

# D.N.R. College (Autonomous), Bhimavaram

(Affiliated to Adikavi Nannaya University)

Revised Choice Based Credit System (w.e.f. 2020-21)

Programme: B.Sc., Year: I, Semester: 2

Core Courses Domain Subject: **CHEMISTRY**, Theory Course– 2

Title: **Organic & General Chemistry**

Total Theory Hours: 60, 4 hours per week, Total Credits: 4

## ORGANIC CHEMISTRY

### UNIT-I

#### Recapitulation of Basics of Organic Chemistry

#### Carbon-Carbon sigma bonds (Alkanes and Cycloalkanes)

#### General methods of preparation of alkanes

Alkanes are hydrocarbons composed solely of carbon-carbon and carbon-hydrogen single bonds. They can be prepared by various methods, mainly involving synthesis from simpler compounds or through natural processes. Here are the general methods of preparation of alkanes:

1. **Direct Synthesis from Elements:**

- **Sabatier-Senderens Process:** This method involves the catalytic hydrogenation of carbon monoxide (CO) under high pressure using a metal catalyst such as nickel or ruthenium. The reaction can be represented as:  
$$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$$
$$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$$
Methane (CH<sub>4</sub>) is the simplest alkane formed in this process.

2. **Cracking of Higher Alkanes:**

- Higher alkanes (e.g., octane, C<sub>8</sub>H<sub>18</sub>) can be cracked (broken down) into smaller alkanes and alkenes under high temperature and pressure conditions. This process is commonly used in petroleum refining to produce a range of smaller alkanes suitable for various industrial applications.

3. **Wurtz Reaction:**

- This is a coupling reaction between alkyl halides (alkyl chlorides, bromides, or iodides) in the presence of metallic sodium or lithium to form higher alkanes. The general reaction is:  
$$2\text{R-X} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaX}$$
$$2\text{R-X} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaX}$$
where RRR represents an alkyl group (e.g., methyl, ethyl) and XXX represents a halogen (e.g., Cl, Br).

○

4. **WurtzFittig reaction**

- a. The Wurtz-Fittig reaction involves the coupling of an alkyl halide (typically a bromide or iodide) with an aryl halide (bromide or iodide) in the presence of a strong base like sodium or potassium metal. This reaction is commonly used to synthesize biaryls, where two aromatic rings are linked together through a carbon-carbon bond.
- b. However, for alkanes (saturated hydrocarbons), the Wurtz-Fittig reaction is not applicable in the traditional sense because alkanes do not have a leaving group like halides that could participate in such a coupling reaction. Alkanes are relatively inert under these conditions and do not readily undergo direct coupling reactions with aryl halides to form new carbon-carbon bonds.
- c. For the synthesis involving alkanes and aryl groups, alternative methods such as cross-coupling reactions (like Suzuki coupling, Heck reaction, etc.) or other methods specific to the functional groups present on the alkane and aryl substrate would be employed. These methods typically require activated or reactive forms of the alkane, such as halogenated derivatives or metalated species, to enable the formation of carbon-carbon bonds with aryl halides or aryl metal reagents

#### 5. Reduction of Alkenes:

- o Alkenes (unsaturated hydrocarbons with a carbon-carbon double bond) can be reduced to alkanes by catalytic hydrogenation (using hydrogen gas and a metal catalyst like platinum, palladium, or nickel). For example:  

$$\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3-\text{CH}_3$$

$$\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3-\text{CH}_3$$
 Ethene (ethylene) is converted to ethane.

#### 6. Hydrogenolysis of Alkyl Halides:

- o Alkyl halides (alkanes with a halogen substituent) can be reduced with hydrogen gas under pressure and heat, often in the presence of a metal catalyst, to form alkanes. For instance:  

$$\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{HBr}$$

$$\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{HBr}$$

#### 7. Decarboxylation:

- o Carboxylic acids (containing a carboxyl group, -COOH) can undergo decarboxylation under high temperature conditions to produce alkanes. The general reaction is:  

$$\text{RCOOH} \rightarrow \text{RH} + \text{CO}_2$$

$$\text{RCOOH} \rightarrow \text{RH} + \text{CO}_2$$
 where R is an alkyl group.

#### 8. Corey House synthesis of alkane

The Corey-House synthesis is a method used to synthesize alkanes, particularly for generating longer chain alkanes. It involves the coupling of two Grignard reagents (alkylmagnesium halides) followed by reduction. Here's a step-by-step outline of the process:

##### 1. Formation of Grignard Reagents:

- o Prepare two different alkylmagnesium halides (R-MgX and R'-MgX). This is typically done by reacting alkyl halides (RX) with magnesium metal in anhydrous ether or THF (tetrahydrofuran).

- 2. Coupling Reaction (Corey-House Reaction):**
  - Mix the two different Grignard reagents ( $R-MgX$  and  $R^1-MgX$ ) in the presence of a suitable catalyst, often a nickel or copper catalyst. The reaction is carried out in anhydrous ether or THF at low temperatures to avoid unwanted side reactions.
- 3. Reduction:**
  - After coupling, the resulting intermediate is typically a dialkyl-substituted alkene. This intermediate is then subjected to hydrogenation using a suitable catalyst like palladium on carbon (Pd/C) or platinum (Pt) to reduce the double bonds, yielding the desired alkane.
- 4. Isolation and Purification:**
  - The alkane product is isolated and purified through techniques such as distillation or recrystallization, depending on its physical properties.

### Key Points:

- **Selectivity:** The Corey-House synthesis is useful for selectively coupling two different alkyl groups to form longer chain alkanes.
- **Scope:** It is particularly effective for synthesizing medium to long-chain alkanes, where traditional methods might not be as efficient.
- **Applications:** This method finds applications in organic synthesis where specific alkane structures are required, especially in pharmaceuticals, materials science, and industrial chemistry.

The Corey-House synthesis is valued for its ability to construct complex carbon frameworks efficiently, making it a versatile tool in synthetic organic chemistry.

These methods provide various routes to synthesize alkanes, catering to different starting materials and conditions depending on the desired alkane and the specific industrial or laboratory application.

## Physical and Chemical properties of alkanes

Alkanes are a family of hydrocarbons characterized by single bonds between carbon atoms and hydrogen atoms. They are known for their relatively inert nature compared to other organic compounds due to the absence of functional groups like hydroxyl (-OH) or carbonyl (C=O) groups. Here are some key physical and chemical properties of alkanes:

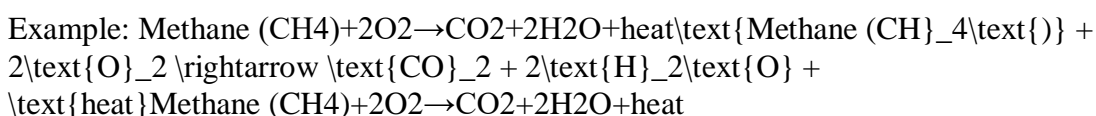
### Physical Properties:

- 1. State of Matter:** Alkanes with fewer carbon atoms (1-4) are gases at room temperature (e.g., methane, ethane), those with 5-17 carbon atoms are liquids (e.g., pentane to octadecane), and those with more than 17 carbon atoms are solids (e.g., nonadecane and beyond).

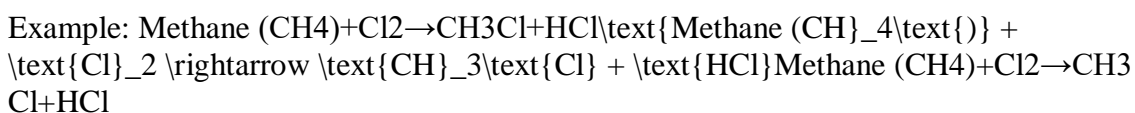
2. **Density:** Generally low density compared to water, with values decreasing as molecular weight decreases.
3. **Melting and Boiling Points:** Increase with increasing molecular weight (size of the molecule). For example, methane (CH<sub>4</sub>) has a boiling point of -161.5°C, while hexane (C<sub>6</sub>H<sub>14</sub>) boils at 68.7°C.
4. **Solubility:** Insoluble in water (hydrophobic) but soluble in non-polar solvents like benzene and chloroform.

## Chemical Properties:

1. **Combustion:** Alkanes burn readily in the presence of oxygen to produce carbon dioxide and water, releasing heat. The combustion of alkanes is a major source of energy.



2. **Halogenation:** Alkanes undergo substitution reactions with halogens (chlorine, bromine) in the presence of UV light or heat, replacing hydrogen atoms with halogen atoms.



3. **Reaction with Oxygen:** In limited oxygen supply (insufficient for complete combustion), alkanes can undergo partial oxidation to form products such as alcohols, aldehydes, or ketones.
4. **Chemical Stability:** Alkanes are relatively inert under normal conditions, making them useful as solvents and as starting materials for various industrial processes.
5. **Cracking:** Alkanes can undergo thermal cracking (heating in the absence of oxygen) to form smaller alkanes, alkenes, and hydrogen. This process is used in the petroleum industry to produce gasoline and other fuels.
6. **Isomerism:** Alkanes exhibit structural isomerism due to different ways carbon atoms can be arranged in a molecule while maintaining the same molecular formula.

Overall, alkanes are characterized by their saturated nature (all carbon-carbon bonds are single bonds), non-polarity, and relatively low reactivity compared to other organic compounds. Their properties make them valuable as fuels, lubricants, and starting materials in chemical synthesis.

## Isomerism and its effect on properties

Isomerism is a phenomenon where two or more compounds have the same molecular formula but different structural arrangements or spatial orientations of atoms. Isomers can be broadly categorized into structural isomers, stereoisomers, and geometric isomers, each of which can affect the properties of the compounds in distinct ways:

### 1. Structural Isomers:

- **Different connectivity:** Structural isomers have different bonding patterns or different arrangements of atoms. For example, butane and isobutane are structural isomers because they have different branching patterns.
- **Effect on properties:** Structural isomers often have different physical properties such as boiling points, melting points, solubility, and density. This is because these properties depend on the intermolecular forces and molecular shape, which vary with the different structural arrangements.

### 2. Stereoisomers:

- **Same connectivity, different spatial arrangement:** Stereoisomers have the same sequence of bonded atoms but differ in the spatial arrangement of these atoms. This can occur due to geometric isomerism (cis-trans isomerism) or due to chirality (handedness).
- **Effect on properties:** Stereoisomers have nearly identical physical properties because they have the same molecular formula and similar intermolecular forces. However, they can differ in biological activity, taste, smell, and optical activity (for chiral compounds), which can be crucial in fields like pharmacology and food chemistry.

### 3. Geometric Isomers:

- **Cis-trans isomerism:** This type of stereoisomerism occurs in compounds with restricted rotation around a double bond or a ring structure, resulting in different spatial arrangements around the double bond or within the ring.
- **Effect on properties:** Geometric isomers can have different physical properties such as melting points, boiling points, and solubility due to differences in spatial arrangement. For example, cis- and trans- forms of alkenes can have different stabilities and reactivities.

In summary, isomerism affects properties primarily by altering the spatial arrangement of atoms within a molecule. This alteration can lead to differences in physical properties like boiling points and solubility for structural isomers, and differences in biological activity or optical properties for stereoisomers. Understanding isomerism is crucial in fields ranging from organic chemistry to drug design, as it helps predict and manipulate the properties of compounds for specific applications.

## Free radical substitutions

Free radical substitutions, particularly halogenation, involve the replacement of a hydrogen atom in an organic compound with a halogen atom (fluorine, chlorine, bromine, or iodine) through a radical mechanism. This process is governed by considerations of relative reactivity and selectivity.

### Relative Reactivity:

#### 1. Bond Dissociation Energy (BDE):

- The reactivity of a hydrogen atom in a molecule is influenced by its bond dissociation energy. Lower BDE indicates easier cleavage of the hydrogen atom, making it more reactive towards halogen radicals.
2. **Radical Stability:**
    - Radicals are stabilized by electron-donating groups (inductive or resonance effects), which can stabilize the developing radical character. For instance, tertiary radicals are more stable than secondary, and primary radicals are the least stable.
  3. **Halogen Reactivity:**
    - Halogens have different reactivity due to their electronegativity and bond strength with carbon. Fluorine is highly reactive and tends to abstract hydrogen atoms even from saturated hydrocarbons. Chlorine is less reactive than fluorine but more reactive than bromine and iodine.

## Selectivity:

1. **Positional Selectivity:**
  - This refers to the preference of a halogen atom to substitute at a particular carbon position in the substrate molecule. Factors influencing positional selectivity include:
    - **Stability of Intermediate Radicals:** More stable radicals are formed preferentially.
    - **Steric Effects:** Hindered positions may be less accessible to the halogen radical.
    - **Electronic Effects:** Resonance or inductive effects can influence radical stability.
2. **Regioselectivity:**
  - Halogenation can occur at different positions if the substrate has multiple reactive sites. The regioselectivity depends on the factors mentioned above, primarily the stability of the resulting radical intermediate.

## Example: Chlorination of Methane

- Methane (CH<sub>4</sub>) undergoes chlorination:  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$
- The process is initiated by radical chain initiation, followed by propagation steps where radicals react to form new radicals until termination by radical combination or disproportionation.
- Relative reactivity dictates that chlorine radicals abstract hydrogen atoms from methane. Once initiated, the propagation steps continue to form various chloromethanes depending on the number of hydrogen atoms replaced.

In summary, halogenation via free radical substitution is governed by both the relative reactivity of hydrogen atoms in the substrate and the selectivity of where halogen atoms preferentially substitute based on radical stability and electronic factors. These concepts are fundamental in understanding and predicting the outcomes of halogenation reactions in organic chemistry

## Conformational analysis of alkanes

Conformational analysis of alkanes involves studying different spatial arrangements (conformations) of the carbon-carbon bonds due to rotation about these bonds. Let's explore the conformations, relative stability, and energy diagrams of ethane, propane, and butane.

### Ethane (C<sub>2</sub>H<sub>6</sub>):

Ethane has a simple structure with two carbon atoms connected by a single bond.

#### 1. Conformations of Ethane:

- **Eclipsed Conformation:** Both methyl groups (CH<sub>3</sub>) on each carbon are in direct alignment with each other. This is the highest energy conformation due to steric hindrance between the hydrogens.
- **Staggered Conformation:** The methyl groups are as far apart from each other as possible, minimizing steric hindrance.
  - **Anti (or trans) Conformation:** Methyl groups are 180 degrees apart.
  - **Gauche Conformation:** Methyl groups are 60 degrees apart.

#### 2. Relative Stability:

- The staggered conformations (anti and gauche) are lower in energy compared to the eclipsed conformation due to less steric hindrance.

#### 3. Energy Diagram:

- The energy diagram of ethane shows two minima (at anti and gauche conformations) and a maximum (at eclipsed conformation).

### Propane (C<sub>3</sub>H<sub>8</sub>):

Propane has a longer carbon chain compared to ethane, introducing more complexity in its conformational analysis.

