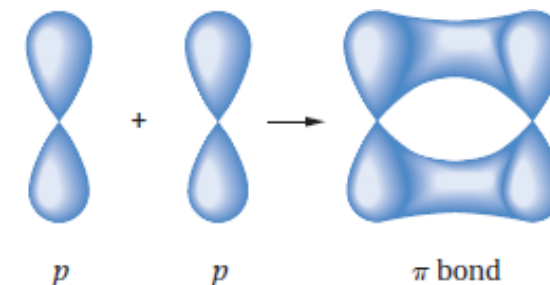
➤ The **end-on overlap** of **two p** atomic orbitals.



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



○ **pi bonds (π bonds)** can be formed from the **side-side overlap** between two p atomic orbitals.



Bond Energy and Bond Length

- **A molecule is more stable than the isolated constituent atoms.**

This stability is apparent in the release of energy during the formation of the molecular bond.

- **Heat of formation (bond energy)**

The amount of energy released when a bond is formed.

- **Bond dissociation energy**

The amount of energy that must be absorbed to break a bond.

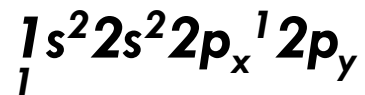
- **Bond length**

The distance between nuclei in the molecular structure.

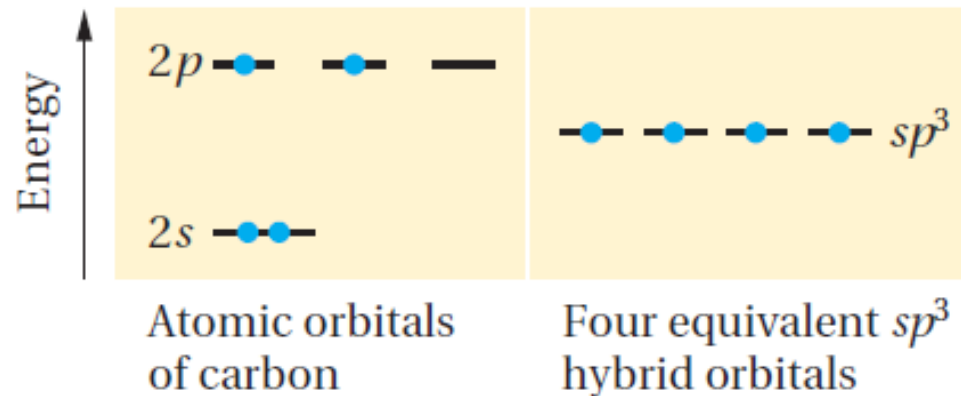
Hybridization (Alkanes sp^3)

