DIRECTOR OF DISTANCE & CONTINUING EDUCATION
MANONMANIAM SUNDARANAR UNIVERSITY
TIRUNELVELI-627012

OPEN LEARNING AND DISTANCE LEARNING (ODL) PROGRAMME

(for those who joined the programmes from the academic year 2023-2024)

B.Sc Chemistry

Course material**- Core III-General Chemistry-II**

Course code-**JMCH21**

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UNIT-I Acids, bases and Ionic equilibria

Concepts of Acids and Bases - Arrhenius concept, Bronsted-Lowry concept, Lewis concept; Relative strengths of acids, bases and dissociation constant; dissociation of poly basic acids, ionic product of water, pH scale, pH of solutions; Degree of dissociation, common ion effect, factors affecting degree of dissociation; acid base indicators, theory of acid base indicators – action of phenolphthalein and methyl orange, titration curves - use of acid base indicators;

Buffer solutions – types, mechanism of buffer action in acid and basic buffer, Henderson-Hasselbalch equation;

Salt hydrolysis - salts of weak acids and strong bases, weak bases and strong acids, weak acids and weak bases - hydrolysis constant, degree of hydrolysis and relation between hydrolysis constant and degree of hydrolysis;

Solubility product - determination and applications; numerical problems involving the core concepts.

Unit-II Chemistry of s - Block Elements

Hydrogen: Position of hydrogen in the periodic table. Alkali metals: Comparative study of the elements with respect to oxides, hydroxides, halides, carbonates and bicarbonates. Diagonal relationship of Li with Mg. Preparation, properties and uses of NaOH, Na_2CO_3, KBr, KClO3 alkaline earth metals. Anomalous behaviour of Be.

Chemistry of p- Block Elements (Group 13 & 14) -preparation and structure of diborane and borazine. Chemistry of borax. Extraction of Al and its uses. Alloys of Al. comparison of carbon with silicon. Carbon-di-sulphide – Preparation, properties, structure and uses. Percarbonates, per monocarbonates and per dicarbonates.

UNIT-III Chemistry of p- Block Elements (Group 15-18)

General characteristics of elementsof Group 15; chemistry of $H_2N\text{-}NH_2$, NH_2OH, NH_3 and HNO_3. Chemistry of PH_3, PCl_3, PCl_5, $POCl_3$, P_2O_5 and oxy acids of phosphorous (H_3PO_3 and H_3PO_4).

General properties of elements of group16 - Structure and allotropy of elements - chemistry of ozone - Classification and properties of oxides - oxides of sulphur and selenium – Oxy acids of sulphur (Caro’s and Marshall’s acids).

Chemistry of Halogens: General characteristics of halogen with reference to electronegativity, electron affinity, oxidation states and oxidizing power. Peculiarities of fluorine. Halogen acids (HF, HCl, HBr and HI), oxides and oxy acids ($HClO_4$). Inter-halogen compounds (ICl, ClF_3, BrF_5 and IF_7), pseudo halogens [$(CN)_2$ and $(SCN)_2$] and basic nature of Iodine.

Noble gases: Position in the periodic table. Preparation, properties and structure of XeF_2, XeF_4, XeF_6 and $XeOF_4$; uses of noble gases - clathrate compounds.

UNIT-IV Hydrocarbon Chemistry-I

Petroproducts: Fractional distillation of petroleum; cracking, isomerisation, alkylation, reforming and uses.

Alkenes-Nomenclature, general methods of preparation – Mechanism of elimination reactions – E1 and E2 mechanism - factors influencing – stereochemistry – orientation – Hofmann and Saytzeff rules. Reactions of alkenes – addition reactions – mechanisms – Markownikoff's rule, Kharasch effect, oxidation reactions – hydroxylation, oxidative degradation, epoxidation, ozonolysis; polymerization.

Alkadienes - Nomenclature - classification – isolated, conjugated and cumulated dienes; stability of conjugated dienes; mechanism of electrophilic addition to conjugated dienes - 1, 2 and 1, 4 additions; free radical addition to conjugated dienes– Diels–Alder reactions – polymerisation – polybutadiene, polyisoprene (natural rubber), vulcanisation, polychloroprene.

Alkynes -Nomenclature; general methods of preparation, properties and reactions; acidic nature of terminal alkynes and acetylene, polymerisation and isomerisation.

Cycloalkanes: Nomenclature, Relative stability of cycloalkanes, Bayer's strain theory and its limitations. Conformational analysis of cyclohexane, mono and di substituted cyclohexanes. Geometrical isomerism in cyclohexanes.

UNIT-V Hydrocarbon Chemistry - II

Benzene: Source, structure of benzene, stability of benzene ring, molecular orbital picture of benzene, aromaticity, Huckel's (4n+2) e- rule and its applications. Electrophilic substitution reactions - General mechanism of aromatic electrophilic substitution - nitration, sulphonation, halogenations.

Friedel-Craft's alkylation and acylation. Mono substituted and disubstituted benzene - Effect of substituent – orientation and reactivity.

Polynuclear Aromatic hydrocarbons: Naphthalene – nomenclature, Haworth synthesis; physical properties, reactions – electrophilic substitution reaction, nitration, sulphonation, halogenation, Friedel – Crafts acylation & alkylation, preferential substitution at o-,p- or m-position – reduction, oxidation – uses. Anthracene – synthesis by Elbs reaction, Diels – Alder reaction and Haworth synthesis; physical properties; reactions - Diels-Alder reaction, preferential substitution at C-9 and C-10; uses.

Reference book

i. Maron S H and Prutton C P, (1972), Principles of Physical Chemistry, 4th ed., The Macmillan Company, Newyork.
ii. Barrow G M, (1992), Physical Chemistry, 5th ed., Tata McGraw Hill, New Delhi.
iii. Lee J D, (1991), Concise Inorganic Chemistry, 4thed., ELBS William Heinemann, London.
iv. Huheey J E, (1993), Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed., Addison Wesley Publishing Company, India.
v. Gurudeep Raj, (2001), Advanced Inorganic Chemistry Vol – I, 26th ed., Goel Publishing House, Meerut.
vi. Agarwal O P, (1995), Reactions and Reagents in Organic Chemistry, 8thed., Goel Publishing House,Meerut.

Website e-learning

i. https://onlinecourses.nptel.ac.inhttp://cactus.dixie.edu/smblack/chem1010/lecture_notes/4B.html
ii. http://www.auburn.edu/~deruija/pdareson.pdfhttps://swayam.gov.in/course/64-atomic-structure-and-chemical-bonding

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CONCEPTS OF ACIDS AND BASES

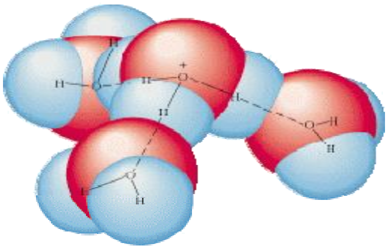
Acid-Base Concepts

- The Arrhenius concept
- The Bronsted Lowry concept
- The Lewis concept

The Arrhenius Definition

According to the Arrhenius concept of acids and bases,

- An acid is a substance that, when dissolved in water, increases the concentration of hydronium ion (H_3O^+) (produces H^+).



The $H_3O^+$is shown here hydrogen bonded to three water molecules.

- A base, in the Arrhenius concept, is a substance that, when dissolved in water, increases the concentration of hydroxide ion, OH^-(aq) (produces OH^-).

Arrhenius Concept of Acids and Bases

In the Arrhenius concept, a strong (100%) acid is a substance that ionizes completely in aqueous solution to give H_3O^+(aq) and an anion.

An example is perchloric acid, $HClO_4$.

$$HClO_{4.(aq)} + H_2O(I) \longrightarrow H_3O^+(aq) + ClO_4^-{}_{(aq)}$$

$$HClO_{4.(aq)} \longrightarrow H^+(aq) + ClO_4^-{}_{(aq)}$$

In the Arrhenius concept, a strong (100%) base is a substance that dissociates completely in aqueous solution to give OH-(aq) and a cation.

An example is sodium hydroxide, NaOH (ionic).

$$NaOH_{(S)} \longrightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)}$$

Some weak acids and bases not completely ionized and exist in reversible reaction with the corresponding ions.

$NH_4OH(aq) \rightleftharpoons NH4^+(aq) + OH^-(aq)$ Since Ammonium hydroxide, NH_4OH, is a weak base

$CH_3COOH(aq) + H_2O(I) \rightleftharpoons H_3O^+(aq) + CH_3COO^-$ Since Acetic acid, CH_3COOH is a weak acid.

The Brønsted-Lowry Definition

According to the Brønsted-Lowry concept,

- An acid is the species donating the proton in a proton-transfer reaction
- A base is the species accepting the proton in a proton-transfer reaction.

In any reversible acid-base reaction, both forward and reverse reactions involve proton transfer.

Consider the reaction of NH_3 and H_2O.

Based on Arrhenius theory (produces OH-) therefore NH_3 is a base in water.

$$NH_3 + H_2O(I) \rightleftharpoons NH4^+(aq) + OH^-(aq)$$

- In the forward reaction, NH_3 accepts a proton from H_2O. Thus, NH_3 is a base and H_2O is an acid.
- In reversible reaction, there are also acid/base components. NH_4^+ donates a proton to OH^-. The NH_4^+ ion is the acid and OH^- is the base.

The species NH_4^+ / NH_3 and H_2O/ OH^- are conjugate acid-base pair.

A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the loss or gain of one proton.

$$NH_3 + H_2O(I) \rightleftharpoons NH4^+(aq) + OH^-(aq)$$

Base 1 Acid 2 Acid 1 Base 2

NH_4^+ is the conjugate acid of NH_3 and NH_3 is the conjugate base of NH_4^+ (NH_4^+ /NH_3).

H_2O is the conjugate acid of OH^- and OH^- is the conjugate base of H_2O (H_2O/OH^-).

An amphoteric species

Some species can act as an acid or a base (it can gain or lose a proton) called an amphoteric species

I. Carbonic acid

For example, HCO_3^- acts as a proton donor (an acid) in the presence of OH-

$$HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$$

Acid base

HCO_3^- acid and CO_3^{2-} conj base & OH^- base and H_2O conj acid

Alternatively, HCO_3^- can act as a proton acceptor (a base) in the presence of HF. Proton accepter and base in this reaction. HCO_3^- base, H_2CO_3 conj acid, HF acid, F^- conj base.

$$HCO_3^-(aq) + HF(aq) \longrightarrow H_2CO_3(aq) + F^-(l)$$

base Acid

HCO_3^- base and H_2CO_3 conj acid & HF acid and F^- conj base

II. Water

The amphoteric characteristic of water is important in the acid-base properties of aqueous solutions.

Water reacts as an acid with the base NH_3.

$$NH_3(aq) + H_2O(I) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Base Acid

NH_3 base and NH_4^+ conj acid & H_2O acid and OH^- conj base

Water can also react as a base with the acid HF

$$HF(aq) + H_2O(I) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Acid base

H_2O base and H_3O^+ conj acid & HF acid and F^- conj base

In the Brønsted-Lowry concept:

i. A base is a species that accepts protons; OH^- is only one example of a base.

ii. Acids and bases can be ions as well as molecular substances.

iii. Acid-base reactions are not restricted to aqueous solution but most of what we do will be.

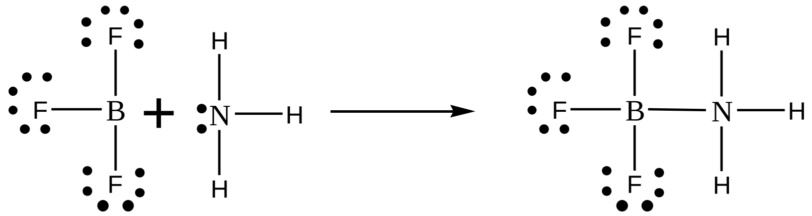
iv. Some species can act as either acids or bases depending the other reactant.

The Lewis concept

The Lewis concept defines an acid as an electron pair acceptor and a base makes available electron pair.

Lewis Concept of Acids and Bases

The reaction of boron trifluoride with ammonia is an example.



Boron trifluoride accepts the electron pair, so it is a Lewis acid. Ammonia makes available the electron pair, so it is the Lewis base.

Relative Strength of Acids and Bases

If an acid loses its H^+, the resulting anion is now in a position to reaccept a proton, making it a Brønsted-Lowry base.

It is logical to assume that if an acid is considered strong, its conjugate base (that is, its anion) would be weak, since it is unlikely to accept a hydrogen ion. It wants to donate proton as soon as it accepts a proton.

In other words, the stronger the acid, the weaker the conjugate base and vice-versa

- The stronger the conj acid is an acid, the weaker its conj base is a base.
- The stronger the conj base is a base, the weaker its conj acid is an acid.

$HCl + H_2O \text{-->} H_3O^+ + Cl^-$

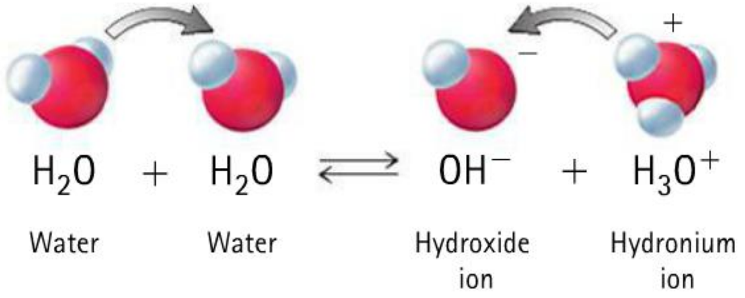
strong acid	extremely weak base,
$HCN + H_2O \text{<-->} H_3O^+ + CN^-$	
weak acid	stronger base than Cl

HCl stronger acid than HCN; therefore, CN- stronger base than Cl-

Ionic product of water

Pure water is a weak electrolyte. Weak because it does not completely disassociates into hydrogen and hydroxide but exist in equilibrium with these two ions. It is neutral in nature, i.e., H+ ion concentration is exactly equal to OH- ion concentration

$$[H^+] = [OH^-]$$



Autoionization of Water

Self-ionization is a reaction in which two like molecules react to give ions (amphiprotic therefore can react with self)

In the case of water, the following equilibrium is established.

$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$

The equilibrium-constant expression for this system is:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The concentration of ions is extremely small (equil lies to far left), so the concentration of H2O remains essentially constant. This gives

$$[H_2O]^2 K_c = [H_3O^+][OH^-]$$

$$H_2O(I) + H_2O(I) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_W = [H_3O^+][OH^-]$$

At 25°C, the value of K_w is 1.0×10^{-14}.

Like any equilibrium constant, K_w varies with temperature. K_w means water + water and basis of acid/base scale in aqueous solutions

Because we often write H_3O^+ as H^+, the ion product constant expression for water can be written:

$$K_w=[H^+][OH^-]$$

Using K_w you can calculate the concentrations of H+ and OH- ions in pure water.

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as salt hydrolysis. It is defined as a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.

The degree of dissociation

The degree of dissociation, usually denoted by the symbol α, is a quantity that quantitatively describes the dissociation of electrolytes in solution. This concept was first introduced by Arrhenius and is often used to compare the strength of electrolytes. The degree of dissociation of the electrolyte α in the first approximation determines the amount of dissociation. It is expressed as the ratio of the number of moles of molecules dissociated into ions to the number of moles of solute molecules.

$$\alpha = \frac{n_z}{n_0} \times 100\ \%$$

where:

n_z – number of moles of molecules dissociated into ions,

n_0 – number of moles of solute molecules.

The value of the degree of dissociation is less than or equal to one.

It can also be expressed as a percentage.

- If the degree of dissociation is equal to or close to one, then the electrolyte is almost completely dissociated into ions and the electrical conductivity of such a solution is significant. It turns out that strong electrolytes completely dissociate ($\alpha = 1$),
- If weak electrolytes have $\alpha < 1$. For weak electrolytes, the dissociation degree values are several percent.

The degree of dissociation depends on:

- type of electrolyte and type of solvent,
- solution concentration,
- temperature,
- presence of other electrolytes in the solution.

i. Type of electrolyte

The basic factor determining the value of the degree of dissociation is the binding strength in the molecule that undergoes dissociation. An example would be the

HF molecule. Although the H – F bond is much more polar than the H – Cl bond, HF is a weak electrolyte and HCl is a strong electrolyte. Part of this is due to the very strong H – F bond, as a result of which hydrogen is difficult to separate.

ii. Type of solvent

The solvent can significantly affect the value of the degree of dissociation of a given electrolyte. For example, under comparable conditions, hydrochloric acid (HCl) is 100% dissociated in water, and in benzene, the dissociation rate of this acid is $\alpha < 1\%$.

iii. Solution concentration

The concentration has an important influence on the degree of dissociation. Measurements showed that α increase with dilution of the electrolyte and in very dilute solutions all electrolytes show a degree of dissociation close to one, i.e. almost all molecules or groups of solute ions dissociate into ions. The above is due to Ostwald's law of dilution.

iv. Temperature

The degree of dissociation increases with increasing temperature, but the effect is small.

The dissociation constant

The dissociation of weak electrolytes can be viewed as a reversible chemical reaction. The weak electrolyte of the general formula AB undergoes dissociation in aqueous solution according to the equation:

$$AB \rightleftharpoons A^{+} + B^{-}$$

Since electrolytic dissociation is a reversible process, there is equilibrium in the electrolyte solution for which you can write the expression for the equilibrium constant(K_c)

$$K_c = \frac{[A^+][B^-]}{AB} = Constant$$

$[A^+][B^-]$ = actual ion concentration at equilibrium,

$[AB]$ =the actual concentration of undissociated molecules.

Example

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^{-}$$

$$K_c = \frac{[Mg^{2+}][OH^-]^2}{Mg(OH)_2} = Constant$$

The constant K_c of electrolytes at a given temperature is practically constant, independent of concentration. Therefore, it can be used as an exact measure of the power of electrolytes, much more accurate than the degree of dissociation (α), which depends on the concentration.

The stronger the electrolyte, the greater the value of the constant Kc.

K_c dissociation constants values for selected acids at 298K

Type of acid	Dissociation constant
Strong acids	
HI	$K= 1.0\times10^{10}$
HBr	$K= 3.0\times10^{9}$
HCl	$K= 1.0\times10^{7}$
H_2SO_4	$K_1= 1.0\times10^{3}$ $K_2= 1.2\times10^{-2}$
Medium-strength acids	
$HClO_2$	$K= 1.0\times10^{-2}$
H_2SO_3	$K_1= 1.6\times10^{-2}$ $K_2= 6.3\times10^{-8}$
H_3PO_4	$K_1= 7.5\times10^{-3}$ $K_2= 6.3\times10^{-8}$ $K_3= 1.3\times10^{-12}$
Weak acids	
HNO_2	$K= 2.0\times10^{-4}$
H_2CO_3	$K_1= 4.5\times10^{-7}$ $K_2= 4.7\times10^{-11}$
H_2S	$K_1= 6\times10^{-8}$ $K_2= 1.0\times10^{-14}$
H_3BO_3	$K_1= 5.8\times10^{-10}$ $K_2= 1.8\times10^{-13}$ $K_3= 1.6\times10^{-14}$

K_b dissociation constants values for selected hydroxides at 298K

Type of hydroxide	Dissociation constant
Strong hydroxides	
NaOH	$K>10^{14}$
KOH	$K>10^{14}$
LiOH	$K>10^{14}$
RbOH	$K>10^{14}$
Weak hydroxides	
$Mg(OH)_2$	$K=2.5\times10^{-3}$
$Fe(OH)_2$	$K=1.3\times10^{-4}$
$Cu(OH)_2$	$K=1.3\times10^{-4}$
$Zn(OH)_2$	$K=4.0\times10^{-5}$
$Al(OH)_3$	$K=1.4\times10^{-9}$

Sum up, in the case of hydroxides, it can be assumed that strong hydroxides form only metals in the I and II main groups, and not all of them, because calcium hydroxide $Ca(OH)_2$ by some authors, due to the value of the constant Kb is considered a medium-strength hydroxide, and magnesium hydroxide $Mg(OH)_2$ and beryllium hydroxide are weak hydroxides. The hydroxides of the metals of the remaining groups form weak hydroxides. Among other common hydroxides, a weak hydroxide is also ammonium hydroxide NH4OH, the constant of which has the value $K_b = 1.8\times10^{-5}$

Ostwald's law

Ostwald's law captures the relationship between the degree of dissociation and the dissociation constant. For e.g. weak acetic acid CH_3COOH, with initial concentration C, dissociation is as follows:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

After the dissociation of acetic acid, the equilibrium state, the concentrations of hydrogen, acetate and undissociated acid in the solution are respectively:

$$K_a = [CH_3COO^-][H^+]/[CH_3COOH]$$

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of Dissociation of CH_3COOH	α	-	-
Number of moles at equilibrium	1- α	α	α
Equilibrium concentration	(1- α)C	αC	αC

Substituting the Equilibrium concentration in the equation

$K_a = (\alpha C)(\alpha C)/(1-\alpha)C$

$K_a = (\alpha^2 C^2)/(1-\alpha)C$

$K_a = \alpha^2 C/(1-\alpha)$ -----------------(i)

We know that weak acid dissociate only to a very small extent compared to one, a is so small

Equation (1) becomes,

$K_a = \alpha^2 C$

$\alpha^2 = K_a/C$

$\alpha = \sqrt{(K_a/C)}$

The concentration of H can be calculated using the k_a value as below

$[H^+] = \alpha C$

$\alpha = [H^+]/C$ -----------------(ii)

Equating (i) & (ii)

$[H^+]/C = \sqrt{(K_a/C)}$

$[H^+] = [\sqrt{(K_a/C)}] \times C$

$$[H^+] = \sqrt{\left\{\frac{K_a \times C^2}{C}\right\}}$$

$[H^+] = \sqrt{K_a} \times C$

For acid $[H^+] = \sqrt{(K_a \times C)}$

For bases $[OH^-] = \sqrt{(K_b \times C)}$

The Common-Ion Effect

- Weak acid or weak base will partially ionize in aqueous solution.
- Ionic compounds (i.e. salts) dissociate completely in aqueous solution
  - ✓ Some salts may contain ions derived from acids or bases
  - ✓ Ions derived from strong acids or bases will not alter the pH

- ✓ Ions derived from weak acids or bases will have a tendency to affect pH, either donate or accept a proton

What happens if a salt is added to a solution of a weak acid, and that salt contains a conjugate base to the weak acid?

Example: Acetic acid CH_3COOH

The ionization of acetic acid, a weak acid, is as follows:

$$CH_3COOH \longrightarrow H^+ + CH_3COO^-$$

Add some Sodium Acetate salt.

Sodium acetate will dissociate completely in solution:

$$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$$

If acetate conjugates base concentration increases by without increasing the concentration of H^+

Le Chatelier's - equilibrium will *shift to the left*

$$CH_3COOH \longleftarrow H^+ + CH_3COO^-$$

- will also result in a decrease in the H^+ concentration – raise pH
- less acid will dissociate

The "Common Ion Effect": The dissociation of a weak electrolyte is decreased by adding to the solution a strong electrolyte (i.e. a salt) that has an ion in common with the weak electrolyte

Example

Acetic acid (CH_3COOH) is a weak acid with the following ionization reaction:

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad K_a = 1.8 \times 10^{-5}$

What is the pH of a solution that is 0.5M in acetic acid and 2.5M in sodium acetate, CH_3COONa?

$$1.8 \times 10^{-5} = [CH_3COO^-][H_3O^+]/[CH_3COOH]$$

X M = amount of acetic acid that dissociates

Then X M of H_3O^+ and $CH3COO^-$ ions are formed

$$1.8 \times 10^{-5} = (X + 2.5)\ (X)/\ (0.5 - X)$$

$$1.8 \times 10^{-5} = (X + 2.5)(X)/(0.5 - X) \approx (2.5)(X)/(0.5)$$

$$9.0 \times 10^{-6} = 2.5X$$

$$X = 3.60 \times 10^{-6}$$

$$= [H^+]$$

$pH = -\log[H^+] = -\log(3.60 \times 10^{-6}) = 5.44$

pH

pH is a measure of how acidic or basic a substance is. In our everyday routine, we encounter and drink many liquids with different pH. Water is a neutral substance.

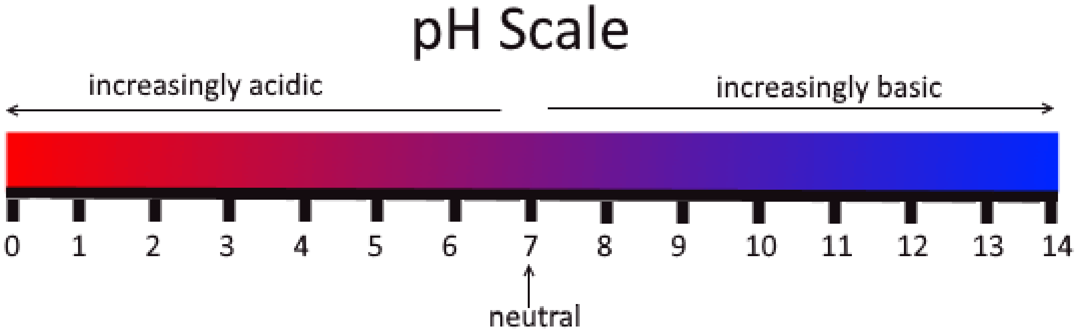
- pH is a measure of how basic or acidic a substance is. pH has a range of 0-14. A pH greater than 7 means the substance is basic. A pH less than 7 means the substance is acidic. When the pH is exactly 7 that indicates that the substance is neutral.
- An acidic substance is anything that will give up a proton. A basic substance will accept a proton.

The pH formula is:

$$\text{pH} = -\log([H^+])$$

The formula for pH is shown above. pH is defined as the negative log base 10 of the hydronium concentration.

This formula for pH is discussed in more detail in a section below, including how to use the pH formula.



The pH scale starts from the number 0 and ends at the number 14. These numbers allow the classification of substances based on their pH;

- The most acidic substances will be close to 0, while the most basic or alkaline substances will be close to 14.
- The lower the pH, the more H^+ ions will be present and the stronger the acid. The most basic or alkaline substances will have a classification between 7 and 14.

Converting pH to H^+

$$[H^+] = 10^{-\text{pH}}$$

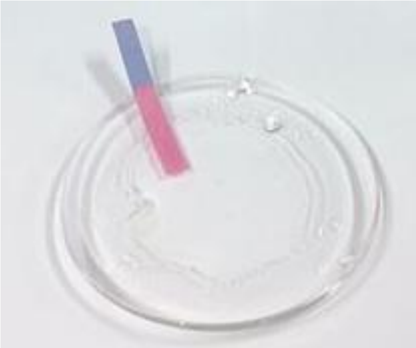
Using this equation, we find that if the pH of a solution is 7, then $[H^+] = 10^{-7}$ M. If the pH of a solution is 0, then $[H^+] = 10^{-0}$ M = 1M (a one molar solution), and if the pH of a solution is 14, then $[H^+] = 10^{-14}$ M.

Measuring pH

There are several ways to measure the pH of a substance in the laboratory, at home, or in the field.

i. pH Probe: A pH probe is an instrument that has an arm with two small electrodes in it. The arm is placed in a substance and the electrodes respond to the pH of the solution. The pH is typically displayed on a small screen. There are both large and small portable models of this instrument

ii. Litmus paper: Litmus paper is a thin strip of paper that changes color based on the pH of the solution it is dipped in to. This pH indicator can be found at some pet supply stores to test the pH of aquariums



iii. Chemical Indicators: Chemical indicators are chemicals you can place into solution that will change the color of the solution as the pH changes. Some common ones are phenolphthalein, bromthymol blue, and litmus.

INDICATORS

INDICATORS are those substance employed to determine the end point of a volumetric titration. Indicators are either organic weak acid or weak bases having different colours in different medium . Phenolphthalein, methyl orange, litmus solution, methyl red and etc are **acid - base indicators.**

An Indicator is also defined as a substance which indicates completion of acid-base titration or end point by changing its colour within limits with variation in PH of the solution to which it is added.

THEORY OF INDICATORS

There are two theory of indicators as given below :-

(1) Ostwald's theory (2) Quinonoid's theory

OSTWALD'S THEORY

Ostwald's theory is as follows:-

- The indicators are weak electrolytes whose ionized form has different colour than the unionized form. The colour change is due to ionization of the indicator.
- Since indicators are weak acids or bases so the ionization of the indicator is largely affected in acids and bases. IF the indicator is weak acid, its ionization is very much low in acids due to common H^+ ions while it is fairly ionized in alkalies . Similarly if the indicator is a weak base, its ionization is large in acids and low in alkalies due to common OH^- ions.

The above theory can be understood by considering two important indicators methyl orange and phenolphthalein as given below:

PHENOLPHTHALEIN

Phenolphthalein is weak acid whose unionized molecule is colourless but its ionized form has pink colour and it ionises as given below

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{Pink}}{Ph^-}$$

When phenolphthalein is added to acid the above equilibrium shifts towards left due to increase in concentration of H^+ and hence the ionization of indicator is suppressed consequently solution becomes colourless. On the other hand when phenolphthalein is added to an alkaline solution eg NaOH , KOH, the OH^- produced by alkali reacts with H^+ and forms feebly dissociated molecule of H_2O due to this above equilibrium shifts towards right and hence concentration of Ph ions increases in solution and solution becomes pink .

$$HPh + OH^- \rightleftharpoons H^+ + Ph^-$$

But when phenolphthalein is added to solution of salt of weak base and strong acid eg NH_4OH then only few OH- ions with which H^+ ions of phenolphthalein may combine and thus equilibrium is not shift sufficiently right and pink colour is not appeared boldly.

METHYL ORANGE

Methyl orange is a weak base and can be represented by MeOH. Its unionized form is yellow which gives red coloured Me+ ions on ionization.

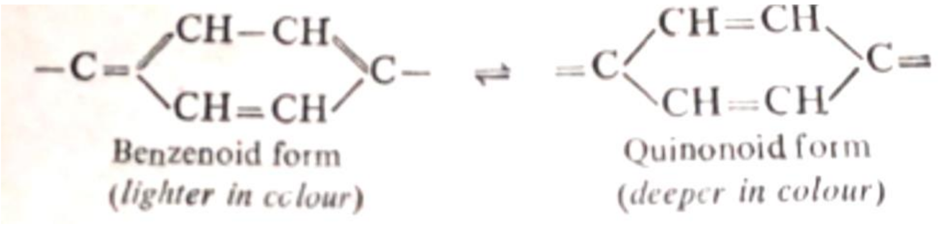
$$\underset{\text{Yellow}}{MEOH} \rightleftharpoons \underset{\text{red}}{Me^+} + \underset{\text{colourless}}{OH^-}$$

When solution of methyl orange is added to an alkali solution, due to excess common ion OH- the ionization of MeOH is suppressed, and the solution remains yellow. When acid is added then H^+ ions of acid combine with OH- ions and form feebly ionized water and due to this above equilibrium shifts towards right and solution becomes red.