#### 1. Conformations of Propane:

- Similar to ethane, propane exhibits eclipsed and staggered conformations.
- The three carbon atoms allow for more possible conformations:
  - **Eclipsed Conformations:** Three types due to different alignments of methyl groups.
  - **Staggered Conformations:** Various types based on the relative positions of methyl groups.

#### 2. Relative Stability:

- Staggered conformations (anti and gauche) are generally lower in energy compared to eclipsed conformations.

#### 3. Energy Diagram:

- The energy diagram of propane will have multiple staggered conformations at lower energies and eclipsed conformations at higher energies.

### Butane (C<sub>4</sub>H<sub>10</sub>):

Butane is more complex due to its four-carbon chain, offering a wider variety of conformations.

1. **Conformations of Butane:**

- Butane can adopt several staggered and eclipsed conformations.
- Staggered conformations include various anti and gauche conformations.
- Eclipsed conformations are higher in energy due to steric hindrance.

2. **Relative Stability:**

- Similar to propane, staggered conformations are more stable than eclipsed conformations.

3. **Energy Diagram:**

- The energy diagram of butane is more complex, with multiple staggered conformations at lower energies and several eclipsed conformations at higher energies.

### General Trends:

- **Steric Hindrance:** Eclipsed conformations are higher in energy due to steric hindrance between the larger groups (methyl or ethyl groups).
- **Conformational Energy:** Staggered conformations (anti and gauche) are typically lower in energy compared to eclipsed conformations.
- **Energy Diagrams:** Energy diagrams show the relative energies of different conformations, with staggered conformations at lower energy levels and eclipsed conformations at higher energy levels.

Conformational analysis of alkanes like ethane, propane, and butane is essential for understanding their physical properties, reactivity, and behavior in various chemical processes.

## Cycloalkanes and relative stability

Cycloalkanes are a class of organic compounds where carbon atoms form a ring structure, similar to alkanes but with a cyclic rather than a linear arrangement. The general molecular formula for cycloalkanes is  $C_nH_{2n}$ , where  $n$  is the number of carbon atoms in the ring. Here are a few examples:

1. **Cyclopropane:**  $C_3H_6$
2. **Cyclobutane:**  $C_4H_8$
3. **Cyclopentane:**  $C_5H_{10}$
4. **Cyclohexane:**  $C_6H_{12}$
5. **Cycloheptane:**  $C_7H_{14}$
6. **Cyclooctane:**  $C_8H_{16}$

### Relative Stability of Cycloalkanes:



The stability of cycloalkanes generally increases with the number of carbon atoms in the ring. This stability is primarily due to the ring strain caused by the bond angles and torsional strain within the cyclic structure.

1. **Cyclopropane:** Cyclopropane is the least stable due to its high ring strain. The bond angles in cyclopropane are approximately  $60^\circ$ , which are significantly smaller than the ideal tetrahedral angle of  $109.5^\circ$ . This leads to considerable angle strain and torsional strain, making cyclopropane highly reactive.
2. **Cyclobutane:** Cyclobutane is slightly more stable than cyclopropane but still experiences some angle strain. The bond angles in cyclobutane are around  $90^\circ$ , which is closer to the ideal tetrahedral angle than in cyclopropane.
3. **Cyclopentane:** Cyclopentane has even lower ring strain compared to cyclobutane. The bond angles in cyclopentane are closer to  $108^\circ$ , which reduces both angle strain and torsional strain.
4. **Cyclohexane:** Cyclohexane is the most stable of the simple cycloalkanes. It adopts a chair conformation, which allows all carbon-carbon bond angles to be close to  $109.5^\circ$ , minimizing ring strain. The chair conformation of cyclohexane is highly stable and essentially free from angle strain and torsional strain when compared to smaller cycloalkanes.
5. **Cycloalkanes with more than six carbons:** As the size of the ring increases beyond cyclohexane (e.g., cycloheptane, cyclooctane, etc.), the ring strain continues to decrease, leading to increasing stability.

In summary, the stability of cycloalkanes increases with ring size due to the reduction in ring strain (angle strain and torsional strain). Cyclohexane, with its chair conformation, represents the point of highest stability among the simple cycloalkanes

## Baeyer strain theory

Baeyer strain theory, proposed by the German chemist Adolf von Baeyer in 1885, is a fundamental concept in organic chemistry related to the strain or instability in cyclic molecules, particularly cycloalkanes.

### Baeyer Strain Theory:

Baeyer proposed that the strain in cycloalkanes arises from two main sources:

1. **Angle Strain:** This is the strain due to bond angles differing from the ideal tetrahedral angle ( $109.5^\circ$ ). In cycloalkanes, particularly smaller rings like cyclopropane and cyclobutane, the bond angles deviate significantly from  $109.5^\circ$ , leading to increased strain.
2. **Torsional Strain:** This refers to the eclipsing interactions between adjacent atoms or groups in the ring. In cyclic compounds, these interactions can lead to increased energy due to unfavorable overlap of electron clouds.

## Cyclohexane Conformations and Energy Diagram:

Cyclohexane is a key example to understand how cycloalkanes alleviate strain through conformational flexibility. It can adopt various conformations, the most stable of which are the chair and boat conformations. Here's a brief overview of these conformations and their energy relationships:

### 1. Chair Conformation:

- The chair conformation of cyclohexane is the most stable and predominant form.
- In the chair conformation, all carbon-carbon bonds are staggered (no torsional strain) and nearly all bond angles are close to  $109.5^\circ$  (minimizing angle strain).
- There are two unique positions for carbon atoms: axial and equatorial.
- Axial positions are vertically oriented above and below the plane of the ring, while equatorial positions are roughly along the plane of the ring.

### 2. Boat Conformation:

- The boat conformation is another possible form of cyclohexane where the molecule appears boat-shaped.
- It is less stable than the chair conformation due to increased torsional strain and some angle strain.

### 3. Energy Diagram:

- An energy diagram for cyclohexane typically shows the relative energies of different conformations.
- The chair conformation is at the lowest energy (most stable), while the boat conformation is higher in energy.
- The diagram illustrates how cyclohexane can undergo conformational changes to minimize strain and stabilize the molecule.

## Conclusion:

Baeyer strain theory helps explain why certain cyclic compounds adopt specific conformations to minimize strain energy. In the case of cyclohexane, the chair conformation is favored due to its low energy and minimal strain, showcasing how molecular shape and strain are intricately linked in organic chemistry

## Conformations of monosubstituted cyclohexane

Monosubstituted cyclohexanes can adopt different conformations due to the ability of the cyclohexane ring to undergo chair, boat, and twist-boat conformations. The most stable conformation for a monosubstituted cyclohexane is typically the one where the substituent (or group) occupies an equatorial position rather than an axial position. This preference is due to the lower steric hindrance experienced by the substituent in the equatorial position.

Here's a brief overview of how this preference influences the conformation:

1. **Chair Conformation:** Cyclohexane can exist in a chair conformation where all carbon atoms lie in one of two planes, with alternating axial and equatorial positions around the ring. In a monosubstituted cyclohexane, the substituent can be placed in either an axial or equatorial position.
  - **Equatorial Position:** This is the most stable conformation for the substituent due to less steric hindrance with neighboring groups.
  - **Axial Position:** Less stable due to greater steric hindrance caused by interactions with adjacent groups.
2. **Boat Conformation:** This is another possible conformation where the ring takes on a boat-like shape. In a monosubstituted cyclohexane, the substituent can occupy either an axial or equatorial position similar to the chair conformation.
  - **Equatorial Position:** Preferred for the same reasons as in the chair conformation.
  - **Axial Position:** Less preferred due to steric interactions.
3. **Twist-Boat Conformation:** A variation of the boat conformation where the ring is twisted slightly, resulting in different axial and equatorial positions compared to the boat conformation.
  - **Equatorial Position:** Still preferred over axial positions.
  - **Axial Position:** Less stable due to steric interactions.

In summary, the stability of a monosubstituted cyclohexane conformation depends largely on minimizing steric hindrance involving the substituent and other groups. Equatorial positions are preferred because they experience less steric hindrance compared to axial positions, leading to a more stable overall conformation.

## UNIT-II

### Carbon-Carbon pi Bonds (Alkenes and Alkynes)

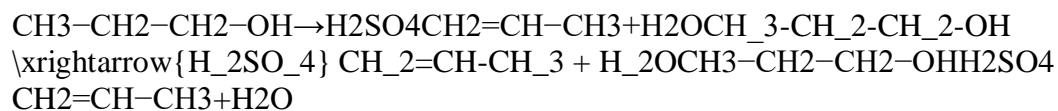
### General methods of preparation, physical and chemical properties of alkenes

Alkenes are a class of hydrocarbons characterized by carbon-carbon double bonds (C=C). Here's a comprehensive overview covering their preparation methods and physical/chemical properties:

#### Preparation Methods of Alkenes:

1. **Dehydrohalogenation of Alkyl Halides (Elimination Reactions):**
  - Alkyl halides (haloalkanes) undergo elimination reactions (typically with strong bases like KOH) to form alkenes. Example:  

$$\text{R-CH}_2\text{-CH}_2\text{-Cl} \xrightarrow{\text{KOH}} \text{R-CH=CH}_2 + \text{HCl}$$
2. **Dehydration of Alcohols:**
  - Alcohols can be dehydrated in the presence of an acid catalyst (e.g., concentrated sulfuric acid, H<sub>2</sub>SO<sub>4</sub>) to yield alkenes. Example:



### 3. Decarboxylation of Carboxylic Acids:

- Carboxylic acids with  $\beta$ -carbons can undergo decarboxylation to form alkenes.  
Example:  $\text{CH}_3\text{-CH}_2\text{-COOH} \xrightarrow{\text{heat}} \text{CH}_2=\text{CH-CH}_3 + \text{CO}_2$

### 4. Cracking of Petroleum Fractions:

- High temperature cracking of larger hydrocarbons (from crude oil) can produce smaller alkenes among other products.

### 5. Wittig Reaction:

- In organic synthesis, the Wittig reaction involves the reaction of a phosphonium ylide with an aldehyde or ketone to produce an alkene.

## Physical Properties of Alkenes:

- State:** Generally, alkenes are colorless gases or liquids at room temperature.
- Boiling Points:** Increase with molecular mass due to increased London dispersion forces; generally lower boiling points compared to alkanes of similar molecular weight.
- Density:** Less dense than water.
- Solubility:** Insoluble in water (due to non-polar nature) but soluble in non-polar organic solvents (like dissolves like).

## Chemical Properties of Alkenes:

### 1. Addition Reactions:

- Alkenes readily undergo addition reactions with electrophiles (like HBr, HCl) to form alkyl halides.
- Example:  $\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br}$

### 2. Oxidation Reactions:

- Alkenes can be oxidized to form diols (with alkaline  $\text{KMnO}_4$  or  $\text{OsO}_4$ ) or epoxides.
- Example:  $\text{CH}_2=\text{CH}_2 + \text{OsO}_4 \rightarrow \text{HO-CH}_2\text{-CH}_2\text{-OH}$

### 3. Polymerization:

- Under appropriate conditions (like high pressure and suitable catalysts), alkenes can undergo polymerization to form polymers (e.g., polyethylene from ethylene).

### 4. Isomerization:

- Alkenes can undergo isomerization (shift of the double bond within the molecule) under the influence of heat or catalysts.

### 5. Halogenation:

- Alkenes can react with halogens (e.g.,  $\text{Br}_2$  or  $\text{Cl}_2$ ) to form vicinal dihalides.
- Example:  $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \rightarrow \text{Br-CH}_2\text{-CH}_2\text{-Br}$

Understanding these methods of preparation and properties is crucial in organic chemistry for the synthesis and manipulation of alkenes in various industrial and laboratory applications

## General methods of preparation, physical and chemical properties of alkynes

Alkynes are a class of hydrocarbons characterized by the presence of a triple bond between carbon atoms. Their general formula is  $C_nH_{2n-2}$ . Here's an overview of their preparation methods, physical properties, and chemical properties:

### Preparation Methods:

- 1. From Calcium Carbide (Acetylene Method):**
  - Calcium carbide ( $CaC_2$ ) reacts with water to produce acetylene gas ( $C_2H_2$ ), which is the simplest alkyne.
  - **Reaction:**  $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
  - Acetylene can be further reacted to form higher alkynes.
- 2. From Vicinal Dihalides (Elimination Method):**
  - Vicinal dihalides (alkenes with two halogen atoms on adjacent carbons) can undergo dehydrohalogenation (elimination of  $HX$ ) to form alkynes.
  - **Reaction:**  $RCHBrCHBrR' + 2KOH \rightarrow RC\equiv CR' + 2KBr + 2H_2O$
- 3. From Terminal Alkynes (Alkylation Method):**
  - Terminal alkynes can be alkylated to form higher alkynes using strong bases like sodium amide ( $NaNH_2$ ).
  - **Reaction:**  $RC\equiv CH + R'Br + NaNH_2 \rightarrow RC\equiv C-R' + NaBr + NH_3$

### Physical Properties:

- **Physical State:** Generally, lower alkynes (up to  $C_4H_6$ ) are gases at room temperature, while higher alkynes ( $C_5H_8$  and above) are liquids or solids.
- **Odor:** Some alkynes have distinct odors (e.g., acetylene has a garlic-like odor).
- **Solubility:** They are relatively insoluble in water but soluble in organic solvents like benzene and ether.

### Chemical Properties:

- 1. Acidic Character:**
  - Terminal alkynes (acetylenes) are acidic due to the presence of a hydrogen atom bonded to a  $sp$  carbon.
  - They react with strong bases to form acetylide ions ( $RC\equiv C^-$ ).
- 2. Addition Reactions:**
  - Alkynes undergo addition reactions similar to alkenes but can also undergo further addition to form polyenes.
  - **Hydrogenation:**  $RC\equiv CR' + H_2$  (catalyst)  $\rightarrow RCH=CHR'$
  - **Hydration:**  $RC\equiv CR' + H_2O$  ( $HgSO_4, H_2SO_4$ )  $\rightarrow RCOH-CR'$

3. **Halogenation:**
  - Alkynes react with halogens (Cl<sub>2</sub>, Br<sub>2</sub>) to form tetrahalo compounds.
  - **Reaction:**  $\text{RC}\equiv\text{CR}' + \text{Br}_2 \rightarrow \text{RBrC}=\text{CR}'\text{Br}$
4. **Oxidation:**
  - Terminal alkynes can be oxidized to produce carboxylic acids.
  - **Reaction:**  $\text{RC}\equiv\text{CH} + 2[\text{O}] \rightarrow \text{RCOOH}$
5. **Polymerization:**
  - Alkynes can polymerize under certain conditions to form polymers known as polyacetylenes.

### Chemical Reactivity:

- Alkynes are generally more reactive than alkenes due to the presence of the triple bond, which provides a larger area of electron density for reactions.