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



Equivalent to $:\dot{C}.$

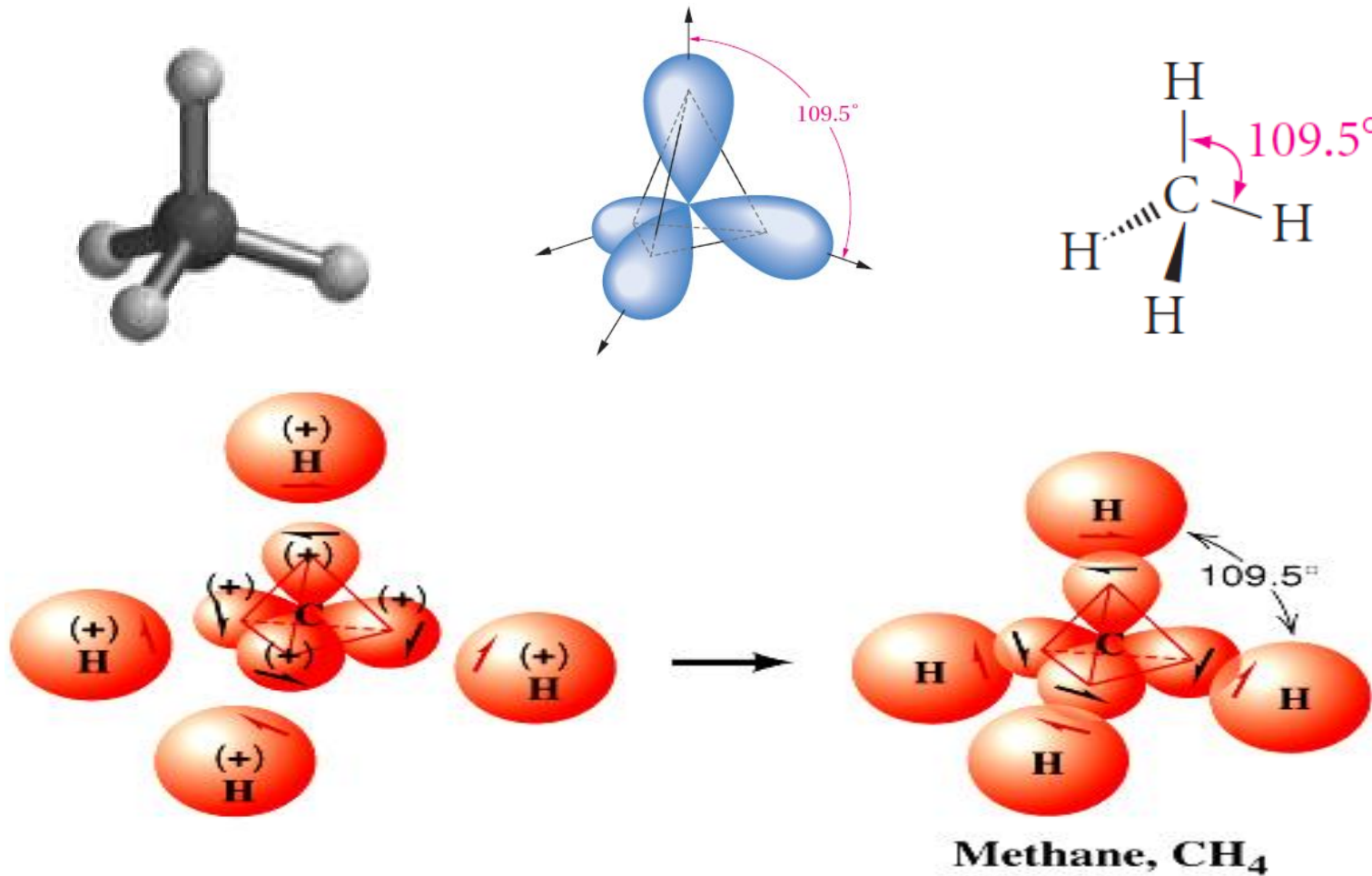


- Mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron.
- In this model, the hybrid orbitals are called **sp^3 hybrid orbitals** because each one has one part s character and three parts p character
- Each sp^3 orbital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

Hybridization (Alkanes sp^3)

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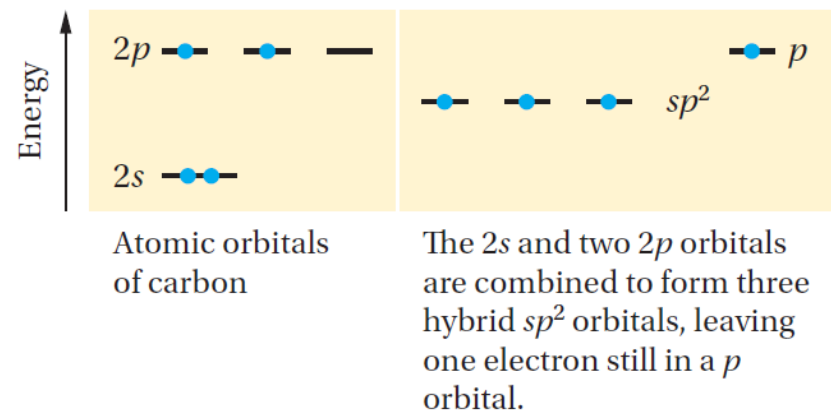
- **Regular tetrahedron** with all **H-C-H bond angles of 109.5°** .