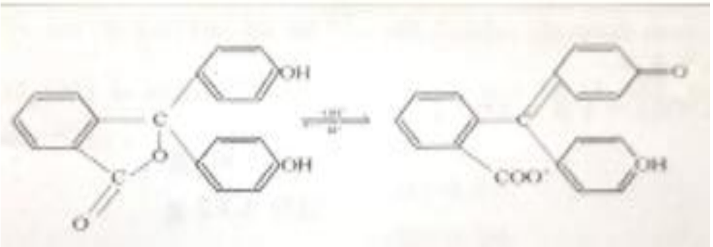
QUINONOID THEORY

QUINONOID THEORY is also known as modern theory. According to this theory, The acid -base indicators used in volumetric titration are organic aromatic compounds which exist in two tautomeric forms having different structures. One form is termed benzenoid form and the other quinonoid form .

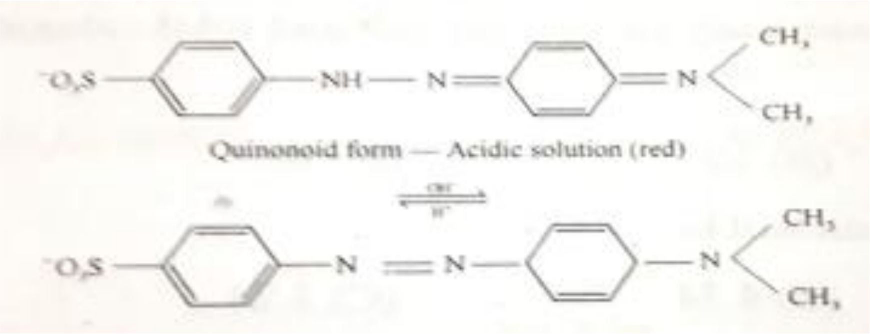
TWO forms having different colour remain in equilibrium. One form exists in acidic medium while other form exists in alkaline medium. The quinonoid form is usually deeper in colour then the benzenoid form. The colour change is due to the interconversion of one tautomeric form into other.



During titration the medium changes from acidic to alkaline or viceversa via neutral medium .The change in PH converts one tautomeric form into other and thus, the colour change occurs. Eg Phenolphthalein in acidic medium exists in benzenoid form so it is colourless but when medium of solution changes into alkaline medium it get converted into quinonoid form and colour of solution changes to pink.



eg methyl orange exists in two tautomeric forms. The quinonoid form has red colour in acidic medium while benzenoid form has yellow colour. when alkali solution is added to converts solution having methyl orange from acidic to alkaline medium then colour changes from red to yellow.



Titration Curve

Titration and indicators are vital tools in analytical chemistry, providing insights into the concentration and nature of acids and bases. This section focuses on the principles and applications of pH titration curves and the selection of appropriate indicators for acid-alkali titrations.

Purpose and Application

- Determining Concentration: Titration helps in calculating the molarity of unknown acids or bases.
- Acid-Base Reactions: Essential in understanding the neutralisation process.
- Quality Control: Widely used in industry for purity assessment.

Titration Curve Characteristics

1. Strong Acid and Strong Base Titration

   Initial pH: Starts low due to the high concentration of hydrogen ions in strong acids.

   Midpoint: Exhibits a rapid increase in pH near the equivalence point.

   Equivalence Point: pH is neutral (around 7) when equal amounts of acid and base have reacted.

Curve Feature: Characterised by a steep and symmetrical profile.

2. Strong Acid and Weak Base Titration

   Initial pH: Similar to strong acid-strong base titrations, it starts low.

   Equivalence Point: pH is acidic (less than 7), reflecting the weak base's inability to completely neutralise the acid.

   Curve Feature: Shows a less steep rise near the equivalence point due to the buffer effect of the weak base.

3. Weak Acid and Strong Base Titration

   Initial pH: Higher than strong acids, as weak acids have a lower concentration of hydrogen ions.

   Equivalence Point: pH is basic (greater than 7), due to the formation of the weak acid's conjugate base.

   Curve Feature: Begins with a gradual rise, followed by a steep increase as it approaches the equivalence point.

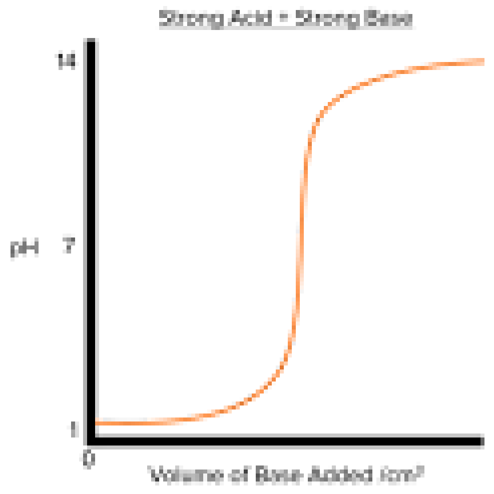
4. Weak Acid and Weak Base Titration

   Initial pH: Varies based on the relative strengths of the acid and base.

   Equivalence Point: Not sharply defined; the pH at this point is influenced by the strengths of the reactants.

   Curve Feature: Exhibits a broad and gradual slope, indicating a less distinct transition

1



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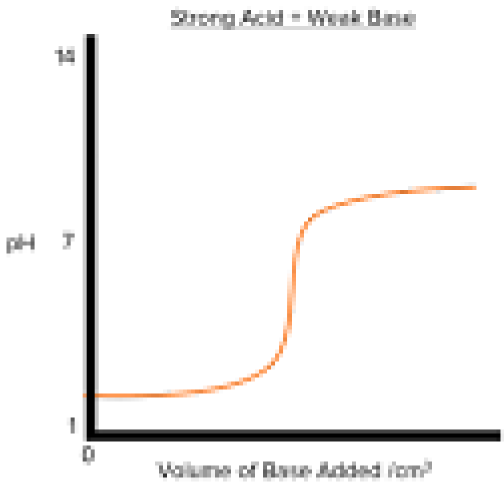

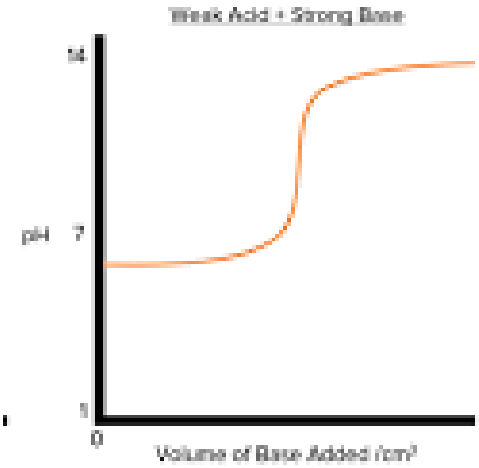

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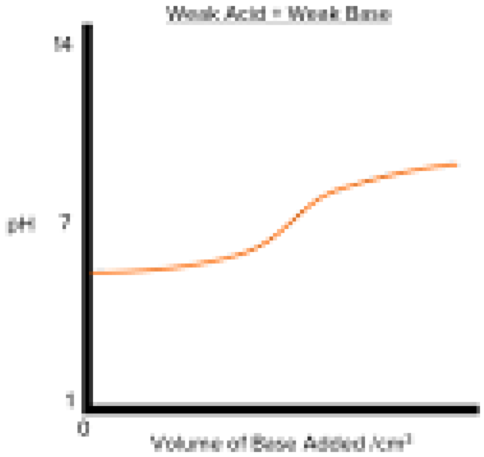

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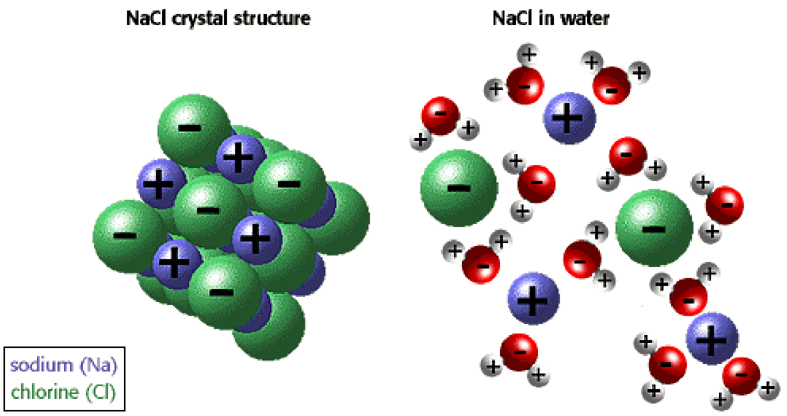
Hydrolysis of NaCl



Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H+ ions. Thus, the solution acquires acidic nature.

$M^+ + \ H_2O \rightleftharpoons MOH + H^+$ MOH= Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH- ions. Thus, the solution becomes basic.

$A^- + \ H_2O \rightleftharpoons HA \ + OH^-$ HA=Weak acid

The process of salt hydrolysis is actually the reverse of neutralization.

Salt + Water ⇌ Acid + Base

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

i. Salt of a strong acid and a weak base.

   Examples: $FeCl_3$, $CuCl_2$, $AlCl_3$, NH_4Cl, $CuSO_4$, etc.

ii. Salt of a strong base and a weak acid.

   Examples: CH_3COONa, NaCN, $NaHCO_3$, Na_2CO_3, etc.

iii. Salt of a weak acid and a weak base.

   Examples: CH_3COONH_4, $(NH_4)_2CO_3$, NH_4HCO_3, etc.

iv. Salt of a strong acid and a strong base.

   Examples: NaCl, K_2SO_4, $NaNO_3$, NaBr, etc.

Salt of a Strong Acid and a Weak Base

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base is reactive. It reacts with water to form a weak base and H+ ions.

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Consider, for example, NH_4Cl. It ionises in water completely into NH_4^+ and Cl^- ions react with water to form a weak base (NH_4OH) and H^+ ions.

$$NH4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$C(1\text{-}x) \qquad Cx \qquad Cx$$

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[Hx][NH_4OH]}{NH_4^+} = \frac{(x^2C)}{(1-x)} \qquad \text{------------(i)}$$

Where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{\left[NH_4^+][OH^-]\right]}{[NH_4OH]} = \frac{(x^2C)}{(1-x)} \qquad \text{------------(ii)}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-] \qquad \text{------------(iii)}$$

From eqs. (ii) and (iii)

$$\frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{NH_4^+} = K_h \qquad \text{------------(iv)}$$

$$\frac{K_w[NH_4^+]}{K_b[NH_4OH]} = [H^+] \qquad \text{------------(iv)}$$

$\log [H^+] = \log K_w - \log K_b + \log[\text{salt}]/[\text{base}]$

$-pH = -pK_w + pK_b + \log[\text{salt}]/[\text{base}]$

$pK_w - pH = pK_b + \log[\text{salt}]/[\text{base}]$

$pOH = pK_b + \log\{[\text{salt}]/[\text{base}]\}$

Relation between Hydrolysis Constant and Degree of Hydrolysis

The extent to which hydrolysis proceeds is expressed as the degree of hydrolysisand is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as *h* or *x.*

h = (Amount of salt hydrolysed)/ (Total salt taken)

Considering again eq. (i),

$K_h = x^2C/(1-x)$ or $K_h = h^2C/(1-h)$

When h is very small (1-h) → 1,

$K_h = h^2C \qquad h^2 = K_h \times 1/C$

$h = \sqrt{(K_h/C)}$

$h = \sqrt{[(K_w/K_b) \times C]}$

$[H^+] = h \times C \qquad = \sqrt{(K_h/C)} \times C$

$= \sqrt{[(K_h/C) \times (\sqrt{C}\times\sqrt{C}]}$

$= \sqrt{[(K_hC)]}$

$$=\sqrt{\left[\left(\frac{K_w}{K_b}\right)C\right]}$$

Taking negative log on both sides

$-\log [H^+] = -½ \log K_w + ½\log K_b - ½\log C$

$pH = ½pK_w - ½pK_b - ½\log C$

$= 7 - ½pK_b - ½\log C$

Salt of a Weak Acid and a Strong Base

A Strong Base The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a weak acid and OH- ions.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a weak acid, CH_3COOH and OH^- ions.

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

C(1-x) Cx Cx

Thus, OH- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$K_h = [CH_3COOH][OH^-]/[CH_3CO^-] = (Cx \times Cx)/C(1\text{-}x) = [(Cx2)/(1\text{-}x)]$ ---------(i)

Other equations present in the solution are:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = [CH_3COO\text{-}][H+]/[CH_3COOH]$ ---------(ii)

$H_2O \rightleftharpoons H^+ + OH^-$

$K_w = [H^+][OH^-]$ ---------
(iii)

From eqs. (ii) and (iii),

$K_w / K_a = [OH^-][CH_3COOH] / [CH_3COO\text{-}]$ ---------(iv)

$$[OH^-] = \frac{K_w[CH_3COO^-]}{K_a[CH_3COOH]}$$ ---------(v)

$\log [OH^-] = \log K_w - \log K_a + \log[salt]/[acid]$

$-pOH = -pK_w + pK_a + \log[salt]/[acid]$

$pK_w - pOH = pK_a + \log[salt]/[acid]$

$pH = pK_a + \log[salt/base]$

Considering eq. (i) again,

$K_x = Cx^2/(1\text{-}x)$ or $K_h = Ch^2/(1\text{-}h)$

When h is very small, (1-h) → 1

$K_h = Ch^2$

$h2 = K_h/C$

$h = \sqrt{}(Kh/C)$

$h = \sqrt{}(K_h/C)$

$h = \sqrt{}[(K_w/K_a) \times C]$

$[OH^-] = h \times C$

$= \sqrt{}(K_h/C) \times C$

$= \sqrt{} [(K_h/C) \times (\sqrt{C} \times \sqrt{C}]$

$=\sqrt{[(K_hC)]}$

$=\left[\ (\frac{K_w}{K_a})C\right]$

$[H^+] \quad = K_w/[OH^-]$

$= K_w / \sqrt{\left[\ (\frac{K_w}{K_a})C\right]}$

$= \sqrt{K_w} \times \sqrt{K_w} /[(\sqrt{K_w} \times \sqrt{C})/ \sqrt{K_a}]$

$= \sqrt{K_w} \times \sqrt{K_w} \times \sqrt{K_a} /[(\sqrt{K_w} \times \sqrt{C})]$

$= \sqrt{K_w} \times \sqrt{K_a} / \sqrt{C}$

Taking negative log on both sides

$-\log [H^+] \quad = -½ \log K_w - ½\log K_a + ½\log C$

$pH \quad = ½pK_w + ½pK_b + ½\log C$

$= 7 + ½pKa + ½\log C.$

Salt of a Weak Acid and a Weak Base

A Weak Base Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H+ and OFT ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt CH3COONH4. It gives CH3COO- and ions in solution. Both react with water.

$NH4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ (or) $CH_3COO^- + NH4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

Both the reaction occur with same speed, the solution is neutral.

CH_3COO^- +	$NH4^+$ +	$H_2O \rightleftharpoons$	CH_3COOH +	NH_4OH
C(1-h)	C(1-h)		Ch	Ch

$$K_h = \frac{[NH_4OH][CH_3COOH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = [CH_3COO^-][H^+]/[CH_3COOH]$ ---------(i)

$NH4OH \rightleftharpoons NH_4^+ + OH^-$

$K_b = [NH_4^+] [OH^-]/[NH4OH]$ ---------(ii)

$H_2O \rightleftharpoons H^+ + OH^-$

$K_w = [H^+][OH^-]$ --------- (iii)

From Eqs. (i), (ii) and (iii),

$$K_h = \frac{K_w}{K_a K_b}$$

$$= \frac{[NH_4OH][CH_3COOH]}{[CH_3COO^-][NH_4^+]} \quad \text{---------(iv)}$$

Let C be the concentration and h be the degree of hydrolysis

$K_h = h^2/(1-h)^2$

When h is small, (1-h) → 1.

$K_h = h^2$

$h = \sqrt{K_h}$

$= \sqrt{[K_w/(K_a \times K_b)]}$

$[H^+] = K_a \times h$

$$= \frac{K_a \times \sqrt{K_w}}{\sqrt{K_a} \times \sqrt{K_b}}$$

$$= \frac{\sqrt{K_a} \times \sqrt{K_a} \times \sqrt{K_w}}{\sqrt{K_a} \times \sqrt{K_b}}$$

$$= \frac{\sqrt{K_a} \times \sqrt{K_w}}{\sqrt{K_b}}$$

Taking negative logarithm on both sides

$-\log [H^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log K_w + \frac{1}{2}\log K_b$

$pH = \frac{1}{2}pK_a + \frac{1}{2}pK_w - \frac{1}{2}pK_b$

$= 7 + \frac{1}{2}pKa - \frac{1}{2}pKb$

- When $pK_a = pK_b$, pH = 7, i.e., solution will be neutral in nature.
- When $pK_a > pK_b$. The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7.
- In case $pK_a < pK_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

Salt of a Strong Acid and a Strong Base

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Such a salt, say NaCl, does not undergo hydrolysis as both the ions are not reactive. The solution is thus, neutral in nature.

Buffer Solutions

A buffer is a solution which can resist small changes in pH, restoring the pH to its original value.

Buffers only work when small amounts of acid or base are added: if large amounts are added then the buffer cannot cope and the pH will change significantly.

Buffers are commonly used in shampoos and biological washing powders.

Acidic Buffer Solutions

- An acidic buffer is made by adding a weak acid to a solution of one of its salts (its conjugate base) like for example, Acetic acid and sodium Acetate
- The Acetic acid is a weak acid and partially ionises setting up equilibrium:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+(aq)$$

- The salt fully ionises:

$$CH_3COONa \rightarrow CH_3COO^-\ (aq) + Na^+(aq)$$

- The buffer solution contains lots of undissociated acid molecules and lots of salt ions of the acid from the salt solution, and enough H+ ions so that the solution is acidic.

Calculating pH of Acidic Buffer Solutions

For calculating the pH of a buffer solution the Ka value of the acid in the buffer and the concentrations of both the acid and its salt has to know. The following assumptions have to be made:

- Equilibrium and initial concentrations of the conjugate base are the same. The salt is assumed to dissociate fully.
- Equilibrium and initial concentrations of the weak acid are the same. The acid only dissociates slightly.

Worked Example:

A buffer solution contains 0.05 mol of sodium acetate in a solution of 750 cm^3 of 0.0500 mol dm^{-3} Acetic acid. The solution is at 298 K. Calculate the pH of the buffer solution formed. Ka of Acetic acid at 298K = 1.76×10^{-5} mol dm^{-3}

Answer

Step 1: Calculate the concentration acetate ions

Concentration of acetate ions = moles/ volume = 0.05/(750/1000) = 0.06 mol dm^{-3}

Step 2: Calculate the H^+ ion concentration using Ka

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

Rearrange and substitute in values to find $[H^+]$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{1.76 \times 10^{-5} \times (0.05)}{(0.06)}$$

$$[H^+]=1.46 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 3: Calculate pH

$$pH = -\log_{10}[H^+]=4.83$$

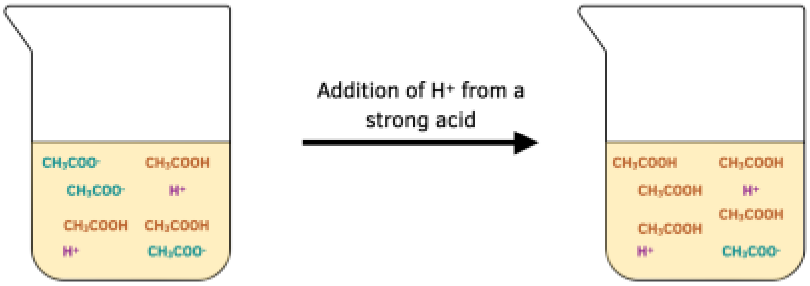
Adding an Acid to an Acidic Buffer

When H^+ ions are added to the acid buffer, they combine with some of the large quantity of acetate ions to make more undissociated acid molecules.

$$H^+ (aq) + CH_3COO^- (aq) \rightarrow CH_3COOH(l)$$

As a result:

- The amount of salt ions decreases. Excess acetate combine with the extra H^+ to form undissociated acetic acid.
- The amount of undissociated acid increases. H+ combines with acetate ions, more undissociated acetic acid forms.
- The pH stays more or less the same. The extra H^+ added immediately combine with the acetate ions and so the pH hardly changes.



Worked Example:

A buffer solution contains 0.05 mol of sodium acetate in a solution of 750 cm^3 of 0.0500 mol dm^{-3} acetic acid. The solution is at 298 K. 7.5 cm^3 of 2 mol dm^{-3} of hydrochloric acid is added to this buffer solution. Calculate the pH of the solution formed. (5 marks)

Ka of acetic acid at 298K = 1.76×10^{-5} mol dm^{-3}

Answer:

Step 1: Calculate the moles of hydrochloric and acetic acids

Moles of hydrochloric acid = 7.5/1000 x 2 = 0.015 mol

Moles of acetic acid = 750/1000 x 0.05 = 0.0375 mol

Step 2: Calculate the moles of acetate ions after the addition of HCl (1 mark)

When H^+ ions are added to the buffer, they react with some of the acetate ions from the salt solution:

H^+ (aq) + CH_3COO^- (aq) → CH_3COOH (l) – --------------- 1

The mole ratio of H^+: CH_3COO- = 1:1

Acetate ions are used up in the reaction, and decrease by the same number of moles of acid added.

Moles of acetate ions = 0.05 – 0.015 = 0.035 mol

Step 3: Calculate the new moles of acetic acid molecules

More acetic acid is made when H^+ ions are added.

Mole ratio of CH_3COOH: H^+ = 1:1 from equation 1

Moles of acetic acid = 0.0375 + 0.015 = 0.05 mol

Step 4: Calculate the H^+ ion concentration using Ka

$$K_a = \frac{[\mathrm{H}^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

Rearrange and substitute in values to find $[H^+]$

$$[\mathrm{H}^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{1.76 \times 10^{-5} \times (0.05)}{(0.035)}$$

$$[\mathrm{H}^+]=2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 5: Calculate pH

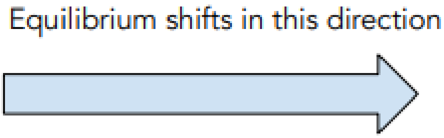
$$\text{pH} = -\log_{10}[\mathrm{H}^+]=4.60$$

Adding a Base to an Acidic Buffer

When OH- ions are added to an acidic buffer, they react with the H+ ions produced from the dissociated acid molecules. As the H+ ions are used up, the equilibrium shifts to the right.

For example with an acetic acid and acetate ion buffer:

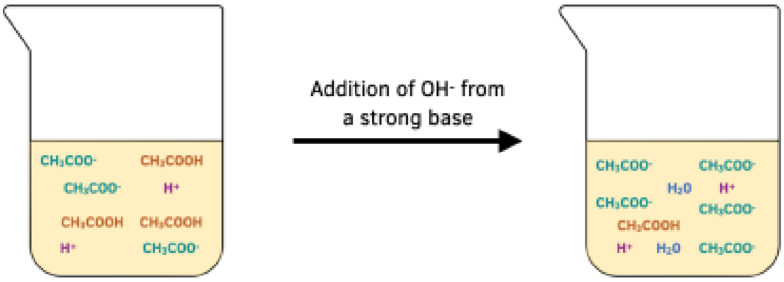
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$



$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+(aq)$$

As a result:

- The amount of undissociated acid decreases. As the position of equilibrium shifts, more undissociated acid is dissociated to replace the H^+ ions
- The amount of salt ions increases. As more undissociated acid is dissociated to replace the H^+ ions, more acetate ions are produced.
- The pH stays more or less the same. The extra OH^- added immediately combine with the H^+ ions in solution, which are quickly replenished as the position of equilibrium shifts to the right.



Worked Example:

A buffer solution contains 0.05 mol of sodium acetate in a solution of 750 cm^3 of 0.0500 mol dm^{-3} acetic acid. The solution is at 298 K.

7.5 cm^3 of 2 mol dm^{-3} of sodium hydroxide is added to this buffer solution. Calculate the pH of the solution formed. Ka of acetic acid at 298K = 1.76×10^{-5} mol dm^{-3}

Answer:

Step 1: Calculate the moles of sodium hydroxide (1) and initial moles of acetic acid

Moles of sodium hydroxide = 7.5/1000 x 2 = 0.015 mol

Moles acetic acid = 750/1000 x 0.05 = 0.0375 mol

Step 2: Calculate the moles of acetic acid after the addition of NaOH

When OH- ions are added to the buffer, they react with hydrogen ions from the dissociated acid molecules.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The mole ratio of $H^+ : OH- = 1:1$

So moles of H^+ ions reacting = 0.015 mol = moles of acetic acid molecules dissociated.

Acetic acid molecules, therefore, decrease by the same number of moles of base added.

Moles of acetic acid = 0.0375 – 0.015 = 0.0225 mol

Step 3: Calculate the new moles of acetate ions

More acetate ions are made is made when OH^- ions are added. The equilibrium reaction shifts to the right as H^+ ions are used up, producing more acetate ions.

Mole ratio of $CH_3COO^- : H^+ = 1:1$ from equation 1

Moles of acetate ions = 0.05 + 0.015 = 0.065 mol

Step 4: Calculate the H^+ ion concentration using Ka

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

Rearrange and substitute in values to find $[H^+]$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{1.76 \times 10^{-5} \times (0.0225)}{(0.065)}$$

$$[H^+]=5.9 \times 10^{-}6 \text{ mol dm}^{-3}$$

Step 5: Calculate pH

$$pH = -\log_{10}[H^+]=5.22$$

Basic Buffer Solutions

Basic buffers have a pH greater than 7. They are made by adding a weak base to its salt. For example, ammonia solution and ammonium chloride act as a basic buffer.

The salt fully dissociates:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

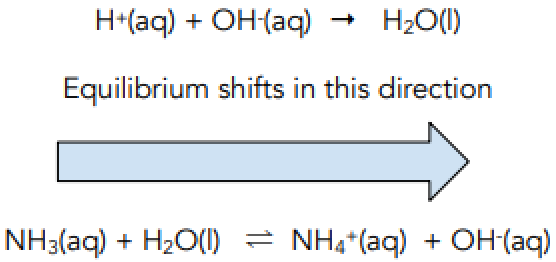
The ammonia solution partially dissociates:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The buffer solution contains lots of undissociated base molecules and lots of salt ions of the base from the salt solution, and enough OH^- ions so that the solution is basic.

Adding an Acid to a Basic Buffer

When H^+ ions are added to the basic buffer, they combine with OHions released when the ammonia molecules dissociate. The equilibrium shifts to the right to replace the OH^- ions.



$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

As a result:

- The amount of undissociated ammonia decreases. As the position of equilibrium shifts, more undissociated ammonia is dissociated to replace the OH^- ions
- The amount of ammonium ions increases. As more undissociated ammonia is dissociated to replace the OH^- ions, more ammonium ions are produced.
- The pH stays more or less the same. The extra H^+ added immediately combine with the OH^- ions in solution, which are quickly replenished as the position of equilibrium shifts to the right.

Adding a Base to a Basic Buffer

When OH^- ions are added to the basic buffer, they combine with NH_4^+ ions from the salt, to make more undissociated ammonia molecules.

$$NH_4^+ (aq) + OH^- (aq) \rightarrow NH_3 (aq) + H_2O(l)$$

As a result:

- The amount of ammonium ions decreases. Excess ammonium ions combine with the extra OH^- to form undissociated ammonia.
- The amount of undissociated ammonia increases. As OH^- combines with ammonium ions, more undissociated ammonia forms.
- The pH stays more or less the same. The extra OH^+ added immediately combine with the ammonium and so the pH hardly changes.

Henderson Hasselbalch Equation

$$pH = pK_a + \ log \frac{conjugate\ base}{weak\ acid}\ (for\ weak\ acid)$$

$$pOH = pK_b + \ log \frac{conjugate\ acid}{weak\ base}\ (for\ weak\ base)$$

- The Henderson-Hasselbalch equation is the equation commonly used in chemistry and biology to determine the pH of a solution.
- This equation shows a relationship between the pH or pOH of the solution, the pKa or pKb, and the concentration of the chemical species involved.
- This type of kinetic analysis has enabled us for nearly a century to relate theoretically the changes of the acidic intensity of dilute solutions to a quantity of acid or base added or subtracted.
- This equation can be considered as the backbone of acid-base physiology.
- This equation is commonly used to determine the amount of acid and conjugate base required to prepare a buffer of the desired pH.

Objectives of Henderson Hasselbalch Equation

The principal objectives of the Henderson Hasselbalch equation include the following:

i. To calculate the pH, pOH, $[H_3O^+]_{tot}$, $[OH^-]_{tot}$, $[H_3O^+]_{water}$, and $[OH^-]_{water}$ in a solution containing a strong acid (base) given the initial concentration of the acid (base).
ii. To describe how a buffer solution (either acidic or basic) can resist significant changes in pH when small amounts of either acid or base are added to the buffer solution.
iii. To describe how either an acidic or basic buffer solution is prepared.
iv. To describe a “buffer solution”.
v. To describe “buffer capacity”.
vi. To determine whether an aqueous solution of salt will be acidic, basic, or neutral given values of Ka and Kb for conjugate acid-base pairs.
vii. To describe how the relative strengths of the conjugate acids or bases can be evaluated using the values of Kb and Ka for the bases and acids, respectively.
viii. To determine the protonation state of different biomolecule functional groups in a pH seven buffer.

Principle/Theory/Derivation of Henderson Hasselbalch Equation

According to the Bronsted-Lowry theory of acids and bases, an acid (HA) can donate a proton (H^+) while a base (B) can accept a proton.

An acid after losing a proton forms a conjugate base (A^-), and the protonated base exists as conjugate acid (BH^+).

The dissociation of acid is expressed in terms of the equilibrium equation as:

$$HA \quad \leftrightarrow \quad H^+ + A^-$$

This relationship can be described in terms of the equilibrium constant as:

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

Now taking negative log on both sides of the equation gives

$$-logKa = -log\frac{[H^+][A^-]}{[HA]}$$

(or)

$$-logKa = -\log[H^+] - log\frac{[A^-]}{[HA]}$$

$$pKa = pH - log\frac{[A^-]}{[HA]}$$

This equation rearranges to give

$$pH = pKa + log\frac{[A^-]}{[HA]}$$

The Henderson Hasselbalch equation can be expressed in two ways

$$pH = pK_a + \ log\frac{conjugate\ base}{weak\ acid}\ (for\ weak\ acid)$$

$$pOH = pK_b + \ log\frac{conjugate\ acid}{weak\ base}\ (for\ weak\ base)$$

Where

pK_a= dissociation constant of acid

pK_b= dissociation constant of base

Applications of Henderson Hasselbalch Equation

Calculating the pH of a solution using pKa

- ✓ This equation can be used to determine the pH of different solutions in different chemical equations as well as in biological systems like enzymes and proteins.

Calculating the ionized and unionized concentrations of chemicals.