In summary, alkynes exhibit distinctive properties and reactivity patterns due to the presence of the triple bond. Their preparation methods involve calcium carbide, elimination reactions of vicinal dihalides, and alkylation of terminal alkynes. Their chemical properties include acidic character, addition reactions, halogenation, oxidation, and polymerization.

### Mechanism of E1 and E2 reactions

E1 and E2 reactions are two fundamental types of elimination reactions in organic chemistry, involving the removal of a leaving group (usually a halide ion, -X) from a substrate to form an alkene. Here's a breakdown of each mechanism:

#### E1 Mechanism (Unimolecular Elimination)

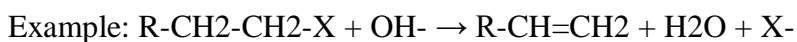
1. **Substrate Formation:** The reaction typically starts with a substrate that is a tertiary or secondary alkyl halide. The leaving group (-X) departs from the substrate, leaving behind a carbocation intermediate.



2. **Carbocation Formation:** After the leaving group departs, a carbocation (C<sup>+</sup>) intermediate is formed. This carbocation is stabilized by adjacent alkyl groups (inductive effect and hyperconjugation).
3. **Elimination:** A base (often a weak base like water or an alcohol) then abstracts a proton from the β-carbon (carbon adjacent to the carbocation), leading to the formation of the double bond.
4. **Product Formation:** The result is the formation of an alkene and a protonated base.

#### E2 Mechanism (Bimolecular Elimination)

1. **Simultaneous Deprotonation and Leaving Group Departure:** The base (usually a strong base like hydroxide ion, OH<sup>-</sup>) abstracts a proton β to the leaving group as the leaving group leaves. This concerted process occurs in a single step.



2. **Transition State:** The transition state involves partial formation of the double bond and simultaneous departure of the leaving group and proton abstraction.
3. **Product Formation:** This results directly in the formation of an alkene and a deprotonated base.

### Comparison:

- **Rate-Determining Step:**
  - **E1:** Formation of the carbocation is the slow, rate-determining step.
  - **E2:** Simultaneous removal of the leaving group and abstraction of a proton occurs in the rate-determining step.
- **Substrate Requirement:**
  - **E1:** Typically requires a tertiary or secondary alkyl halide due to the stability of the carbocation intermediate.
  - **E2:** Works well with primary, secondary, and some tertiary alkyl halides.
- **Base Strength:**
  - **E1:** Can proceed with weak bases because the reaction is driven by the stability of the carbocation intermediate.
  - **E2:** Requires a relatively strong base to abstract a proton effectively.
- **Regioselectivity:**
  - **E1:** Can lead to both Markovnikov and anti-Markovnikov products depending on the stability of the carbocation intermediate.
  - **E2:** Usually follows Zaitsev's rule (more substituted alkene is major product), although Hofmann elimination can occur under certain conditions.

In summary, E1 and E2 reactions are distinguished by their mechanisms: E1 involves the formation of a carbocation intermediate, while E2 proceeds through a single, concerted step involving both base abstraction and leaving group departure. The choice between E1 and E2 mechanisms depends on factors such as substrate structure, base strength, and reaction conditions

### Saytzeff and Hoffmann eliminations

Sure, let's talk about the Saytzeff and Hofmann eliminations, which are concepts in organic chemistry related to elimination reactions.

**Saytzeff Elimination (Zaitsev's Rule):** Saytzeff elimination, often referred to as Zaitsev's rule, states that in an elimination reaction (such as in the dehydrohalogenation of alkyl halides to form alkenes), the more substituted alkene (having more alkyl substituents on the double-bonded carbons) is typically the major product. This rule is based on the principle that the transition state

leading to the more substituted alkene is lower in energy, making it more favorable and hence more likely to be formed.

For example, in the elimination of 2-bromobutane, you can form two possible alkenes:

- 1-Butene (less substituted)
- 2-Butene (more substituted)

According to Saytzeff's rule, 2-Butene (more substituted) would be the major product.

**Hofmann Elimination:** Hofmann elimination, on the other hand, refers to a type of elimination reaction where the least substituted alkene is the major product. This occurs under certain specific conditions, typically involving a bulky base like potassium tert-butoxide (KOtBu). The bulky base prefers to abstract a proton from the carbon that will lead to the formation of the least substituted alkene, due to steric hindrance.

For instance, in the elimination of quaternary ammonium salts (such as tetraalkylammonium salts), the least substituted alkene (Hofmann product) is often favored due to steric reasons caused by the large size of the base.

To summarize:

- **Saytzeff Elimination** (Zaitsev's rule): Forms the more substituted alkene as the major product.
- **Hofmann Elimination:** Forms the least substituted alkene as the major product, usually favored by bulky bases.

These principles are important in predicting the major products of elimination reactions in organic chemistry

## **Electrophilic Additions, mechanism (Markownikoff/Antimarkownikoff addition)**

Electrophilic addition reactions are common in organic chemistry, especially with alkenes and alkynes. These reactions involve the addition of an electrophilic species (electron-deficient reagent) to a double or triple bond. The regiochemistry of the addition (whether the electrophile adds to the more substituted or less substituted carbon) can be explained using Markovnikov's rule or its opposite, Antimarkovnikov's rule.

**Markovnikov's Rule:** Markovnikov's rule states that in the addition of a protic acid HX (where X is a halogen) to an alkene, the hydrogen atom of HX adds to the carbon of the double bond that already has more hydrogen atoms, while the halogen atom adds to the other carbon.

**Antimarkovnikov's Rule:** Antimarkovnikov's rule states that in certain reactions, the electrophile adds to the carbon of the double bond that already has fewer hydrogen atoms.



Let's illustrate both rules with suitable examples:

### **Markovnikov Addition:**

#### **Example 1: Addition of HBr to Propene**

**1. Mechanism:**

- Propene ( $\text{CH}_2=\text{CHCH}_3$ ) reacts with hydrogen bromide (HBr).
- The pi electrons of the double bond attack the proton ( $\text{H}^+$ ) from HBr, forming a carbocation intermediate ( $\text{CH}_2\text{CHCH}_3^+$ ).
- The bromide ion ( $\text{Br}^-$ ) then attacks the carbocation, leading to the formation of 2-bromopropane ( $\text{CH}_2\text{BrCH}_2\text{CH}_3$ ).

**2. Product:**

- The product formed is 2-bromopropane ( $\text{CH}_2\text{BrCH}_2\text{CH}_3$ ).

**3. Explanation (Markovnikov's Rule):**

- In this reaction, the hydrogen atom from HBr adds to the carbon of the double bond that already had more hydrogen atoms (the more substituted carbon), while the bromine adds to the less substituted carbon.

### **Antimarkovnikov Addition:**

#### **Example 2: Hydroboration-Oxidation of Alkenes**

**1. Mechanism:**

- Alkenes react with borane ( $\text{BH}_3$ ) followed by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and hydroxide ions ( $\text{OH}^-$ ).
- Initially, the alkene coordinates with  $\text{BH}_3$  to form a cyclic transition state where boron bonds to the less substituted carbon of the alkene (the carbon with more hydrogens).
- After oxidation with hydrogen peroxide and hydroxide ions, the boron is replaced by a hydroxyl group (OH), yielding an alcohol.

**2. Product:**

- An example reaction is 1-butanol formed from the hydroboration-oxidation of 1-butene.

**3. Explanation (Antimarkovnikov's Rule):**

- In hydroboration-oxidation, the boron atom initially adds to the less substituted carbon (the carbon with more hydrogens), which follows Antimarkovnikov's rule. This results in the alcohol product where the hydroxyl group is attached to the less substituted carbon.

These examples illustrate the application of both Markovnikov's and Antimarkovnikov's rules in electrophilic addition reactions. These rules are crucial in predicting the regiochemistry of addition reactions and understanding how the electronic and steric factors influence the outcome of these reactions.

## syn and anti-addition; addition of H<sub>2</sub>, X<sub>2</sub>, HX

In organic chemistry, "syn" and "anti" additions refer to the orientation of the substituents or atoms relative to each other in a chemical reaction involving an addition to a double bond.

### 1. Syn Addition:

- In syn addition, the substituents or atoms add to the same side (or face) of the double bond. This means they end up on adjacent carbon atoms after the addition.
- For example, in the addition of hydrogen (H<sub>2</sub>) to an alkene, if both hydrogen atoms end up on the same side of the double bond, it is termed syn addition.

### 2. Anti Addition:

- In anti addition, the substituents or atoms add to opposite sides (or faces) of the double bond. This results in them ending up on opposite carbon atoms after the addition.
- For example, in the addition of hydrogen (H<sub>2</sub>) to an alkene, if the hydrogen atoms end up on opposite sides of the double bond, it is termed anti addition.

Let's apply these concepts to specific addition reactions:

- **Hydrogenation (H<sub>2</sub> addition):**
  - **Syn Addition:** Both hydrogen atoms add to the same side of the double bond, resulting in a cis-alkane product.
  - **Anti Addition:** Hydrogen atoms add to opposite sides of the double bond, resulting in a trans-alkane product.
- **Halogenation (X<sub>2</sub> addition, where X = halogen):**
  - **Syn Addition:** Both halogen atoms add to the same side of the double bond.
  - **Anti Addition:** Halogen atoms add to opposite sides of the double bond.
- **Hydrohalogenation (HX addition):**
  - **Syn Addition:** The hydrogen and the halogen (X) add to the same side of the double bond.
  - **Anti Addition:** The hydrogen and the halogen (X) add to opposite sides of the double bond.

These addition modes (syn and anti) are important in determining the stereochemistry of the products formed in organic reactions and can have significant implications for the properties and reactivity of the resulting compounds.

## oxymercuration-demercuration, hydroboration-oxidation, ozonolysis, hydroxylation

It seems like you've listed several different chemical reactions or reaction sequences commonly studied in organic chemistry. Let's briefly describe each one:

### 1. Oxymercuration-demercuration:

- This reaction involves the addition of a mercuric acetate ( $\text{Hg}(\text{OAc})_2$ ) and water to an alkene to form an alcohol. The intermediate formed is then reduced with a reducing agent such as sodium borohydride ( $\text{NaBH}_4$ ) to yield the alcohol product.
2. **Hydroboration-oxidation:**
    - In this reaction sequence, an alkene reacts with borane ( $\text{BH}_3$ ) in the presence of a basic hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution to form an organoboron intermediate. This intermediate is then oxidized by hydrolysis (usually with alkaline hydrogen peroxide) to yield an alcohol.
  3. **Ozonolysis:**
    - Ozonolysis involves the cleavage of carbon-carbon double bonds or triple bonds by ozone ( $\text{O}_3$ ). This reaction produces carbonyl compounds (aldehydes, ketones, or carboxylic acids) depending on the nature of the starting material and work-up conditions.
  4. **Hydroxylation:**
    - Hydroxylation refers to the introduction of a hydroxyl group ( $-\text{OH}$ ) into a molecule. This can occur in various ways depending on the reagents used and the specific reaction conditions. One common example is the hydroxylation of alkenes using potassium permanganate ( $\text{KMnO}_4$ ) or osmium tetroxide ( $\text{OsO}_4$ ) to form diols.

These reactions are fundamental in organic chemistry for synthesizing various functional groups and understanding reaction mechanisms. Each plays a significant role in the synthesis and modification of organic molecules

## Diels Alder reaction, 1,2- and 1,4-addition reactions in conjugated dienes

The Diels-Alder reaction and 1,2- vs 1,4-addition reactions are fundamental concepts in organic chemistry, particularly in the context of conjugated dienes.

### Diels-Alder Reaction:

**Definition:** The Diels-Alder reaction is a concerted [4+2] cycloaddition reaction between a conjugated diene (typically a 1,3-diene) and a dienophile (an alkene or alkyne). It forms a six-membered ring structure known as a cyclohexene ring.

### Key Features:

- **Conjugated Dienes:** These are hydrocarbons containing two double bonds separated by one single bond (e.g., 1,3-butadiene).
- **Dienophiles:** These are typically alkenes or alkynes that react with the diene to form a new ring.

**Mechanism:** The reaction proceeds through a single transition state where all bonds form simultaneously. It is highly stereospecific and generally favors the endo product, where the substituents of the dienophile are positioned on the same face of the newly formed ring.

**Applications:** Diels-Alder reactions are widely used in organic synthesis to form complex ring systems in a predictable and efficient manner.

## 1,2- vs 1,4-Addition Reactions in Conjugated Dienes:

### 1,2-Addition (or Markovnikov Addition):

- **Definition:** In conjugated dienes, 1,2-addition involves the addition of a reagent (such as HX or H<sub>2</sub>O) across the C1 and C2 carbons of the diene.
- **Outcome:** This results in the formation of a product where the addition occurs directly adjacent to one of the double bonds.
- **Regioselectivity:** The addition typically occurs at the carbon that stabilizes the resulting carbocation more effectively, following Markovnikov's rule.

### 1,4-Addition (or Conjugate Addition):

- **Definition:** In conjugated dienes, 1,4-addition involves the addition of a reagent across the C1 and C4 carbons of the diene, forming a conjugate addition product.
- **Outcome:** This results in the addition of a reagent to the carbon atoms that are separated by one double bond in the conjugated system.
- **Regioselectivity:** It occurs due to the stabilization of the resulting intermediate via conjugation, which is often favored over direct 1,2-addition under certain conditions.

### Examples:

- **1,2-Addition:** Reaction with HBr to form a bromo-substituted product.
- **1,4-Addition:** Reaction with electrophiles like H<sup>+</sup>, forming an enolate intermediate that subsequently reacts to form a 1,4-addition product.

**Importance:** Understanding the regioselectivity of 1,2- vs 1,4-addition reactions is crucial for predicting the outcome of reactions involving conjugated dienes, especially in the context of organic synthesis and functional group transformations.

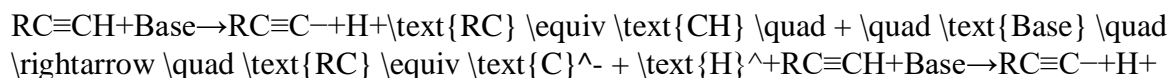
In summary, the Diels-Alder reaction is a powerful tool for forming cyclic structures from conjugated dienes and dienophiles, whereas 1,2- and 1,4-addition reactions involve the addition of reagents across different positions of the conjugated system, influencing the regiochemistry of the final products

**Reactions of alkynes; acidity, electrophilic and nucleophilic additions, hydration to form carbonyl compounds, Alkylation of terminal alkynes.**

Certainly! Alkynes, which are hydrocarbons with a triple bond between carbon atoms, exhibit several characteristic reactions due to the presence of this triple bond. Here's a breakdown of the reactions you mentioned:

## 1. Acidity of Alkynes

Alkynes are weakly acidic due to the presence of a sp-hybridized carbon atom at the end of the triple bond. This hydrogen can be removed by a strong base to form an acetylide ion:

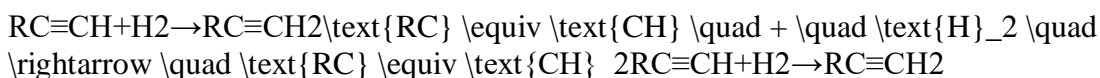


The acetylide ion ( $\text{RC}\equiv\text{C}^-$ ) is stabilized by resonance and can undergo various nucleophilic reactions.