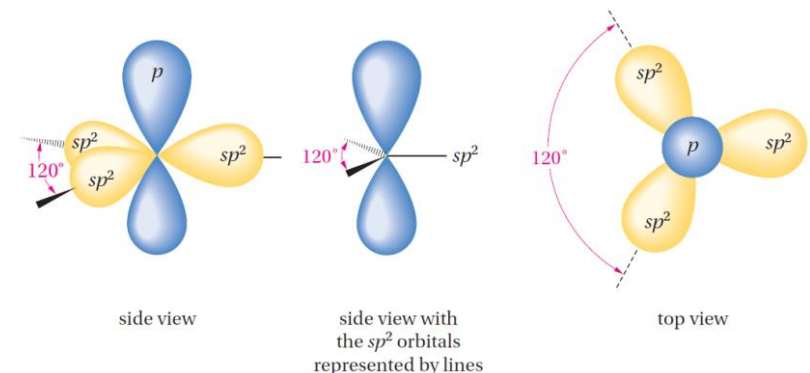
Hybridization (Alkenes sp^2)

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- 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

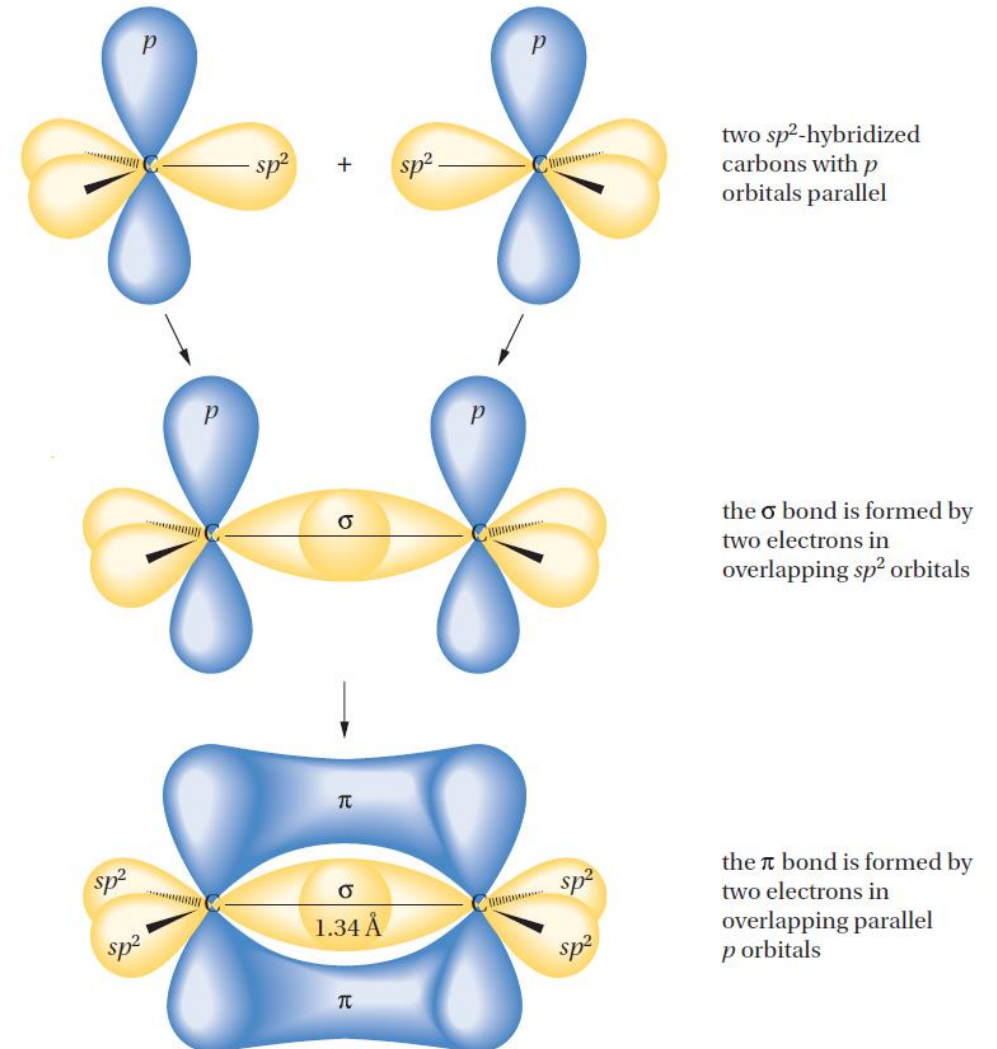


- **A trigonal carbon with bond angles of 120° .**

Hybridization (Alkenes sp^2)