- ✓ One of the most potent applications of the Henderson Hasselbalch equation is the ability to determine the concentrations of ionized and unionized chemicals.
- ✓ Generally, the amount of ionized and unionized species is detected using some spectroscopic technique, and thus, this equation is useful in the condition where spectroscopic studies are not feasible.
- ✓ The knowledge of the concentration of ionized and unionized chemicals is essential in fields like organic chemistry, analytical chemistry, and pharmaceuticals sciences,

Calculating pKa of a molecule using pH

- ✓ Determining the pKa of a molecule is important as the pKa is an essential characteristic of the chemistry of the structure of the molecule.
- ✓ Henderson Hasselbalch equation can be used to determine the pKa when the ratio of ionized and unionized forms and the pH of the solution is known.

Determination of solubility

- ✓ It has been observed that the Henderson Hasselbalch equation is important in determining the pH dependency of solubility.
- ✓ Based on the pH of a solution, the solubility of the solution can be determined, and there is also a close relationship between pH and solubility of various components in a solution.

Calculating the isoelectric point of protein

- ✓ This equation can also be used in determining the isoelectric point of different proteins (pH at which proteins neither lose nor accept protons).

Limitations

- ⅄ The most critical assumption of this equation is that the concentration of acid and its conjugate base will remain the same during the equilibrium.
- ⅄ The significance of hydrolysis of water and its effect on the pH of the overall solution is neglected.
- ⅄ Similarly, the hydrolysis of the base and dissociation of acid is also neglected.
- ⅄ The assumption made in the equation might fail while dealing with strong acids or bases.

UNIT –II -CHEMISTRY OF S-BLOCK ELEMENTS

Hydrogen: Position of Hydrogen in the Periodic Table:

Hydrogen is the first element in the periodic table. Its atomic number is 1 and atomic mass 1.008 a.m.u. The nucleous of the hydrogen atom contains one proton but no neutron. There is only one planetary electron arranged in the s-Orbital of the K shell. The hydrogen atom has a tendency to lose this electron and change into H^+ ion. Hydrogen, therefore, has an electropositive character like alkali metals. The hydrogen atom has also a tendency to gain an electron to complete the 1s sub shell and thus has an electronegative character like the halogens. Thus,in some respects it resembles alkali metals(Group 1) while in some other respects it resembles the halogens(Group 17). The points of resemblance and the point of difference of hydrogen with alkali metals on one hand and the halogens on the other hand are discussed below.

Resemblance with alkali metals.

1. Like alkali metals , Hydrogen has only one electron in its outer shell
2. The atoms of alkali metals have a strong tendency to loose the solitary electron from their outer shell and change into positive ions .Hydrogen also has a tendency, though not as strong as the alkali metals, to lose the solitary electron to change into H^+ion.
3. The normal valency of hydrogen as well as of alkali metals is 1
4. Hydrogen forms a stable oxides, H_2O. Alkali metals also form stable oxides, Hydrogen forms a peroxide, H_2O_2. Alkali metals also form peroxides.
5. Alkali metals are good reducing agents and so is hydrogen

Resemblance with the Halogens

1. Hydrogen has also a tendency to gain one electron more so as to complete its outer K shell and acquire helium configuration and thus change into negative ions H^-.
2. The ionization energy of hydrogen os of the same order as that of the halogens.
3. Hydrogen molecule is diatomic and so are the molecules of the halogens.
4. Hydrogens forms hydrides with carbon. Halogens also form well known halides with carbon.
5. Hydrogen in organic compounds can be substituted by halogens by suitable.

Alkali metals: Comparative study of the elements with respects to Oxides, Hydroxides, Halides, Carbonates and Bi- Carbonates

All the common compounds of alkali metals are ionic in character and contain the alkali metals as colorless electropositive monovalent ions. Most of the compounds are soluble in water. With the exception of a few lithium salts, all the alkali metal slts are insoluble in alcohol. The alkali metal cations are extremely stable because of their noble gas configurations.The compounds of alkali metals are colorless except those having coloured anions like MnO_4^{--}.

Oxides:

When the alkali metals are burnt in air, they form oxides. Different kinds of oxides are formed depending upon the alkali metal. Thus, lithium forms monoxide, when burnt in oxygen. Sodiun forms Peroxide. Potassium, rubidium and cesium form superoxides of the type$MO_2$when burnt in air.

The normal oxide contains O^{2-} ion, the peroxide contains O_2^{2-} ion and superoxide contains O_2^-ion.the peroxides and superoxides become more stable with increase in atomic number of the alkali metals. The formation and stability of these oxides can be explained on the basis of their *lattice energy*. Li^+ ion being a small ion has a strong positive field around it and can stabilize only a small anion, O^{2-}, whereas Na^+ ion being a large cation can stabilize a large anion and so on. Thus, smaller cation can stabilize smaller anion and larger cation can stabilize larger anion.

The typical oxides are the monoxides, Which are strongly basic and highly soluble in water. They give strongly alkaline solutions to formation of hydroxides, which are very largely ionized.

The higher oxides, peroxides and super oxides are important oxidizing agents. They react with dilute acids forming hydrogen peroxide and oxygen.

Hydroxides:

The hydroxides of alkali metals have the general formula MOH. These are white crystalline solids, highly soluble in water as well ass in alcohol. They act as strong bases in aqueous solutions, as shown above. Since electropositive character of alkali metals increases on moving from lithium to cesium, their hydroxides become more and more basic on moving down the group. Thus , out of the hydroxides of lithium, sodium and potassium, lithium hydroxide is the weakest and potassium m hydroxide is the strongest alkali.

All the hydroxides are stable towards heat and this stability increases on moving from Li to Cs. They melt without decomposing and are good conductors of electricity in the fused state.

The hydroxides sublime at about 400^0C giving vapours which consists of dimmers $(MOH)_2$.

Halides:

Halides of alkali metals have, generally, high melting points. They are good conductors of electricity in fused state and are really soluble in water.

Their structure is determined by the radius ratio and lattice energy effects. The radius ratio M^+/Cl^- for chlorides of various alkali metals are given in table. The co-ordination number expected from a given radius ratio, as discussed. The actual coordination numbers as observed from X-ray structure of the crystals are shown in the last column.

Radius ratios and coordination number of alkali metal halides

Formula of chloride	**Radius ratio M^+,Cl^-**	**Coordination number expected from the radius ratio**	**Observed coordination number**
LiCl	0.338	4	6
NaCl	0.524	6	6
KCl	0.732	6	6
RbCl	0.822	8	6 or 8
CaCl	0.930	8	8

Thus, while observed coordination numbers for Na, K, Rb and Cs are according to expectations, that for Li is higher. The anomaly in the case of Li is due the fact that higher coordination number leads to higher lattice energy and, therefore, adds to the stability of the crystal.

The alkali metal halides have essentially ionic character. Lithium halides, however, have partly covalent character in addition to ionic character. This is due to the polarization of the halide ion by the lithium ion, as has already been discussed.

Carbonates and Bicarbonates:

The alkali metals are highly electropositive, their carbonates(M_2CO_3) and in most cases, also the bicarbonates($MHCO_3$), are highly stable to heat. As the electropositive character increases on moving down the group, the stability of the carbonates and bicarbonates increases in the same order. Thus lithium carbonate is not so stable to heat as the other alkali metal carbonates. Lithium bicarbonate does not exist as solid.

Diagonal relationship of Li with Mg:

Lithium resembles magnesium in several respects, as illustrated below.

1. Atomic radius of lithium is $1.34A^0$while that of magnesium, being $1.364A^0$, is not very much different.
2. The radii of Li^+ ion$(0.60A^0)$ and Mg^{2+} ion ($0.65A^0$) are not much different from each other.
3. Polarising powers of Li^+ ion and Mg^{2+}ion are about the same.
4. Electro negativities of Li and Mg, being 1.0 and 1.3 respectively, are not much different from each other.
5. Like magnesium, lithium decomposes water only slowly liberating hydrogen.
6. Like magnesium and lithium hardly reacts with liquid bromine.
7. Lithium reacts with nitrogen to give lithium nitride, Li_3N. Magnesium also reacts with nitrogen to give magnesium nitride Mg_3N_2.
8. Lithium forms only the monoxides, Li_2O. Magnesium also prefers to form only the monoxide, MgO.
9. Lithium hydroxide, like magnesium hydroxide, is very slightly soluble in water.
10. Lithium hydroxide, like magnesium hydroxide, is a weak base.
11. Lithium fluoride, phosphate, oxalate and carbonate, like the corresponding salts of magnesium, are sparingly soluble in water.
12. Lithium chloride, like magnesium chloride, seperates out from aqueous solutions as hydrated crystals.
13. Lithium chloride, like magnesium chloride, is deliquescent.
14. Lithium chloride, like magnesium chloride, undergoes hydrolysis in hot water though to a smaller extent than magnesium chloride.
15. Lithium nitrate, like magnesium nitrate, evolves nitrogen dioxide and oxygen on heating, leaving behind the oxide.

Preparation, properties and uses of $NaOH, Na_2CO_3$, KBr, $KClO_3$:

Sodium hydroxide-NaOH-Caustic Soda:

Preparation of Caustic Soda

Sodium hydroxide can be prepared by various methods like:

1. Castner-Kellner process
2. Nelson Diaphragm cell
3. Loewig's process

Castner-Kellner process

Principle: In the Castner-Kellner method, electrolysis of brine solution is performed in order to obtain sodium hydroxide.

Castner-Kellner cell: It is a steel tank that is rectangular. Ebonite is lined inside the tank. Titanium acts as an anode and a layer of mercury at the bottom of the tank acts as the cathode.

Ionization of brine solution occurs according to the following reaction:

$$2NaCl \rightarrow 2Na^+ + 2Cl^-$$

When the brine solution comes in contact with electric current, ionization takes place. As a result positive and the negative ions move towards the electrodes. Sodium ions get deposited at the mercury cathode forming a sodium amalgam. Chlorine ions move towards the anode and exit the cell from the top.

Reaction at the anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Reaction at the cathode: $2Na^+ + 2e^- \rightarrow 2Na$

Formation of NaOH

The amalgam formed is then transferred to another chamber called denuder. In the denuder, it is treated with water to obtain a sodium hydroxide solution. On evaporation of the solution, solid sodium hydroxide is formed. This is a very efficient process in order to obtain pure caustic soda.

Properties of NaOH:

- Sodium Hydroxide is a solid ionic compound.
- Sodium hydroxide is produced as a co-product in the production of chlorine.
- It is highly corrosive and can cause severe skin burns and irritation to the eyes and other body parts.
- It is a white solid which has a melting point of 591K

- It is a stable compound.
- NaOH is bitter and has a soapy feel to it.
- It is highly soluble in water and moderately soluble in alcohol.
- Sodium hydroxide is strongly alkaline in nature.
- Sodium hydroxide is an odourless and colourless crystalline solid in its pure state.
- It has a molar mass of 39.997 g/mol
- The high melting and boiling points of sodium hydroxide are 318°C and 1388°C, respectively.
- It is denser than water with viscosity and density of 78 mPas and 2.13g/cm
- Sodium hydroxide has the ability to form hydrates. Tetrahydrate, Trihemihydrate, Trihydrate, Dihydrate, Heptahydrate, Pentahydrate, and Monohydrate are the most common hydrates formed by sodium hydroxide.
- The hydrogen bond donor, as well as the acceptor count of sodium hydroxide, is one.
- Sodium hydroxide is soluble in glycerol, water, and ethanol. It is insoluble in nonpolar solvents such as ether and sparingly soluble in propanediol.
- The process of saponification on the skin due to the reaction between NaOH and natural skin oils gives a slippery feel to sodium hydroxide.

Chemical Properties

- Sodium hydroxide is an ionic compound formed by the creation of an ionic bond between The covalent bond still exists between the oxygen and hydrogen atoms of the hydroxyl group.
- Sodium hydroxide is a strong base that reacts with acids to form salt and water.
- The sodium hydroxide solution has extremely high alkalinity.
- At high temperatures, sodium hydroxide reacts with metals to form the respective metal oxides. For example, the reaction between iron and sodium hydroxide at 500°C, results in the production of iron(III)oxide and sodium metal along with the hydrogen gas.
- Sodium hydroxide performs a reaction between acidic oxides to purify the harmful acidic acid.

Uses of Sodium hydroxide:

- It is used as a cleansing agent and in the manufacturing of washing soda.
- Sometimes, sodium hydroxide is also used as a reagent in the laboratories.
- It is used in the preparation of soda lime.
- It is used in the extraction of aluminium by purifying bauxite.
- It is used in the manufacturing of detergents and soaps.
- It is used in the production of bleach-like chlorine.
- It is used in drain cleaners.
- It is used in the removal of heavy metals from the water by the municipal water treatment facility.
- It is used in food preservatives to prevent bacteria and mould growth.
- It is used for canning.
- It is used in papermaking and paper recycling.
- Soaps and a number of detergents used in households and businesses are made with sodium hydroxide. By mixing chlorine with sodium hydroxide, chlorine bleach is created in the cleaning industry. Fats and grease that can clog pipes are transformed into soap by sodium hydroxide-containing drain cleaners.
- Aspirin and other widely used painkillers, as well as anticoagulants that can help prevent blood clots and cholesterol-lowering pharmaceuticals, are all manufactured with the aid of sodium hydroxide.
- In the energy industry, the manufacture of fuel cells uses sodium hydroxide. Fuel cells function similarly to batteries to create electricity cleanly and effectively for a variety of uses, such as transportation, material handling, fixed, portable, and emergency backup power applications. Wind turbines also use sodium hydroxide-produced epoxy resins.
- Sodium hydroxide is used in municipal water treatment facilities to reduce water acidity and aid in the removal of heavy metals. The water disinfectant sodium hypochlorite is also produced using sodium hydroxide.
- Sodium hydroxide is one of the dominant reagents used in the chemical industry.
- To prepare tomatoes, potatoes, and other fruits and vegetables for canning, sodium hydroxide is used to remove the skins. It is also an important component of food preservatives that work to inhibit mold and bacteria from growing in food.

- A solution comprising sodium hydroxide and sodium sulfide is frequently used to treat wood during the paper-making process. As a result, the majority of the undesirable substances in the wood are dissolved leaving cellulose comparatively clean.
- Sodium hydroxide is also used in the recycling of paper to separate the paper fibres from the ink, allowing the paper fibres to be used again.
- It is also used in the metal cleaning and processing, oxide coating, electroplating, and electrolytic extraction industries, as well as in the textile sector to produce dyes, process cotton fabric, launder, and bleach.

Sodium Carbonate-Na_2CO_3- Soda ash- Washing Soda- Soda Crystals

Preparation:

Sodium carbonate is now exclusively manufactured by the ***Solvay process.*** In this process carbon dioxide and ammonia are passed into a cold saturated solution of sodium chloride. In the reactions which occur sodium hydrogen carbonate is formed which is only very slightly soluble in the presence of sodium ions, is almost completely precipitated. It is removed by filtration and ignited to produce sodium carbonate.

The ingredients of this process are readily available and inexpensive. These are salt brine (NaCl), ammonia (NH_3) and limestone ($CaCO_3$). In this process, $CaCl_2$ is an important by-product obtained.

The reactions can be represented by the following equation.

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$

Addition of common salt to the solution containing NH_4^+ and HCO_3^- results in the precipitation of $NaHCO_3$ which is the least soluble. It is then filtered off.

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium bicarbonate is then heated to give Na_2CO_3.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

The CO_2 gas evolved can be reused again. Anhydrous sodium carbonate is dissolved in water and recrystallizes to get washing soda crystals containing 10 molecules of water of crystallization.

Properties:

Physical Properties of Sodium Carbonate

Sodium carbonate possesses the following physical properties:

- It exists in a hydrated form with 10 molecules of water of crystallization.
- It is basic in nature and turns red litmus blue.
- It is white in color and odorless in nature.
- It possesses a molecular weight/ molar mass of 105.9888 g/mol.
- It has a density of 2.54g/cm3.
- It has a boiling point of 1600o C and a melting point of 851o C
- Sodium carbonate has a pH value of 11 and is a very strong base.
- This inorganic compound is water-soluble and when dissolved in water, it forms carbonic acid and sodium hydroxide.
- In its pure form, it is a white powder and odourless. It is a strong base and acts as an antacid.
- it is a weak acid it is slightly soluble in ethanol and insoluble in alcohol.
- pH is about 11.

Chemical Properties of Sodium Carbonate

Sodium carbonate possesses the following chemical properties:

- It is highly stable and melts without decomposition.
- When dissolved in water it forms a slightly basic solution as it reacts with water to form sodium hydroxide (NaOH).

$$Na_2CO_3 + H_2O \rightarrow Na^+ + OH^- + H_2CO_3$$

When dissolved in water, it absorbs carbon dioxide leading to the formation of sodium hydrogen carbonate.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

- Sodium carbonate reacts with acids to form sodium chloride, water, and carbon dioxide.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_{2(}g)$$

Uses:

The uses of sodium carbonate are listed below.

- It is used in the ***manufacture of detergents, soaps, and paper.***
- Also used in the manufacture of water glass (sodium silicate), borax, sodium phosphate, and many other sodium compounds.
- It is used as a wetting agent in the brick industry
- It is used as an abrasive and foaming agent in toothpaste

- It is used as a ***pH modifier***
- It is used as a ***water softener*** – Hard water which consists of magnesium and calcium ions are precipitated by carbonate.
- As a laboratory reagent to standardize acids and as an analytical reagent
- In the brick-making industry, it can be used for welting purposes.
- It is used for tanning in the leather industry.
- Rayon is also manufactured using sodium carbonate
- It is used as a food additive as an anticaking agent, raising agent, stabilizer etc.
- It is used in cooking for example ramen noodles get their authentic flavor due to Sodium Carbonate.

Potassium Bromide-KBr-Kali Bromidium

Preparation:

One of the traditional methods of producing KBr is by reacting potassium carbonate with an iron (III, II) bromide, Fe3Br8, produced by treating scrap iron in water with excess bromine. The chemical equation for the same is given as follows:

$$4K_2CO_3 + Fe_3Br_8 \rightarrow 8KBr + Fe_3O_4 + 4CO_2$$

Properties:

Properties	Details
The chemical formula of potassium bromide	KBr
The molar mass of potassium bromide	119.002 gram/mol
Density of KBr	2.74 gram/cm^3
Appearance in standard condition	White solid
Structure	Cubic
Occurrence	It does not present in nature
Taste	Bitter, Salty, Pungent, Strong
Odour	Odourless
Soluble in	Water, Glycerol, Ethanol

Solubility in water	535 g/L in 0°C, 678 g/L in 25°C, and 1020 g/L in 100°C
Solubility in glycerol	217 g/L
Solubility in ethanol	47.6 g/L in 80°C
Meting point	734°C
Boiling point	1435°C

Uses:

- During the 19th or 20th century, this compound was utilized as a medicine against convulsions. However, nowadays, it is majorly used as an antiepileptic medicine for veterinary uses.
- One of the most vital usages is as sedatives.
- Commonly, this is also operated in the infrared spectroscopy technique. This utilization is majorly performed because of its transparent crystal formation with zero optical absorption.
- In the photographic plates and paper manufacturing industry, it is one of the most widespread chemical compounds.
- As a heat stabilizer in nylon production, potassium bromide is regarded as a popular chemical agent.
- Used in the water treatment of aquariums
- Used as plasticizers.
- Some other potassium bromide used are as laboratory agents and manufacture chemicals
- Potassium Bromide is used to manufacture photographic papers and plates.
- Used as a laboratory agent.
- Used to manufacture chemicals

Potassium Chlorate-$KClO_3$.

Preparation:

Potassium chlorate can be produced in three ways:

1. On the industrial scale, it can be produced via the Liebig process:

Step 1. Take hot calcium hydroxide.

Step 2. Pass chlorine into it.

Step 3. Add potassium chloride.

$6\ Ca(OH)_2 + 6\ Cl_2 \rightarrow Ca(ClO_3)_2 + 5\ CaCl_2 + 6\ H_2O$

$Ca(ClO_3)_2 + 2\ KCl \rightarrow 2\ KClO_3 + CaCl_2$

2. Potassium chlorate produced by disproportionation:

Step 1. In this method, first sodium chloride and sodium chlorate are formed by disproportionation of sodium hypochlorite.

Step 2. Then metathesis reaction takes place between potassium chlorate and potassium chloride.

$3\ NaOCl(aq) \rightarrow 2\ NaCl(s) + NaClO_3(aq)$

$KCl(aq) + NaClO_3(aq) \rightarrow NaCl(aq) + KClO_3(s)$

3. Method three:

Step 1. Consider a hot solution of caustic potash.

Step 2. Pass chlorine gas into it.

$3\ Cl_2(g) + 6\ KOH(aq) \rightarrow KClO_3(aq) + 5\ KCl(aq) + 3\ H_2O(l)$

Properties:

Potassium Chlorate has following physical and chemical properties –

- In its pure form, it is a white crystalline solid.
- Its molar mass is 122.55 g/mol.
- Its density is 2.32 g/cm3.
- Its melting point is 356°C.
- Its boiling point is 400°C.
- It is soluble in water. As the temperature increases, solubility of Potassium Chlorate in water also increases.
- It is soluble in glycerol as well.
- It is slightly soluble in acetone and liquid ammonia as well.
- Its oxidizing properties make it suitable for ignition.
- It is hygroscopic.
- Its crystal structure is monoclinic.
- Potassium Chlorate immediately decomposes if heated in the presence of a catalyst such as MnO_2.

- If it is heated in the absence of a catalyst, then on decomposition it gives potassium perchlorate and Potassium Chloride.On further heating potassium perchlorate decomposes into oxygen and Potassium Chloride.

Uses:

- It is used as an oxidizing agent.
- It is used in the preparation of oxygen.
- It can be used as a disinfectant.
- It is used in safety matches in a very small amount.
- It is used in explosives.
- It helps in early arrival of the blossoming stage of longan trees. Thus, causing it to produce fruit in the warmer climate.
- It is used in firearms and percussion caps.
- It is used in propellants.
- It is used in combination with silver fulminate in trick noise makers such as snappers, pop – its, bang – snaps etc.
- It is used in pyrotechnics.
- It is used in smoke grenades.
- It is used in laboratories as well.
- It is used in chlorate candles or oxygen candles.
- It is used in oxygen supply systems of aircrafts, space stations and submarines etc.
- It is used in limelights (A type of stage lighting which was used in theaters and music halls in old time) as well.
- It is also used as a pesticide.
- Molten Potassium Chlorate is used in dramatic screaming jelly babies, Gummy bear, Haribo and Trolli candy etc.

Alkaline Earth Metals: Anomalous behavior of Beryllium:

Beryllium, the first element of Group II, differs considerably from the rest of the elementsof this group.this is partly due to its small size and partly due to its relatively high electronegativity. The main point of difference are as follows.

1.Tendency to form ionic compounds: Ionisation energy of Be(899KJmol^{-1}) is the highest, Consequently, it hhas the lowest tendency to form the ion,Be^{2+}.Accordingly it does not form ionic compounds readily.

2. Tendency to form Covalent compounds Electronegativity of Be(1.5) is more than that of any other element of the family. Hence, its compounds with Oxygen, chlorine, Nitrogen, Sulphur, etc., are more covalent in character than the corresponding compounds of magnesium, Calcium, Strontium and Barium.

3. Reaction with Water: Beryllium does not reacts with water even at elevated temperatures. its reaction with steam forming beryllium oxide, BeO and liberating hydrogen is doubtful.

4.Oxidation potential: Be has the lowest oxidation potential which indicates that it has the lowest electropositive character. Consequently, BeO and Be(OH)$_2$are not at all basic in character. They are , in fact, amphoteric and dissolve in acids to form salts and in alkalis to form beryllates Na_2BeO_2.

The oxides and hydroxides of the other metals are basic in character. The basic character increases on moving down the group. Magnesium hydroxide is weakly basic while calcium, strontium and barium hydroxides are distinctly basic, their strengths increasing in the order of their mention.

5.Reaction with acids: Beryllium, on account of its relatively lower oxidation potential, does not liberate hydrogen from acids so readily as the rest of the metals of group 2 do.

6.Reaction with hydrogen: Beryllium does not combine directly with hydrogen to give the hydride. All other elements of the group do. Beryllium hydride is a covalent compound. Magnesium hydride is also a covalent compound. The hydrides of remaining elements are, however, electrovalent in character.

7. Reaction with halogens: All the metals of this group form halides by direct combination with the halogens at appropriate temperature. Beryllium halides are, however, covalent while the other halides are electrovalent compounds.

8.Reaction with Nitrogen: All the elements of this group react with nitrogen to give nitrides, M_3N_2,as already stated. However, beryllium nitride is volatile while the other nitrides are not.

9.Formation of Carbides: All the elements, from Mg to Ba, give ionic carbides, MC_2,when the metals or their oxides are heated with carbon. Beryllium, on the other hand, gives

Be_2C and not BeC_2 when heated with carbon. Beryllium carbide, Be_2C, evolves methane on treatment with water while the other carbides evolve acetylene.

$$Be_2C + 2H_2O \rightarrow 2BeO + CH_4$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

10. Formation of Complexes: The alkaline earth metal ions do not form many complexes. However, beryllium ion, on account of its small size, gives a number of stable complexes, such as $[BeF_3]^-$ and the tendency to form complexes decreases on moving down the group. Thus, barium forms very few complexes.

Chemistry of p-Block Elements:

Preparation and structure of diborane and Borazine:

Diborane:

Preparation:

It is the simplest of the hydrides of boron and can be prepared by the following methods:

1. By the reaction of iodine on sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2NaI + H_2$$

2. By passing silent electric discharge through a mixture of hydrogen and boron trichloride at a low pressure.

$$2BCl_3 + 6H_2 \xrightarrow{\text{Electric discharge}} B_2H_6 + 6HCl$$

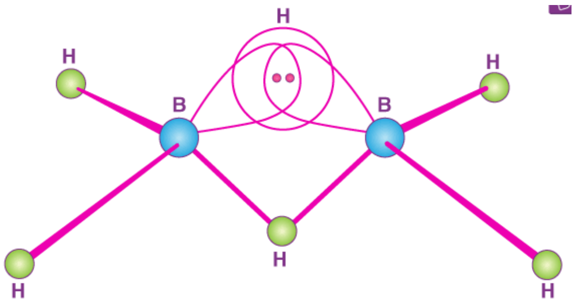
3. By the reduction of boron trichloride with lithium aluminum hydride.

$$4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

4. By reducing gaseous boron tri fluoride with sodium hydride at 180^0C

$$2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$$

Structure:



Boron atom in excited state has three half filled orbitals, it has three available for sharing. therefore, it can link to itself three hydrogen atoms. Thus, each boron atom in diborane can link to itself three hydrogen atoms, there are no electrons left to form a bond between the two boron atoms.

Four hydrogen atoms, two on the left and two on the right, known as terminal hydrogen's, are in different environments from the other two hydrogen atoms which are known as the bridging atoms. The two boron atoms and the four terminal hydrogen atoms lie in the same plane while the two boron atoms and the two bridging hydrogen atoms, one above and the other below, lie in a plane perpendicular to this plane.

The bridged structure discussed above is supported by the following:

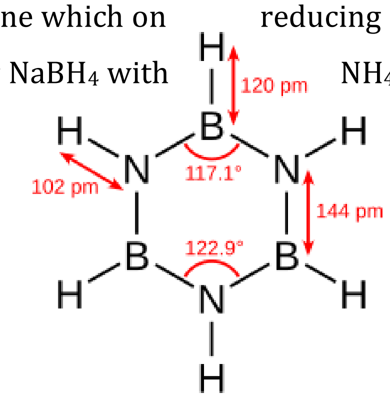
1. Heat capacity measurements have shown that the rotation of the two ends of the molecule against each other is very much hindered. This indicates that the bridging hydrogen atoms lie in a plane at right angles to the plane in which the rest of the molecule lies. In a molecule like ethane, in which there are no bridging hydrogen atoms, the hindrance to this type of rotation is very low.
2. Nuclear magnetic resonance and Roman spectra have shown that four hydrogen's are of one type and two hydrogen's are of another type. In ethane all the six hydrogen's are known to be equivalent.
3. Diborane can not be methylated beyond$(CH_3)_4B_2H_2$. The hydrogen's which cannot be methylated, evidently, are in a environment.

Borazine:

Preparation:

Borazine can be prepared by heating together BCl_3 and NH_4Cl.the initial product formed is trichloroborazine which on reducing with$NaBH_4$ yields Borazine. It can also prepared by treating $NaBH_4$ with NH_4Cl.

Structure



It is similar to that of Benzene, In this structure, the valence shell orbital's of both boron and nitrogen atoms are sp^2 hybridized. Each nitrogen atom has one lone pair of electrons while each boron atom has an empty p orbital. The bonding in Borazine is dative and it arises from the sidewise overlapping of fully filled p- orbital's of nitrogen and empty p orbital's of boron. Because of the similarity of the structures of Borazine and benzene, Borazine ia also known as Inorganic Benzene.

Chemistry of Borax:

- The structure of borax according to X-ray crystallography. From the chemical perspective, borax contains the $[B_4O_5(OH)_4]^{2-}$ ion. In this structure, there are two four-coordinate boron centers and two three-coordinate boron centers.
- It is a proton conductor at temperatures above 21 °C. Conductivity is maximum along the *b*-axis.
- Borax is also easily converted to boric acid and other borates, which have many applications. Its reaction with hydrochloric acid to form boric acid is:
- $Na_2B_4O_7 \cdot 10H_2O + 2\ HCl \rightarrow 4\ H_3BO_3 + 2\ NaCl + 5\ H_2O$
- rem :$Na_2B_4O_5(OH)_4 \cdot 8H_2O + 2\ HCl \rightarrow 4\ B(OH)_3 + 2\ NaCl + 5H_2O$
- Borax is sufficiently stable to find use as a primary standard for acid-base titrimetry.
- Molten borax dissolves many metal oxides to form glasses. This property is important for its uses in metallurgy and for the borax bead test of qualitative chemical analysis.
- Borax is soluble in a variety of solvents; however, it is notably insoluble in ethanol
- The term *borax* properly refers to the so-called "decahydrate" $Na_2B_4O_7 \cdot 10H_2O$,
- It is actually octahydrate. The anion is not tetraborate $[B_4O_7]^{2-}$ but tetrahydroxy tetraborate $[B_4O_5(OH)_4]^{2-}$,so the more correct formula should be $Na_2B_4O_5(OH)_4 \cdot 8H_2O$.
- Borax "pentahydrate" has the formula $Na_2B_4O_7 \cdot 5H_2O$, which is actually a trihydrate $Na_2B_4O_5(OH)_4 \cdot 3H_2O$.
- It is a colorless solid with a density of 1.880 kg/m^3 that crystallizes from water solutions above 60.8 °C in the rhombohedral crystal system.
- It occurs naturally as the mineral tinkhanite

- It can be obtained by heating the decahydrate above 61 °C
- Borax "dihydrate" has the formula $Na_2B_4O_7\cdot 2H_2O$, which is actually anhydrous, with the correct formula $Na_2B_4O_5(OH)_4$. It can be obtained by heating the "decahydrate" or "pentahydrate" to above 116-120 °C.
- Anhydrous borax is sodium tetraborate proper, with formula $Na_2B_4O_7$. It can be obtained by heating any hydrate to 300 °C.
- It has one amorphous (glassy) form and three crystalline forms – α, β, and γ, with melting points of 1015, 993 and 936 K respectively. α-$Na_2B_4O_7$ is the stable form.