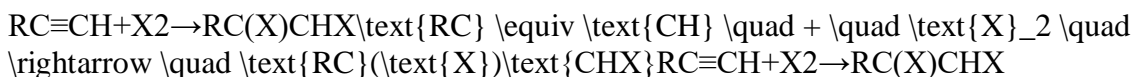
## 2. Electrophilic Addition Reactions

Alkynes readily undergo electrophilic addition reactions across the triple bond to form various organic compounds:

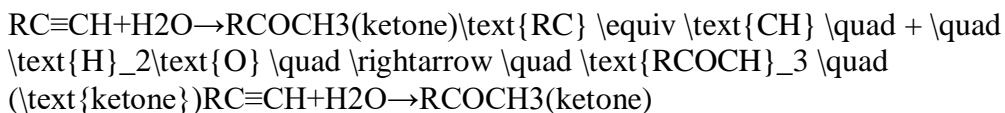
- **Hydrogenation:** Alkynes can be hydrogenated in the presence of a metal catalyst (like platinum or palladium) to form alkanes.



- **Halogenation:** Alkynes react with halogens (e.g.,  $\text{Cl}_2$ ,  $\text{Br}_2$ ) to form dihaloalkanes.



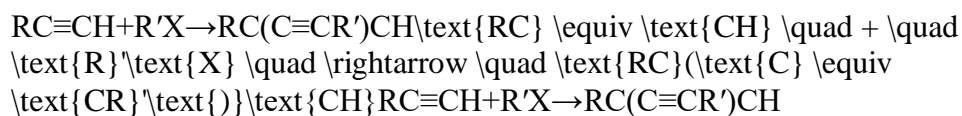
- **Hydration:** Alkynes react with water in the presence of a strong acid catalyst (such as  $\text{HgSO}_4$ ) to form carbonyl compounds (ketones or aldehydes, depending on the structure of the alkyne).



## 3. Nucleophilic Addition Reactions

Alkynes can undergo nucleophilic addition reactions with various nucleophiles, especially the acetylide ion formed in basic conditions:

- **Alkylation:** Terminal alkynes (alkynes with a hydrogen atom on one of the carbons adjacent to the triple bond) can be alkylated using alkyl halides in the presence of a strong base to form a new carbon-carbon bond.



These reactions demonstrate the versatility of alkynes in organic synthesis, allowing for the formation of a wide range of organic compounds through both electrophilic and nucleophilic addition pathways.

## UNIT-III

### Benzene and its reactivity

#### Concept of Aromaticity

Aromaticity is a fundamental concept in organic chemistry that describes the stability and unique reactivity of certain cyclic compounds. Here's an in-depth look at the concept:

#### *Key Characteristics of Aromatic Compounds*

1. **Cyclic Structure:** The compound must be cyclic, meaning that the atoms in the molecule form a ring.
2. **Conjugation:** There must be continuous overlap of p-orbitals across the ring, creating a conjugated system. This means that every atom in the ring must be capable of participating in delocalization of  $\pi$ -electrons.
3. **Planarity:** The molecule must be planar or nearly planar, allowing for effective overlap of the p-orbitals.
4. **Hückel's Rule:** Aromatic compounds must contain a specific number of  $\pi$ -electrons, following the  $4n + 2$  rule, where  $n$  is a non-negative integer (0, 1, 2, 3, ...). This means the molecule has 2, 6, 10, 14, etc.,  $\pi$ -electrons.

#### *Hückel's Rule and $\pi$ -Electron Count*

- **$4n + 2$  Rule:** For a compound to be aromatic, it must have a number of  $\pi$ -electrons that fits this formula. For example:
  - Benzene ( $\text{C}_6\text{H}_6$ ) has 6  $\pi$ -electrons ( $n=1$ ), making it aromatic.
  - Naphthalene ( $\text{C}_{10}\text{H}_8$ ) has 10  $\pi$ -electrons ( $n=2$ ), making it aromatic.
  - Cyclobutadiene ( $\text{C}_4\text{H}_4$ ), with 4  $\pi$ -electrons ( $n=1$ ), does not follow the rule and is anti-aromatic.

### *Aromaticity vs. Anti-Aromaticity vs. Non-Aromaticity*

- **Aromatic Compounds:** These compounds are highly stable due to the delocalization of  $\pi$ -electrons. Examples include benzene, pyridine, and naphthalene.
- **Anti-Aromatic Compounds:** These compounds have a cyclic, conjugated system but have  $4n$   $\pi$ -electrons. They are typically unstable and highly reactive. An example is cyclobutadiene.
- **Non-Aromatic Compounds:** These compounds do not meet the criteria for aromaticity, either because they are not fully conjugated, not planar, or do not have the right number of  $\pi$ -electrons. Examples include cyclohexane and many non-cyclic compounds.

### *Stability and Reactivity*

Aromatic compounds are more stable than would be expected based on their structure alone. This stability is often referred to as "aromatic stabilization" or "resonance energy." This makes aromatic compounds less reactive in many types of chemical reactions compared to their non-aromatic analogs.

### *Applications and Importance*

- **Pharmaceuticals:** Many drugs are aromatic compounds due to their stability and ability to interact with biological molecules.
- **Materials Science:** Aromatic compounds are used in the production of polymers, dyes, and other materials.
- **Chemical Synthesis:** Understanding aromaticity is crucial for designing and synthesizing new organic compounds in research and industry.

## Summary

Aromaticity is a concept that explains the enhanced stability and unique properties of certain cyclic, conjugated, planar compounds with a specific number of  $\pi$ -electrons. By understanding and applying the principles of aromaticity, chemists can predict the behavior of molecules and design new compounds with desirable properties.

## Huckel's rule

Hückel's rule is a fundamental principle in organic chemistry that helps predict whether a planar ring molecule will have aromatic properties. According to Hückel's rule, a planar ring molecule will be aromatic if it has  $4n+2$   $\pi$ -electrons, where  $n$  is a non-negative integer (0, 1, 2, 3, ...).

## Application to Benzenoid Compounds

**Benzene:**

- Structure: Benzene ( $C_6H_6$ ) is a planar, hexagonal ring with alternating double and single bonds.
- $\pi$ -electrons: Benzene has six  $\pi$ -electrons.
- Hückel's Rule:  $4n+2=6$   $4n+2=6 \Rightarrow 4n=4 \Rightarrow n=1$
- Conclusion: Since  $n$  is a whole number, benzene is aromatic.

### Naphthalene:

- Structure: Naphthalene ( $C_{10}H_8$ ) consists of two fused benzene rings.
- $\pi$ -electrons: Naphthalene has ten  $\pi$ -electrons.
- Hückel's Rule:  $4n+2=10$   $4n+2=10 \Rightarrow 4n=8 \Rightarrow n=2$
- Conclusion: Since  $n$  is a whole number, naphthalene is aromatic.

## Application to Non-Benzenoid Compounds

### Cyclopropenyl Cation:

- Structure: Cyclopropenyl cation ( $C_3H_3^+$ ) is a triangular ring with one double bond.
- $\pi$ -electrons: The cation has two  $\pi$ -electrons.
- Hückel's Rule:  $4n+2=2$   $4n+2=2 \Rightarrow 4n=0 \Rightarrow n=0$
- Conclusion: Since  $n$  is a whole number, the cyclopropenyl cation is aromatic.

### Cyclopentadienyl Anion:

- Structure: Cyclopentadienyl anion ( $C_5H_5^-$ ) is a five-membered ring with alternating double and single bonds.
- $\pi$ -electrons: The anion has six  $\pi$ -electrons (four from double bonds and two from the negative charge).
- Hückel's Rule:  $4n+2=6$   $4n+2=6 \Rightarrow 4n=4 \Rightarrow n=1$
- Conclusion: Since  $n$  is a whole number, the cyclopentadienyl anion is aromatic.

### Tropylium Cation:

- Structure: Tropylium cation ( $C_7H_7^+$ ) is a seven-membered ring with three double bonds.
- $\pi$ -electrons: The cation has six  $\pi$ -electrons.
- Hückel's Rule:  $4n+2=6$   $4n+2=6 \Rightarrow 4n=4 \Rightarrow n=1$
- Conclusion: Since  $n$  is a whole number, the tropylium cation is aromatic.

## Summary

- **Benzenoid Compounds:**
  - **Benzene:** Aromatic (6  $\pi$ -electrons,  $n=1$ )
  - **Naphthalene:** Aromatic (10  $\pi$ -electrons,  $n=2$ )
- **Non-Benzenoid Compounds:**
  - **Cyclopropenyl Cation:** Aromatic (2  $\pi$ -electrons,  $n=0$ )
  - **Cyclopentadienyl Anion:** Aromatic (6  $\pi$ -electrons,  $n=1$ )



- **Tropylium Cation:** Aromatic ( $6 \pi$ -electrons,  $n=1$   $n = 1n=1$ )

These examples demonstrate how Hückel's rule is applied to determine the aromaticity of both benzenoid and non-benzenoid compounds.

## General mechanism of electrophilic aromatic substitution

Electrophilic Aromatic Substitution (EAS) is a common and important reaction mechanism in organic chemistry where an electrophile replaces a hydrogen atom on an aromatic ring. The general mechanism involves several key steps, and it's typically broken down into two main phases: the formation of the sigma complex (or arenium ion) and the deprotonation to restore aromaticity. Here's a step-by-step outline of the mechanism:

### 1. Generation of the Electrophile

Before the reaction begins, the electrophile ( $E^+$ ) must be generated. This can happen in various ways depending on the specific reaction:

- **Halogenation:** A halogen ( $X_2$ ) is activated by a Lewis acid (e.g.,  $FeX_3$ ) to form the electrophile  $X^+$ .
- **Nitration:** Nitric acid ( $HNO_3$ ) and sulfuric acid ( $H_2SO_4$ ) react to form the nitronium ion ( $NO_2^+$ ).
- **Sulfonation:** Sulfur trioxide ( $SO_3$ ) and sulfuric acid ( $H_2SO_4$ ) produce the sulfonium ion ( $SO_3H^+$ ).
- **Friedel-Crafts Alkylation/Acylation:** An alkyl or acyl halide is activated by a Lewis acid (e.g.,  $AlCl_3$ ) to form the corresponding carbocation or acylium ion.

### 2. Formation of the Sigma Complex (Arenium Ion)

The aromatic ring, rich in  $\pi$ -electrons, acts as a nucleophile and reacts with the electrophile. This step involves the following:

- **Attack on the Electrophile:** One of the  $\pi$ -electrons from the aromatic ring forms a bond with the electrophile, resulting in the formation of a non-aromatic carbocation intermediate known as the sigma complex or arenium ion.
- **Resonance Stabilization:** The positive charge on the arenium ion is delocalized through resonance, spreading over the ortho and para positions relative to the site of electrophilic attack. This stabilization is crucial for the intermediate's existence.

### 3. Deprotonation and Restoration of Aromaticity

To restore the aromaticity of the ring, the sigma complex must lose a proton ( $H^+$ ):

- **Deprotonation:** A base (often the conjugate base of the acid used in the reaction) abstracts the proton from the carbon atom that formed the new bond with the electrophile.

This step restores the aromatic system by re-establishing the delocalized  $\pi$ -electron system of the benzene ring.

## Overall Reaction Scheme

The overall EAS mechanism can be summarized as follows:

### 1. Electrophile Generation:

Generation of  $E^+$  (Electrophile)  
 $\text{Generation of } E^+ \text{ (Electrophile)}$

### 2. Formation of the Sigma Complex:

$\text{ArH} + E^+ \rightarrow \text{Ar-E}^+ \rightarrow (\text{Sigma Complex})$   
 $\text{ArH} + E^+ \rightarrow \text{Ar-E}^+ \rightarrow (\text{Sigma Complex})$

### 3. Deprotonation:

$\text{Sigma Complex} + \text{Base} \rightarrow \text{Ar-E} + \text{HBase}^+$   
 $\text{Sigma Complex} + \text{Base} \rightarrow \text{Ar-E} + \text{HBase}^+$

## Example: Bromination of Benzene

### Step-by-step Example for Bromination:

#### 1. Generation of the Electrophile:

$\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$   
 $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$

#### 2. Formation of the Sigma Complex:

$\text{Benzene} + \text{Br}^+ \rightarrow \text{Sigma Complex (with Br attached)}$   
 $\text{Benzene} + \text{Br}^+ \rightarrow \text{Sigma Complex (with Br attached)}$

#### 3. Deprotonation:

$\text{Sigma Complex} + \text{FeBr}_4^- \rightarrow \text{Bromobenzene} + \text{HFeBr}_3$   
 $\text{Sigma Complex} + \text{FeBr}_4^- \rightarrow \text{Bromobenzene} + \text{HFeBr}_3$

In this process, the aromaticity of the benzene ring is temporarily lost during the formation of the sigma complex but is restored after deprotonation. The specific details can vary slightly

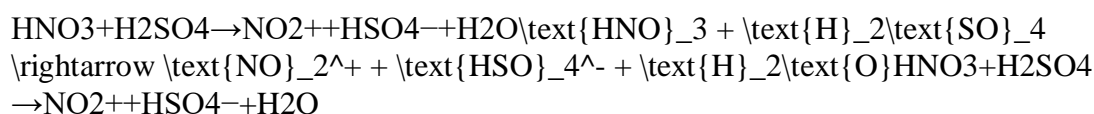
depending on the electrophile and the conditions, but the overall mechanism remains consistent across different types of electrophilic aromatic substitutions.

## Mechanism of nitration of benzene

The nitration of benzene is an electrophilic aromatic substitution reaction that involves the introduction of a nitro group (-NO<sub>2</sub>) into the benzene ring. The mechanism proceeds through several steps and can be summarized as follows:

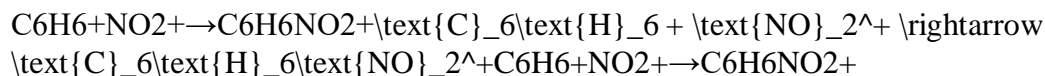
### 1. Generation of the Electrophile:

- The nitration reaction is typically carried out using a mixture of concentrated nitric acid (HNO<sub>3</sub>) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).
- Sulfuric acid acts as a catalyst and protonates nitric acid to form the nitronium ion (NO<sub>2</sub><sup>+</sup>), which is the actual electrophile in the reaction.