23

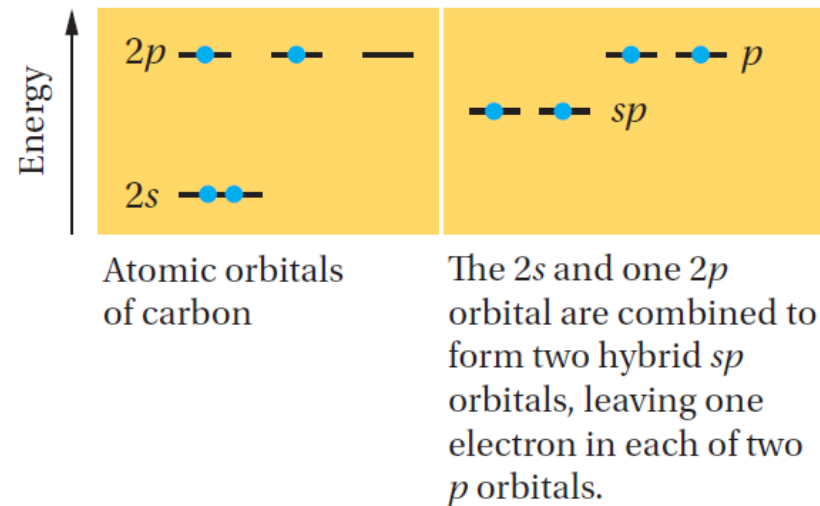
Schematic formation of a carbon–carbon double bond. Two sp^2 carbons form a sigma (σ) bond (end-on overlap of two sp^2 orbitals) and a pi (π) bond (lateral overlap of two properly aligned p orbitals).



Hybridization (Alkynes sp)

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- 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°**

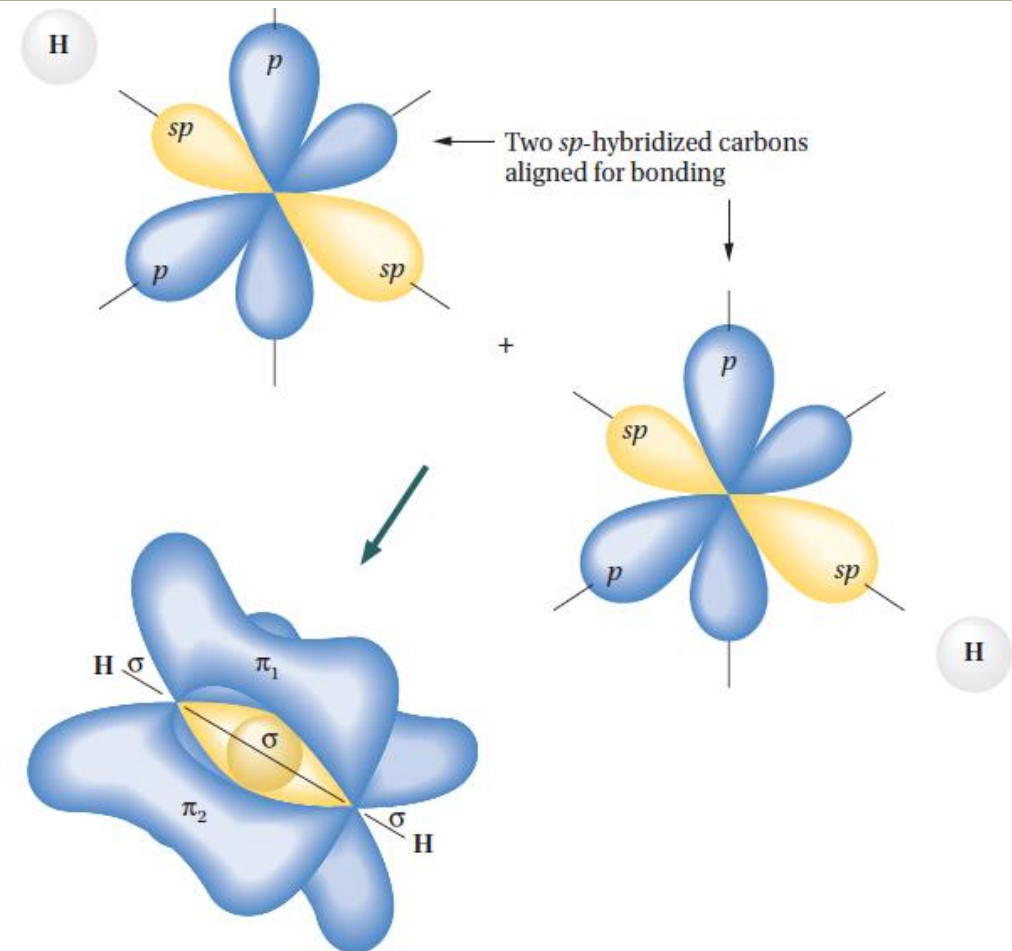
- Linear**



Hybridization (Alkynes sp)

25

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.