Uses of Borax

- Borax is used in pest control solutions because it is toxic to ants.
- Borax is used in various household laundry and cleaning products, including the 20 Mule Team Borax laundry booster, Boraxo powdered hand soap, and some tooth bleaching formulas
- Borate ions (commonly supplied as boric acid) are used in biochemical and chemical laboratories to make buffers,
- Borax as a source of borate has been used to take advantage of the co-complexing ability of borate with other agents in water to form complex ions with various substances.
- Borate and a suitable polymer bed are used to chromatograph non-glycated hemoglobin differentially from glycated hemoglobin (chiefly HbA1c), which is an indicator of long-term hyperglycemia in diabetes mellitus.
- Borax alone does not have a high affinity for *hardness cations*, although it has been used for water-softening.

$$Mg^{2+}(aq) + Na_2B_4O_7(aq) \rightarrow MgB_4O_7(s)\downarrow + 2\ Na^+(aq)$$

- A mixture of borax and ammonium chloride is used as a flux when welding iron
- Borax is also mixed with water as a flux when soldering jewelry metals such as gold or silver
- Borax is also a good flux for "pre-tinning" tungsten with zinc, making the tungsten soft-solderable. Borax is often used as a flux for forge welding.
- A rubbery polymer sometimes called Slime, Flubber, 'gluep' or 'glurch' (or erroneously called Silly Putty, which is based on silicone polymers), can be made by cross-linking polyvinyl alcohol with borax.

- Borax, given the E number *E285*, is used as a food additive but this use is banned in some countries, In addition to its use as a preservative, borax imparts a firm, rubbery texture to food.
- Component of glass, pottery, and ceramics

Extraction of Aluminium and its uses:

Next to silica and oxygen, Aluminium is the most widely distributed element. It is present to the extent of 7.3 per cent in the earth's crust. The important ores are: (i) *Bauxite,* $Al_2O_3.3H_2O$ *(ii)Cryolite* Na_3AlF_6 and (iii)*Corundum,* Al_2O_3. Aluminium is generally obtained from the bauxite ore.

The Bauxite ore is powdered and digested with sodium hydroxide in an autoclave under pressure at 130^0C for several hours when alumina of the ore dissolves ass sodium meta aluminate whereas impurities such a ferric oxide, silica, etc., being insoluble in NaOH, settle down. The sodium meta aluminate solution is then stirred with carbon dioxide gas when a precipitate of $Al(OH)_3$ is obtained. It is ignited at 1500^0Cto get pure alumina Al_2O_3 which is dissolved in molten cryolite at $800-1000^0C$ and the melt electrolyzed to get the pure metal.

Uses:

- Aluminium, being very light, is used in manufacturing household utensils, aeroplane parts, precision and surgical instruments, etc.,
- It is un attacked by nitric acid, it is used in chemical plants and also for transporting nitric acid.
- Mixed with oil, it is used in paints for steam pipes and other metal objects.
- Aluminium foil is used for packing chocolates, cigarettes, etc.,
- Alums are used as mordants in dyeing and paints
- It is used ass a reducing agent for the production of certain metals such ass chromium and manganese, etc.,
- Alumina is used in making refractory bricks and ultramarine.
- In certain forms such as feldspar and mica it is used in the construction of buildings.
- Along with organic colloids, it is used for sizing of paper.
- The evolution of enormous quantities of heat in the oxidation of Aluminium is made use of in Thermite welding of metals.

Alloys of Aluminium

- An **Aluminium alloy** is an alloy in which Aluminium (Al) is the predominant metal.
- The typical alloying elements are copper, magnesium, manganese, silicon, tin, nickel and zinc. There are two principal classifications, namely casting alloys and wrought alloys, both of which are further subdivided into the categories heat-treatable and non-heat-treatable.
- About 85% of Aluminium is used for wrought products, for example rolled plate, foils and extrusions.
- Cast Aluminium alloys yield cost-effective products due to the low melting point, although they generally have lower tensile strengths than wrought alloys.
- The most important cast Aluminium alloy system is Al–Si, where the high levels of silicon (4–13%) contribute to give good casting characteristics.
- Aluminium alloys are widely used in engineering structures and components where light weight or corrosion resistance is required.
- Alloys composed mostly of Aluminium have been very important in aerospace manufacturing since the introduction of metal-skinned aircraft.
- Aluminium–magnesium alloys are both lighter than other Aluminium alloys and much less flammable than other alloys that contain a very high percentage of magnesium.
- Aluminium alloy surfaces will develop a white, protective layer of Aluminium oxide if left unprotected by anodizing and/or correct painting procedures.
- In a wet environment, galvanic corrosion can occur when an Aluminium alloy is placed in electrical contact with other metals with more positive corrosion potentials than Aluminium, and an electrolyte is present that allows ion exchange. Also referred to as dissimilar-metal corrosion, this process can occur as exfoliation or as inter granular corrosion. Aluminium alloys can be improperly heat treated, causing internal element separation which corrodes the metal from the inside out.

Uses & Properties

- Aluminium alloys with a wide range of properties are used in engineering structures.
- Alloy systems are classified by a number system (ANSI) or by names indicating their main alloying constituents (DIN and ISO).
- Selecting the right alloy for a given application entails considerations of its tensile strength, density, ductility, formability, workability, weldability, and corrosion resistance, to name a few.
- A brief historical overview of alloys and manufacturing technologies is given in Ref. Aluminium alloys are used extensively in aircraft due to their high strength-to-weight ratio.
- Pure aluminium metal is much too soft for such uses, and it does not have the high tensile strength that is needed for building airplanes and helicopters.

Comparison of Carbon with Silicon:

Silicon is the element with atomic number 14, and it is also in group 14 of the periodic table, just below carbon whereas carbon is the element with atomic number 6, and it is also in the group 14 of the periodic table, just above silicon. However, the difference between silicon and carbon is that the carbon is a nonmetal whereas the silicon is a metalloid.

Furthermore, carbon and silicon have the same common electron configuration as s^2, p^2. But, there is a difference between silicon and carbon. In silicon, the electrons spread into the 3rd energy level, whereas in carbon, it is only to the 2nd energy level. This difference occurs because of carbon in the 2nd period, but silicon in the 3rd. Silicon atom is larger than the carbon atom. Moreover, another difference between silicon and carbon is that the silicon is less reactive than carbon. Also, pure carbon compounds occur in nature such as diamond, graphite, and coal. But pure silicon compounds are hardly found. They exist as oxides or silicates. The below inforgraphic summarizes the difference between silicon and carbon in tabular form.

	Silicon	**Carbon**
Definition	The element with atomic number 14, and it is also in the group 14 of the periodic table. Just below carbon	The element with atomic number6 and it is also in the group 14 of the periodic table. Just above silicon
Chemical catagory	Metalloid	Nonmetal
Election Configuration	The electrons are spread into the3rd energy level	Spread only to the 2nd energy leveite and coall
Reactivity	Less reactive	Comparatively more reactive
Size of atom	Comparatively a large atom	Comparatively a small atom
Pure form	Hardly found	Common in nature such such as diamond.Grap

Preparation, Properties, Structure and uses of Carbon-Di-Sulphide

Preparation

1. Carbon-disulphide is prepared by directly heating sulphur and coke in iron retorts at 750^0C-1000^0C

$$C+2S \rightarrow CS_2$$

2. It is also prepared from natural gas as follows:

$$CH_4+4S \xrightarrow{SiO_2/Al_2O_3} CS_2+2H_2S$$

Physical Properties

Pure CS_2 is a colorless, volatile liquid boiling at 46.2^0C. It freezes -111.6^0C and has a flash point of -30^0C. Its vapour are toxic and have an adverse effect on the nervous system.

Chemical Properties:

1.CS_2 is highly inflammable and burns in air to give CO_2 and SO_2.

$$CS_2+3O_2 \longrightarrow CO_2+2SO_2$$

2. It combines with metal sulphides to give thiocarbonates

$$MS+CS_2 \longrightarrow MCS_2$$

3.It reacts with aqueous NaOH to give a mixture of Na_2CO_3 and Na_2CS_3

$$3CS_2+6NaOH \longrightarrow Na_2CO_3+2Na_2CS_3+3H_2O$$

4. It reacts with ammonia and primary and secondary amines to give Dithiocarbonate
5. Water reacts with CS_2 slowly to give COS and H_2S at 200^0C and $CO_2$and H_2S at higher temperatures.

$$\begin{tikzcd}
CS_2+H_2O \arrow[r] & COS+H_2S \arrow[d, "H_2O"'] \\
 & CO_2+H_2S
\end{tikzcd}$$

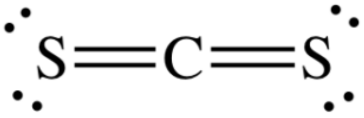
6. MGO,SO_3HSO_3Cl convert CS_2 to COS in a similar manner. For example

$$\begin{tikzcd}
MGO+CS_2 \arrow[r] & COS+MgS \arrow[d, "MgO"'] \\
 & CO_2+MgS
\end{tikzcd}$$

7. CS_2 reacts with ethanol in the presence of alkalies to give sodium ethyl dithiocarbonate, also known as sodium xanthate
8. CS_2 reacts with Cl_2 to give CCl_4.
9. Fluorine reacts with CS_2 to form a variety of fluorinated products such as SF_4,SF_6, S_2F_{10}.The exact nature of the product depends upon the reaction condition.
10. It readily undergoes insertion reaction introducing thereby a SCS group in between a metal- nitrogen bond as also in some other bonds.
11. CS_2 is an efficient complexing agent.

Structure of CS_2

- Electron diffraction studies show that CS_2 molecule in gaseous phase is linear like CO_2.
- The dipole moment of CS_2 is also zero like that of CO_2.
- The CS bond distance in CS_2 is found to be $1.54A^0$ which is quite close to C=s distance.
- The C-S single bond distance is known to be $1.8A^0$. which is obviously far greater than the observed C=S distance in CS_2.



Uses

It is used in the manufacture of viscose rayon and cellophane. It is also used in the vulcanization of rubber and for manufacturing insecticides.

Percarbonates

Percarbonates are supposed to be derived from percarbonic acids known as permonocarbonic acid and perdicarbonic acid. The formulae and structure of these acids in relation to carbonic acid are represented as

H_2CO_3	H_2CO_4	H_2CO_5
Carbonic acid	Permonocarbonic acid	Perdicarbonic acid

These acids have not been isolated so far but their salts, Permonocarbonates and perdicarbonates are known. However, they are not very stable.

Permonocarbonates:

Permonocarbonates of sodium and potassium can be prepared by passing CO_2 through a solution of the corresponding alkali peroxide.

$$O=C=O+Na\text{-}O\text{-}O\text{-}Na \rightarrow Na_2CO_4$$

These can be prepared by the action of hydrogen peroxide on the corresponding alkali carbonate.

$$Na_2CO_3+H_2O_2 \rightarrow Na_2CO_4+H_2O$$

The permonocarbonates when freshly prepared contain waterof crystallization. They are soluble in water, the solution behaving as if it is a mixture of simple carbonate and hydrogen peroxide. The salts, therefore, may be regarded as simple hydrated carbonates conaining also hydrogen peroxide as a molecule of crystallization, the composition of the sodium salt being represented as $Na_2CO_3.H_2O_2.H_2O$.

The formula is supported by the fact that the compound slowly liberates iodine from a solution of potassium iodide and that hydrogen peroxide can be extracted by shaking the aqueous solution with ether.

Perdicarbonates

Sodium or potassium perdicarbonates can be prepared by the electrolysis of a concentrated aqueous solution of the corresponding carbonate at a temperature of -110^0. The electrolytic reaction may be represented as

$$K_2CO_3 \rightarrow K^++KCO_3^- \qquad H_2O \leftrightarrow H^++OH^-$$

Potassium perdicarbonates appears as a bluish precipitate. It is washed with cold water, alcohol and ether and finally dried. It is stable at ordinary temperatures in the absence of moisture. In water it decomposes to give potassium carbonate.

$$2K_2C_2O_6 \rightarrow 2K_2CO_3+2CO_2+O_2$$

It also decomposes on heating. It acts as an oxidizing agent and liberates iodine from potassium iodide. It can also oxidize lead sulphide to lead sulphate.

UNIT-III CHEMISTRY OF P-BLOCK ELEMENTS (GROUP 15-16)

General Characteristics of elements of Group 15 :

Group 15 elements are also called the ***Nitrogen family.*** It includes nitrogen, phosphorus, arsenic, antimony and bismuth elements. The p-block elements are also known as the ***Representative Elements*** which are placed on the right side of the main periodic table.

Group 15 elements as you would move down a group, starting with the lightest element and finishing with the heavy ones; you'd notice a general flow in properties as you move down the order. For eg, Nitrogen is a gas and non-metal but as you move down the group, we encounter metalloids and then at the bottom, metal i.e. Bismuth. These trends in the periodic table help us better understand the behaviour of atoms and also helps us predict new elements.

Property	**Nitrogen**	**Phosphorus**	**Arsenic**	**Antimony**	**Bismuth**
Atomic symbol	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
Valence electron configuration	$[He]2s^2\ 2p^3$	$[Ne]3s^2\ 3p^3$	$[Ar]3d^{10}\ 4s^2\ 4p^3$	$[Kr]4d^{10}\ 5s^2 5p^3$	$[Xe]4f^{14}\ 5d^{10}6s^2 6p^3$
Melting point Boiling point (°C)	– 210 -196	44.15 281	817 603(sublimes)	631 1587	271 1564
Density (g/cm3) at 25°C	1.15(g/L)	1.8	5.7	6.68	9.79
Atomic radius (pm)	56	98	114	133	143
First Ionization energy (kJ/mol)	1402	1012	947	834	703
Common Oxidation state(s)	-3 to +5	+5, +3, -3	+5, +3	+5, +3	+3
Ionic radius (pm)	146(-3)	212(-3)	58(+3)	76(+3)	103(+3)
Electronegativity	3.0	2.2	2.2	2.1	1.9

Some of the trends in the modern periodic table with respect to group 15 elements of the p-Block elements are discussed below.

1. Electronic Configuration

- The valence shell electronic configuration plays a major role in how an element behaves. The valence electron shell configuration of group 15 elements is ns^2np^3.
- All the group 15 elements have the same arrangement and this is why they're similar.

- The s-orbital in this group is completely filled and ***the p-orbitals are half filled and this makes their configuration extra stable.***

2. Atomic and Ionic Radii

- The electronic configuration of elements in the table above, it is noticed that with, every step you move downwards, new orbitals are added to the atom.
- This addition of new orbitals increases both the Atomic and the Ionic radii of group 15 elements.
- If move from Arsenic to Bismuth only a small increase in ionic radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

3. Ionization Enthalpy

- Ionization Energy is the amount of energy required to remove an electron from the outermost orbit of the atom.
- This is basically a measure of how hard the nucleus is holding on to the electron.
- The closer the electron is to the nucleus the stronger its hold and thus the energy required is more.
- As we move down the group, the radius of the atom increases, and therefore the Ionization energy decreases due to the weaker hold of the nucleus.

4. Electronegativity

- The electronegativity value decreases down the group with increasing atomic size.
- This again is due to the increasing distance between the nucleus and the valence shell as we move down the group.

5. Physical Properties

- All the elements of the group exist in a polyatomic state.
- First, Nitrogen is gas, but as you move down, there is a significant increase in the metallic character of the elements.
- Nitrogen and Phosphorus are non-metals, Arsenic and Antimony are metalloids and Bismuth is a metal.
- These changes can be attributed to the decrease in Ionization enthalpy and increase in atomic size.
- Boiling points also, in general, show an increasing trend as you move down.
- Except for Nitrogen, all the other elements have allotropes.

6. Chemical Properties

- The valence shells of the p-Block elements have a configuration of ns^2 np^3.
- So the elements here can either lose 5 electrons or gain 3.

- The common oxidation states of these elements are -3, +3 and +5.
- With a decrease in the Ionization enthalpy and electronegativity due to the increasing atomic radius, the tendency to gain three electrons to create -3 oxidation state decreases down the group.
- In fact, Bismuth hardly forms any compounds with a -3 oxidation state.
- As we go down, the stability of the +5 state decreases and that of +3 increases due to the inert pair effect.

Chemistry N_2H_4-Hydrazine

N_2H_4 is an inorganic compound with chemical name Hydrazine and also called as Diamine or Diazane or Nitrogen hydride and is a strong base. It is an azane and dangerously unstable. Each subunit of H_2N-NH_2 is pyramidal and the N−N bond distance is about 1.45 Å.

Diamine in its anhydrous form, is a colourless, fuming oily liquid which smells like ammonia. It has a flash point value of 99°F. In case if traces of air is present during the process of distillation, it explodes. It is toxic and corrosive to tissues. When it undergoes combustion, it generates toxic oxides of nitrogen.

Properties of Hydrazine – N_2H_4

N_2H_4	**Hydrazine**
Molecular weight/molar mass of N_2H_4	32.0452 g/mol
Density of Hydrazine	1.021 g/cm^3
Boiling Point of Hydrazine	114 °C
Melting Point of Hydrazine	2 °C

Hydrazine Structure – N_2H_4 **NH_2-NH_2**

Production of Hydrazine

Diamine can be obtained from hydrogen peroxide and ammonia in the ketazine process or Pechiney-Ugine-Kuhlmann process. The reaction is as follows:

$$2NH_3 + H_2O_2 \rightarrow H_2NNH_2 + 2H_2O$$

Chloramine reacts with ammonia to generate nitrogen–nitrogen single bond and hydrogen chloride as by products. The reaction is as follows:

$$NH_2Cl + NH_3 \rightarrow H_2NNH_2 + HCl$$

N_2H_4 Uses (Hydrazine)

- Hydrazine is used as a propellant in space vehicles.
- It is used as a precursor in several pharmaceutical products.

- It is used as a reducing agent for selenium, arsenic, and tellurium
- It is used as a corrosion inhibitor in cooling water reactor.
- It is used in the process of electrolytic plating of metals on plastic and glass.
- Used in the manufacturing of agricultural chemicals.
- Used as a solvent for inorganic compounds.

Hydroxylamine –NH_2OH

Hydroxylamine was first prepared as hydroxylammonium chloride in 1865 by the German chemist Wilhelm Clemens Lossen (1838-1906); he reacted tin and hydrochloric acid in the presence of ethyl nitrate It was first prepared in pure form in 1891 by the Dutch chemist Lobry de Bruyn and by the French chemist Léon Maurice Crismer (1858-1944) The coordination complex $ZnCl_2(NH_2OH)_2$ (zinc dichloride di(hydroxylamine)), known as Crismer's salt, releases hydroxylamine upon heating.

Hydroxylamine (also known as hydroxyammonia) is an inorganic compound with the chemical formula NH_2OH. The compound is in a form of a white hygroscopic crystals. Hydroxylamine is almost always provided and used as an aqueous solution. It is consumed almost exclusively to produce Nylon-6.

Production

Hydroxylamine or its salts (salts containing hydroxylammonium cations $[NH_3OH]^+$) can be produced via several routes but only two are commercially viable. It is also produced naturally as discussed in a section on biochemistry.

From nitric oxide

NH_2OH is mainly produced as its sulfuric acid salt, hydroxylammonium hydrogen sulfate ($[NH_3OH]^+[HSO_4]^-$), by the hydrogenation of nitric oxide over platinum catalysts in the presence of sulfuric acid.

$$2\ NO + 3\ H_2 + 2\ H_2SO_4 \rightarrow 2\ [NH_3OH]^+[HSO_4]^-$$

Other methods

Julius Tafel discovered that hydroxylamine hydrochloride or sulfate salts can be produced by electrolytic reduction of nitric acid with HCl or H_2SO_4 respectively.

$$HNO_3 + 3\ H_2 \rightarrow NH_2OH + 2\ H_2O$$

Hydroxylamine reacts with electrophiles, such as alkylating agents, which can attach to either to yield Nylon 6.

Laboratory uses

Hydroxylamine and its salts are commonly used as reducing agents in myriad organic and the oxygen or the nitrogen atoms:

$$R{-}X + NH_2OH \rightarrow R{-}O{-}NH_2 + HX$$

$$R{-}X + NH_2OH \rightarrow R{-}NH{-}OH + HX$$

Uses

- Conversion of cyclohexanone to caprolactam involving the Beckmann rearrangement. Approximately 95% of hydroxylamine is used in the synthesis of cyclohexanone oxime, a precursor to Nylon 6. The treatment of this oxime with acid induces the Beckmann rearrangement to give caprolactam (**3**) The latter can then undergo a ring-opening polymerization inorganic reactions.
- They can also act as antioxidants for fatty acids.
- High concentrations of hydroxylamine are used by biologists to introduce mutations by acting as a DNA nucleobase amine-hydroxylating agent.
- This route also involves the Beckmann Rearrangement, like the conversion from cyclohexanone to caprolactam. An alternative industrial synthesis of paracetamol developed by Hoechst–Celanese involves the conversion of ketone to a ketoxime with hydroxylamine.
- Some non-chemical uses include removal of hair from animal hides and photographic developing solutions.
- In the semiconductor industry, hydroxylamine is often a component in the "resist stripper", which removes photoresist after lithography.
- Hydroxylamine can also be used to better characterize the nature of a post-translational modification onto proteins. For example, poly(ADP-Ribose) chains are sensitive to hydroxylamine when attached to glutamic or aspartic acids but not sensitive when attached to serines. Similarly, Ubiquitin molecules bound to serines or threonines residues are sensitive to hydroxylamine, but those bound to lysine (isopeptide bond) are resistant

<u>Ammonia-</u>Preparation-NH_3

Ammonia is the most important compound of nitrogen. It is present in small quantities in air and soil where it is formed by thee decay of nitrogeneous organic matter eg.urea

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \leftrightarrow 2NH_3 + CO_2 + H_2O$$

Laboratory Preparation

Ammonia is prepared in the laboratory by heating ammonium salt.NH_4Cl, $(NH_4)_2SO_4$ with a strong alkali like NaOH.

$$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$

$$(NH_4)_2SO_4 + 2\,NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

It can also be prepared by heating Ammonium chloride with alkali lime

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

It can also be prepared by the hydrolysis of magnesium nitride.

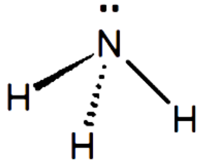
$$Mg_3N_2 + H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

Ammonia can be manufactured by Haber's process which involves the reaction

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

This is a reversible exothermic reaction. The favourable conditions for high yield of ammonia can be understood by applying **Le chartelier's Principle.**

Structure of Ammonia:



Ammonia is expected to have a tetrahedral geometry because the central nitrogen atom involves sp^3 hybridisation as already discussed. It has one position occupied by a loan pair. The lone pair distorts its geometry and the molecule has pyramidal geometry with nitrogen atom at the apex. The N-H bond length is 101.7 pm and HNH bond angle is 107.8^0

Properties of Ammonia:

The Properties of Ammonia are given as follows-

- It is lighter than air
- Ammonia can be easily liquefied under pressure.
- Ammonia is a gas which is colourless in nature and has a pungent smell.
- It boils at 198.4K and 239.7K.
- This gas is highly dissolvable in water. The aqueous solution of NH_3 is a weak base as OH- ions are formed. $NH_3 + H_20 \rightarrow NH_4^+ + OH^-$
- Ammonium salts are formed when it reacts with an acid.

$$ZnSO_4 + 2NH_4OH\ (g) \rightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

Uses of Ammonia:

- It is used in the manufacture of nitric acid and sodium carbonate
- Liquid ammonia is used as a refrigerant
- It is used in the manufacture of rayon
- It is commonly used for preparing various nitrogenous fertilizers such as ammonium nitrate, ammonium sulphate, ammonium phosphate and urea.
- It is an important reagent and is used as a solvent in the laboratory.

Nitric acid-HNO_3

Nitrogen fporms numerous oxoacids through several are unstable in the free state and are known only in aqueous solution or as their salts. Out of oxoacids of nitrogen, nitric acid is the most important. It is very strong oxidizing agent and is quite useful.Nitrogen shown in oxidation state of +5 in nitric acid.

Preparation

In the laboratory, nitric acid can be prepared by heating sodium or potassium nitrate with concentrated sulphuric acid to about 423-475K

$$NaNO_2+H_2SO_4 \rightarrow NaHSO_4+HNO_3$$

Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with P_4O_{10}

Manufacture of Nitric acid

Nitric acid is commonly manufactured by Ostwald process in which its prepared by the catalytic oxidation of ammonia by atmospheric oxygen. The reaction is carried out at about 500K and $9*10^5$ Pa pressure in the pressure of Pt or Rh gauge as catalyst.

$$NH_3+5O_2 \rightarrow 4NO+6H_2O \quad \Delta H=-90.2kJ$$

Nitric oxide thus formed combine with oxygen to form nitrogen dioxide

$$2NO+O_2 \rightarrow 2NO_2$$

Nitrogen dioxide so formed, dissolves in water to give nitric acid

$$3NO_2+H_2O \rightarrow 2HNO_3+NO$$

The NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto about 68% by mass. Dilute nitric acid is further concentrated by dehydration with concentrated sulphuric acid to get about 98% acid.

Properties of Nitric acid:

- Pure nitric acid is colourless liquid
- It has boiling point-355.6K and freezing point 231.4K
- Laboratory grade nitric acid contains about 68% nitric acid by mass and has a specific Gravity of 1.504
- The impure acid is generally yellow due to the presence of nitrogen dioxide as impurity. Nitric acid containing dissolved nitrogen dioxide is known as fuming nitric acid.
- It has a corrosive action on skin and produces painful blisters.

Structure of Nitric acid

Uses of Nitric acid:

1. It is used in the manufacture of ammonium nitrate for fertilizers
2. It is used in the manufacture of sulphuric acid by lead chamber process
3. It is used in the manufacture of explosives such as trinitro toluene (TNT), Nitroglycerine, Picric acid etc.,
4. It is used in the manufacture of dyes, perfumes and silk.
5. It is used for the manufacture of nitrates for use in explosive and pyrotechnics
6. It is used in Pickling(cleaning) of stainless steel and etching of metals.
7. It is also used as an oxidizer in rocket fuels
8. It is used in the purification of gold and silver ass aqua regia.

Chemistry of PH_3, PCl_3,PCl_5,$POCl_3$, P_2O_5 and oxoacids of phosphorous(H_3PO_3,H_3PO_4)

PH_3- Phosphine –Preparation

1. **From Phosphides**: By the action of water or dilute mineral acid on metallic phosphides

$$Ca_3P_2+6H_2O \rightarrow 3Ca(OH)_2+2PH_3$$

$$Ca_3P_2+6HCl \rightarrow 3CaCl_2+2PH_3$$

$$AlP+3HCl \rightarrow AlCl_3+PH_3$$

2. **From phosphorous acid:**

   Pure phosphine can also be prepared by heating phosphorous acid at 478-473K.

   $H_3PO_3 \rightarrow H_3PO_4 + PH_3$

3. **From phosphonium salts:**

   Pure phosphine can also be obtained by heating phosphonium iodide with caustic soda solution.

   $PH_4I + NaOH \rightarrow NaI + H_2O + PH_3$

   Phosphonium iodide is obtained from phosphorous

   $P_4 + 2I_2 + 8H_2O \rightarrow 2PH_4I + 2HI + 2H_3PO_4$

4. **Laboratory preparation**

Phosphine is prepared in the laboratory by heating white phosphorous with concentrated NaOH solution in an inert atmosphere of carbon dioxide or coal gas.

$$4P + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

Structure of PH_3

- Phosphine has pyramidal structure
- sp^3 Hybridisation
- Three bonds are formed by the overlap of sp^3hybrid orbitals of phosphorous with 1s-orbital of hydrogen.
- One of the orbital is occupied by a lone pair of electrons
- The HPH bond angle in PH_3 is 93.6^0 and PH bond distance 142 pm

Properties of Phosphine

- It is a colorless gas with unpleasant smell of rotten fish or garlic,
- It is highly poisonous in nature
- It is heavier than air and is slightly soluble in water
- On cooling to 1855 K, Phosphine condenses to a liquid and on cooling to 139.5K, it solidifies
- It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorous and hydrogen.

Uses of Phosphine

- In semiconductor industries, it is used in small amounts as a dopant.
- PH_3 is used in Holme's signal due to its property of spontaneous combustion.

- It is used to prepare Smoke screens in warfare.

PCl_3-Phosphorous trichloride

Preparation

It is prepared in the laboratory by passing dry chlorine gas over heated white phosphorous. The vapours of PCl_3 distil over and are collected in a receiver cooled by water.

$$P_4+6Cl_2 \rightarrow 4PCl_3$$

The receiver ha a calcium chloride tube attached to it which protects it from the reactions of outside moisture. It can be purified by distilling over white phosphorous to remove the excess of chlorine. It can also be obtained by the reaction of thionyl chloride with white phosphorous.

$$P_4+8SOCl_2 \rightarrow 4PCl_3+4SO_2+2S_2Cl_2$$

Structure:

Phosphorous in PCl_3 undergoes sp^3 hybridization. Three of the sp^3hybrid orbital's overlap with p-orbital's of chlorine to form three P-Cl σ bonds while the fourth sp^3 hybrid orbital contains a lone pair of electrons. Therefore ,like PH_3PCl_3 has pyramidal structure. The bond angle of ClPCl in PCl_3 is 100.4^0 which is greater than HPH bond angle in PH_3 (96.9^0).this is due to stearic crowding of two large Cl atoms in comparison to H atoms. As expected the P-Cl bond is much larger than PH bond because of larger size of Cl atom.

Properties

- It is a colorless oily liquid fuming constantly is the moist air
- Its specific gravity is 1.6
- Its boiling point and freezing point values are 347K and 161K respectively
- It has highly pungent smell

Uses:

- It is mainly employed in the organic chemistry as an important reagent to replace the hydroxyl group by chlorine atom in organic reactions.