### 2. Attack of the Electrophile on the Benzene Ring:

- The nitronium ion (NO<sub>2</sub><sup>+</sup>) attacks the π-electron-rich benzene ring to form a sigma complex (also known as an arenium ion or carbocation intermediate). This is the rate-determining step of the reaction.

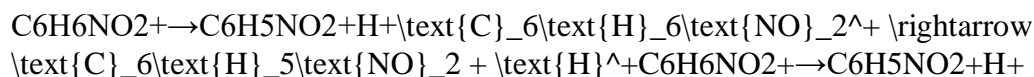


### 3. Formation of the Sigma Complex:

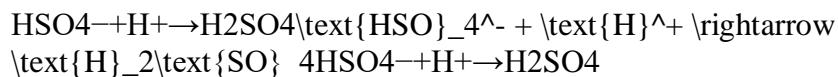
- The benzene ring donates a pair of π-electrons to the nitronium ion, forming a new C-N bond and creating a positively charged intermediate.

### 4. Deprotonation and Restoration of Aromaticity:

- The positively charged intermediate (sigma complex) then loses a proton (H<sup>+</sup>) from the carbon that formed the new bond, restoring the aromaticity of the benzene ring and yielding nitrobenzene as the final product.

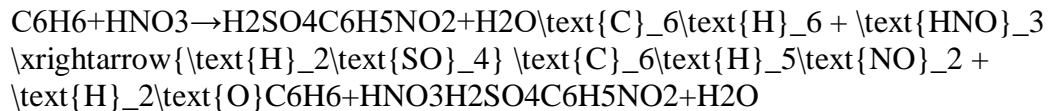


- The proton (H<sup>+</sup>) is typically abstracted by the bisulfate anion (HSO<sub>4</sub><sup>-</sup>) generated in the first step, forming sulfuric acid again and completing the catalytic cycle.



## Summary of the Overall Reaction:

The overall balanced chemical equation for the nitration of benzene can be written as:



### Key Points:

- **Electrophile:** The nitronium ion ( $\text{NO}_2^+$ ) is the electrophile in this reaction.
- **Catalyst:** Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) acts as a catalyst by generating the nitronium ion.
- **Intermediate:** The formation of a sigma complex (arenium ion) is a key intermediate step.
- **Restoration of Aromaticity:** The loss of a proton restores the aromatic nature of the benzene ring, resulting in the formation of nitrobenzene.

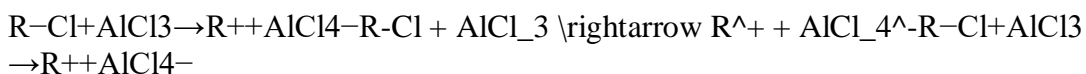
This mechanism explains how the nitro group is introduced into the benzene ring through an electrophilic aromatic substitution reaction.

## Friedel- Crafts' alkylation of benzene

Friedel-Crafts alkylation is a type of electrophilic aromatic substitution reaction in which an alkyl group is introduced onto an aromatic ring, such as benzene. The general reaction involves the use of an alkyl halide and a Lewis acid catalyst, typically aluminum chloride ( $\text{AlCl}_3$ ). Here is the step-by-step process for the Friedel-Crafts alkylation of benzene:

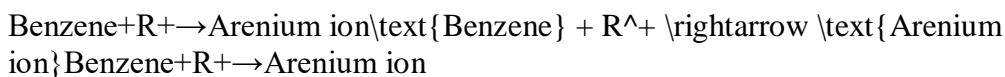
### Reaction Mechanism

1. **Formation of the Electrophile:** The Lewis acid catalyst ( $\text{AlCl}_3$ ) interacts with the alkyl halide ( $\text{R-Cl}$ ) to generate a more electrophilic species. This can be depicted as:

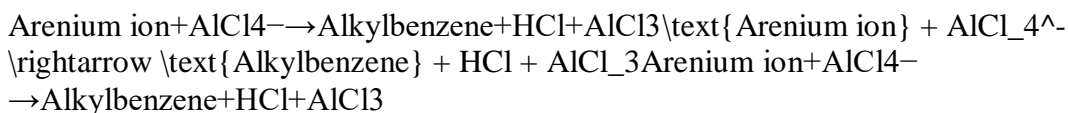


Here,  $\text{R}^+$  (the alkyl carbocation) is the electrophile that will react with benzene.

2. **Formation of the Arenium Ion:** The benzene ring, acting as a nucleophile, reacts with the carbocation. The  $\pi$ -electrons of the benzene attack the carbocation, forming a non-aromatic cyclohexadienyl cation (also known as an arenium ion or sigma complex).



3. **Deprotonation:** The arenium ion loses a proton ( $\text{H}^+$ ) to restore aromaticity. The proton is abstracted by the  $\text{AlCl}_4^-$  ion, which was formed in the first step.



## Overall Reaction

The overall balanced equation for the Friedel-Crafts alkylation of benzene can be written as:



## Example

As an example, consider the alkylation of benzene using methyl chloride (CH<sub>3</sub>Cl) and aluminum chloride (AlCl<sub>3</sub>) as the catalyst:

1. Formation of the methyl cation:  $\text{CH}_3\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3^+ + \text{AlCl}_4^-$
2. Formation of the arenium ion:  $\text{C}_6\text{H}_6 + \text{CH}_3^+ \rightarrow \text{arenium ion}$
3. Deprotonation to form toluene:  $\text{arenium ion} + \text{AlCl}_4^- \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl} + \text{AlCl}_3$

## Key Points and Considerations

- **Regioselectivity:** The position where the alkyl group attaches depends on the existing substituents on the benzene ring. For example, electron-donating groups (EDGs) direct the incoming alkyl group to ortho and para positions.
- **Rearrangement:** Carbocations can rearrange to form more stable carbocations before reacting with benzene. For example, a 1° carbocation may rearrange to a 2° or 3° carbocation.
- **Polyalkylation:** Multiple alkyl groups can be introduced if not carefully controlled, resulting in polyalkylated products.
- **Catalyst Regeneration:** The catalyst (AlCl<sub>3</sub>) is regenerated in the reaction, which allows it to catalyze multiple cycles.

Friedel-Crafts alkylation is a valuable method for introducing alkyl groups onto aromatic rings, expanding the versatility and utility of aromatic compounds in organic synthesis.

## Friedel-Craft's acylation of benzene

Friedel-Crafts acylation is a classic organic reaction used to attach an acyl group (RCO-) to an aromatic ring, typically benzene. Here's how the reaction proceeds:

### Reaction Overview:

1. **Reagents:** The reagents typically used are an acyl chloride (RCOCl) and a Lewis acid catalyst such as aluminum chloride (AlCl<sub>3</sub>).
2. **Mechanism:**
  - o **Formation of Acylium Ion:** The acyl chloride reacts with the Lewis acid catalyst (AlCl<sub>3</sub>) to form an acylium ion (RCO<sup>+</sup>).
  - o **Electrophilic Attack:** Benzene (or another aromatic compound) then reacts with the acylium ion as an electrophile.
  - o **Regeneration of Catalyst:** The Lewis acid catalyst (AlCl<sub>3</sub>) serves to regenerate during the reaction, making it catalytic.

### Detailed Steps:

- **Step 1: Formation of Acylium Ion**  $\text{RCOCl} + \text{AlCl}_3 \rightarrow \text{RCO}^+ + \text{AlCl}_4^-$  Here, AlCl<sub>3</sub> acts as a Lewis acid catalyst, facilitating the departure of Cl<sup>-</sup> from the acyl chloride (RCOCl) and generating the acylium ion (RCO<sup>+</sup>).
- **Step 2: Electrophilic Attack**  $\text{RCO}^+ + \text{Benzene} \rightarrow \text{RCO-benzene}^+$  The benzene ring, acting as a nucleophile due to its electron-rich aromatic system, attacks the acylium ion, leading to the substitution of a hydrogen atom on the benzene ring with the acyl group (RCO-).
- **Step 3: Catalyst Regeneration**  $\text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{Cl}^-$  The AlCl<sub>4</sub><sup>-</sup> ion formed in the initial step is recycled back to AlCl<sub>3</sub>, thus completing the catalytic cycle.

### Key Points:

- **Conditions:** Friedel-Crafts acylation typically requires a dry, non-polar solvent (such as dichloromethane or chlorobenzene) and low temperatures to minimize side reactions.
- **Selectivity:** The reaction is highly regioselective, typically placing the acyl group in the ortho and para positions relative to existing substituents on the benzene ring.
- **Limitations:** Friedel-Crafts acylation can be sensitive to steric hindrance and can undergo further reactions (such as Friedel-Crafts alkylation) under certain conditions.

This reaction is fundamental in organic synthesis for creating aromatic ketones and is an important tool in the toolbox of organic chemists.

### Orientation of aromatic substitution

In organic chemistry, the orientation of aromatic substitution reactions (such as electrophilic aromatic substitution) is influenced by the presence of substituents on the benzene ring. These substituents can be classified into groups that direct incoming substituents to either the ortho, para, or meta positions relative to themselves. Here's a breakdown of these directing effects:

1. **Ortho-Para Directing Groups:** Substituents that are ortho-para directing enhance the electrophilic substitution at the ortho and para positions relative to themselves. These groups typically stabilize the developing positive charge on the ortho and para carbons through resonance or inductive effects.

Examples of ortho-para directing groups include:

- **-OH (hydroxyl group)**
- **-NH<sub>2</sub> (amino group)**
- **-NHR (alkylamino group)**
- **-NR<sub>2</sub> (dialkylamino group)**
- **-OR (alkoxy group)**
- **-SR (alkylthio group)**
- **-X (halogens such as F, Cl, Br, I)**
- **-CN (cyano group)**

These groups donate electron density through resonance or inductive effects, stabilizing the carbocation intermediate at the ortho and para positions.

2. **Meta Directing Groups:** Substituents that are meta directing direct incoming electrophiles to the meta position relative to themselves. This is because they withdraw electron density from the benzene ring through resonance or inductive effects, making the ortho and para positions less attractive for electrophilic attack.

Examples of meta directing groups include:

- **-NO<sub>2</sub> (nitro group)**
- **-COR (acyl group)**
- **-COOH (carboxylic acid group)**
- **-SO<sub>3</sub>H (sulfonic acid group)**
- **-CONH<sub>2</sub> (amide group)**
- **-CN (cyano group when strongly deactivated)**

These groups withdraw electron density from the benzene ring, destabilizing carbocation intermediates at the ortho and para positions and thus favoring substitution at the meta position.

Understanding whether a substituent is ortho-para directing or meta directing is crucial for predicting the products of electrophilic aromatic substitution reactions. This predictive ability is based on the electronic effects of the substituents on the benzene ring, which can be analyzed through resonance structures and inductive effects

## Ring activating and deactivating groups

In organic chemistry, the concept of activating and deactivating groups refers to how substituents on a benzene ring affect the reactivity of the ring towards electrophilic aromatic substitution reactions. Here's an electronic interpretation of activating and deactivating groups with examples:

### Activating Groups:

1. **Alkyl groups (e.g., methyl, ethyl):**
  - **Effect:** These groups donate electron density through their sigma bonds into the benzene ring.
  - **Example:** Toluene (methylbenzene) - the methyl group activates the ring towards electrophilic substitution.
2. **Hydroxyl group (-OH) on an aromatic ring (Phenolic group):**
  - **Effect:** The lone pairs on oxygen can donate electron density into the ring through resonance and inductive effects.
  - **Example:** Phenol - the hydroxyl group activates the ring towards electrophilic substitution.
3. **Amino group (-NH<sub>2</sub>):**
  - **Effect:** The amino group is an electron-donating group through both resonance and inductive effects.
  - **Example:** Aniline - the amino group activates the ring towards electrophilic substitution.
4. **Methoxy group (-OCH<sub>3</sub>):**
  - **Effect:** The methoxy group donates electron density through resonance effects.
  - **Example:** Anisole (methoxybenzene) - the methoxy group activates the ring towards electrophilic substitution.

### Deactivating Groups:

1. **Nitro group (-NO<sub>2</sub>):**
  - **Effect:** The nitro group is strongly electron-withdrawing through both inductive and resonance effects.
  - **Example:** Nitrobenzene - the nitro group deactivates the ring towards electrophilic substitution.
2. **Carbonyl group (C=O) directly attached to the ring (e.g., -COR, -COOH):**
  - **Effect:** These groups withdraw electron density through resonance and inductive effects.
  - **Example:** Benzaldehyde (PhCHO) - the aldehyde group deactivates the ring towards electrophilic substitution.
3. **Halogen substituents (e.g., -Cl, -Br, -I):**
  - **Effect:** These groups withdraw electron density through inductive effects.
  - **Example:** Chlorobenzene - the chlorine atom deactivates the ring towards electrophilic substitution.
4. **Sulfonic acid group (-SO<sub>3</sub>H):**
  - **Effect:** The sulfonic acid group is strongly electron-withdrawing through both inductive and resonance effects.
  - **Example:** Benzenesulfonic acid - the sulfonic acid group deactivates the ring towards electrophilic substitution.

### Summary:

- **Activating groups** donate electron density to the benzene ring, making it more reactive towards electrophiles.



- **Deactivating groups** withdraw electron density from the benzene ring, making it less reactive towards electrophiles.

These effects are crucial in predicting where electrophilic substitution reactions will occur on substituted benzene rings and are fundamental in organic chemistry synthesis and analysis.

## Orientation of benzene

Sure, let's categorize the orientation of these groups in terms of electron-donating (EDG) and electron-withdrawing (EWG) effects relative to a benzene ring in organic chemistry:

### (i) Amino, Methoxy, and Methyl Groups:

- **Amino Group (-NH<sub>2</sub>):**
  - **EDG:** Amino groups are electron-donating due to the lone pair on the nitrogen atom. They are ortho/para-directing on a benzene ring in electrophilic aromatic substitution reactions.
- **Methoxy Group (-OCH<sub>3</sub>):**
  - **EDG:** Methoxy groups are also electron-donating via inductive and resonance effects. They are ortho/para-directing in electrophilic aromatic substitution.
- **Methyl Group (-CH<sub>3</sub>):**
  - **EDG:** Methyl groups are weakly electron-donating via hyperconjugation and inductive effects. They are weakly ortho/para-directing in electrophilic aromatic substitution.

### (ii) Carboxy, Nitro, Nitrile, Carbonyl, and Sulphonic Acid Groups:

- **Carboxylic Acid Group (-COOH):**
  - **EWG:** Carboxylic acids are electron-withdrawing due to the electronegative oxygen atoms. They are meta-directing in electrophilic aromatic substitution.
- **Nitro Group (-NO<sub>2</sub>):**
  - **EWG:** Nitro groups are strongly electron-withdrawing due to both inductive and resonance effects. They are meta-directing in electrophilic aromatic substitution.
- **Nitrile Group (-CN):**
  - **EWG:** Nitrile groups are electron-withdrawing primarily through inductive effects. They are meta-directing in electrophilic aromatic substitution.
- **Carbonyl Group (-C=O):**
  - **EWG:** Carbonyl groups are mildly electron-withdrawing due to the electronegative oxygen atom. They are meta-directing in electrophilic aromatic substitution.
- **Sulphonic Acid Group (-SO<sub>3</sub>H):**
  - **EWG:** Sulphonic acid groups are strongly electron-withdrawing due to the multiple electronegative oxygen atoms and the sulfonic acid group itself. They are meta-directing in electrophilic aromatic substitution.