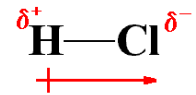


The resulting carbon-carbon triple bond, with a hydrogen atom attached to each remaining sp bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

Inductive Effect

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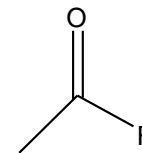
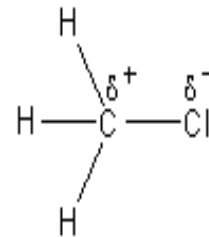
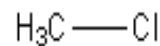
- **Inductive effect** can be defined as *the permanent displacement of electrons forming a covalent bond (sigma σ bonds) towards the more electronegative element or group.*



- The inductive effect is represented by the symbol, the arrow pointing towards the more electronegative element or group of elements.

(+ I) effect if the substituent electron-donating

(- I) effect if the substituent electron-withdrawing



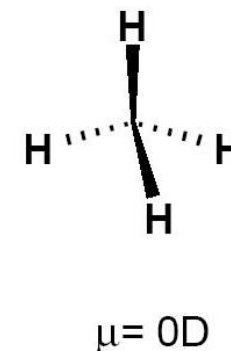
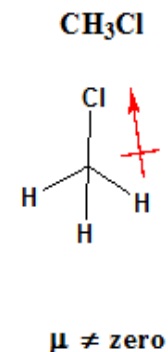
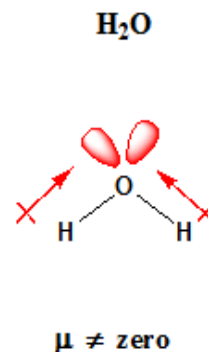
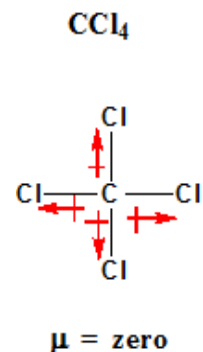
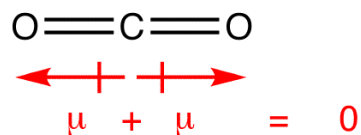
Electron-donating substituents (+I): $-\text{CH}_3$, $-\text{C}_2\text{H}_5$,

Electron-withdrawing substituents (-I): $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, COOH , COOR , NH_2 , OH , OCH_3

Bond Polarity and Dipole Moment (μ)

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- **Dipole moment** (depends on the inductive effect).
- A bond with the electrons shared equally between two atoms is called a **nonpolar bond** like in Cl-Cl and C-C bond in ethane.
- A bond with the electrons shared unequally between two different elements is called a **polar bond**.
- The **bond polarity** is measured by its dipole moment (μ).
- **Dipole moment (μ)** defined to be the amount of charge separation ($+\delta$ and $-\delta$) multiplied by the bond length.



Functional Groups

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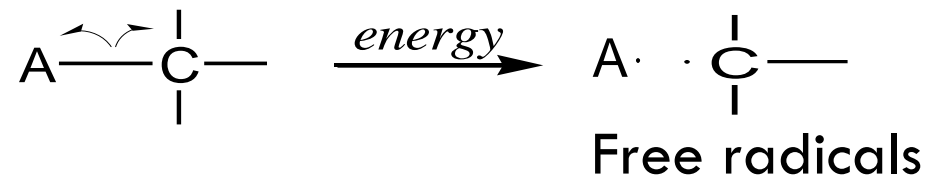
Functional Group is a reactive portion of an organic molecule, an atom, or a group of atoms that confers on the whole molecule its characteristic properties.