Phosphorous pentachloride-PCl_5

Preparation

- Phosphorous pentachloride is prepared by the reaction of white phosphorous with excess of dry chlorine.

$$P_4+10Cl_2 \rightarrow 4PCl_5$$

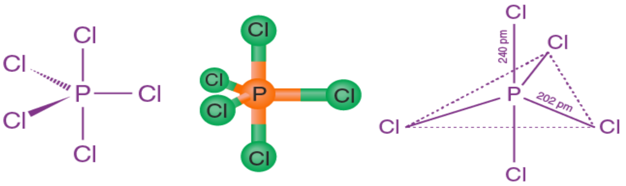
- It can also obtained by the reaction of dry chlorine on phosphorous trichloride

$$PCl_3+Cl_2 \rightarrow PCl_5$$

- PCl_5 can also be prepared by the action of SO_2Cl_2 on phosphorous.

$$P_4+10SO_2Cl_2 \rightarrow 4PCl_5+10SO_2$$

Structure



In PCl_5, Phosphorous undergoes sp^3d hybridization and has Trigonal bipyramidal structure . It has three equatorial P-Cl bonds and two axial P-Cl bonds which are different. Therefore, all the five P-Cl bonds are not equal. The axial bonds are larger than equatorial bonds as P-Cl axial=219pm, P-Cl equatorial= 204pm

Properties of PCl_5

- It is yellowish white powder having pungent smell
- It fumes in moist air due to its strong affinity for water
- On heating it sublimes at 433K and can be melted(318K) only by heating it under pressure.

Uses:

- It is extremely useful in organic reactions to replacea hydroxyl group by chlorine atom such as for the synthesis of Ethyl chloride and Acetyl Chloride.

Phosphorous oxychloride –$POCl_3$

$POCl_3$ is an inorganic compound which is commonly referred to as phosphorous oxychloride or phosphoryl chloride”. At room temperature & pressure, this compound is a colourless liquid that forms fumes in moist air. These fumes are released because $POCl_3$ undergoes hydrolysis in the presence of moisture to yield phosphoric acid and hydrogen chloride (which evolve as fumes).

The synthesis of $POCl_3$ on an industrial scale is done by reacting phosphorus trichloride (PCl_3) with oxygen or phosphorus pentoxide (P_2O_5). It is important to note that $POCl_3$ is not soluble in water since it reacts with it to form hydrogen chloride and phosphoric acid.

Preparation of $POCl_3$

The oxidation of PCl_3 (phosphorus trichloride) with oxygen yields phosphorus oxychloride as the product. The chemical equation for this reaction is provided below.

$$2PCl_3 + O_2 \rightarrow 2POCl_3$$

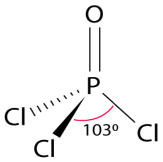
Alternately, this compound can also be prepared from phosphorus trichloride by treating it with potassium chlorate. The chemical equation is:

$$3PCl_3 + KClO_3 \rightarrow KCl + 3POCl_3$$

$POCl_3$ can also be prepared by reacting phosphorus pentachloride with phosphorus pentoxide. The balanced chemical equation for this reaction is given by:

$$P_4O_{10} + 6PCl_5 \rightarrow 10POCl_3$$

Structure of $POCl_3$



$POCl_3$ molecules feature 3 phosphorus-chlorine single bonds and one phosphorus-oxygen double bond. This molecule assumes a tetrahedral shape. The structure of a $POCl_3$ molecule is illustrated below. It can be noted that the P=O bond is much stronger than the P-Cl bond. The bond length of the P=O bond is 158 pm whereas that of the P-Cl bond is 202 pm. It can also be noted that the bond dissociation energy of the P=O bond is approximately 533.5 $kJ.mol^{-1}$.

Properties of $POCl_3$

Physical Properties

- The molar mass of $POCl_3$ is 153.33 grams per mole.
- This colourless liquid has a musty, pungent odour.
- The density of $POCl_3$ in its liquid state is 1.645 grams per cubic centimetre.
- The melting and boiling point of this compound corresponds to 274.4 K and 378.9 K respectively. Therefore, the liquid range of phosphorus oxychloride is quite similar to that of water.

Chemical Properties

- $POCl_3$ is highly soluble in chloroform, benzene, carbon tetrachloride, and carbon disulfide.
- When treated with an excess of some phenols or alcohols, this compound yields organophosphates (or phosphate esters).

- This compound can behave like a Lewis base by forming adducts with several Lewis acids for example, titanium tetrachloride.
- In the presence of Lewis acid catalysts, $POCl_3$ reacts with HBr to obtain $POBr_3$.

Uses of $POCl_3$

- $POCl_3$ is widely used in the industrial manufacture of phosphate esters. Some important examples include the synthesis of triphenyl phosphate and tricresyl phosphate.
- It is also used in the semiconductor industry as a safe source of liquid phosphorus in diffusion processes.
- $POCl_3$ is a commonly used dehydrating agent in chemical laboratories. It is used as a dehydrating agent in the preparation of nitriles from primary amides.
- It is also used as a dehydrating agent in the Bischler-Napieralski reaction.
- Phosphorus oxychloride is also used in the preparation of Vilsmeier's reagent, which is an integral part of the Vilsmeier-Haack reaction.

Phosphorus Pentoxide –P_2O_5 or P_4O_{10}.

Phosphorus Pentoxide is a chemical compound whose empirical formula is P_2O_5 and whose molecular formula is P_4O_{10}. At ambient temperatures, this compound exists as a white solid that is crystalline in nature. Phosphorus pentoxide is an acid anhydride that is obtained from phosphoric acid. It is highly hygroscopic and is, therefore, used as a dehydrating agent and as a desiccant.

Preparation of Phosphorus Pentoxide

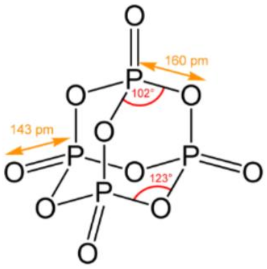
P_2O_5 (or P_4O_{10}) can be prepared by burning elemental P_4 (tetra-phosphorus) in an environment containing a sufficient amount of oxygen. The chemical reaction for the preparation of P_2O_5 is provided below.

$$\mathbf{P_4 + 5O_2 \rightarrow P_4O_{10}}$$

This compound is a source of pure phosphoric acid.

Structure of Phosphorus Pentoxide

It can be noted that the P=O bond length in this compound is 143 picometers and the P-O bond length is 160 picometers.



Physical Properties of Phosphorus Pentoxide

- Phosphorus pentoxide is a white solid which does not have any distinct odour.
- The chemical formula of this compound is P_4O_{10}. However, it is named after its empirical formula, which is P_2O_5.
- The molar mass of phosphorus pentoxide corresponds to 283.9 g/mol.
- The density of this solid is 2.39 g/cm^3.
- The melting point of this P_2O_5 is 613K. Its boiling point corresponds to 633K (however, it undergoes sublimation at this temperature).

Chemical Properties of Phosphorus Pentoxide

- Phosphorus pentoxide undergoes violent hydrolysis when exposed to water. This reaction is highly exothermic.
- This compound crystallizes in four different polymorphs.
- It is highly corrosive and must, therefore, be kept away from metals.

Uses of Phosphorus Pentoxide

- This compound is a very potent dehydrating agent (since it undergoes hydrolysis in an exothermic manner).
- Phosphorus pentoxide is also used in some organic synthesis reactions. For example, it is used in the preparation of nitriles from primary amides.
- It is a vital component of the Onodera reagent, which is widely used in the oxidation of alcohols.
- This compound can also be used to convert certain mineral acids into their anhydrides. For example, N_2O_5 can be prepared from HNO_3 with the help of P_2O_5.

Phosphorous acid- trihydroxy-Orthophosphorus acid- H_3PO_3

Phosphorous acid which is also called phosphonic acid is a colourless oxyacids of phosphorus.Phosphorous acid is produced in the form of a white volatile powder by the slow combustion of phosphorus. Its salts are called ***phosphites***. It is conveniently prepared by allowing phosphorous trichloride to react with water. In industrial synthesis PCl_3 is sprayed into steam at 190°C the heat of reaction is used to distill off the hydrogen chloride and excess water vapour.

H_3PO_3	Phosphorous Acid
Density	1.65 g/cm³
Molecular Weight/ Molar Mass	82 g/mol
Boiling Point	200 °C
Melting Point	73.6 °C
Chemical Formula	H_3PO_3

Phosphorous Acid Structure – H_3PO_3

Physical Properties of Phosphorous Acid – H_3PO_3

Odour	Sour odour
Appearance	White solid, deliquescent
Covalently-Bonded Unit	1
Hydrogen Bond Acceptor	3
Complexity	8
Solubility	Soluble in water

Chemical Properties of Phosphorous Acid – H_3PO_3

- Phosphorous acid has strong reducing properties it tends to be converted to phosphoric acid. On being heated dry phosphorous acid disproportionates to give phosphine and phosphoric acid.

$$\mathbf{H_3PO_3 + 3H_3PO_3 \rightarrow PH_3 + 3H_3PO_4}$$

- Phosphorous acid reacts with a base like sodium hydroxide forms sodium phosphate and water.

$$\mathbf{H_3PO_3 + 3NaOH \rightarrow Na_3PO_3 + 3H_2O}$$

Uses of Phosphorous Acid – H_3PO_3

- Used in the production of basic lead phosphonate PVC stabilizer, aminomethylene phosphonic acid and hydroxyethane diphosphonic acid.
- Used as a strong reducing agent.

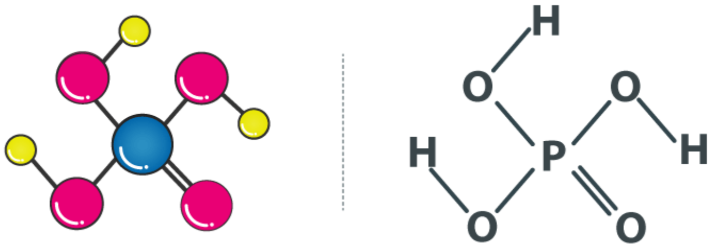
- Used in the production of raw materials of phosphorous acid, synthetic fibres and organophosphorus pesticides etc.
- Used in the production of high efficient water treatment agent amino trimethylene phosphonic acid.

Phosphoric Acid- H_3PO_4.

Orthophosphoric acid refers to phosphoric acid. Phosphoric Acid is a weak acid with the chemical formula H_3PO_4. ***Phosphoric Acid*** is an acid-containing four atoms of oxygen, one atom of phosphorus, and three atoms of hydrogen. It is also known as phosphoric(V) acid or orthophosphoric acid. It is present in teeth and bones and helps in metabolic processes. In its liquid form, it appears as a clear, colourless solution and in its solid form, it appears as a transparent, crystalline solid.

As a sequestering agent, it helps in the binding of divalent cations. It is widely used in orthodontics and dentistry. Phosphoric acid is important in biogeochemistry and biochemistry. It is a tribasic acid. All three hydrogens are acidic, the pKa value of first, second and third hydrogen are respectively $pKa_1 = 2.14$, $pKa_2 = 7.20$, and $pKa_3 = 12.37$

Structure of Phosphoric Acid (H_3PO_4)



Physical Properties of Phosphoric Acid (H_3PO_4)

H_3PO_4	Phosphoric Acid
Molecular Weight/ Molar Mass	97.994 g/mol
Density	1.88 g/cm³
Boiling Point	158 °C
Melting Point	42.35 °C

1. Phosphoric acid is an odourless, colourless, viscous liquid, possessing in a high degree the property of reddening litmus. It cannot be obtained free from water.
2. When exposed to a red heat and afterward cooled it forms a transparent brittle glass.
3. This fusion should be effected in a platinum crucible since phosphoric acid when heated to redness attacks either glass or porcelain.

4. The acid if examined after this exposure to heat is found although its composition remains the same to have acquired new properties.
5. On this account the name of para phosphoric has been given to it; while the term phosphoric is applied to designate the acid in the state first described.
6. Nitrate of silver yields with phosphoric acid a yellow precipitate with para phosphoric acid a white one. Albumen is coagulated by the latter but not by the former.

Preparation of Phosphoric acid

It can be conveniently prepared by dissolving P_2O_5 in water followed by boiling the solution to form a thick syrup.

$$\mathbf{P_2O_5 + 3H_2O \rightleftharpoons 2H_3PO_4}$$

Red phosphorus when heated with conc. HNO_3 yields orthophosphoric acid.

$$\mathbf{P + 5HNO_3 \rightarrow H_3PO_4 + H_2O + 5NO_2}$$

On a large scale, it is prepared by treating phosphorite rock with dil.H2SO4.

$$\mathbf{Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4}$$

Synthesis of Phosphoric Acid – H_3PO_4

- Phosphoric acid may be obtained by adding sulphuric acid to the phosphate of baryta suspended in water.
- The sulphuric acid unites with the baryta forming an insoluble salt which precipitates while the phosphoric acid remains in solution.
- When phosphorus is gradually added to nitric acid, phosphoric acid is generated and remains mingled with the residual nitric acid.

Chemical Properties of Phosphoric Acid (H_3PO_4)

- Phosphoric acid is a deliquescent solid, generally encountered as a viscous aqueous solution.
- It is weakly acidic, with three possible sequential deprotonation steps, forming phosphates.
- Like carboxylic acids, phosphoric acid can dimerize via a dehydration reaction to form phospho anhydrides.
- Phosphoric acid undergoes dehydration in three steps and is referred to as tribasic.
- As a result mono and di sodium and potassium salts of phosphoric acid are routinely used as pH buffers.
- One of the most important reactions of phosphoric acid and its derivatives is multimerization.

- As with carboxylic acids, two phosphoric acid molecules may combine with the loss of water to form a di phosphate ester also referred to as pyrophosphate.
- However, as phosphoric acid has further -OH functionalities triphosphates may also be formed.
- Salts of phosphoric acid are solid and many are relatively water-insoluble unless a strong mineral acid is present.

Uses of Phosphoric Acid (H_3PO_4)

Phosphoric acid (H_3PO_4) has many essential applications, in particular in the manufacture of fertilizers. Many acids are derived from phosphate rocks by a wet process based on the reaction between phosphate rocks and acid solutions. This acid (H_3PO_4) is a medium-strong acid, but is also highly corrosive to ferrous or ferrous alloys.

- Around 90% of phosphoric acid produced is used as fertilizers
- It is used as a supplement feed for pigs, cattle, poultry
- It is used in skincare products, cosmetics as a pH adjuster
- It is used in brewing, food and dairy industries as a sanitizing agent
- It is used in beverages and food like jam and cola to acidify them
- It is used to remove rust from the surface to metals

General properties of elements of group 16

The chalcogens are the elements that belong to group 16 of the modern periodic table (or the oxygen family). Chalcogens consist of five elements – oxygen, sulfur, selenium, tellurium, and polonium. It can be noted that the synthetic element livermorium (denoted by the symbol Lv) is also believed to belong to the chalcogen family. It can also be noted that it is not uncommon for oxygen to be excluded from the chalcogen family while generalizing their chemical properties since its chemical behaviour is quite different from the rest of the member elements.

All chalcogens have a total of 6 electrons in their respective valence shells. These elements are also known as ore-forming elements since a large number of metals are known to exist in the form of sulfides or oxides in the earth’s crust. Many chalcogens are known to occur in different allotropes. For example, oxygen is known to have a total of 9 allotropes and sulfur is known to have over 20. However, it can be noted that only one allotrope of tellurium has been discovered so far.

General Electronic Configuration of the Chalcogens

The general electronic configuration of the chalcogens can be written as ‘ns^2np^4’, where ‘n’ denotes the value of the principal quantum number corresponding to the valence shell of the element. The electronic configurations of the chalcogens are tabulated below.

Chalcogen	Electron Configuration
Oxygen (O)	$[He]2s^22p^4$
Sulfur (S)	$[Ne]3s^23p^4$
Selenium (Se)	$[Ar]3d^{10}4s^24p^4$
Tellurium (Te)	$[Kr]4d^{10}5s^25p^4$
Polonium (Po)	$[Xe]4f^{14}5d^{10}6s^26p^4$

Physical Properties of the Chalcogens

Atomic/Ionic Radii of the Chalcogens

The atomic radii or the ionic radii of elements increases while progressing down a group. The chalcogen with the lowest atomic radius and ionic radius is oxygen, whereas the chalcogen with the largest atomic/ionic radius (excluding livermorium) is polonium.

It can also be noted that the atomic radii of elements decrease across the period due to the addition of protons and the increase in the effective nuclear charge. Therefore, the atomic radius of oxygen will be much smaller than that of lithium.

Ionization Enthalpies of the Chalcogens

As the size or the radius of the atom increases, the ionization enthalpy decreases (it is easier to remove an electron from an atom with a large atomic radius since the distance between the nucleus and the valence shell will be relatively large). Therefore, the ionization enthalpies of the chalcogens decrease while progressing down the group. Oxygen has the highest ionization enthalpy among the chalcogens.

It can also be noted that ionization enthalpy increases across a period (due to the increase in the effective nuclear charge across the period). Therefore, the ionization enthalpy of oxygen will be much higher than that of lithium.

Electron Gain Enthalpies of the Group 16 Elements

As the size of the atom increases, the electron gain enthalpy decreases. Therefore, the electron gain enthalpies of the chalcogens decrease down the group. It is important to note that oxygen has a less negative electron gain enthalpy when compared to sulfur, which can be explained by the compressed atomic structure of oxygen, which contributes to interelectronic repulsion between the valence electrons and any other approaching electron.

Electronegativities of the Chalcogens

Electronegativity decreases moving down a group due to many factors such as the increase in the atomic radius and the increase in the electron-electron repulsion. The most electronegative chalcogen is oxygen and the least electronegative chalcogen is polonium (livermorium not considered).

Metallic Nature of the Group 16 Elements

- Oxygen and sulfur are classified as non-metals.
- Selenium and tellurium are classified as metalloids.
- Under standard conditions, polonium exhibits metallic characteristics. However, it is important to note that polonium is a radioactive element.

Trends in the Melting and Boiling Points of the Chalcogens

Due to the increase in atomic sizes and atomic masses down a group, the melting and boiling points of the elements also increase while progressing down a group (as a result of increased intermolecular forces of attraction). Among the chalcogens, oxygen is known to have the lowest melting and boiling point.

The considerable difference in the melting and boiling points of sulfur and oxygen can be explained by the fact that oxygen exists in the atmosphere as a diatomic molecule whereas sulfur usually exists in the form of a polyatomic molecule.

Chemical Properties of the Chalcogens

Allotropy Exhibited by Group 16 Elements

Almost all chalcogens have more than one allotrope. The most common allotropes of oxygen are dioxygen and ozone. In fact, oxygen has 9 known allotropes. Furthermore, sulfur is known to have over 20 known allotropes.

Selenium is known to have at least 5 different allotropes and polonium is known to have 2 allotropes. The two most stable allotropic forms of sulfur are monoclinic sulfur and rhombic sulfur. It can be noted that selenium and tellurium can exist in both crystalline and amorphous forms.

Oxidation States Exhibited by the Chalcogens

Since the general electronic configuration of the chalcogens is ‘ns^2np^4’, they can obtain a stable electronic configuration by gaining two electrons or participating in covalent bonding. When they gain 2 electrons, the general formula of the ion formed is M^{2-} (where M denotes a chalcogen). The regular oxidation states shown by the chalcogens include -2, +2, +4, and +6.

Reactions between Group 16 Elements and Hydrogen

When reacted with dihydrogen, the chalcogens usually form hydrides with the general formula H_2M (where M denotes any chalcogen – oxygen, sulfur, selenium, tellurium, or polonium). The general format of this chemical reaction is:

M (chalcogen) + H_2 (dihydrogen) → H_2M (hydride of the chalcogen)

To learn more about the chalcogens and other related concepts, such as the physical and chemical properties of the noble gases, register with BYJU'S and download the mobile application on your smartphone.

Allotropy of Group 16 Elements

Allotropy refers to the different forms of elements which have different physical properties but similar chemical properties. The allotropes for Group 16 Elements are discussed below:

- Dioxygen and ozone are two forms of oxygen.
- Sulphur comes in yellow ortho-rhombic, α and β monoclinic forms.
- There are eight allotropes of selenium, three of which are red monoclinic forms with Se_8 rings. The thermodynamically stable form of selenium is grey hexagonal metallic selenium with polymeric helical chains.
- Amorphous black selenium is the most prevalent form of the element. The only selenium allotrope that conducts electricity is grey selenium.
- There is just one crystalline form of tellurium, which has a chain structure similar to grey selenium.
- Polonium has 33 isotopes and all exhibit radioactivity.

Allotropes of Sulphur

Sulphur generates a number of allotropes. The first is yellow rhombic sulphur (α-sulphur), and the second is monoclinic sulphur (β-sulphur). The most intriguing feature is that the allotropes of the sulphur compound are interconvertible in terms of thermal stability. It means that rhombic sulphur produces monoclinic sulphur when heated above 369K.

Rhombic sulphur (α-sulphur)

Rhombic sulphur is a crystalline substance with an octahedral shape. When we heat the roll sulphur solution in the CS_2, we get rhombic sulphur. It has a yellow colour, a specific gravity of 2.06, and a melting point of 385.8K. Rhombic sulphur compounds are not soluble in water, but they are soluble in ether, benzene, or alcohol.

Monoclinic sulphur (β-sulphur)

When we melt rhombic sulphur in a dish and cool it, we get monoclinic sulphur. In this process, we poke two holes in the crust and pour out the remaining liquid. When the crust is removed after this process, we get colourless needle-shaped crystals of -sulphur.

Colloidal Sulphur

It is created by passing hydrogen sulphide through a saturated and cooled sulphur dioxide solution in water. The other method is to mix an alcohol and sulphur solution into the water. It also serves as a solvent in the carbon disulfide reaction. It can be used in pharmaceuticals.

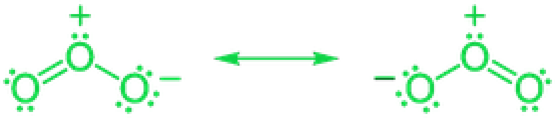
Ozone-O_3

Ozone, O_3, an unstable, blue, diamagnetic gas with a characteristic pungent odor, protects the earth and its inhabitants from intense ultraviolet radiation from the sun.

Ozone is an allotropic molecular form of oxygen containing three atoms of oxygen (O_3). Ozone O3 is generated through the passage of oxygen O_2 through a high voltage potential resulting in the attachment and formation of a third oxygen atom. The molecular formula for ozone (O_3) was established by Soret (1863) by taking the ratio of the change in volumes when O_3/O_2 mixtures were either heated or exposed to turpentine and cinnamon oil. The word ‘ozone’ comes from the Greek word ‘ozein’ which means ‘to smell’. This meaning comes from ozone at the ground level, which gives off a pungent, acrid odour.

O_3	Ozone
Density	2.14 kg/m^3
Molecular Weight/ Molar Mass	48 g/mol
Boiling Point	-112 °C
Melting Point	-192.2 °C
Chemical Formula	O_3

Ozone Structure – O_3



Ozone is a bent molecule with symmetry similar to water, according to microwave spectroscopy experiments. The angle formed by O-O-O is 116.78°. One lone pair is sp^2 hybridised with the centre atom. The molecule ozone is polar. The molecule can be described as a resonance hybrid with two contributing structures, one with a single bond on one side and the other with a double bond. It has the same isoelectronic properties as the nitrite anion.

Physical Properties of Ozone – O_3

1. Ozone is a colourless or pale blue gas that is mildly soluble in water but much more soluble in inert nonpolar solvents like carbon tetrachloride or fluorocarbons, where it forms a blue solution.
2. It condenses to create a dark blue liquid around 161K.
3. Allowing this liquid to reach its boiling point is dangerous since both concentrated gaseous and liquid ozone has the potential to explode.
4. At temperatures below 80 degrees Celsius, it solidifies as a violet-black liquid.
5. Most people can detect ozone in the air because it has a distinct sharp odour that is similar to chlorine bleach.
6. Ozone exposure causes headaches, burning eyes, and irritation of the respiratory passages.
7. Modest levels of ozone in the air are extremely damaging to organic materials such as latex, polymers, and animal lung tissue.
8. Ozone has a weak paramagnetic property.

Odour	Similar to chlorine
Appearance	Pale blue gas
Covalently-Bonded Unit	1
Hydrogen Bond Acceptor	2
Complexity	4.8
Solubility	Soluble in water, CCl4, Sulfuric acid

Chemical Properties of Ozone – O_3

- Ozone dissolves in water resulting in the formation of hydrogen peroxide. The chemical equation is given below.

$$O_3 + 3H_2O \rightarrow 3H_2O_2$$

- Ozone reacts with lead sulfide resulting in the formation of lead sulfate. The chemical equation is given below.

$$3PbS + 4O_3 \rightarrow 3PbSO_4$$

Uses of Ozone – O_3

- Ozone used at water treatment plants without filtration systems.

- Ozone may also be formed by commonly used equipment such as photocopiers, laser printers, and other electrical devices.
- In medicine, by limiting the effects of bacteria, viruses, fungi, yeast, and protozoa, ozone therapy is used to disinfect and treat diseases.
- Several ozone-depleting compounds possess properties that make them good refrigerants that is, they can efficiently transfer heat from one location to another

Classification Of Oxides

This topic educates with the **classification of oxides** based on the nature and properties of compounds. Oxides are binary compounds formed by the reaction of oxygen with other elements. Oxygen is highly reactive in nature. They react with metals and non-metals to form oxides.

Oxides

The classification of oxides is done into neutral, amphoteric and basic or acidic based on their acid-base characteristics.

1. An acidic oxide is an oxide that when combined with water gives off an acid.
2. A basic oxide is an oxide that when combined with water gives off a base.
3. When a substance reacts chemically, both as a base or acid is termed as amphoteric oxide.
4. Neutral Oxide is one that neither has an acidic characteristic nor a basic one.

Metal Oxides have an oxidation number of -2 and generally comprise an oxygen anion. The Earth’s crust is mostly made up of oxides that are solid. Oxide coatings can get formed over pure elements too, for instance, a foil made of aluminium gets covered by a thin skin of Al_2O_3, and this skin defends the rest of the foil from corrosion.

Classification Of Oxides

Depending upon nature and the properties exhibited by compounds, they are classified into

- Acidic oxides
- Basic oxides
- Amphoteric oxides
- Neutral oxides

Basic oxide:

Metals react with oxygen to give basic compounds of oxygen. These compounds are usually ionic in nature. Group 1, 2 and lanthanides form basic compounds of oxygen when they react with dioxygen. During the formation of these compounds, a large amount of energy is released. These compounds readily react with water except for a few exceptions.

Examples: M_2O_3, MO_2, ThO_2

$$Na_2O + H_2O \rightarrow 2NaOH$$

Acidic oxide:

Non-metals react with oxygen to form acidic compounds of oxides which are held together by covalent bonds. These compounds can also be called acid anhydrides. Acid anhydrides usually have a low melting and boiling point except for compounds like B_2O_3 and SiO_2 which have high melting points and form giant molecules.

Examples: NO, CO_2

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$B_2O_3 + H_2O \rightarrow 2H_3BO_3$$

Amphoteric oxide:

Amphoteric oxides are compounds of oxygen which exhibit both acidic as well as basic characteristics. These oxides when reacting with acid undergo a neutralization reaction to form water and salt. This exhibits the basic property of the compounds. Similarly amphoteric oxides reacts with the alkali to form salt and water, exhibiting acidic properties.

Example: aluminium oxide

Acidic characteristics:

$$Al_2O_3 + 6HCl \rightarrow 2Al_3^+ + 6Cl^- + 3H_2O$$

Basic characteristics:

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al\,(OH)_4]^-$$

Neutral Oxides:

Some compounds react with oxygen to form oxides which do not exhibit acidic nor basic characteristics. Such compounds are called neutral compounds of oxygen.

Example: NO, CO.

Oxides of sulphur

The **oxides of sulphur** are inorganic compounds made up entirely of sulphur and oxygen atoms. In the Earth's lower atmosphere, the most commonly found oxides of sulphur are sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Some other notable classes of sulphur oxides are listed below.

- The lower sulphur oxides have the general formula S_mO_n (m>2n).

- Sulphur monoxide (SO) and disulphur dioxide (S_2O_2) which are formed from the dimerisation of sulphur monoxide.
- Disulphur monoxide (S2O)
- The higher sulphur oxides, in which sulphur exhibits an oxidation state of +6.

Normally, oxides of sulphur are formed when substances containing sulphur are burnt in air containing plenty of oxygen. It can be found during the roasting of sulphide ores, burning of fossil fuels, coals, etc. One of the most common sources of sulphur oxide that we can relate to is the emission from vehicles. Sulphur dioxide can be formed naturally due to volcanic activity and also as a byproduct during the metallurgy of copper. Sulphur trioxide, on the other hand, is prepared industrially as a precursor to sulphuric acid and is, therefore, referred to as sulphuric anhydride. The lower oxides of sulphur are formed as intermediates during the combustion of elemental sulphur and are relatively less stable when compared to SO_2 and SO_3.

Important Oxides of Sulphur

While there are many types of oxides of sulphur, the two most important ones are

1. Sulphur dioxide (SO_2)
2. Sulphur trioxide (SO_3)

Sulphur Dioxide

Sulphur dioxide is one of the most common sulphur oxides that is found on the Earth and even in space. It is a colourless gas. It is sometimes poisonous and is also soluble in water. Exposure to this gas in high concentration can be harmful to living beings. It can cause adverse health effects in humans.

Properties of Sulphur Dioxide

- Sulphur dioxide is a colourless, acidic gas with a pungent and suffocating smell.
- It can be liquefied easily.
- It is highly soluble in water, and its aqueous solution (H2SO3), is acidic in nature.
- It acts as a strong reducing agent and, as such, reduces halogens to halogen acids, turning acidified $K_2Cr_2O_7$ solution green.

  $$\mathbf{K_2Cr_2O_7+3SO_2+H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+H_2O}$$

- Decolourises KMnO4 solution and reduces ferric to ferrous salts, PbO_2 to $PbSO_4$ and Na_2O_2 to Na_2SO_4.
- Being acidic, it reacts with NaOH solution to give sodium sulphite (Na_2SO_3), which then reacts with more SO_2 to form sodium hydrogen sulphite ($NaHSO_3$).

  $$\mathbf{2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O}$$

Na_2SO_3+ SO_2+H_2O→ $NaHSO_3$

- It also decomposes carbonates and bicarbonates, evolving CO_2 gas.

Na_2CO_3 + $2SO_2$+ H_2O → NaHSO3 + CO_2

$NaHCO_3$ + SO_2 → $NaHSO_3$ + CO_2

- With lime water, it forms milkiness due to the formation of insoluble calcium sulphite ($CaSO_3$), which disappears on further passing SO_2 for a long time as a result of the formation of soluble sodium bisulphite ($NAHSO_3$).

$Ca(OH)_2$ + SO_2 → $CaSO_3$ + H_2O

$CaSO_3$ + SO_2 + H_2O → $Ca(HSO_3)_2$+ H_2O

- SO2, in reaction with PCL_5, gives thionyl chloride (SOCI), which fumes in moist air and is used in organic chemistry.

PCI_5 + SO_2 → $SOCl_2$ + $POCI_3$

- It also acts as an oxidising agent and a Lewis base. For example, it oxidises H_2S to S.

$2H_2S$ + SO_2 → $2H_2O$ +3S.

Lighted magnesium ribbon and heated potassium metal keep on burning in SO_2 and are oxidised.