### Halogens (F, Cl, Br, I):

- **Halogens:**
  - **EWG:** Halogens are electron-withdrawing due to their electronegativity. They generally destabilize the aromatic ring and can lead to ortho/para-directing effects in electrophilic aromatic substitution, but this can vary depending on the halogen and substituent pattern.

In summary, the groups you mentioned can be categorized based on their electron-donating (EDG) or electron-withdrawing (EWG) effects on a benzene ring, which influences their orientation in electrophilic aromatic substitution reactions.

## GENERAL CHEMISTRY

### UNIT-IV

#### Surface chemistry and chemical bonding Surface chemistry

#### Colloids

Certainly! Let's break down each of these topics related to colloids:

1. **Colloids:** Colloids are heterogeneous mixtures where one substance is evenly dispersed in another but does not settle out or dissolve. The particles in colloids are larger than those in solutions but smaller than those in suspensions. Examples include fog (liquid dispersed in gas), milk (fat dispersed in water), and gelatin (protein dispersed in water).
2. **Coagulation of Colloids:** Coagulation refers to the process where colloidal particles aggregate and settle out of the dispersion medium. This destabilization can be induced by various factors such as adding electrolytes (salting out), changing pH, or by heating. Coagulation disrupts the stability of the colloid, causing it to separate into distinct phases.
3. **Hardy-Schulze Rule:** The Hardy-Schulze rule describes how the coagulating power of an electrolyte (salt) depends on its charge and valency. According to this rule, multivalent ions (ions with higher charges) have greater coagulating power than monovalent ions. For instance, a trivalent ion like  $\text{Al}^{3+}$  can precipitate colloids more effectively than a monovalent ion like  $\text{Na}^+$ .
4. **Stability of Colloids:** Colloidal stability refers to the ability of colloidal particles to remain dispersed in the medium without aggregating or settling out. Stability depends on factors such as particle size, charge (electrostatic stabilization), and the presence of stabilizing agents (such as surfactants or polymers).
5. **Protection of Colloids:** Colloidal stability can be enhanced through various methods:
  - **Electrostatic stabilization:** Adding electrolytes or adjusting pH to manipulate the charge on particles.
  - **Steric stabilization:** Using polymers or surfactants to create a barrier around particles, preventing them from coming close enough to coagulate.
  - **Peptization:** Breaking down aggregates into smaller particles through the addition of small amounts of a stabilizing agent.
6. **Gold Number:** The Gold number is a measure of the minimum amount of protective colloid (usually gelatin) needed to prevent coagulation of 10 ml of gold sol when 1 ml of

10% NaCl solution is added. It quantifies the effectiveness of a protective colloid in preventing coagulation, with lower numbers indicating better protective action.

These concepts are fundamental in understanding the behavior, stability, and manipulation of colloidal systems in various applications ranging from industrial processes to biological systems.

## Adsorption

Adsorption is a surface phenomenon where molecules or atoms from a fluid phase (liquid or gas) accumulate on the surface of a solid or a liquid (adsorbent). It can be broadly classified into two types based on the nature of forces involved: physical adsorption (physisorption) and chemical adsorption (chemisorption).

### Physical Adsorption (Physisorption):

1. **Nature of Bonding:** Physisorption involves relatively weak van der Waals forces between the adsorbate molecules (the ones being adsorbed) and the adsorbent surface.
2. **Bond Strength:** The energy of adsorption in physisorption is low, typically in the range of 5 to 40 kJ/mol.
3. **Temperature Dependence:** Physisorption is usually reversible and depends strongly on temperature. Adsorption increases with decreasing temperature and vice versa.
4. **Surface Coverage:** It occurs primarily on the outer surface of the adsorbent material.
5. **Examples:** Adsorption of gases on activated carbon, adsorption of water vapor on silica gel, etc.

### Chemical Adsorption (Chemisorption):

1. **Nature of Bonding:** Chemisorption involves the formation of strong chemical bonds (covalent or ionic) between the adsorbate molecules and the adsorbent surface.
2. **Bond Strength:** The energy of adsorption in chemisorption is higher than in physisorption, typically more than 40 kJ/mol.
3. **Temperature Dependence:** Chemisorption is not as strongly dependent on temperature as physisorption. It often requires activation energy to proceed and can be irreversible under certain conditions.
4. **Surface Coverage:** Chemisorption can occur both on the outer and inner surfaces of the adsorbent material, depending on the nature of the chemical bonds formed.
5. **Examples:** Adsorption of hydrogen on a metal surface, adsorption of ammonia on silica-alumina catalysts, etc.

### Key Differences:

- **Bonding:** Physical adsorption involves weak van der Waals forces, whereas chemical adsorption involves stronger chemical bonds.
- **Energy:** Chemical adsorption typically releases more energy (heat) compared to physical adsorption.

- **Reversibility:** Physical adsorption is generally reversible and depends strongly on temperature, while chemical adsorption can be irreversible under certain conditions.
- **Surface Coverage:** Chemical adsorption can occur on both outer and inner surfaces of the adsorbent material, whereas physical adsorption usually occurs on the outer surface.

Both types of adsorption are important in various industrial processes, such as purification of gases, catalysis, and separation techniques. The choice between physical and chemical adsorption depends on factors such as the specific application, required efficiency, and the nature of the substances involved

## Langmuir adsorption isotherm

The Langmuir adsorption isotherm is a model that describes the adsorption of gas molecules onto a solid surface. It was proposed by Irving Langmuir in 1916 and remains widely used in surface chemistry and catalysis.

### Formulation of Langmuir Adsorption Isotherm:

The Langmuir isotherm assumes the following:

1. **Assumptions:**
  - Adsorption occurs at specific homogeneous sites on the surface.
  - Each site can only accommodate one adsorbate molecule.
  - Adsorption and desorption are reversible processes.
  - There is no lateral interaction between adsorbed molecules.
2. **Equation:** The Langmuir adsorption isotherm can be expressed mathematically as:
 
$$\theta = \frac{K \cdot P}{1 + K \cdot P}$$
 where:
  - $\theta$  is the fractional coverage of the surface by adsorbed molecules.
  - $P$  is the pressure of the gas phase.
  - $K$  is the Langmuir adsorption equilibrium constant, which is related to the binding energy of the adsorbate to the surface.

Alternatively, it can also be written in terms of the Langmuir adsorption equilibrium constant  $K$ :
 
$$\theta = \frac{K \cdot P}{1 + K \cdot P}$$
 where  $K$  is related to the standard free energy of adsorption.

3. **Interpretation:**
  - At low pressures (low  $P$ ),  $\theta$  increases linearly with  $P$ , indicating that adsorption sites are being filled.
  - At high pressures (high  $P$ ),  $\theta$  approaches a maximum value of 1, indicating that all available adsorption sites are occupied (saturation).
4. **Applications:**
  - The Langmuir adsorption isotherm is particularly useful in understanding surface area and adsorption capacity of materials used in catalysts, gas separations, and in environmental science for studying pollutant adsorption onto surfaces.
5. **Limitations:**

- Assumes uniform adsorption sites, which may not always be the case.
- Does not account for surface heterogeneity or lateral interactions between adsorbed molecules, which can be significant in some systems.
- Experimental deviations from the Langmuir model can occur, leading to the development of more complex isotherms like the BET (Brunauer-Emmett-Teller) model.

In summary, the Langmuir adsorption isotherm provides a fundamental model for understanding how gas molecules adsorb onto surfaces and is a cornerstone in surface science and catalysis.

## Applications of adsorption

Adsorption finds numerous applications across various fields due to its ability to concentrate substances on surfaces. Some key applications include:

1. **Water Purification:** Activated carbon is widely used to remove contaminants like organic compounds, chlorine, and heavy metals from water through adsorption.
2. **Air Purification:** Adsorbents like activated alumina or silica gel are used in air purification systems to remove pollutants such as volatile organic compounds (VOCs), odors, and moisture.
3. **Catalysis:** Catalysts often use adsorption to hold reactants close to active sites, enhancing reaction rates and selectivity in processes such as petroleum refining and chemical production.
4. **Gas Separation:** Adsorption processes like pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are used for separating gases based on their affinity for an adsorbent material.
5. **Chromatography:** Various forms of chromatography, such as gas chromatography and liquid chromatography, utilize adsorbents to separate components of a mixture based on their affinity for the stationary phase.
6. **Drug Delivery:** Adsorption can be employed in pharmaceuticals for drug delivery systems where drugs are adsorbed onto solid surfaces (like nanoparticles) and released in a controlled manner.
7. **Environmental Protection:** Adsorption is used in environmental cleanup efforts, such as soil remediation to remove contaminants, and in controlling emissions from industrial processes.
8. **Food and Beverage Industry:** Adsorbents like activated carbon are used for decolorization, purification, and removal of impurities in food processing and beverage industries.
9. **Energy Storage:** Adsorption processes are explored for energy storage applications, such as storing natural gas in porous materials for vehicular fueling.
10. **Personal Care Products:** Adsorption is used in products like facial masks and skin cleansers to remove impurities from the skin surface.

These applications illustrate the versatility of adsorption across industries, from environmental protection to healthcare and industrial processes.

## Chemical Bonding

### Valence bond theory

The valence bond theory (VB theory) is a model in chemistry used to describe the formation of chemical bonds between atoms. It was developed primarily by Linus Pauling and others in the early 20th century and provides a qualitative understanding of bonding based on quantum mechanics principles. Here are the key points of the valence bond theory:

1. **Atomic Orbitals Overlap:** According to VB theory, a chemical bond is formed when two atoms approach each other closely enough so that their atomic orbitals overlap. Atomic orbitals are regions around the nucleus where electrons are likely to be found.
2. **Formation of Bonding and Antibonding Orbitals:** When atomic orbitals overlap, two new molecular orbitals are formed:
  - **Bonding Molecular Orbital ( $\sigma$  bond):** Formed by the overlap of atomic orbitals with the same sign (phase). The electron density between the nuclei increases, resulting in a stable bonding interaction.
  - **\*Antibonding Molecular Orbital ( $\sigma$  bond)\*\*:** Formed by the overlap of atomic orbitals with opposite signs (out of phase). The electron density between the nuclei decreases, resulting in an unstable antibonding interaction.
3. **Bond Types:** Valence bond theory explains the formation of different types of bonds:
  - **Single Bonds:** Formed by the overlap of one pair of orbitals (e.g.,  $\sigma$  bond).
  - **Double Bonds:** Formed by the overlap of two pairs of orbitals (e.g., one  $\sigma$  bond and one  $\pi$  bond).
  - **Triple Bonds:** Formed by the overlap of three pairs of orbitals (e.g., one  $\sigma$  bond and two  $\pi$  bonds).
4. **Hybridization:** VB theory also introduced the concept of orbital hybridization to explain molecular shapes and bond angles. Hybrid orbitals are formed by mixing atomic orbitals from the same atom. For example,  $sp$ ,  $sp^2$ , and  $sp^3$  hybrid orbitals explain the geometry of molecules like methane ( $CH_4$ ), ethylene ( $C_2H_4$ ), and ethane ( $C_2H_6$ ), respectively.
5. **Resonance:** The theory can also account for resonance structures, where electrons are delocalized over multiple atoms or bonds. Resonance is described as a combination of contributing structures that together represent the actual electronic structure of the molecule.
6. **Strengths and Limitations:** Valence bond theory provides a qualitative understanding of bonding, especially in simple molecules. It emphasizes the role of overlap and orbital directionality in bond formation. However, it has limitations in explaining molecular spectra and bonding in more complex molecules, where molecular orbital theory (which builds upon VB theory) is often more useful.

In summary, valence bond theory is a foundational concept in chemistry that explains how atoms bond together by overlapping their atomic orbitals, leading to the formation of stable molecular orbitals and various types of chemical bonds.

### Hybridization

Hybridization in chemistry refers to the mixing of atomic orbitals to form new hybrid orbitals suitable for bonding. This concept helps explain the shapes, bond angles, and reactivity of molecules. Here's a simplified explanation:

1. **Atomic Orbitals:** Atoms have different types of orbitals (s, p, d, etc.) where electrons are located.
2. **Hybrid Orbitals:** When atoms bond, their orbitals can mix to form hybrid orbitals with different characteristics than the original orbitals. For example, mixing an s orbital with a p orbital can create sp hybrid orbitals.
3. **Types of Hybridization:**
  - **sp Hybridization:** One s and one p orbital mix to form two sp hybrid orbitals, which are linear and have bond angles of  $180^\circ$ .
  - **sp<sup>2</sup> Hybridization:** One s and two p orbitals mix to form three sp<sup>2</sup> hybrid orbitals, which are trigonal planar with bond angles of  $120^\circ$ .
  - **sp<sup>3</sup> Hybridization:** One s and three p orbitals mix to form four sp<sup>3</sup> hybrid orbitals, which are tetrahedral with bond angles of approximately  $109.5^\circ$ .
  - **sp<sup>3</sup>d Hybridization:** One s, three p, and one d orbital mix to form five sp<sup>3</sup>d hybrid orbitals, which are trigonal bipyramidal with bond angles of  $90^\circ$  and  $120^\circ$ .
  - **sp<sup>3</sup>d<sup>2</sup> Hybridization:** One s, three p, and two d orbitals mix to form six sp<sup>3</sup>d<sup>2</sup> hybrid orbitals, which are octahedral with bond angles of  $90^\circ$ .
4. **Application:** Hybridization explains the geometry and bond angles observed in molecules. For instance, methane (CH<sub>4</sub>) has sp<sup>3</sup> hybridization, forming a tetrahedral shape with bond angles of  $109.5^\circ$ , while ethene (C<sub>2</sub>H<sub>4</sub>) has sp<sup>2</sup> hybridization, resulting in a planar structure with bond angles of  $120^\circ$ .

Understanding hybridization helps predict molecular shapes and reactivity, crucial for fields like organic chemistry and biochemistry.

## VB theory as applied to ClF<sub>3</sub>, Ni(CO)<sub>4</sub>

In the context of VB (Valence Bond) theory, let's apply it to understand the bonding in two different molecules: ClF<sub>3</sub> and Ni(CO)<sub>4</sub>.