Class	General formula	Functional group	Specific
Alkane	RH	C – C (single bond)	H ₃ C – CH ₃
Alkene	R – CH = CH ₂	C = C (double bond)	H ₂ C = CH ₂
Alkyne	R – C ≡ CH	C ≡ C (triple bond)	HC ≡ CH
Alkyl halide	RX	-X (X = F, Cl, Br, I)	H ₃ C - Cl
Alcohol	R – OH	-OH	H ₃ C - OH
Ether	R – O – R'	- C - O - C -	H ₃ C – O – CH ₃
Aldehyde	R – $\overset{\text{O}}{\parallel}$ C – H	$\text{---} \overset{\text{O}}{\parallel}$ C – H	H – $\overset{\text{O}}{\parallel}$ C – H, H ₃ C – $\overset{\text{O}}{\parallel}$ C – H
Ketone	R – $\overset{\text{O}}{\parallel}$ C – R	$\text{---} \overset{\text{O}}{\parallel}$ C – ---	H ₃ C – $\overset{\text{O}}{\parallel}$ C – CH ₃
Carboxylic acid	R – $\overset{\text{O}}{\parallel}$ C – OH	$\text{---} \overset{\text{O}}{\parallel}$ C – OH	H – $\overset{\text{O}}{\parallel}$ C – OH, H ₃ C – $\overset{\text{O}}{\parallel}$ C – OH
Ester	R – $\overset{\text{O}}{\parallel}$ C – OR	$\text{---} \overset{\text{O}}{\parallel}$ C – OR	H – $\overset{\text{O}}{\parallel}$ C – OCH ₃ H ₃ C – $\overset{\text{O}}{\parallel}$ C – OCH ₃
Amine	R – NH ₂	$\text{---} \overset{\text{I}}{\underset{\text{I}}{\text{C}}} \text{---} \text{NH}_2$	H ₃ C – NH ₂

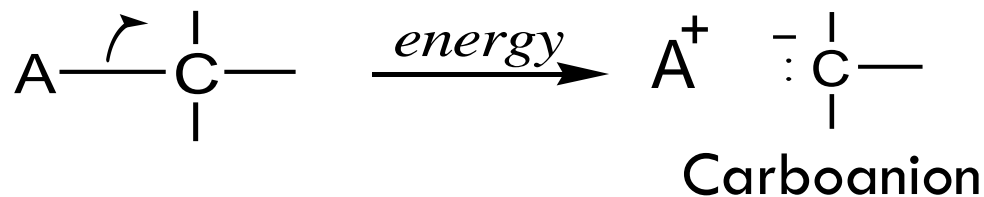
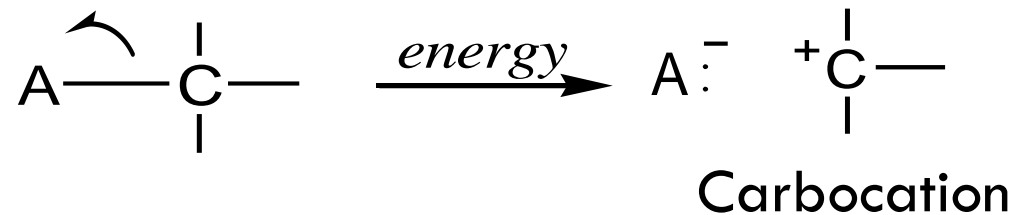
Notations for bond breaking and bond making