2Mg + SO_2 → 2MgO + S

3Mg + SO_2 → 2MgO + MgS

4K+$3SO_2$ → K_2SO_3 + $K_2S_2O_3$

3Fe + SO_2 → 2FeO + FeS

CO is oxidised to CO_2.

2CO+ SO_2 → $2CO_2$ +S

In the presence of HCl, stannous and mercurous salts are oxidised to stannic and mercuric salts.

$2SnCl_2$+ SO_2+ 4HCl→ $2SnCl_4$ + $2H_2O$ + S

2 Hg_2Cl_2+ SO_2 +4HCl → $4HgCl_2$+ $2H_20$ + S

It combines with O2 in the presence of platinised asbestos at 723 K or in the presence of V_2O_5 at 773 K to give SO_3.

2 SO_2+ O_2 → 2 SO_3

- It reacts with Cl2 in the presence of charcoal as a catalyst to form sulphuryl chloride SO_2Cl_2.

SO_2 + Cl_2 → SO_2Cl_2

Preparation

It can be prepared by

● Burning of sulphur in the air.

$$S + O_2 \rightarrow SO_2$$

● Heating of iron pyrites and by the action of dilute acids on sulphites and bisulphites.

$$4FeS_2 + 11O_2 \rightarrow Fe_2O_3 + 8SO_2$$

In the laboratory, it is prepared by the action of concentrated H2SO4 on copper turnings.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Uses of Sulphur Dioxide

- Sulphur dioxide is used in the manufacture of H_2SO_4.
- It is used in the refining of cane juice in the sugar industry.
- For fumigation, as a germicide and for preserving fruits.
- Liquid SO_2 is used as a non-aqueous solvent and as a refrigerant.

Sulphur Trioxide (SO_3)

Sulphur trioxide is often formed when sulphur dioxide is oxidised. This chemical compound can occur in different forms more widely in a white crystalline solid. When it is in liquid form, it is colourless. It is a highly reactive substance and tends to react violently with water. When sulphur trioxide is in vapour form, it is considered to be a major pollutant and is one of the components of acid rain. It also tends to fume to a great degree in the atmosphere, and its vapour is also highly corrosive. This compound should be handled with extreme caution.

Properties

- It is an acidic oxide and dissolves in H_2O to form H_2SO_4. As such, it reacts with CaO to form $CaSO_4$ and decomposes carbonates to evolve CO.
- It reacts with HCl to form chlorosulphonic acid ($HOSO_2CI$).
- It acts as a strong oxidising agent.

Preparation

It can be prepared by

(i) Passing a mixture of SO_2 and O_2 overheated Pt or V_2O_5.

(ii) By dehydration of H_2SO_4 with P_2O_5 or by heating ferric sulphate.

$$2\ SO_2 + O_2 \Leftrightarrow 2\ SO_3$$

$$H_2SO_4 + P_2O_5 \rightarrow SO_3 + 2\ HPO_3$$

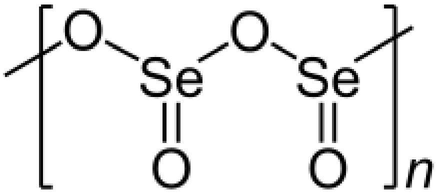
$$Fe_2(SO4)_3 \rightarrow Fe_2O_3 + 3\ SO_3$$

Uses

- Used in the preparation of sulphuric acid and other chemicals.
- It is an important reagent in sulphonation reactions.

Oxides of Selenium

Selenium dioxide



Selenium dioxide is the chemical compound with the formula SeO_2. This colorless solid is one of the most frequently encountered compounds of selenium. It is used in making specialized glasses as well as a reagent in organic chemistry

Properties

SeO_2 is a one-dimensional polymer, the chain consisting of alternating selenium and oxygen atoms. Each Se atom is pyramidal and bears a terminal oxide group. The bridging Se-O bond lengths are 179 pm and the terminal Se-O distance is 162 pm. The relative stereochemistry at Se alternates along the polymer chain (syndiotactic). In the gas phase selenium dioxide is present as dimers and other oligomeric species, at higher temperatures it is monomeric. The monomeric form adopts a bent structure very similar to that of sulfur dioxide with a bond length of 161 pm. The dimeric form has been isolated in a low temperature argon matrix and vibrational spectra indicate that it has a centrosymmetric chair formDissolution of SeO_2 in selenium oxydichloride give the trimer $[Se(O)O]_3$ Monomeric SeO_2 is a polar molecule, with the dipole moment of 2.62 D pointed from the midpoint of the two oxygen atoms to the selenium atom.

The solid sublimes readily. At very low concentrations the vapour has a revolting odour, resembling decayed horseradishes. At higher concentrations the vapour has an odour resembling horseradish sauce and can burn the nose and throat on inhalation. Whereas SO_2 tends to be molecular and SeO_2 is a one-dimensional chain, TeO_2 is a cross-linked polymer

SeO_2 is considered an acidic oxide: it dissolves in water to form selenous acid Often the terms *selenous acid* and *selenium dioxide* are used interchangeably. It reacts with base to form selenite salts containing the SeO^{2-} anion. For example, reaction with sodium hydroxide produces sodium selenite:

$$SeO_2 + 2\,NaOH \rightarrow Na_2SeO_3 + H_2O$$

Preparation

Selenium dioxide is prepared by oxidation of selenium by burning in air or by reaction with nitric acid or hydrogen peroxide, but perhaps the most convenient preparation is by the dehydration of selenous acid.

$$2\ H_2O_2 + Se \rightarrow SeO_2 + 2\ H_2O$$

$$3\ Se + 4\ HNO_3 + H_2O \rightarrow 3\ H_2SeO_3 + 4\ NO$$

$$H_2SeO_3 \rightleftharpoons SeO_2 + H_2O$$

Uses

- SeO_2 is an important reagent in organic synthesis. Oxidation of paraldehyde (acetaldehyde trimer) with SeO_2 gives glyoxal.
- Selenium dioxide can also be used to synthesize 1,2,3-selenadiazoles from acylated hydrazone derivatives.
- Selenium dioxide imparts a red colour to glass. It is used in small quantities to counteract the colour due to iron impurities and so to create (apparently) colourless glass. In larger quantities, it gives a deep ruby red colour.
- Selenium dioxide is the active ingredient in some cold-bluing solutions.
- It was also used as a toner in photographic developing.

Oxo acids of sulphur(Caro's acid and Marshall's acid)

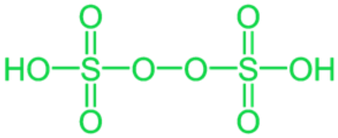
Oxoacids are oxygen-containing acids. Many oxoacids, such as H_2SO_4, H_2SO_3, and others, are known to be formed by sulphur. When sulphur is coordinated to oxygen, it forms a tetrahedral structure in oxoacids. Sulfur oxoacids are sulphur, oxygen, and hydrogen-containing chemical compounds. Sulfuric acid is the most well-known and widely utilised in industry. Sulfur contains various oxoacids; however, some of these are only recognised through their salts. The acids that have been described have a variety of structural characteristics.

Peroxodisulphuric acid

- Sulphur in the +6 oxidation state is present in peroxodisulphuric acid. As a result, it is a strong oxidizing agent and a highly explosive substance in nature. Marshall's acid is the common name for it. It has one peroxide group that forms a bridge between the two sulphur atoms.

- Other than the peroxide group, each sulphur atom is linked to one hydroxyl group (S-OH bond) and two oxygen atoms (S=O bond). We can make it by reacting chlorosulfuric acid with hydrogen peroxide. The following is the reaction:

- **$2ClSO_3H + H_2O_2 \rightarrow H_2S_2O_8 + 2HCl$**

- 

Peroxodisulphuric acid

Peroxomonosulphuric acid

Synthesis and production

The laboratory scale preparation of Caro's acid involves the combination of chlorosulfuric acid and hydrogen peroxide:

Published patents include more than one reaction for preparation of Caro's acid, usually as an intermediate for the production of potassium monopersulfate (PMPS), a bleaching and oxidizing agent. One patent for production of Caro's acid for this purpose gives the following reaction:

This is the reaction that produces the acid transiently in "piranha solution".

Uses in industry

- It has been used for a variety of disinfectant and cleaning applications, e.g., swimming pool treatment and denture cleaning
- It is also used in laboratories as a last resort in removing organic materials
- It used in the plastics industry as radical initiators for polymerization. They are also used as etchants, oxidative desizing agents for textile fabrics, and for decolorizing and deodorizing oils.
- It is widely used as an oxidizing agent.

Chemistry of Halogens:

General characteristics of halogen with reference to electronegativity, electron affinity, Oxidation states and oxidizing power

Periodic Trends

The periodic trends observed in the halogen group:

Melting and Boiling Points (increase down the group)

The melting and boiling points increase down the group because of the van der Waals forces. The size of the molecules increases down the group. This increase in size means an increase in the strength of the van der Waals forces.

F<Cl<Br<I<At

Melting and Boiling Points of Halogens		
Halogen	**Melting Point (°C)**	**Boiling Point (°C)**
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7.2	58.8
Iodine	114	184
Astatine	302	337

Atomic Radius (increases down the group)

The size of the nucleus increases down a group (F < Cl < Br < I < At) because the numbers of protons and neutrons increase. In addition, more energy levels are added with each period. This results in a larger orbital, and therefore a longer atomic radius.

Halogen	Covalent Radius (pm)	Ionic (X-) radius (pm)
Fluorine	71	133
Chlorine	99	181
Bromine	114	196
Iodine	133	220
Astatine	150	

Ionization Energy (decreases down the group)

If the outer valence electrons are not near the nucleus, it does not take as much energy to remove them. Therefore, the energy required to pull off the outermost electron is not as high for the elements at the bottom of the group since there are more energy levels. Also, the high ionization energy makes the element appear non-metallic. Iodine and astatine display metallic properties, so ionization energy decreases down the group (At < I < Br < Cl < F).

Halogen	First Ionization Energy (kJ/mol)
Fluorine	1681
Chlorine	1251
Bromine	1140
Iodine	1008
Astatine	890±40

Electronegativity (decreases down the group)

The number of valence electrons in an atom increases down the group due to the increase in energy levels at progressively lower levels. The electrons are further from the nucleus; therefore, the nucleus and the electrons are not as attracted to each other. An increase in shielding is observed. Electronegativity therefore decreases down the group (At < I < Br < Cl < F).

Halogen	Electronegativity
Fluorine	4.0
Chlorine	3.0
Bromine	2.8
Iodine	2.5
Astatine	2.2

Electron Affinity (decreases down the group)

Since the atomic size increases down the group, electron affinity generally decreases (At < I < Br < **F** < Cl). An electron will not be as attracted to the nucleus, resulting in a low electron affinity. However, fluorine has a lower electron affinity than chlorine. This can be explained by the small size of fluorine, compared to chlorine.

Halogen	Electron Affinity (kJ/mol)
Fluorine	-328.0
Chlorine	-349.0
Bromine	-324.6
Iodine	-295.2

Reactivity of Elements (decreases down the group)

The reactivities of the halogens decrease down the group (At < I < Br < Cl < F). This is due to the fact that the atomic radius increases in size with an increase of electronic energy levels. This lessens the attraction for valence electrons of other atoms, decreasing reactivity. This decrease also occurs because electronegativity decreases down a group; therefore, there is less electron "pulling." In addition, there is a decrease in oxidizing ability down the group.

Oxidation States of Halogens in Compounds

As a general rule, halogens usually have an oxidation state of -1. However, if the halogen is bonded to oxygen or to another halogen, it can adopt different states: the -2 rule for oxygen takes precedence over this rule; in the case of two different halogens bonded together, the more electronegative atom takes precedence and adopts the -1 oxidation state.

Halogen	**Oxidation States in Compounds**
Fluorine	(always) -1*
Chlorine	-1, +1, +3, +5, +7
Bromine	-1, +1, +3, +4, +5
Iodine	-1, +1,+5, +7

Peculiarities of fluorine:

- Ionization enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.
- The anomalous behaviour of fluorine is due to its small size,
- Highest electronegativity,
- Low F-F bond dissociation enthalpy, and non availability of d- orbitals in valence shell.
- Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).
- It forms only one oxoacid while other halogens form a number of oxoacids.
- Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.
- Other halogens except fluorine have d- orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

- Each halogen has one electron less than the nearest noble¬ gas and hence has a strong tendency to share its unpaired electron with another atom of the same halogen to form diatomic molecules.
- The acidic strength of HF, HCl, HI acid in water is, HF<HCl <HI
- Because the bond dissociation energy of H-X bond decreases as size of halogen increases.
- ICl is more reactive than I_2, because I-Cl bond is weaker than I-I bond.
- The electron gain enthalpy of fluorine is less negative a compared to chlorine, fluorine is a stronger oxidizing agent than chlorine, because the standard reduction potential of fluorine(i.e. +2.87 V) is more positive than chlorine (i.e. =1.36 V).
- The decreasing order of bond dissociation enthalpies of different diatomic halogens is $Cl_2 > Br_2 > F_2 > I_2$.
- Bleaching of substances by chlorine is permanent while that by sulphur dioxide is temporary, it is because chlorine bleaches coloured materials by oxidation and hence permanent on the other hand, sulphur dioxide bleaches coloured materials by reduction and hence bleaching is temporary because when the bleached material is exposed to air, it gets oxidized and colour is restored.
- More metal fluorides are ionic than metal fluorides, because Clis¬ bigger in size than Fion so it get easily polarized (Fajan’s rule)

Hydrogen Halides:

A halide is formed when a halogen reacts with another, less electronegative element to form a binary compound. Hydrogen, for example, reacts with halogens to form halides of the form HX:

- Hydrogen Fluoride: HF
- Hydrogen Chloride: HCl
- Hydrogen Bromide: HBr
- Hydrogen Iodide: HI

Hydrogen halides readily dissolve in water to form hydrohalic (*hydrofluoric, hydrochloric*, *hydrobromic*, *hydroiodic*) acids. The properties of these acids are given below:

- The acids are formed by the following reaction: $HX\ (aq) + H_2O\ (l) \rightarrow X^-(aq) + H_3O^+\ (aq)$

- All hydrogen halides form strong acids, except HF
- The acidity of the hydrohalic acids increases as follows: HF < HCl < HBr < HI

Hydrofluoric acid can etch glass and certain inorganic fluorides over a long period of time.

It may seem counterintuitive to say that HF is the weakest hydrohalic acid because fluorine has the highest electronegativity. However, the H-F bond is very strong; if the H-X bond is strong, the resulting acid is weak. A strong bond is determined by a short bond length and a large bond dissociation energy. Of all the hydrogen halides, HF has the shortest bond length and largest bond dissociation energy.

Hydrogen Chloride-HCl

In Chemistry, even though Hydrogen Chloride and Chlorine are different elements we tend to study them together. Besides, they share a close relationship, for example, most HCl is produced as a co-product of reactions involving chlorine. So this basically makes it desirable to consider the two chemical substances together. That being said, here we will look at the methods for the preparation of Hydrogen Chloride and Chlorine.

Hydrogen Chloride was first prepared in the year 1648 by Glauber by heating sodium chloride with concentrated. In the year 1840, Davy showed that HCl is a compound of chlorine and hydrogen. The common name for hydrochloric acid is **muriatic acid.**

Preparation of Hydrogen Chloride

Muriatic acid is prepared by warming NaCl crystals with concentrated H2SO4 (Sulphuric acid).

$$NaCl+H_2SO_4 \rightarrow Na_2SO_4+HCl$$

Usually, most of the hydrogen chloride/hydrochloric acid that is formed is a co-product of some other chemical reactions. HCl is also formed by the chlorination of hydrocarbons.

Properties of Hydrogen Chloride

- HCl is an uncoloured gas and has a pungent aroma.
- Hydrochloric acid is the aqueous solution of hydrogen chloride.
- HCl is soluble in water.
- It liquefies at 189K to form a colourless liquid and freezes at 159k to form a white solid.

Uses of Hydrogen Chloride

- HCl is used in the preparation of chlorine, aqua regia, and other chlorides.

- It is used as a solvent to dissolve noble gases.
- It acts as a reagent in laboratories.

Hydrogen Bromide-HBr

Hydrobromic Acid: Properties, Preparation and Uses

Hydrobromic acid is a type of strong acid which is prepared by dissolving the molecule of hydrogen bromide in water. It is a chemical compound of bromine used to produce zinc, calcium and sodium.

- At 124.3 °C, an aqueous solution of "constant boiling" hydrobromic acid distils, yielding 47.6 per cent HBr by mass, or 8.77 mol/L.
- Hydrobromic acid is one of the most potent mineral acids.
- With a pKa of 9, it is stronger than **hydrochloric acid.**
- It is not as powerful as hydroiodic acid.
- The chemical formula of hydrobromic acid is HBr.
- It is a colourless liquid which is highly soluble in water.
- The acid is used in the anti-Markovnikov hydrohalogenation of **alkenes.**
- The molecule is bonded by a single covalent bond between the bromine and **hydrogen** atom.

Hydrobromic acid is made when the diatomic molecule hydrogen bromide (HBr) is dissolved in water. In industrial syntheses, hydrobromic acid (HBr) is employed as a source of bromine.

- It's a strong acid in **aqueous solution** that's used to make PTA/PET catalysts.
- The compound is responsible for forming electrolytes for energy storage.
- Hydrobromination agents are used in various chemical processes like pharma and agro applications.
- In the formation of hydrobromic **acid**, hydrogen ions are easily ionized by highly electronegativity Br atom.
- The compound is highly corrosive in nature, which can easily burn your skin.
- Graphite is the most suitable catalyst for bromine **electrodes**.
- It can easily attack the bromine atom dissolved in hydrobromic acid.

Physical Properties of Hydrobromic Acid

The physical properties of hydrobromic acid are as follows:

- It is a colourless liquid that has a pungent odour.
- The molecular mass or **molar mass** of hydrobromic acid is 80.9 g/mol.

- Another name for hydrobromic acid is bromane or hydrogen bromane.
- It has a **boiling point** of 122 °C.
- In its anhydrous form, the compound appears as a colorless gas.
- It is a strong acid that is corrosive in nature.

Formula	**HBr**
Molecular Weight	80.9 g/mol.
Melting Point	−11 °C
Boiling Point	122 °C
Density	1.49 g/cm^3

Preparation of Hydrobromic Acid

Reaction of bromine with sulphur oxide and water

In this reaction, bromine reacts with the water molecules and **sulphur oxide**, which will produce hydrobromic acid. Sulphuric acid is the additional by-product formed.

$$\mathbf{Br_2 + SO_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ HBr}$$

- The manufacture of anhydrous HBr, which is then dissolved in water, is more commonly used in laboratory preparations.
- Bromine, sulphur, or phosphorus, and water are often used in the industrial production of hydrobromic acid.
- It can, however, be generated electrolytically.
- It's also possible to make it by combining bromides with non-oxidizing acids like phosphoric or **acetic acids.**

Types of Chemical Reactions

Reaction of sulphuric acid and potassium bromide

Alternatively, dilute (5.8M) sulphuric acid and **potassium bromide** can be used to make the acid. The yield is estimated to be over 85%.

$$\mathbf{H_2SO_4 + KBr \rightarrow KHSO_4 + HBr}$$

- HBr is further oxidised to bromine gas by using more concentrated **sulphuric acid**.
- Another way of making hydrobromic acid involves allowing the reaction solution to approach 75 °C.
- Filtering out the $KHSO_4$ and distilling the water further purifies the acid until it achieves an azeotrope (126 °C at 760 torr).
- Hydrobromic acid is commercially available in a variety of concentrations and purities.

Hydrobromic acid is manufactured by using one of the following ways:

- Bromine, sulphur, or phosphorus, and water are often used in the industrial production of hydrobromic acid.
- It can, however, be generated electrolytically.
- It's also possible to make it by combining bromides with non-oxidizing acids like phosphoric or acetic acids.

Uses of Hydrobromic Acid

Some of the uses of hydrobromic acid are as follows:

- Inorganic bromides, such as zinc, **calcium**, and sodium bromides, are mostly made with hydrobromic acid.
- It's an excellent reagent for the preparation of organobromine compounds.
- Certain ethers can be cleaved using HBr.
- Some of the extraction of **ores** and alkylation processes are catalysed by hydrobromic acid.
- Alkyl bromide, tetrabromo bis(phenol), and bromoacetic acid are all important organic chemicals from HBr.
- HBr is used almost entirely for anti-Markovnikov hydrohalogenation of alkenes.
- In industrial syntheses, hydrobromic acid (HBr) is employed as a source of bromine.

Hydrobromic acid is a strong acid with an acid dissociation constant pK_a of −9. The acid is strongly dependent upon the concentration of its own aqueous solution.

Hydrofluoric Acid

The chemical formula for hydrofluoric acid is HFHF. It is water soluble. Hydrofluoric acid was discovered in 1771 by Swedish pharmaceutical chemist Carl Wilhelm Scheele while investigating fluorite minerals. The other names for hydrofluoric acid are Hydronium fluoride and fluorhydric acid.

Hydrofluoric Acid Structure

Hydrofluoric acid is a diatomic molecule with strong intermolecular hydrogen bonding. Hydrogen fluoride is formed when fluorine bonds with hydrogen by sharing electrons, and a single bond is formed. The bond between hydrogen and fluoride is covalent and it is highly polarized. Hydrofluoric acid is a linear molecule, and the bond length of the molecule is 0.91 Å. In the lewis structure of hydrofluoric acid, total 3 lone pairs of electrons are observed. This makes hydrofluoric acid an electron-rich hydride. Only one pair of electrons is shared between hydrogen and Fluorine.

Preparation of Hydrofluoric Acid

Hydrofluoric acid is prepared by treating mineral fluorite with concentrated sulphuric acid at 265°C. The chemical reaction equation for this reaction is given as-

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$$

Hydrofluoric acid is also formed as a byproduct of the production of phosphoric acid from apatite and fluorapatite. Apatite and fluorapatite react with sulphuric acid at high temperatures, and a mixture of gases is released, which includes hydrogen fluoride.

Properties of Hydrofluoric Acid

Physical Properties of Hydrofluoric Acid

The physical properties of hydrofluoric acid are-

Property	**Value**		
Chemical Formula	HF	Density	1.15g/cm31.15
Appearance	Colourless	Solubility	Water soluble
Odour	Strong, pungent odour	pH	3.4
Melting Point	-83.6℃	Pka	3.17
Boiling Point	19.5℃	Molar mass	20.0063 g/mol

Chemical Properties of Hydrofluoric Acid

The chemical properties of hydrofluoric acid are-

- In aqueous solution, hydrogen fluoride acts like a weak acid as the bond between hydrogen and fluorine is quite short. The dissociation of hydrofluoric takes place as-

  $$H2O + HF \rightleftharpoons H3O^{+}.F^{-}$$

- Hydrofluoric acid reacts with silicon dioxide to produce water-soluble silicon fluoride and gaseous silicon fluoride. The reaction takes place as-

  $$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2OSiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

- It reacts with sodium hydroxide to yield sodium fluoride along with water. The reaction equation is-

  $$HF + NaOH \longrightarrow NaF + H2O$$

Hydrofluoric Acid Uses

The uses of hydrofluoric acid are-

- It is employed for making herbicides and pharmaceuticals.
- It is utilized as a reagent to dissolve silicates and oxides.
- It is used as a cleansing agent.
- It is used in industries for manufacturing stain removers.
- In fluorescent light bulbs, hydrofluoric acid is used as an electrical component.

- Fluorine compounds like Teflon, freon, fluorocarbons, and fluoxetine use hydrofluoric acid.
- It is used in phenomenons like glass etching, metal cleaning, and rust removal.
- In semiconductors, it is used for cleaning silicon wafers.
- Hydrofluoric acid is a non-oxidizing acid. It is mainly employed in the pharmaceutical industry and also to make herbicides.

Hydro iodic acid-HI

Hydroiodic acid also called Hydriodic acid is a colourless gas, which reddens litmus strongly, and produces dense white fumes in moist air. The chemical formula for **hydroiodic acid is HI.** Hydroiodic acid is a strong acid made by dissolving hydrogen iodide in water. However both differ in the physical state-one is gas and the other is an aqueous solution. It is one of the strongest of all common halide acids due to high stability of its corresponding conjugate base.

Other names – Hydrogen iodide, iodane

HI	Hydroiodic acid
Density	1,700 g/cm³
Molecular Weight/ Molar Mass	127.911 g/mol
Boiling Point	-35.36 °C
Melting Point	-51 °C
Chemical Formula	HI

Preparation

We can prepare the hydroiodic acid commercially by conducting the reaction of the iodine (I2) with the hydrazine, giving the hydrogen iodide and nitrogen gas as a result.

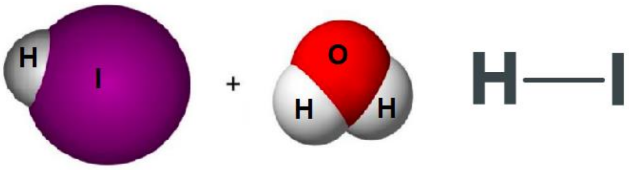
$$\mathbf{2I_2 + NH_2NH_2 \rightarrow 4HI + N_2}$$

We can also prepare the hydroiodic acid by the process of bubbling the hydrogen sulfide gas through an aqueous solution of the iodine.

$$\mathbf{H_2S + I_2 \rightarrow 2HI + S}$$

At the end of this reaction, the HI is distilled to provide the hydroiodic acid in the concentrations that we desire.

Hydroiodic Acid Structure – HI



Physical Properties of Hydroiodic Acid – HI

Odour	Pungent odour
Appearance	Colorless liquid
Covalently-Bonded Unit	1
Heat of vaporization	17.36 kJ/mol at 25ºC
Hydrogen Bond Donor	1
Solubility	Soluble in water

Chemical Properties of Hydroiodic Acid – HI

- Hydroiodic acid reacts with fuming nitric acid forms iodine, nitrogen oxide and water. The chemical equation is given below.

$$2HNO_3 + 6HI \rightarrow 2NO + 3I_2 + 4H_2O$$

- Hydroiodic acid reacts with a base say sodium hydroxide forms sodium iodide and water. The chemical equation is given below.

$$HI + NaOH \rightarrow NaI + H_2O$$

Uses of Hydroiodic Acid – HI

- Used in the manufacture of iodides and as a reducing agent and in disinfectants and pharmaceuticals.
- Used as one of the primary sources of iodine in organic and inorganic synthesis.
- Hydroiodic acid in addition to potassium iodide, a logical choice as a source of a nucleophile in ketal deprotection.
- It is utilised as a catalyst to speed up chemical reactions within other substances. Hydroiodic acid is frequently used to prepare acetic acid due to its potent reducing power and acidity.
- Preparing and producing organic and inorganic iodide, including hydroiodic acid, even though it is one of the most expensive catalytic agents used in this procedure.
- Hydroiodic acid is strongly acidic and can eradicate several viruses and bacteria. It is frequently used to clean and disinfect medical equipment and supplies.

- It is employed as a pharmaceutical intermediary in syrup form. However, it is highly unstable to create a variety of medications for ailments such as chronic bronchitis, scrofula, and malarial infections.
- It also produces alkyl iodides via reaction with alkenes or primary alcohols.

The oxides of halogens

All halogens form multiple oxides due to the covalent nature of halogen and oxygen. While most **halogen** oxides are unstable, there is a large similarity between the electronegativity of **halogens** and oxygen. As fluorine is more electronegative than oxygen, hence all compounds of fluorine with oxygen are termed fluorides of oxygen instead of termed as oxides of fluorine.

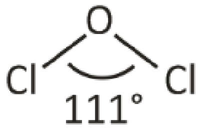
Fluorine is one of the most abundant halogens that are present in the earth's crust in combined form. All these elements show great resemblance to one another in terms of chemical and physical properties. Their oxides and oxoacids are formed widely but only a few of them are known due to their reactive nature.

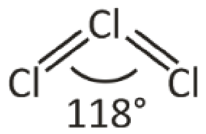
When it comes to stability, I2O5 is the only oxide of **halogen** that remains stable with respect to the dissociation of the elements. The oxides of bromine are the least stable while chlorine oxides decompose violently.

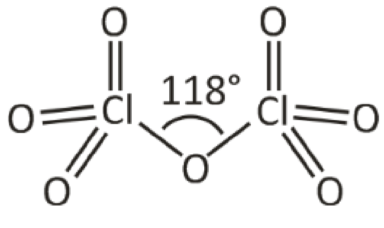
The top **use of halogens** includes the use of Cl20 and ClO2 as bleaching agents in the pulp and flour industries. When it comes to employing the I2O5, it is achieved in the estimation of CO. Some of the famous oxides of **halogens** include:

- Fluorides: These are in the form of OF_2(-1 oxidation state) and O_2F_2 (-1 oxidation state).
- Chlorine oxides: These are Cl_2O (+1 oxidation state), ClO_2(+4 oxidation state), Cl_2O_6(+6 oxidation state), and Cl_2O_7 (+7 oxidation state).
- Bromine oxides: These are Br_2O (+1 oxidation state), BrO_2 (+4 oxidation state), BrO_3 (+6 oxidation state).
- Iodine oxide: I_2O_5 (+5 oxidation state).

Structure:







Out of all the **halogen** oxides, a few of their structures are known. The monoxide structures can be explained based on VSEPR theory. These have a tetrahedral structure with two lone oxygen pairs that give the molecule an angular and “V” shape. The value of bond angle differs based on the position of electrons.

F-O-F< Cl-O-Cl< Br-O-Br

The bonded electron pairs are closer to oxygen in Br2O and Cl2O that makes them repel each other and reduces the lone pair-lone pair repulsion on oxygen.

Properties:

The **halogen elements** form unstable oxides as they encompass free positive energies of formation. OF_2 is the exception as it is stable up to 475 Kelvin with respect to the dissociation of the elements. The stability of these oxides decreases in the below range based on the kinetic and thermodynamic factors:

$I > Cl > Br$

All the higher oxides are stable compared to the lower ones and all oxides except that of iodine are explosive. Iodine pentoxide I2O5 is in the form of a white solid that is stable up to 575 Kelvin. Cl_2O and ClO_2 are further used as germicides and bleaching agents.

The oxoacids of halogens

Any acid containing hydrogen, oxygen, and any other element is called oxoacid. If oxygen is present in acid, the suffixes “ous” and “ic” are used to represent the lower and higher number of oxygen atoms in the acid formula.

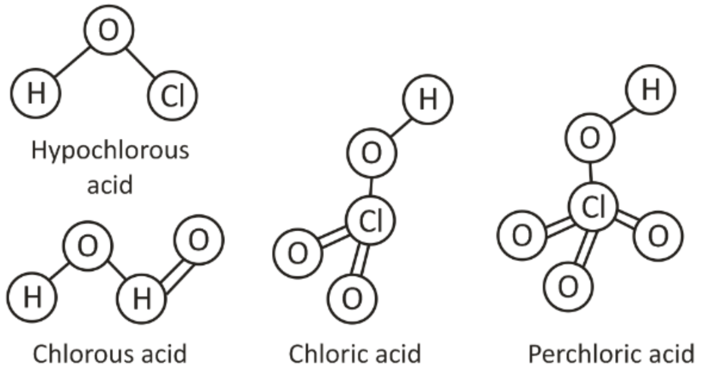
Group 17 of the periodic table- fluorine, chlorine, bromine, iodine, and astatine are the salt producers. A regular gradation in the physical and chemical properties of all elements is observed while moving from up to the bottom.