### 1. ClF<sub>3</sub> (Chlorine Trifluoride)

**Structure:** ClF<sub>3</sub> molecule consists of one chlorine atom bonded to three fluorine atoms.

#### Valence Bond Description:

- **Chlorine (Cl):** Chlorine has 7 valence electrons ( $3s^2 3p^5$ ). In ClF<sub>3</sub>, chlorine uses its 3p atomic orbitals to form three  $\sigma$  bonds with three fluorine atoms. Each  $\sigma$  bond is formed by the overlap of a singly occupied 3p orbital from chlorine and a singly occupied 2p orbital from fluorine.

Chlorine also has a lone pair of electrons in a 3p orbital, which is localized and occupies a different orbital from those involved in bonding.

- **Fluorine (F):** Fluorine has 9 electrons ( $1s^2 2s^2 2p^5$ ). Each fluorine atom uses its 2p orbitals to form  $\sigma$  bonds with chlorine, resulting in three  $\sigma$  bonds in total.

**Bonding Description:** In terms of VB theory:

- The central chlorine atom contributes three unpaired electrons from its 3p orbitals.
- Each fluorine atom contributes one unpaired electron from its 2p orbital.
- The  $\sigma$  bonds are formed by the overlap of these singly occupied orbitals between chlorine and fluorine.

## 2. Ni(CO)<sub>4</sub> (Tetracarbonyl Nickel)

**Structure:** Ni(CO)<sub>4</sub> consists of a nickel atom bonded to four carbon monoxide (CO) ligands.

**Valence Bond Description:**

- **Nickel (Ni):** Nickel has 10 valence electrons ( $3d^8 4s^2$ ). In Ni(CO)<sub>4</sub>, nickel uses its 4s and 3d orbitals to form bonding interactions with the carbon monoxide ligands.
- **Carbon Monoxide (CO):** Carbon monoxide has 10 electrons ( $1s^2 2s^2 2p^4$ ). Each CO ligand donates a pair of electrons from its lone pair on carbon into a  $\sigma$  bonding orbital with nickel. Additionally, the carbon and oxygen atoms of CO each donate one electron into a  $\pi^*$  antibonding orbital.

**Bonding Description:** In VB theory:

- The bonding in Ni(CO)<sub>4</sub> is mainly described by  $\sigma$  and  $\pi$  interactions.
- $\sigma$  bonds are formed by the overlap of electron pairs from the lone pairs on carbon with empty orbitals on nickel.
- $\pi$  bonds are formed by the sideways overlap of the  $\pi^*$  antibonding orbitals from CO with the d orbitals of nickel.

**Conclusion:**

Valence Bond theory provides a detailed description of the bonding in both ClF<sub>3</sub> and Ni(CO)<sub>4</sub>:

- In ClF<sub>3</sub>, the bonding is mainly through  $\sigma$  bonds formed by the overlap of singly occupied orbitals on chlorine and fluorine atoms.
- In Ni(CO)<sub>4</sub>, the bonding involves both  $\sigma$  and  $\pi$  interactions between nickel and carbon monoxide ligands, with nickel utilizing its d and s orbitals to form these bonds.

These examples illustrate how VB theory can be applied to understand the specific bonding interactions in different types of molecules.

## Molecular orbital theory -LCAO method



Molecular orbital theory (MO theory) and the Linear Combination of Atomic Orbitals (LCAO) method are fundamental concepts in quantum chemistry used to describe the behavior of electrons in molecules.

### Molecular Orbital Theory (MO Theory):

1. **Concept:** MO theory treats electrons in a molecule as occupying molecular orbitals, which are formed by combining atomic orbitals (AOs) from the constituent atoms.
2. **Molecular Orbitals:** These are wavefunctions that describe the distribution of electrons over the entire molecule rather than just individual atoms. They are solutions to the Schrödinger equation for the molecule.
3. **Formation of Molecular Orbitals:**
  - **Bonding Molecular Orbitals:** Formed by in-phase combination (constructive interference) of atomic orbitals. Electrons in bonding MOs stabilize the molecule.
  - **Antibonding Molecular Orbitals:** Formed by out-of-phase combination (destructive interference) of atomic orbitals. Electrons in antibonding MOs destabilize the molecule.
  - **Non-bonding Molecular Orbitals:** Formed when atomic orbitals do not combine perfectly in or out of phase.
4. **Energy Levels:** MOs are arranged in energy levels, similar to atomic orbitals, but they now span the entire molecule rather than just individual atoms.

### Linear Combination of Atomic Orbitals (LCAO):

1. **Concept:** LCAO is a method used in MO theory to construct molecular orbitals by linearly combining atomic orbitals from the constituent atoms. Mathematically, a molecular orbital  $\psi$  can be represented as:

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n$$

where  $\phi_i$  are atomic orbitals and  $c_i$  are coefficients.

2. **Coefficients:** The coefficients  $c_i$  are determined by solving the Schrödinger equation for the molecule. These coefficients depend on the overlap and energy difference between the atomic orbitals involved.
3. **Overlap Integral:** The effectiveness of the overlap between atomic orbitals is quantified by the overlap integral, which influences the bonding character of the resulting molecular orbital.
4. **Application:** LCAO is used to calculate the electronic structure of molecules, predict bond order and stability, and understand properties such as bond lengths and bond angles.

### Key Points:

- **Bonding and Antibonding:** Bonding molecular orbitals are lower in energy than the original atomic orbitals, while antibonding orbitals are higher.

- **Electron Occupation:** According to the Aufbau principle, electrons occupy molecular orbitals starting from the lowest energy level.
- **Prediction of Properties:** MO theory can predict magnetic properties, electronic spectra, and chemical reactivity based on the arrangement and occupancy of molecular orbitals.

In essence, MO theory with the LCAO method provides a powerful framework for understanding and predicting the electronic structure and properties of molecules, linking the behavior of electrons to the structure of the molecule as a whole

## Construction of M.O. diagrams

Molecular Orbital (M.O.) diagrams are graphical representations used to show the relative energies of molecular orbitals in a molecule. They are crucial in understanding the bonding and properties of molecules. Here's a basic guide on constructing M.O. diagrams:

### Steps to Construct M.O. Diagrams:

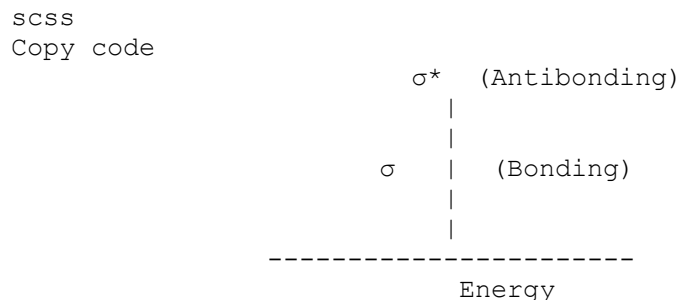
1. **Determine the Atomic Orbitals Involved:** Identify the atomic orbitals (s, p, d, etc.) of each atom participating in bonding. For example, in a diatomic molecule like  $\text{H}_2$ :
  - Each hydrogen atom has 1s atomic orbitals.
2. **Construct Molecular Orbitals:** Molecular orbitals are formed by the linear combination of atomic orbitals (LCAO). The number of molecular orbitals formed equals the number of atomic orbitals used.
  - **Bonding Molecular Orbitals ( $\sigma$ ,  $\pi$ ,  $\delta$ , etc.):**
    - **$\sigma$  (sigma) orbitals:** Formed by head-to-head overlap of atomic orbitals.
    - **$\pi$  (pi) orbitals:** Formed by side-to-side overlap of atomic orbitals.
    - **$\delta$  (delta) orbitals:** Formed by double side-to-side overlap of atomic orbitals.
  - *Antibonding Molecular Orbitals ( $\sigma$ ,  $\pi$ ,  $\delta^*$ , etc.):\*\**
    - These are formed by the subtraction (or phase difference) of the atomic orbitals.
3. **Energy Ordering:**
  - In general, bonding molecular orbitals are lower in energy than the atomic orbitals from which they are formed.
  - Antibonding molecular orbitals are higher in energy than the corresponding atomic orbitals.
4. **Fill Electrons:**
  - Electrons fill the molecular orbitals following the Pauli exclusion principle (no two electrons can have the same set of quantum numbers) and Hund's rule (electrons occupy orbitals singly before pairing).
5. **Label and Interpret:**
  - Label each molecular orbital with its type ( $\sigma$ ,  $\pi$ , etc.) and its relative energy level.
  - Interpret the diagram to determine the bond order, stability, and other properties of the molecule.

## Example: Hydrogen Molecule ( $\text{H}_2$ ) M.O. Diagram

For  $\text{H}_2$ , the M.O. diagram shows:

- **Bonding Orbitals:**  $\sigma_{1s}$  and  $\sigma^*_{1s}$
- **Antibonding Orbitals:**  $\sigma^*_{1s}$

The diagram typically looks like this:



In this diagram:

- The  $\sigma$  orbital is lower in energy compared to the original atomic orbitals (1s), indicating a stable bonding interaction.
- The  $\sigma^*$  orbital is higher in energy, indicating an antibonding interaction.

### Key Points:

- M.O. diagrams are essential tools to visualize the bonding and properties of molecules.
- They illustrate how atomic orbitals combine to form molecular orbitals.
- Energy levels determine stability and the nature of bonding (bonding or antibonding).

By following these steps, you can construct and interpret M.O. diagrams for different molecules, providing insights into their bonding and properties.

## M.O. diagrams for $\text{N}_2$ , $\text{O}_2$ , $\text{CO}$ and $\text{NO}$

Molecular orbital (MO) diagrams provide a way to understand the electronic structure and bonding in diatomic molecules. Let's construct MO diagrams for the diatomic molecules  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{NO}$ , considering both homo-nuclear (same atom) and hetero-nuclear (different atoms) cases.

### Homo-nuclear molecules: $\text{N}_2$ and $\text{O}_2$

## N<sub>2</sub>:

1. **Atomic Orbitals (AOs) involved:** Each nitrogen atom contributes 2s and 2p atomic orbitals (1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>).
2. **MO Diagram ( $\sigma$  and  $\pi$  bonds):**
  - There are 10 electrons to place (5 from each N atom).
  - The MO diagram for N<sub>2</sub> includes  $\sigma$  and  $\pi$  bonding and antibonding orbitals.
  
  - Key features:
    - $\sigma_{2s}$  and  $\sigma^*_{2s}$  are lower in energy.
    - $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are bonding.
    - $\pi_{2p}$  and  $\sigma^*_{2p}$  orbitals are antibonding.

## O<sub>2</sub>:

1. **Atomic Orbitals (AOs) involved:** Each oxygen atom contributes 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> atomic orbitals.
2. **MO Diagram ( $\sigma$  and  $\pi$  bonds):**
  - There are 12 electrons to place (6 from each O atom).
  - The MO diagram for O<sub>2</sub> also includes  $\sigma$  and  $\pi$  bonding and antibonding orbitals.
  
  - Key features:
    - $\sigma_{2s}$  and  $\sigma^*_{2s}$  are lower in energy.
    - $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are bonding.
    - $\pi_{2p}$  and  $\sigma^*_{2p}$  orbitals are antibonding.

## Hetero-nuclear molecules: CO and NO

### CO:

1. **Atomic Orbitals (AOs) involved:** Carbon contributes 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, and oxygen contributes 2s and 2p atomic orbitals.
2. **MO Diagram ( $\sigma$  and  $\pi$  bonds):**
  - There are 14 electrons to place (6 from C and 8 from O).
  - The MO diagram for CO includes  $\sigma$  and  $\pi$  bonding and antibonding orbitals.
  
  - Key features:
    - $\sigma_{2s}$  and  $\sigma^*_{2s}$  are lower in energy.

- $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are bonding.
- $\pi_{2p}$  and  $\sigma_{2p}^*$  orbitals are antibonding.

### NO:

1. **Atomic Orbitals (AOs) involved:** Nitrogen contributes 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, and oxygen contributes 2s and 2p atomic orbitals.
2. **MO Diagram ( $\sigma$  and  $\pi$  bonds):**

  - There are 15 electrons to place (7 from N and 8 from O).
  - The MO diagram for NO also includes  $\sigma$  and  $\pi$  bonding and antibonding orbitals.

  - Key features:
    - $\sigma_{2s}$  and  $\sigma_{2s}^*$  are lower in energy.
    - $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are bonding.
    - $\pi_{2p}^*$  and  $\sigma_{2p}^*$  orbitals are antibonding.

These diagrams illustrate the relative energies of molecular orbitals and how electrons are distributed among them in each molecule, thereby indicating the bonding and stability characteristics of each species.

## HSAB

### Pearson's concept, HSAB principle

Pearson's concept, also known as the Hard and Soft Acids and Bases (HSAB) principle, is a qualitative theory used in chemistry to explain and predict the stability of metal complexes and the outcomes of chemical reactions. Here's a breakdown of the key aspects:

#### Pearson's Concept (HSAB Principle)

1. **Acids and Bases Classification:**
  - **Hard Acids (HA):** These are species that are small, highly charged, and have relatively low polarizability. They prefer to interact with hard bases.
  - **Soft Acids (SA):** These species are larger, less charged, and more polarizable. They prefer to interact with soft bases.
2. **Hard Bases (HB) vs Soft Bases (SB):**
  - **Hard Bases:** Species with small size, high electronegativity, and low polarizability (e.g., oxygen in water).
  - **Soft Bases:** Larger, less electronegative, and more polarizable species (e.g., phosphines, sulfur in thiolates).
3. **Applications and Importance:**

- **Predicting Stability:** The HSAB principle helps predict which metal ions will form stable complexes with which ligands. Hard acids tend to form stable complexes with hard bases, and soft acids with soft bases.
- **Bioinorganic Chemistry:** It's crucial in understanding interactions in biological systems where metal ions coordinate with ligands such as proteins or DNA.
- **Organic Chemistry:** Helps in understanding reactivity and selectivity in organic synthesis involving metal catalysts.

## Bonding in Hard-Hard and Soft-Soft Combinations

### 1. Hard-Hard (HH) Interactions:

- **Nature of Bonding:** Hard acids and hard bases interact through primarily ionic or electrostatic interactions.
- **Examples:**  $\text{Li}^+$  with  $\text{F}^-$ ,  $\text{Mg}^{2+}$  with  $\text{O}^{2-}$ , etc.
- **Bond Strength:** Typically strong bonds due to the high charge density and small size of hard acids and bases.

### 2. Soft-Soft (SS) Interactions:

- **Nature of Bonding:** Soft acids and soft bases interact through more covalent or polar covalent bonding.
- **Examples:**  $\text{Hg}^{2+}$  with thiolates ( $\text{RS}^-$ ),  $\text{Pt}^{2+}$  with phosphines ( $\text{PR}_3$ ), etc.
- **Bond Strength:** Bonds can be relatively weaker than in hard-hard interactions due to the larger size and higher polarizability of the soft acids and bases.