○ A covalent bond can be broken in either two ways,

▪ **Homolytic cleavage.**



▪ **Heterolytic cleavage.**

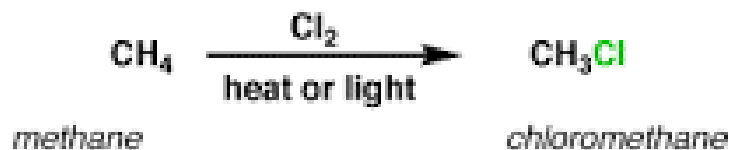


Substitution Reactions

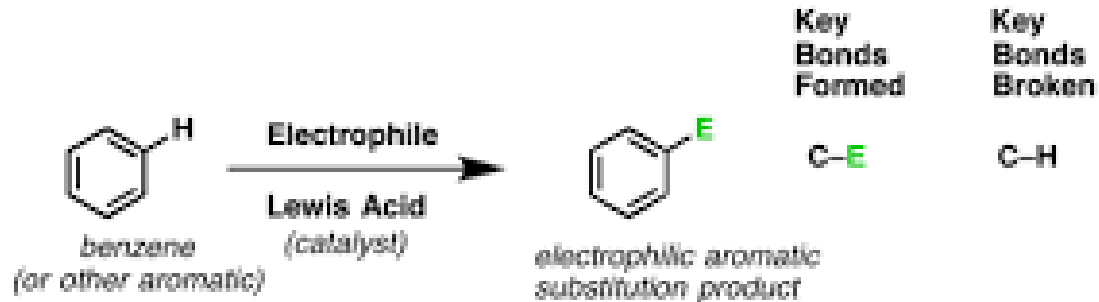
Types of Organic Reactions

Based on the nature of substituents involved

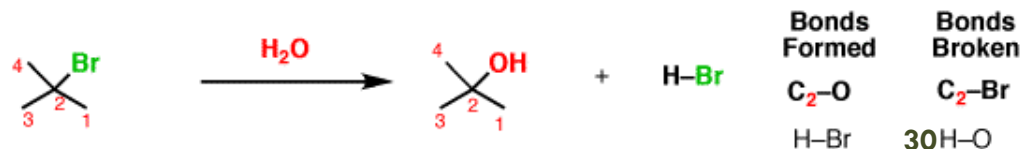
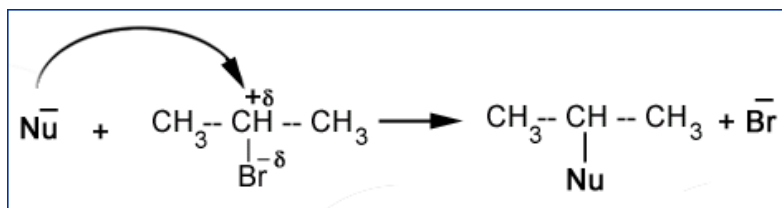
Free Radical Substitution Reactions



Electrophilic Substitution Reactions



Nucleophilic Substitution Reactions

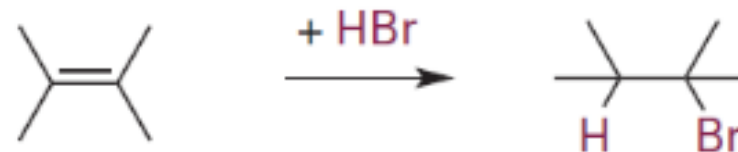




Elimination Reactions

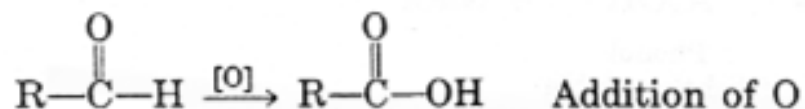
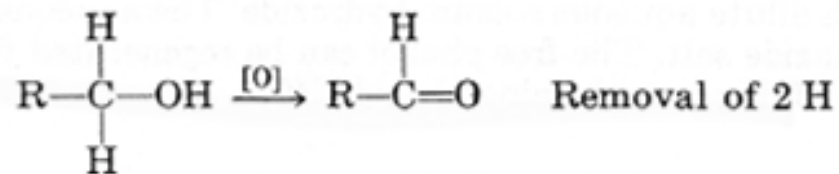


Addition Reactions



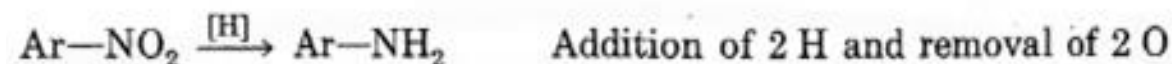
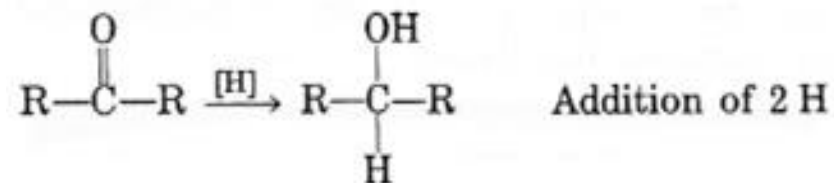
Oxidation-Reduction Reactions

- Oxidation** is the removal of H from a compound and/or the addition of O to a compound.



An oxidizing agent is the chemical reagent that does the oxidation.

- Reduction** is the addition of H to a compound and/or the removal of O from a compound.



A reducing agent is a substance that does the reduction.