While all these elements are highly related, Astatine is the only radioactive element in the group. The electronic configuration of these elements indicates that they have seven electrons in the valence shell with ns2np5 configuration. Hence, instead of losing electrons, these elements gain one electron to achieve stable configurations. Due to the small size and effective nuclear charge, the different oxoacids formed by these elements include:

- Hypohalous acid: It is HOX and has a +1 oxidation state. Some of its examples are HOF, HOCl, HOBr, HOI, etc.
- Halous acid: It is HXO_2 and has a +3 oxidation state. Some of its examples are $HClO_2$, etc.

- Halic acid: It is HXO_3 and has a +5 oxidation state. Some of its examples are $HClO_3$, $HBrO_3$, HIO_3, etc.
- Perhalic acid: It is HXO_4 and has a +7 oxidation state. Some of its examples are $HClO_4$, $HBrO_4$, HIO_4, etc.

Structure:



Hypochlorous acid

Chlorous acid

Chloric acid

Perchloric acid

Perchloric acid

$HClO_4$ is a chlorine oxoacid with the chemical name Perchloric acid. It is also called Hyperchloric acid ($HClO_4$) or hydroxidotrioxidochlorine. It is corrosive to tissue and metals. When closed containers containing perchloric acid are exposed to heat for a long duration they can rupture violently.

Production of Perchloric acid

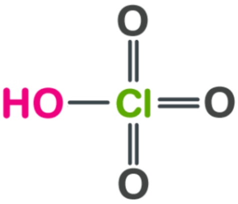
At an industrial level it can be produced in two methods. The traditional method makes full use of the high aqueous solubility of sodium perchlorate (NaClO4) in the production of perchloric acid. Treating sodium perchlorate solution with hydrochloric acid (HCl) produces perchloric acid by precipitating solid sodium chloride. The chemical equation for the same is given as follows:

$$\mathbf{NaClO_4 + HCl \rightarrow NaCl + HClO_4}$$

The second route involves the use of electrodes in which the anodic oxidation of chlorine which is dissolved in water takes place at a platinum electrode. However, the alternate method is considered to be more expensive.

It can also be prepared in laboratories by treating barium perchlorate ($Ba(ClO_4)_2$) with sulphuric acid (H_2SO_4) which precipitates barium sulphate ($BaSO_4$) and leaves perchloric acid. Alternatively, it can be prepared by mixing nitric acid (HNO_3) with ammonium perchlorate (NH_4ClO_4) and by addition of hydrochloric acid during boiling.

Perchloric acid structure – $HClO_4$



Properties of Perchloric acid – $HClO_4$

$HClO_4$	Perchloric acid
Molecular weight of $HClO_4$	100.46 g/mol
Density of Perchloric acid	1.768 g/cm^3
Melting point of Perchloric acid	−17 °C
Boiling point of Perchloric acid	203 °C

$HClO_4$ Uses (Perchloric acid)

- Perchloric acid is used as an oxidiser in the separation of sodium and potassium.
- Used in making explosives.
- Used for plating of metals.
- Used as a reagent to determine the 1H-Benzotriazole.
- Used as a catalyst.
- Used in rocket fuel.
- Used for electropolishing or etching of molybdenum.

<u>Interhalogen Compounds:</u> Iodine monochloride, ICI

Preparation :

i. It is prepared by adding iodine to liquid chlorine and the mixture is kept at 35∘C for 24 hours to ensure a complete reaction.

$$I_2+Cl_2\longrightarrow 2Cl$$

It is obtained as a dark liquid that solidifies on long-standing at room temperature.

ii. It is also prepared by heating iodine with potassium chlorate.

$$KClO_3+I_2\longrightarrow KIO_3+ICl$$

iii. It is also formed in an aqueous solution when hydrochloric acid reacts with a mixture of potassium iodide and potassium iodate.

$$6HCl+KIO_3+5KI\longrightarrow KKCl + 3H_2O + 3l_2$$

$$KIO_3+2l_2+6HCl\longrightarrow KCl+5Cl + 3H_2O$$

The reaction is quantitative and the two stages can be observed by the appearance and disappearance of the red colour of the free iodine.

Properties:

i. It is a dimorphic solid. Its stable form is b-form which is ruby red needle-like crystals, m.p. 27.2°C and the metastable form is b-form which is a red rhombic solid, m.p.14°C and b.p. 97.4°C. These two forms are identical in a gaseous state. These can be separated by cooling the liquid 1Cl below 14°C and by adding to the liquid a crystal of either of the two forms.

ii. Some metal chlorides like those of potassium, rubidium, caesium, and ammonium dissolve in the liquid iodine monochloride to form polyhalides.

$$KCl+ICl \longrightarrow KICl_2$$

while LiCl , NaCl and $BaCl_2$ are insoluble in liquid ICl.

iii. It is readily hydrolyzed by water (in a neutral solution).

$$ICl+3H_2O \longrightarrow 5HCl+HI+2l_2$$

iv. It reacts with alkali to liberate Iodine.

$$5ICl+6NaOH \longrightarrow 5NaCl+NaIO_3+2I_2+3H_2O$$

v. On electrolysis, Iodine is set free at the cathode and chlorine at the anode thereby indicating that the compound is a chloride of monovalent iodine (1+).

$$2Cl \longrightarrow 1^+ + ICl_2^-$$

At Cathode :$21^+ + 2e^- \longrightarrow I$

At Anode : $2Cl_2^- - 2e^- \longrightarrow I_2+2Cl_2$

Therefore. |Cl is used as an ionizing solvent in which the heavier alkali-metal chlorides (KCl, RbCl, CsCl) dissolve.

vi. It reacts with AlC_{l3} and $AgClO_4$ in nitrobenzene.

$$AlCl_3 + ICl \longrightarrow H^+ + (AlCl_4)^-$$

At Anode : $AgClO_4+ICl \longrightarrow AgCl+IClO_4$

vii. In strong hydrochloric acid it forms $HICl_2$.

$$H^+ + Cl^+ + Cl \longrightarrow H^+ + HCl_2^-$$

viii. It reacts with many metals such as Mg, Ca, Ni, Cu, Zn, Fe, Co, etc. to form chlorides.

ix. It converts acetanilide into 4−iodo ocetahylides and salicylic acid into 3,5 di-iodosalicylic acid.

x. ICl forms charge transfer-type complexes with organic bases like pyridine and dioxane.

Chlorine trifluoride, ClF_3

Preparation:

lt may be prepared by treating chlorine or chlorine monofluoride with an excess of chlorine.

$$Cl_2+3F_2 \longrightarrow 2CIF_3$$

$$CIF+F_2 \longrightarrow CIF_3$$

Properties:

i. It is a colorless liquid that gives dense white fumes to air and decomposes in the presence of moist air. Its freezing point is −82.6°C and its boiling point is 12.1°C.
ii. It reacts with almost all elements except for inert gases, nitrogen.
iii. It is an extremely reactive and powerful fluorinating agent. It reacts with AgF and CoF_2 to form AgF_2^- and CoF_3^- respectively.
iv. It destroys glass and quartz and inflames organic substances.
v. It reacts with water to give a red liquid which crystallizes at −70°C and is found to be CIFO. $ClF_3+H_2O \longrightarrow ClFO+H_2F_2$

Uses:

- It is used in incendiary and in cutting off well tubes.
- It is used for fluorination of various compounds.
- It is recommended as an oxidizer for propellants.

Bromine pentafluoride, **-BrF_6**

BrF_5, is an interhalogen compound and a fluoride of bromine. It is a strong fluorinating agent.

BrF_5 finds use in oxygen isotope analysis. Laser ablation of solid silicates in the presence of BrF_5 releases O_2 for subsequent analysis. It has also been tested as an oxidizer in liquid rocket propellants and is used as a fluorinating agent in the processing of uranium.

Preparation

BrF_5 was first prepared in 1931 by the direct reaction of bromine and fluorine. This reaction is suitable for the preparation of large quantities] and is carried out at temperatures over 150 °C (302 °F) with an excess of fluorine:

$$Br_2 + 5\,F_2 \rightarrow 2\,BrF_5$$

For the preparation of smaller amounts, potassium bromide is used:

$$KBr + 3\,F_2 \rightarrow KF + BrF_5$$

Reactions

BrF_5 reacts with water to form bromic acid and hydrofluoric acid:

$$BrF_5 + 3\ H_2O \rightarrow HBrO3 + 5\ HF$$

It is an extremely effective fluorinating agent, being able to convert most metals to their highest fluorides even at room temperature. With uranium and uranium compounds, it can be used to produce uranium hexafluoride:

$$5\ U + 6\ BrF_5 \rightarrow 5\ UF_6 + 3\ Br_2$$

Uses

BrF5 finds use in oxygen isotope analysis. Laser ablation of solid silicates in the presence of BrF5 releases O2 for subsequent analysis. It has also been tested as an oxidizer in liquid rocket propellants and is used as a fluorinating agent in the processing of uranium.

It is used as an oxidizer and a fluorinating agent in making Fluorocarbons.

Hazards

BrF_5 reacts violently with water, and is severely corrosive and toxic. Its vapors are also extremely irritating to all parts of the human body, especially the skin, eyes and other mucous membranes. Like many other interhalogen compounds, it will release "smoke" containing acidic vapors if exposed to moist air, which comes from its reaction with the water in the air. Exposure to 100 ppm or more for more than one minute is lethal to most experimental animals. Chronic exposure may cause kidney damage and liver failure.

Additionally, BrF_5 is a strong oxidizing agent and may spontaneously ignite or explode upon contact with flammable substances such as organic materials and metal dust.

Iodine heptafluoride -IF_7

Iodine heptafluoride is an interhalogen compound with the chemical formula IF_7 It has an unusual pentagonal bipyramidal structure, with D_{5h} symmetry, as predicted by VSEPR theory The molecule can undergo a pseudorotational rearrangement called the Bartell mechanism, which is like the Berry mechanism but for a heptacoordinated system

Below 4.5 °C, IF_7 forms a snow-white powder of colorless crystals, melting at 5-6 °C. However, this melting is difficult to observe, as the liquid form is thermodynamically unstable at 760 mmHg: instead, the compound begins to sublime at 4.77 °C. The dense vapor has a mouldy, acrid odour.

Preparation

IF_7 is prepared by passing F_2 through liquid IF_5 at 90 °C, then heating the vapours to 270 °C. Alternatively, this compound can be prepared from fluorine and dried palladium or potassium iodide to minimize the formation of IOF_5, an impurity arising by hydrolysis. Iodine heptafluoride is also produced as a by-product when dioxygenyl hexafluoroplatinate is used to prepare other platinum(V) compounds such as potassium hexafluoroplatinate(V), using potassium fluoride in iodine pentafluoride solution

$$2\ O_2PtF_6 + 2\ KF + IF_5 \rightarrow 2\ KPtF_6 + 2\ O_2 + IF_7$$

Reactions

Iodine heptafluoride decomposes at 200 °C to fluorine gas and iodine pentafluoride.[11]

Uses.

Iodine heptafluoride is used as a fluorinatingagent

Safety considerations

IF_7 is highly irritating to both the skin and the mucous membranes. It also is a strong oxidizer and can cause fire on contact with organic material.

Pseudohalides:-

- Pseudohalides are univalent anions having a resemblance to halides.
- They are weak Lewis bases that carry a formal -1 charge.
- The difference between halogens and pseudohalides is that the halogens are from group 17 whereas the pseudohalides are from other groups.
- Examples: Cyanide (CN-), Azide ion (N_3-)

Pseudohalogens:-

- Pseudohalogens are polyatomic compounds whose chemical properties resemble that of true halogens.
- They are groups formed by the combination of two or more p- block elements with a -1 charge.
- Examples: Cyanogen ($(CN)_2$), Thiocyanogen ($(SCN)_2$).

Cyanogen

- **Cyanogen** is the chemical compound with the formula $(CN)_2$. The simplest stable carbon nitride, it is a colorless and highly toxic gas with a pungent odor. The molecule is a pseudohalogen. Cyanogen molecules consist of two CN groups – analogous to diatomic halogen molecules, such as Cl_2, but far less oxidizing. The two cyano groups are bonded together at their carbon atoms: N≡C–C≡N, although other isomers have been detectedThe name is also used for the CN radical,[7] and hence is used for compounds such as cyanogen bromide (NCBr) (but see also *Cyano radical*.)

- Cyanogen is the anhydride of oxamide:

$$H_2NC(O)C(O)NH_2 \rightarrow NCCN + 2\ H_2O$$

- although oxamide is manufactured from cyanogen by hydrolysis

$$NCCN + 2\ H_2O \rightarrow H_2NC(O)C(O)NH_2$$

Preparation

- Cyanogen is typically generated from cyanide compounds. One laboratory method entails thermal decomposition of mercuric cyanide:
- $2\ Hg(CN)_2 \rightarrow (CN)_2 + Hg_2(CN)_2$
- Alternatively, one can combine solutions of copper(II) salts (such as copper(II) sulfate) with cyanides; an unstable copper(II) cyanide is formed which rapidly decomposes into copper(I) cyanide and cyanogen
- $2\ CuSO_4 + 4\ KCN \rightarrow (CN)_2 + 2\ CuCN + 2\ K_2SO_4$
- Industrially, it is created by the oxidation of hydrogen cyanide, usually using chlorine over an activated silicon dioxide catalyst or nitrogen dioxide over a copper salt. It is also formed when nitrogen and acetylene are reacted by an electrical spark or discharge

Uses

Used in organic synthesis; Also used as a fuel (for cutting and welding heat-resistant metals), a rocket fuel, and a fumigant; Produced in internal combustion engines burning gasoline with nitrogen additives and in blast furnaces

Thiocyanogen

Thiocyanogen, $(SCN)_2$, is a pseudohalogen derived from the pseudohalide thiocyanate, $[SCN]^-$, with behavior intermediate between dibromine and diiodine. This hexatomic compound exhibits C2 point group symmetry and has the connectivity NCS-SCN

Thiocyanogen was originally prepared by the reaction of iodine with a suspension of silver thiocyanate in diethyl ether, but this reaction suffers from competing equilibria attributed to the weak oxidizing power of iodine. Those same investigations led to the isolation of sulfur dicyanide.

An improved method for generating thiocyanogen entails oxidation of plumbous thiocyanate, which precipitates when aqueous solutions of lead(II) nitrate and sodium thiocyanate are combined. A suspension of anhydrous $Pb(SCN)_2$ is treated with bromine in glacial acetic acid to afford a 0.1M solution of thiocyanogen that is stable for days

Alternatively, a solution of bromine in methylene chloride is added to a suspension of $Pb(SCN)_2$ in methylene chloride at 0°C

$$Pb(SCN)_2 + Br_2 \rightarrow (SCN)_2 + PbBr_2$$

In general, the compound is stored in solution, as pure thiocyanogen explodes above 20 °C. However, the sulfur atoms disproportionate in water:

$$3(SCN)_2 + 4H_2O \rightarrow H_2SO_4 + HCN + 5SCN^- + 5H^+$$

Thiocyanogen adds trans to alkenes to give 1,2-bis(thiocyanato) compounds; the intermediate thiiranium ion can be trapped with many nucleophiles. Radical addition is the most likely side-reaction, and yields improve when cold and dark. Similarly titanacyclopentadienes give (Z,Z)-1,4-bis(thiocyanato)-1,3-butadienes, which in turn can be converted to 1,2-dithiins. Selenocyanogen, (SeCN)2, prepared from reaction of silver selenocyanate with iodine in tetrahydrofuran at 0 °C, reacts in a similar manner to thiocyanogen

Xenon Difluoride XeF_2

Xenon Difluoride is a chemical compound with the formula XeF_2. It was discovered in the year 1962. It is a powerful fluoridating agent. XeF_2 was considered to be a possible convenient replacement for elemental fluorine especially in addition reactions to a double bond. The oxidation state of xenon in Xenon Difluoride is +2. Xenon tetrafluoride has a negligible vapour pressure at -78° and about 3 mm-Hg at room temperature. Xenon difluoride is a hazardous chemical, reacting with water moisture to form hydrofluoric acid.

Other names – Difluoroxenon, Xenon fluoride

XeF_2	Xenon Difluoride
Density	4.32 g/cm³
Molecular Weight/ Molar Mass	169.29 g/mol
Boiling Point	155 °C
Melting Point	128.6 °C
Chemical Formula	XeF_2

Synthesis

- When a mixture of xenon and fluorine in the ratio of 2:1 is heated at 400°C in a sealed nickel vessel, XeF_2 is formed.

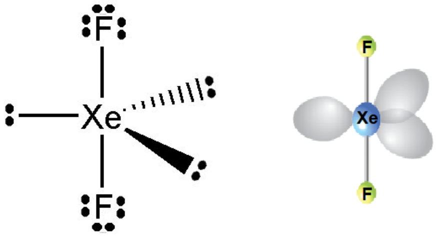
$$\mathbf{Xe + F_2 \rightarrow XeF_2}$$

- Dioxygen difluoride reacts with xenon at about 118°C to give XeF_2.

$$\mathbf{Xe + O_2F_2 \rightarrow XeF_2 + O_2}$$

Xenon Difluoride Structure – XeF_2

- The structure of xenon difluoride is illustrated below.
- XeF2 structure features two covalent bonds between one xenon atom and two fluorine atoms. The xenon atom also holds 3 lone pairs of electrons.



Physical Properties of Xenon Difluoride – XeF_2

Odour	Nauseating odour
Appearance	White solid
Covalently-Bonded Unit	1
Hydrogen Bond Acceptor	2
Complexity	2.8
Solubility	Insoluble in water

Uses of Xenon Difluoride – XeF_2

- Used to oxidize and fluorinate the hetero element in an organometallic compound, but does not attack the alkyl or aryl groups
- Used as a very convenient for the detection and determination of very small amounts of iodine and iodide based on the oxidation of iodine to periodate.
- Used to kill bacteria, power lasers and tracers as an antiseptic. It is preferred to power spacecraft in deep space as fuel for ion engines.

Xenon tetra fluoride-XeF_4

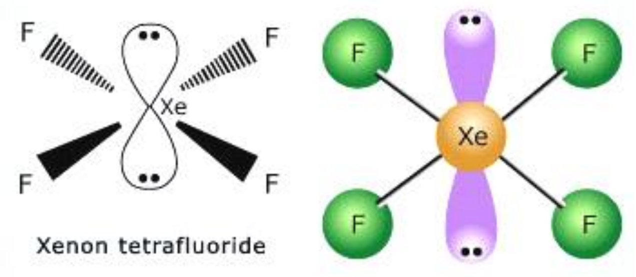
Preparation:

XeF_4 is obtained in good amounts by heating a mixture of xenon and fluorine in the molar ratio **1:5** at 873 K and 7 bar pressure in an enclosed nickel vessel for a few hours.

$$Xe\,(g) + 2F_2\,(g) \xrightarrow{873K.7\ bar} XeF_4$$

Physical properties:

- It is colourless crystalline solid, and can be sublimed.
- It melts at 390 K. XeF_4 is a strong oxidising and fluorinating agent.



Chemical Properties:

- With hydrogen, at 130°C, it gets reduced to xenon.

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

- With fluorine it produces higher fluorides.

$$XeF_4 + F_2 \longrightarrow XeF_6$$

- It acts as a strong oxidising agent. It oxidises iodide to iodine.

$$XeF_4 + 4KI \longrightarrow 4KF + 2I_2 + Xe$$

- It is a good fluorinating agent.

$$XeF_4 + 2C_2H_6 \longrightarrow Xe + 2C_2H_5F + 2HF$$

- It reacts violently with water.

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 3/2\ O_2$$

- With SbF_5 : XeF_4 reacts with covalent pentafluorides such as PF_5, AsF_5 and SbF_5 to form adducts. In these reactions, XeF_4 acts as a fluoride ion donor (Lewis base) and the pentafluoride, a fluoride ion acceptor (Lewis acid). With SbF_5, the reaction is,

$$XeF_4 + SbF_5 \longrightarrow XeF_4.SbF_5 \text{ or } [XeF_3^+]\ [SbF_5^-]$$

Uses

Xenon tetra fluoride has few applications. It has been shown to degrade silicone rubber for analyzing trace metal impurities in the rubber. XeF_4 reacts with the silicone to form simple gaseous products, leaving a residue of metal impurities.

Xenon Hexafluoride-XeF_6

Preparation

- XeF_6 can be prepared by heating a mixture of xenon and fluorine in the ratio 1:20 in a nickel vessel at 600 K under 60–70 bar pressure.

$$Xe\ (g) + 3F_2\ (g) \xrightarrow[60\ -\ 70\ bar]{600\ K} XeF_6\ (s)$$

- It can also be obtained by reacting XeF_4 with O_2F_2 at −130°C.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Properties

- It is a strong fluorinating and oxidising agent.
- With HF, it gives an ionic compound $[XeF_5]^+[HF_2]^-$.

$$HF + XeF_6 \longrightarrow [XeF_5]^+ [HF_2]^- \rightleftharpoons XeF_5^+ + HF_2^-$$

- On heating, it decomposes to give XeF_2 and XeF_4.

$$2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4 + 3F_2$$

- It is reduced by H_2, HCl and NH_3.

$$XeF_6 + 3H_2 \rightarrow Xe + 3H_2F_2$$
$$XeF_6 + 6HCl \rightarrow Xe + 3H_2F_2 + 3Cl_2$$
$$XeF_6 + 8NH_3 \rightarrow Xe + 6NH_4F + N_2$$

- The hydrolysis of XeF_6 with water yields new compounds.

$$XeF_6 + H_2O \rightarrow XeOF_4 + H_2F_2$$

- XeF_6 dissolves in HF according to the following reaction.

$$XeF_6 + HF \rightarrow [XeF_5]^+ + [HF_2]^-$$

- XeF_6 undergoes thermal decomposition.

$$2XeF_6 \rightarrow XeF_2 + XeF_4 + 3F_2$$

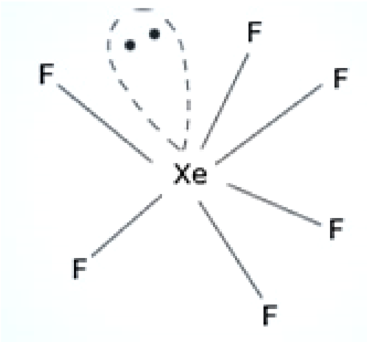
- Like XeF_2 and XeF_4, XeF_6 also acts as fluorinating agent. XeF_6 has strongest fluorinating tendency. XeF_6 undergoes addition reactions with Lewis acids, e.g.,

$$XeF_6 + AsF_5 \rightarrow [XeF_5]^+ [AsF_6]^-$$
$$XeF_6 + BF_3 \rightarrow [XeF_5]^+ [BF_4]^-$$
$$XeF_6 + NaF \rightarrow NaXeF_7$$

- Hexafluoride undergoes hydrolysis in strongly alkaline medium.

$$2XeF_6 + 16OH^- \longrightarrow 8H_2O + 12F^- + XeO_6^{4-} + Xe + O_2$$

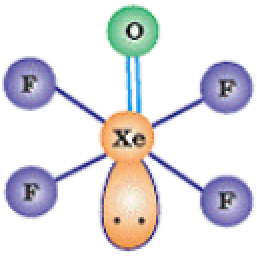
Structure of XeF_6



Xenon oxy tetra fluoride-$XeOF_4$

$XeOF_4$ is having a square pyramidal structure. It is prepared by treating XeF_6 withH_2O.

$$XeF_6 + H_2O \text{ ------> } XeOF_4 + 2\ HF$$



The xenon atom must bond with the four fluorine atoms into four single bonds and double-bonded with an oxygen atom. It has one lone pair of electrons. As per VSEPR theory, sp^3d^2 has a square pyramidal shape. Therefore, the Xenon oxyfluoride is square pyramidal in shape with sp^3d^2 hybridization.

Uses of Noble Gases

- In metallurgical processes, **argon** is widely used in order to provide the necessary inert atmosphere. This inert atmosphere plays an important role in welding titanium, aluminium, stainless steel, and magnesium. It is also used in the production of titanium.
- A limited amount of **argon** is used in germanium and silicon crystals which are used in electric light bulbs, transistors, etc.
- The boiling point of **helium** is the least when compared to any other liquid. It is used to obtain the lowest temperatures required in lasers.
- **Helium** is used in nuclear reactors as a cooling gas and used as a flow-gas in liquid-gas chromatography. It finds its application in airships and helium balloons.
- **Helium** balloons are used to check the weather of a particular region. Helium is preferred over hydrogen though hydrogen is cheaper, as helium is readily available and hydrogen is highly inflammable. Hence, due to safety issues helium is preferred in aircraft.
- It is used by divers to dilute oxygen over nitrogen in the gas cylinders used by them as nitrogen can easily be dissolved in the blood which results in a painful condition called bends. The risk of **helium** causing bends is slightly lower than nitrogen.
- **Neon** is used in discharge tubes which is the reason behind the reddish-orange glow produced by neon lights.

- **Xenon** and **krypton** find their application in photographic flash units due to the generation of very bright light. It is also used in lighthouses.
- **Neon**, **xenon,** and **krypton** are used to produce different colour lights.

Clatherate compounds

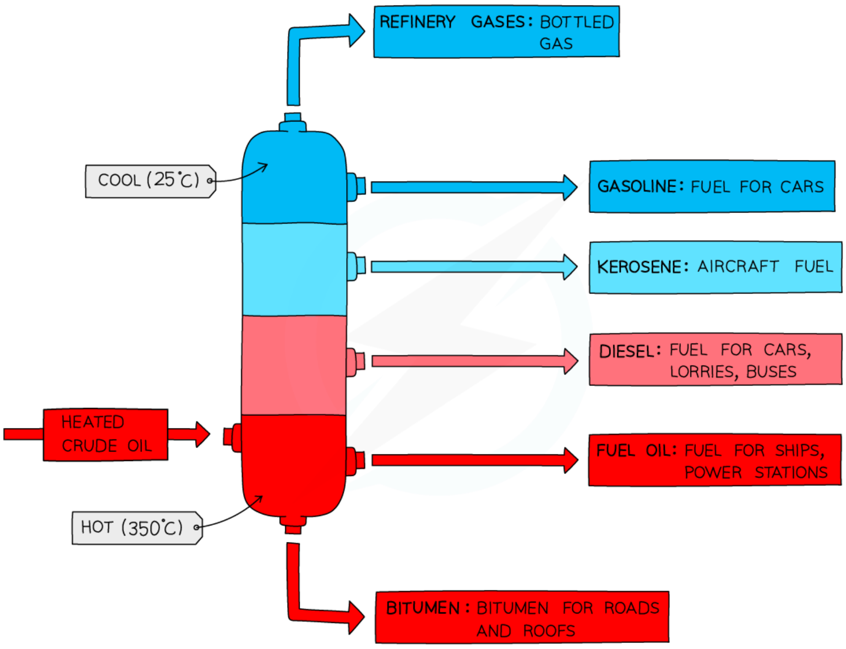
- A **clathrate** is a chemical substance consisting of a lattice that traps or contains molecules. The word *clathrate* is derived from the Latin *clathratus* (*clatratus*), meaning 'with bars, latticed'.
- Most clathrate compounds are polymeric and completely envelop the guest molecule, but in modern usage clathrates also include host–guest complexes and inclusion compounds.
- According to IUPAC, clathrates are inclusion compounds "in which the guest molecule is in a cage formed by the host molecule or by a lattice of host molecules."
- The term refers to many molecular hosts, including calixarenes and cyclodextrins and even some inorganic polymers such as zeolites.
- Clathrate cavities. For example, 5^{12} (dodecahedral) and $5^{12}6^{2}$ (tetrakaidecahedral) make up a Type I (sI) structure.
- Clathrates can be divided into two categories: clathrate hydrates and inorganic clathrates. Each clathrate is made up of a framework and guests that reside the framework. Most common clathrate crystal structures can be composed of cavities such as dodecahedral, tetrakaidecahedral, and hexakaidecahedral cavities.

UNIT IV- HYDROCARBON CHEMISTRY II

FRACTIONAL DISTILLATION OF CRUDE OIL

- Crude oil as a mixture is not a very useful substance but the different hydrocarbons that make up the mixture, called fractions, are enormously valuable, with each fraction having many different applications
- Each fraction consists of groups of hydrocarbons of similar chain lengths
- The fractions in petroleum are separated from each other in a process called fractional distillation
- The molecules in each fraction have similar properties and boiling points, which depend on the number of carbon atoms in the chain
- The size and length of each hydrocarbon molecule determines in which fraction it will be separated into
- The size of each molecule is directly related to how many carbon and hydrogen atoms the molecule contains
- Most fractions contain mainly alkanes, which are compounds of carbon and hydrogen with only single bonds between them

Diagram showing the process of fractional distillation to separate crude oil in a fractionating column



- Fractional distillation is carried out in a fractionating column which is very hot at the bottom and cool at the top
- Crude oil enters the fractionating column and is heated so vapours rise

- Vapours of hydrocarbons with very high boiling points will immediately condense into liquid at the higher temperatures lower down and are tapped off at the bottom of the column
- Vapours of hydrocarbons with low boiling points will rise up the column and condense at the top to be tapped off
- The different fractions condense at different heights according to their boiling points and are tapped off as liquids
- The fractions containing smaller hydrocarbons are collected at the top of the fractionating column as gases
- The fractions containing bigger hydrocarbons are collected at the lower sections of the fractionating column

Petrochemicals are the substances obtained from petroleum and natural gas. They are used in the manufacture of detergents, fibres, polythene, etc.

What is Petroleum?

It is dark brownish to green coloured viscous liquid fossil fuel. It has a strong foul smell due to the presence of sulphur-containing compounds. It is commonly called crude oil. The economy of a nation depends to a great extent on petroleum wealth, that's why petroleum is called black gold. Its name is derived from Latin words Petra (meaning rock) and O1eum (meaning oil). Thus, petroleum literally means "rock oil".

Origin of Petroleum

Petroleum is a complex mixture of solid, liquid and hydrocarbons, mixed with saltwater and earthy particles. It is always found trapped between two impervious rocks.

It is believed that petroleum is formed by the anaerobic decomposition of extremely small sea animals and plants which got buried in the sea bed millions of years ago. Let us see how this happened. Petroleum occurs at a moderate depth (500 m to 200 m) between the 2 layers of impervious rocks. The petroleum is lighter than It water & hence, floats over it. Natural gas is found above petroleum, trapped between the rock cap & petroleum layer.