## Importance of Hard-Hard and Soft-Soft Combinations:

- **Stability of Complexes:** Hard-hard interactions often lead to more stable complexes in aqueous environments or under conditions where ionic interactions are favored.
- **Selectivity in Reactions:** Soft-soft interactions can lead to selective reactions or catalytic processes where the conditions favor covalent bonding and more flexibility in coordination geometry.
- **Biological Relevance:** Understanding these interactions is crucial in bioinorganic chemistry, where metal ions play critical roles in biological processes and enzyme catalysis.

In summary, Pearson's concept of hard and soft acids and bases (HSAB) provides a valuable framework for understanding and predicting chemical reactivity and stability, particularly in metal-ligand interactions. Hard-hard and soft-soft combinations illustrate how the nature of bonding can vary based on the electronic and steric properties of the acids and bases involved.

## UNIT-V

### Stereochemistry of carbon compounds

### Molecular representations

Certainly! Here's an overview of each molecular representation:

1. **Wedge Formula (Solid-Wedge and Dashed-Wedge):**
  - **Purpose:** Used to show the three-dimensional orientation of substituents around a central atom.
  - **Representation:** Solid wedges (pointing out of the plane of the paper) indicate substituents coming towards the viewer, while dashed wedges (pointing into the plane of the paper) indicate substituents going away from the viewer.
2. **Fischer Projection:**
  - **Purpose:** Represents the three-dimensional arrangement of molecules in a two-dimensional format, typically used for sugars and amino acids.
  - **Representation:** Vertical lines represent bonds going into the plane of the paper (wedges), while horizontal lines represent bonds coming out of the plane of the paper (dashes).
3. **Newman Projection:**
  - **Purpose:** Shows the relative orientation of substituents attached to two atoms joined by a single bond, viewed along the bond axis.
  - **Representation:** Consists of two perpendicular lines intersecting at the central bond axis. The front carbon is represented with its substituents shown around it, while the back carbon is represented as a circle with substituents projecting away from it.
4. **Sawhorse Projection:**
  - **Purpose:** Similar to the Newman projection, it shows the three-dimensional structure of a molecule but with a slight angle rather than directly along the bond axis.
  - **Representation:** It resembles a combination of Newman and perspective projection, giving a skewed view of the molecule with substituents shown in a more realistic three-dimensional arrangement.

Each of these representations serves specific purposes in visualizing molecular structures, from simple spatial relationships (like in Wedge and Fischer projections) to detailed stereochemical configurations (like in Newman and Sawhorse projections).

## Optical isomerism

Optical isomerism is a phenomenon that arises in certain molecules where different spatial arrangements of atoms result in molecules that are non-superimposable mirror images of each other, known as enantiomers. This property is important in chemistry and biochemistry, especially in the context of pharmaceuticals and biological molecules.

### Optical Activity:

- **Definition:** Optical activity refers to the ability of a substance (usually a chiral molecule) to rotate the plane of polarized light.
- **Chirality:** Molecules that exhibit optical activity are chiral, meaning they lack an internal plane of symmetry and exist in left-handed (levorotatory) and right-handed (dextrorotatory) forms.

- **Measurement:** The extent of optical activity is measured using a polarimeter, which quantifies the angle of rotation caused by the substance in a polarized light beam passing through it.

### Wave Nature of Light:

- **Polarized Light:** Light consists of oscillating electric and magnetic fields that are perpendicular to each other and to the direction of propagation. When these oscillations occur in a single plane, the light is polarized.
- **Plane-Polarized Light:** Polarized light where the electric field vector oscillates in a single plane as the light travels.
- **Interaction with Chiral Molecules:** When plane-polarized light passes through a solution of chiral molecules, the rotation of the plane of polarization occurs due to the interaction between the light's electric field and the asymmetric arrangement of atoms in the molecules.

### Optical Rotation:

- **Principle:** When plane-polarized light passes through a substance that is optically active (chiral), the plane of polarization rotates.
- **Direction:** The direction of rotation (clockwise or counterclockwise) depends on the specific enantiomer (left-handed or right-handed form) of the molecule present in the solution.
- **Measurement:** The amount of rotation is measured using a polarimeter and is expressed in degrees.

### Specific Rotation:

- **Definition:** Specific rotation ( $\alpha$ ) is a standardized measure of the optical activity of a substance. It is defined as the observed rotation of the plane of polarized light per unit length (typically in decimeters) and per unit concentration (typically in grams per milliliter) of the substance.
- **Formula:** Mathematically, specific rotation ( $\alpha$ ) is calculated using the formula:

$$\alpha = \frac{\text{Observed rotation}}{l \cdot c}$$

where  $l$  is the path length in decimeters and  $c$  is the concentration in g/mL.

In summary, optical isomerism involves the interaction between chiral molecules and polarized light, where the molecular arrangement determines whether the substance is optically active and in which direction it will rotate the plane of polarized light. Specific rotation quantifies this effect in a standardized manner, allowing for precise characterization of optical activity in chemical substances.

## Chiral molecules



Chiral molecules are a fundamental concept in chemistry and refer to molecules that are not superimposable on their mirror images. This non-superimposability arises due to their lack of internal plane(s) of symmetry and occurs when a molecule contains at least one chiral center (often a carbon atom bonded to four different groups).

### Criteria for Chirality:

1. **Chiral Center (Stereocenter):** A chiral center is an atom, typically carbon, that is bonded to four different substituents. This configuration leads to non-superimposability of the molecule on its mirror image. For example, in a molecule like 2-chlorobutane ( $\text{CHClCH}_2\text{CH}_3$ ), the carbon bonded to Cl, H,  $\text{CH}_2\text{CH}_3$ , and  $\text{CH}_3$  is a chiral center.
2. **Absence of a Plane of Symmetry:** A molecule is chiral if it lacks a plane of symmetry (mirror plane). A plane of symmetry is a plane that divides the molecule into two mirror-image halves. If such a plane exists, the molecule is achiral (not chiral).
3. **Axis of Symmetry (Improper Axis of Rotation):** For some molecules, chirality can also be determined by the presence or absence of an improper axis of rotation (also known as a rotational axis of improper rotation). If a molecule has an improper axis of rotation (such as an  $S_4$  axis), it is achiral.

### Symmetry Elements in Chirality:

- **Mirror Plane ( $\sigma$ ):** A chiral molecule cannot have a mirror plane of symmetry. If a mirror plane exists, the molecule is achiral.
- **Center of Symmetry (i):** The presence of a center of symmetry (also known as inversion center) makes a molecule achiral. A center of symmetry means there is a point in the molecule where every atom has a counterpart at an equal distance on the opposite side, effectively creating a mirror image.
- **Rotation Axis ( $C_n$ ):** Chiral molecules can have rotation axes ( $C_n$ ) but only if combined with other elements like rotation or reflection (e.g.,  $C_2$  and  $\sigma$ ) to maintain chirality.

Understanding these symmetry elements helps in identifying whether a molecule is chiral or achiral, crucial for understanding its properties and behavior, especially in biological and chemical contexts where chirality plays a significant role.

## Enantiomers and Diastereomers

Enantiomers and diastereomers are terms used in stereochemistry to describe different types of stereoisomers:

1. **Enantiomers:**
  - Enantiomers are a type of stereoisomer that are non-superimposable mirror images of each other.
  - They have the same connectivity of atoms but differ in their spatial arrangement due to the presence of one or more chiral centers.

- Enantiomers have identical physical properties (melting point, boiling point, solubility, etc.) except for their interaction with other chiral substances (like enzymes or chiral selectors in chromatography).
  - Examples include L- and D-alanine.
2. **Diastereomers:**
- Diastereomers are stereoisomers that are not mirror images of each other and are not superimposable.
  - They arise when molecules have two or more chiral centers and differ in their configuration at some, but not all, of these centers.
  - Diastereomers have different physical properties from each other and may exhibit different chemical reactivity in certain reactions.
  - Examples include cis-trans isomers in alkenes and meso compounds with internal planes of symmetry.

In summary, enantiomers are mirror images that are non-superimposable, while diastereomers are stereoisomers that are not mirror images and are non-superimposable.

## Optical isomerism of Glyceraldehyde, Lactic acid, Alanine, Tartaric acid 2,3-dibromopentane

Optical isomerism, also known as chirality, arises in molecules that are non-superimposable mirror images of each other. These molecules are called enantiomers. Chirality occurs when a molecule has a chiral center — an atom, usually carbon, bonded to four different groups. Here's an explanation of optical isomerism with examples of each compound you mentioned:

1. **Glyceraldehyde:**
  - Glyceraldehyde is a simple sugar and exists in two enantiomeric forms: D-glyceraldehyde and L-glyceraldehyde.
  - The chiral center in glyceraldehyde is the carbon atom bonded to an aldehyde group ( $\text{-CHO}$ ), a hydrogen atom ( $\text{H}$ ), an OH group ( $\text{-OH}$ ), and an H or  $\text{CH}_2\text{OH}$  group (depending on whether it is D or L glyceraldehyde).
2. **Lactic acid:**
  - Lactic acid has one chiral carbon atom. It can exist in two enantiomeric forms: L-lactic acid and D-lactic acid.
  - The chiral center in lactic acid is the carbon atom bonded to a carboxyl group ( $\text{-COOH}$ ), a hydrogen atom ( $\text{H}$ ), a hydroxyl group ( $\text{-OH}$ ), and a methyl group ( $\text{-CH}_3$ ).
3. **Alanine:**
  - Alanine is an amino acid with one chiral carbon atom.
  - It can exist in two enantiomeric forms: L-alanine and D-alanine.
  - The chiral center in alanine is the carbon atom bonded to an amino group ( $\text{-NH}_2$ ), a carboxyl group ( $\text{-COOH}$ ), a hydrogen atom ( $\text{H}$ ), and a methyl group ( $\text{-CH}_3$ ).
4. **Tartaric acid:**
  - Tartaric acid is a dicarboxylic acid with two chiral carbon atoms, which gives rise to multiple stereoisomers.

- The two most common forms are meso-tartaric acid (which is achiral despite having chiral centers due to its internal plane of symmetry) and D-tartaric acid and L-tartaric acid (which are enantiomers).
5. **2,3-dibromopentane:**
- 2,3-dibromopentane is a compound with two chiral centers.
  - It can exist as a pair of enantiomers, where each chiral carbon (at position 2 and 3 in the pentane chain) is bonded to different bromine atoms and hydrogen atoms.

In each of these examples, optical isomerism arises due to the presence of chiral centers. Enantiomers exhibit identical physical properties (melting point, boiling point, solubility) but rotate plane-polarized light in opposite directions (one rotates it clockwise, the other counterclockwise), a phenomenon known as optical activity

## D,L, R,S and E,Z- configuration

In organic chemistry, especially when discussing stereochemistry, terms like D/L and R/S configurations are used to describe the spatial arrangement of atoms or groups around a chiral center. Similarly, E/Z notation is used to describe the configuration of double bonds in organic molecules. Here's a brief explanation and examples of each:

### D/L Configuration:

- **D/L notation** is used to describe the configuration of the highest numbered chiral center in a molecule, based on its relationship to glyceraldehyde.
- **D** indicates that the hydroxyl group (OH) on the highest numbered chiral center is on the right side in a Fischer projection of the molecule.
- **L** indicates that the hydroxyl group (OH) on the highest numbered chiral center is on the left side in a Fischer projection.

### Example:

- **D-Glucose:** In D-glucose, the hydroxyl group on the highest numbered chiral center (C5) is on the right side in a Fischer projection.

### R/S Configuration:

- **R/S notation** is used to describe the absolute configuration of each chiral center in a molecule based on the Cahn-Ingold-Prelog priority rules.
- **R** (rectus) indicates a clockwise arrangement of substituents around a chiral center.
- **S** (sinister) indicates a counterclockwise arrangement of substituents around a chiral center.

### Example:

- **R-2-Chlorobutane:** In R-2-chlorobutane, the chlorine atom is attached to the chiral center (C2) with a configuration that is clockwise when viewed from above.

## E/Z Configuration:

- **E/Z notation** is used to describe the configuration of double bonds in alkenes based on the priority of substituents around the double bond.
- **E** (entgegen) indicates that the highest priority substituents on each carbon of the double bond are on opposite sides.
- **Z** (zusammen) indicates that the highest priority substituents on each carbon of the double bond are on the same side.

### Example:

- **E-2-Butene:** In E-2-butene, the two highest priority groups (H and CH<sub>3</sub>) on each carbon of the double bond are on opposite sides.

These notations are crucial in organic chemistry for accurately describing the three-dimensional structures of molecules, especially when they have chiral centers or double bonds that can exist in different spatial arrangements.

## Racemic mixture – Resolution of racemic mixtures

### Racemic Mixture:

A racemic mixture, in chemistry, refers to a mixture that contains equal amounts of two enantiomers (mirror-image stereoisomers) of a chiral molecule. Enantiomers are molecules that are non-superimposable mirror images of each other and differ only in their spatial arrangement around one or more chiral centers.

### Resolution of Racemic Mixtures:

Resolution of racemic mixtures involves separating the two enantiomers from each other, thereby obtaining pure samples of each enantiomer separately. This process is crucial in many fields, especially in pharmaceuticals where often only one enantiomer (the "active" or "desired" form) is therapeutically effective, while the other might be inactive or even harmful.

Here are three common techniques for the resolution of racemic mixtures:

1. **Crystallization with Chiral Resolving Agents:**
  - **Principle:** A chiral resolving agent, which is itself a chiral compound, is added to the racemic mixture. The resolving agent selectively forms a diastereomeric crystalline complex with one of the enantiomers, leaving the other enantiomer in solution.
  - **Procedure:** The mixture is treated with the resolving agent, and then the diastereomeric crystals are separated from the solution by filtration or other means. The pure enantiomer can then be obtained by dissociating the complex or by further purification steps.
2. **Enzymatic Resolution:**

- **Principle:** Enzymes are highly stereoselective catalysts that can selectively react with one enantiomer of a racemic mixture. This method is particularly useful because enzymes often exhibit high specificity and efficiency under mild conditions.
  - **Procedure:** The racemic mixture is treated with an enzyme that preferentially reacts with one enantiomer, converting it into a product that can be separated from the unchanged enantiomer. After separation, the enzyme can sometimes be recovered and reused.
3. **Chromatographic Resolution:**
- **Principle:** Chromatography techniques exploit differences in the interaction between the stationary phase and the enantiomers to separate them.
  - **Methods:**
    - **High-Performance Liquid Chromatography (HPLC):** Uses a chiral stationary phase (CSP) that interacts differently with each enantiomer, leading to their separation as they pass through the column.
    - **Gas Chromatography (GC):** Similar to HPLC but with a gas phase, where enantiomers are separated based on differences in volatility and interactions with the stationary phase.
    - **Thin-Layer Chromatography (TLC):** Enantiomers are separated on a thin layer of adsorbent material by differential migration.

Each of these techniques has its advantages and limitations depending on factors such as the nature of the racemic mixture, the desired purity of the enantiomers, and the scale of the separation required.