The hole is drilled in the Earth's crust & when it reached the rock cap, the natural gas comes out first with great pressure. When the pressure of gas subsidies, petroleum starts flowing out due to the pressure of natural gas.

Refining of Petroleum

Petroleum is a mixture of several hydrocarbons. It also contains water, salt and rocky materials. It cannot be used in this made form either as a fuel or a basic material to produce other useful components. Before being put to use, it has to be purified or refined. The process of separating the various components of petroleum from one another is known as the refining of petroleum. This is done by a process called fractional distillation which is based on the fact that the different components of petroleum have distinctly different boiling points. In fractional distillation, crude petroleum is heated to a temperature of, 400°C or slightly above in a furnace.

From the refining process, we get the three most important fractions of petroleum which are as follows:

Petroleum Gas

Petroleum gas is a flammable mixture of hydrocarbon gases Liquefied Petroleum Gas is used in heating appliances and even in cooking types of equipment. It is also used as a refrigerant, replacing chlorofluorocarbons in an effort to reduce damage to the ozone layer.

LPG is formed from refining petroleum. It is being manufactured during the refining of petroleum (crude oil) or extracted from petroleum or natural gas streams as they emerge from the ground. It has a very wide variety of uses, mainly used for cylinders across many different markets as an efficient fuel container in the agricultural, recreation, hospitality, industrial etc. It can serve as fuel for cooking, central heating and water heating and is a particularly cost-effective and efficient way to heat off-grid homes.

Petrol

Billions of years ago, animals and plants lived near to seas. After dying, the dead bodies got buried. Over the next billions of years under high pressure and high temperature, the organic matter transformed into what we know today as Petroleum or simply Petrol.

Today, petrol is found underground exactly where ancient seas were located. Petroleum reservoirs can be found beneath land or the ocean floor. Petrol is widely used in automobiles and it has become a basic necessity. Since it is getting exhausted very rapidly, scientists are looking for alternatives to Petrol. Petrol is the need of the current hour as automobiles have become a basic necessity in this 21st century. Petrol is used in automobiles.

Kerosene

It is derived from petroleum. Kerosene is a combustible liquid. The name “Kerosene” is derived from the Greek word “Keros” meaning Wax. It is used as fuel for stoves, lamps and for jet aircraft.

It is often spelt as kerosine in scientific and industrial usage. Kerosene smoke contains high levels of harmful particles, and household use of kerosene results in higher risks of cancer, respiratory infections, asthma and many more. It is obtained from the fractional distillation of petroleum between 150 and 275 °C.

It can be also used to prevent air from re-dissolving in a boiled liquid and to store highly reactive metals like potassium, sodium etc.

Constituents of Petroleum	**Uses**
Liquefied Petroleum Gas (LPG)	It is used as fuel for home and industry.
Petrol	It is used as motor fuel and as a solvent for dry cleaning
Kerosene	It is used as fuel for stoves, lamps and for jet aircraft.
Diesel	It is used as fuel for heavy motor vehicles, electric generators
Lubricating Oil	It is used for lubrication.
Paraffin Wax	It is used in ointments, candles, vaseline, etc.
Bitumen	It is used for making paints, surfacing roads

Catalytic Reforming

Catalytic reforming converts low-octane, straight-run naphtha fractions, particularly heavy naphtha that is rich in naphthenes, into a high-octane, low-sulfur reformate, which is a major blending product for gasoline. The most valuable byproduct from catalytic reforming is hydrogen to satisfy the increasing demand for hydrogen in hydrotreating and hydrocracking processes. Most reforming catalysts contain platinum as the active metal supported on alumina, and some may contain additional metals such as rhenium and tin in bi- or tri-metallic catalyst formulations. In most cases, the naphtha feedstock needs to be hydrotreated before reforming to protect the platinum catalyst from poisoning by sulfur or nitrogen species.

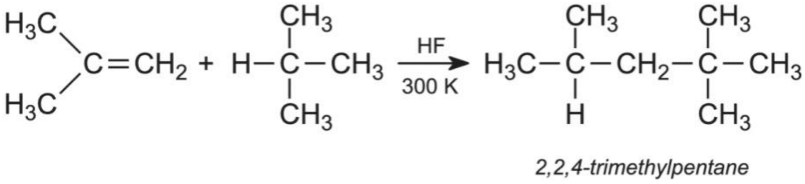
Alkylation

The alkylation process combines light iso-paraffins, most commonly isobutane, with C3–C4 olefins, to produce a mixture of higher molecular weight iso-paraffins (i.e., alkylate) as a high-octane number blending component for the gasoline pool. Iso-butane and C3–C4 olefins are produced as by-products from FCC (fluid catalytic cracking process) and other catalytic and thermal conversion processes in a refinery. The alkylation process was developed in the 1930s and 1940s to initially produce high-octane aviation gasoline, but later it became important for producing motor gasoline because the spark ignition engines have become more powerful with higher compression ratios that require fuel with higher octane numbers. With the recent restrictions on benzene and the total aromatic hydrocarbon contents of gasoline by environmental regulations, alkylation has gained favor as an octane number booster over catalytic reforming. Alkylate does not contain any olefinic or aromatic hydrocarbons.

Alkylation reactions are catalyzed by strong acids (i.e., sulfuric acid [H_2SO_4] and hydrofluoric acid [HF]) to take place more selectively at low temperatures of 70°F for H_2SO_4 and 100°F for HF. By careful selection of the operating conditions, a high proportion of products can fall in the gasoline boiling range with motor octane numbers (MONs) of 88–94 and RONs of 94–99. Early commercial units used H_2SO_4, but more recently, HF alkylation has been used more commonly in petroleum refineries. HF can be more easily regenerated than H_2SO_4 in the alkylation process, and HF alkylation is less sensitive to temperature fluctuations than H_2SO_4 alkylation. In both processes, the volume of acid used is approximately equal to the volume of liquid hydrocarbon feed. Important operating variables include acid strength, reaction temperature, iso-butane/olefin ratio, and olefin space velocity. The reactions are run at sufficiently high pressures to keep the hydrocarbons and the acid in the liquid phase. Good mixing of acid with hydrocarbons is essential for high conversions.

Alkylation is the transfer of an alkyl group from one molecule to another. In a refinery, alkylation refers to the alkylation of alkanes, for example, 2-methylpropane (isobutane) with alkenes, in the presence of a strong acid catalyst such as hydrofluoric acid or sulfuric acid. The reaction is carried out at mild temperatures (between 273 and 303K). Cooling is needed as the reaction is exothermic.

The product from 2-methylpropane and 2-methylpropene (isobutene) is a mixture of, branched-chain alkanes, mainly 2,2,4-trimethylpentane (isooctane):



With propene, 2-methylpropane forms a mixture containing a high proportion of 2,3- and 2,4-dimentylpentanes. These mixtures have very good antiknock properties and are added to petrol to increase the octane rating.

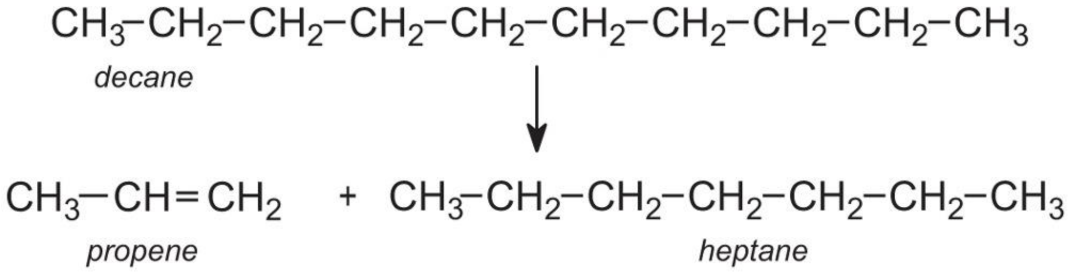
If sulfuric acid is used as the catalyst. many refineries will have a dedicated plant which takes in the waste sulfuric acid from the alkylation plant. In the recycling of sulfuric acid, the diluted acid is heated strongly to form sulfur dioxide which is then fed into a contact process plant, regenerating pure acid.

Isomerization

Isomerization processes have been used to isomerize n-butane to iso-butane used in alkylation and C5 /C6 n-paraffins in light naphtha to the corresponding iso-paraffins to produce high-octane number gasoline stocks after the adoption of lead-free gasoline. Catalytic isomerization processes that use hydrogen have been developed to operate under moderate conditions. Typical feedstocks for the isomerization process include hydrotreated light straight-run naphtha, light natural gasoline, or condensate. The fresh C5/C6 feed combined with make-up and recycled hydrogen is directed to a heat exchanger for heating the reactants to reaction temperature. Hot oil or high-pressure steam can be used as the heat source in this exchanger. The heated feed is sent to the reactor. Typical isomerate product ($C5^+$) yields are 97 wt% of the fresh feed, and the product octane number ranges from 81 to 87, depending on the flow configuration and feedstock properties.

Cracking

Cracking, as the name suggests, is a process in which large hydrocarbon molecules are broken down into smaller and more useful ones, for example:



The cracking products, such as ethene, propene, buta-1,3-diene and C4 alkenes, are used to make many important chemicals. Others such as branched and cyclic alkanes are added to the gasoline fraction obtained from the distillation of crude oil to enhance the octane rating.

Cracking is conducted at high temperatures, by two processes

- Steam cracking which produces high yields of alkenes
- Catalytic cracking in which a catalyst is employed and which produces high yields of branched and cyclic alkanes

Steam cracking

Steam cracking plants use a variety of feedstocks, for example

- ethane, propane and butane from natural gas
- naphtha, a mixture of C5 to C10 hydrocarbons, from the distillation of crude oil
- gas oil and residues, also from the primary distillation of oil

Very recently a cracking plant has come on stream in which crude oil itself is the feedstock, the first time that this has been done. It is important to ensure that the feedstock does not crack to form carbon, which is normally formed at this temperature. This is avoided by passing the gaseous feedstock very quickly and at very low pressure through the pipes which run through the furnace. There is however, a problem; if the plant is run at sub-atmospheric pressure, there may be a leak that allows air to enter into the gases and form an explosive mixture. This is prevented by mixing the feedstock with steam. The steam also acts as a diluent and inhibits carbonisation.

This endothermic reaction occurs in less than a second as the hydrocarbon mixture passes through tubes within the radiant section of the cracking furnace. The products are cooled rapidly (quenched) to prevent loss via side reactions and separated in a series of processes including compression, absorption, drying, refrigeration, fractionation and selective hydrogenation.

- The advantages of this are that it cuts out the expensive distillation processes needed, for example to produce naphtha, and that it produces a wider range of products.
- However the disadvantage is that it may not produce the product that is needed in high enough yield.

Catalytic Cracking

A catalyst allows lower reaction temperatures to be used. In fluidised catalytic cracking, the feedstock is gas oil which is vaporised and passed through a zeolite, produced as a fine powder (Unit 2), heated to about 700-800 K in the reactor. It is so fine that it behaves like a fluid and continuously flows out of the furnace with the cracking products. The temperature, residence time and the catalyst determine the product proportions. After cracking, the catalyst is separated from the products, regenerated by burning off deposited carbon in air (900 K), and subsequently recycled.

The products are:

- a gas of which ethene and propene are the main constituents
- a liquid which is used for petrol and contains branched- chain alkanes, cycloalkanes and aromatic hydrocarbons
- a high boiling residue used as a fuel oil

The relative proportions of the products, as noted above, can be altered by changing the catalyst and temperature. One of several zeolites can be used. For example, if the chosen zeolite contains ZSM-5, the propene yield is increased.

A variant of the process is known as hydrocracking. The cracking is carried out with hydrogen at a pressure of 80 atm and a catalyst of finely divided platinum on silica or alumina. Because excess hydrogen is present no alkenes are formed, and high proportions of branched alkanes, cycloalkanes and aromatics are produced which are essential in the formulation of high grade 'green' petrol. The hydrogen also decreases the tendency for the hydrocarbons to form finely divided carbon on the catalyst surface. The reaction products are separated by fractionation.

Hydrocracking is also used to crack heavy gas oils (which have over 20 carbon atoms in the hydrocarbon molecule) to shorter chain molecules similar to those in naphtha, which can then be steam cracked to form alkenes.

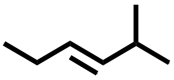
ALKENES

Nomenclature

- Name the parent hydrocarbon by locating the longest carbon chain that contains the double bond and name it according to the number of carbons with the suffix -ene.
- Number the carbons of the parent chain so the double bond carbons have the lowest possible numbers

2-hexene

- If the double bond is equidistant from each end, number so the first substituent has the lowest number.



2-methyl-3-hexene

- Write out the full name, numbering the substituents according to their position in the chain and list them in alphabetical order.
- Indicate the double bond by the number of the first alkene carbon.

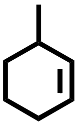
2-hexene

- If more than one double bond is present, indicate their position by using the number of the first carbon of each double bond and use the suffix -diene (for 2 double bonds), -triene (for 3 double bonds), -tetraene (for 4 double bonds), etc.

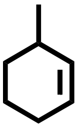
1,4-pentadiene

1,3-pentadiene

- Cycloalkenes are named in a similar way. Number the cycloalkene so the double bond carbons get numbers 1 and 2, and the first substituent is the lowest possible number.

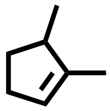


3-methylcyclohexene

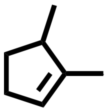


NOT
6-methylcyclohexene

- If there is a substituent on one of the double bond carbons, it gets number 1.



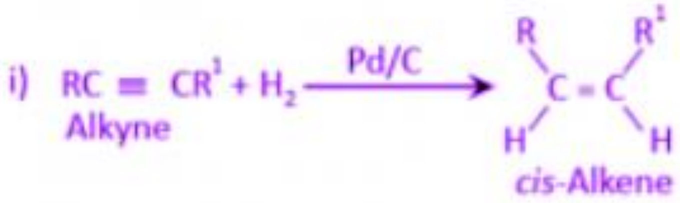
1,5-dimethylcyclopentene

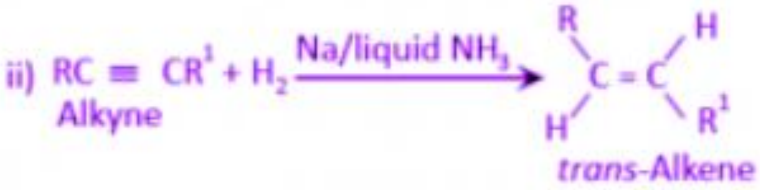


NOT
2,3-dimethylcyclopentene

Preparations

From alkynes: Alkynes can be used for the preparation of alkenes. Alkyne to alkene conversion is carried out by the reduction of alkynes with hydrogen in the presence of palladised charcoal. The charcoal used is moderately deactivated with the help of quinoline or sulphur compounds. This reaction results in the formation of alkenes. Palladised charcoal which is halfway deactivated is called as Lindlar's catalyst. The alkenes obtained from the above reaction have cis geometry. In order to form trans alkenes, alkynes are made to undergo reduction with sodium in liquid ammonia.

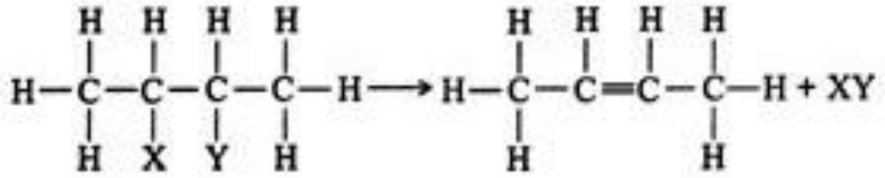




iii) $CH{\equiv}CH + H_2 \xrightarrow{Pd/C} CH_2{=}CH_2$
Ethyne → Ethene

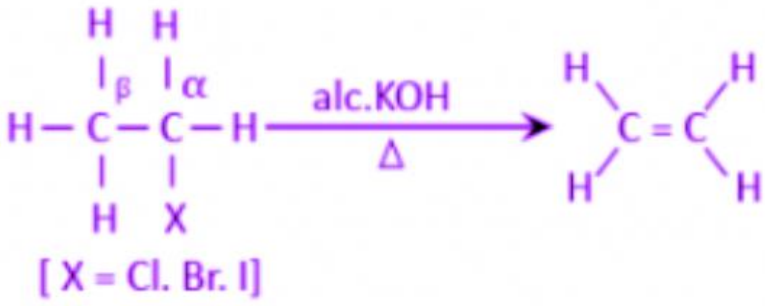
iv) $CH_3{-}C{\equiv}CH + H_2 \xrightarrow{Pd/C} CH_3{-}CH{=}CH_2$
Propyne → Propene

Alkenes are generally prepared through β elimination reactions, in which two atoms on adjacent carbon atoms are removed, resulting in the formation of a double bond.



Preparations include the dehydration of alcohols, the dehydrohalogenation of alkyl halides, and the dehalogenation of alkanes.

<u>From alkyl halides:</u> Alkenes are obtained by heating alkyl halides with alcoholic potash. Alcoholic potash is obtained by dissolving potassium hydroxide in alcohol. In this reaction, dehydrohalogenation takes place i.e. a single molecule of halogen acid is removed. The rate of reaction depends upon the alkyl group and the nature of the halogen group attached.

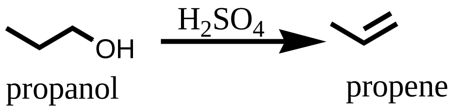


<u>From vicinal halides</u>: Vicinal dihalides can be defined as the dihalides in which two adjacent carbon atoms are attached to two halogens. When such dihalides react with zinc metal, they lose halogen molecules which result in the formation of alkenes. Such a reaction of preparation of alkenes from Vicinal dihalides is known as dehalogenation.

$$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$$

$$CH_3CHBr - CH_2Br + Zn \longrightarrow CH_3CH=CH_2 + ZnBr_2$$

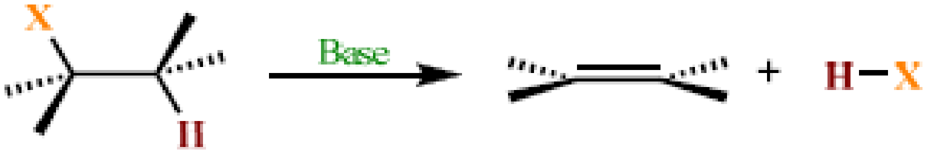
<u>Dehydration of alcohols.</u> In dehydration reactions, a molecule of water is eliminated from an alcohol molecule by heating the alcohol in the presence of a strong mineral acid. A double bond forms between the adjacent carbon atoms that lost the hydrogen ion and hydroxide group.



The mechanism of this dehydration reaction consists of the following steps.

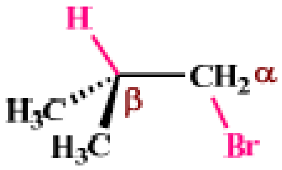
- Protonation of the alcohol.- This step is a simple acid-base reaction, which results in the formation of an **oxonium ion**, a positively charged oxygen atom.
- Dissociation of the oxonium ion- Dissociation of the oxonium ion produces a **carbocation**, which is a positively charged carbon atom and an unstable intermediate.
- Deprotonation of the carbocation. The positively charged end carbon of the carbocation attracts the electrons in the overlap region that bond it to the adjacent a carbon. This electron movement makes the α carbon slightly positive, which in turn attracts the electrons in the overlap regions of all other atoms bonded to it. This results in the hydrogen on the α carbon becoming very slightly acidic and capable of being removed as a proton in an acid-base reaction.

ELIMINATION REACTIONS



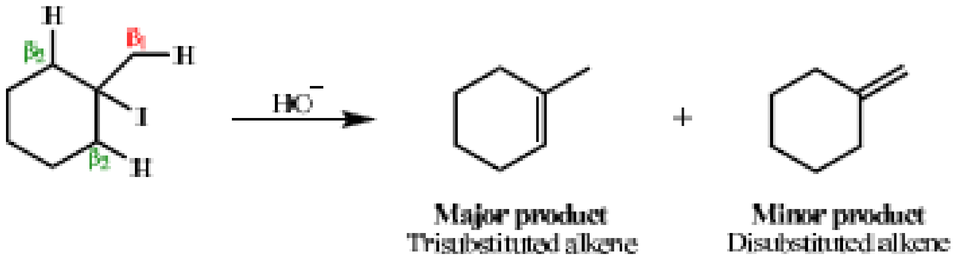
- E2 mechanism — bimolecular elimination
- E1mechanism—unimolecular elimination

Base removes a proton from the β-carbon atom, while the halogen atom leaves from the α-carbon resulting in the formation of a π-bond. Such eliminations are also called β-elimination reactions



The Zaitsev (Saytseff) Rule

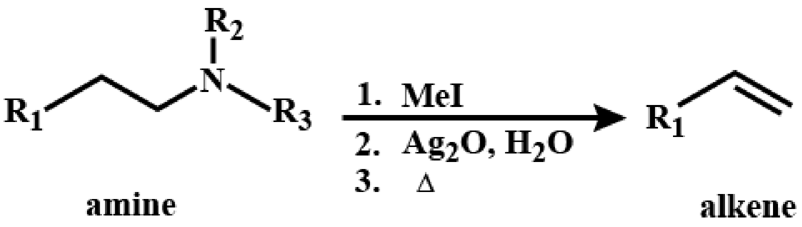
When alkyl halides have two or more different β carbons, more than one alkene product is formed. In such cases, the major product is the more stable product—the one with the more substituted double bond. This phenomenon is called the Zaitsev rule.



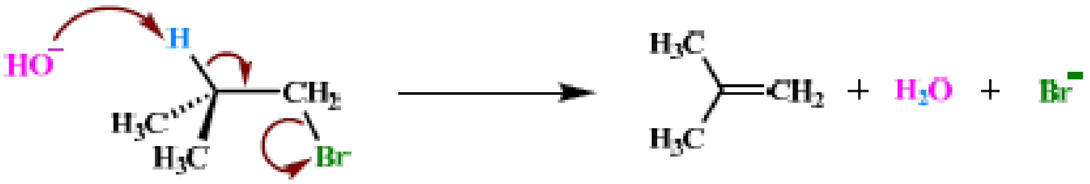
- The Zaitsev product or the more substituted alkene product is more stable than the less substituted product. The stability of the more substituted alkene is a result of number of different contributing factors, including hyperconjugation.
- Each alkyl group that can involve in hyperconjugation with the double bond stabilizes it by approximately 6 kcal/mol

The Hoffmann elimination Rule

The Hoffmann elimination is an organic reaction used to convert an amine with a B-hydrogen to an alkene using methyl iodide, silver oxide and water under thermal conditions The mechanism begins with an attack of the amine on methyl iodide to form an ammonium iodide salt. The iodide reacts with silver oxide to form silver iodide which is insoluble it deprotonates water to form hydroxide ion floating the mixture facilitates an elimination to an give alkene.



The E2 Mechanism

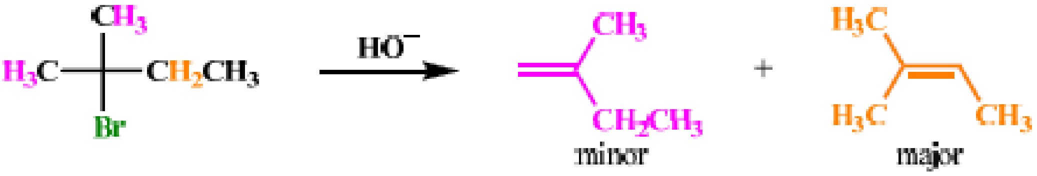


The most common mechanism for dehydrohalogenation is the E2 mechanism.

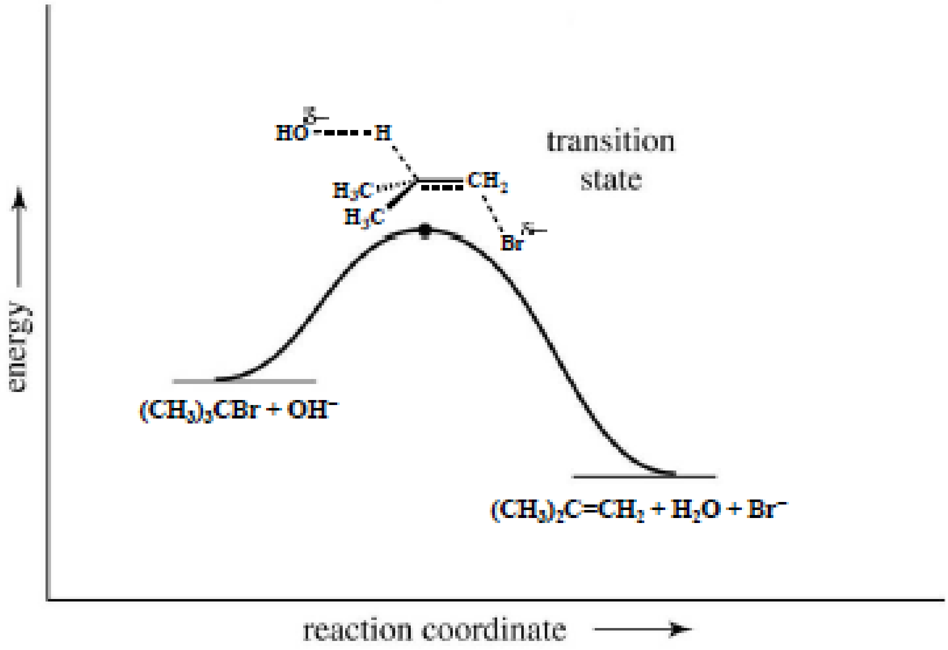
It exhibits second-order kinetics, and , both the alkyl halide and the base appear in the rate equation rate = $k[(CH_3)_3CBr][HO^-]$

The reaction is concerted—all bonds are broken and formed in a single step.

E2 reactions are regioselective and favor the formation of Zaitsev products.



Energy Profile for an E2 Reaction



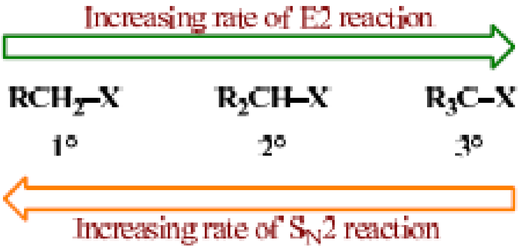
Factors Affecting the Rate of an E2 Reaction

- There are close parallels between E2 and S_N2 mechanisms in how the identity of the base, the leaving group and the solvent affect the rate.
- The base appears in the rate equation, so the rate of the E2 reaction increases as the strength of the base increases.
- E2 reactions are generally run with strong, negatively charged bases like OH- and OR^-.

- Polar aprotic solvents increase the rate of E2 reactions
- There is a partial breaking of the bond to the leaving group in the transition state. So, the better the leaving group the faster the E2 reaction.

Rate of reaction follows the order, R–I > R–Br > R–Cl > R–F

As the number of R groups on the carbon with the leaving group increases, the rate of the E2 reaction increases.



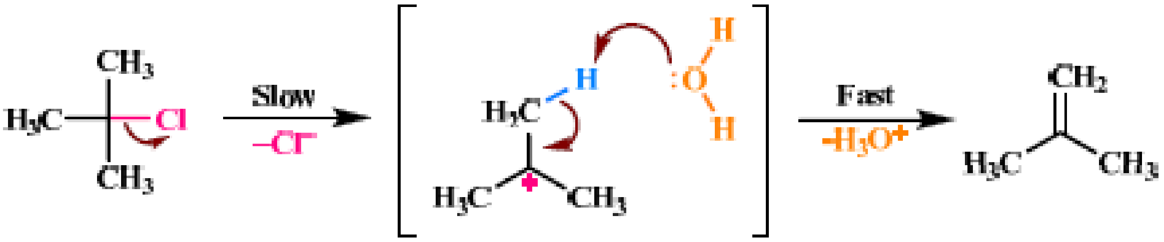
The increase in E2 reaction rate with increasing alkyl substitution can be rationalized in terms of transition state stability. In the transition state, the double bond is partially formed. Thus, the transition state for a more substituted alkene is lower in energy, reducing the activation energy for the reaction and making the reaction faster

Characteristics of an E2 Reaction

Kinetics - Second order
Mechanism - Single step
Identity of R group - More substituted halides react faster
Rate: $R_3CX > R_2CHX > RCH_2X$
Strength of the base - Stronger bases favor the reaction
Leaving group - Better leaving group leads to faster reaction rates
Type of solvent - Favored by polar aprotic solvents

E2 reactions are stereoselective, resulting in the formation of trans-double bonds preferably.

The E1 Mechanism

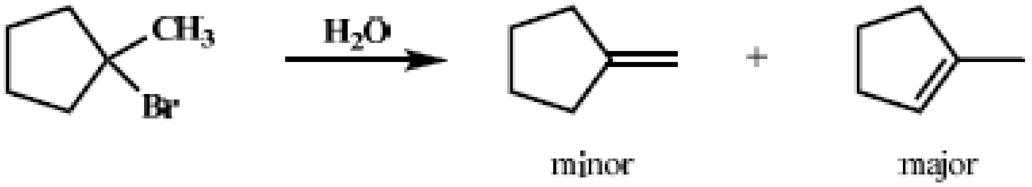


The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the π bond is formed. The slow step is unimolecular, involving only the alkyl halide.

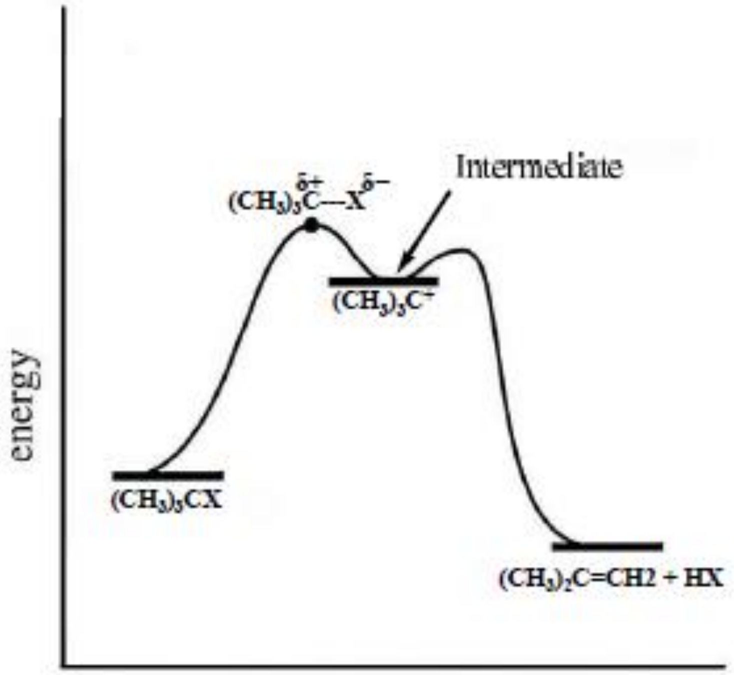
It exhibits first-order kinetics,

$$\text{rate} = k[(CH_3)_3CCl]$$

E1 reactions also are regioselective and follow Zaitsev rule

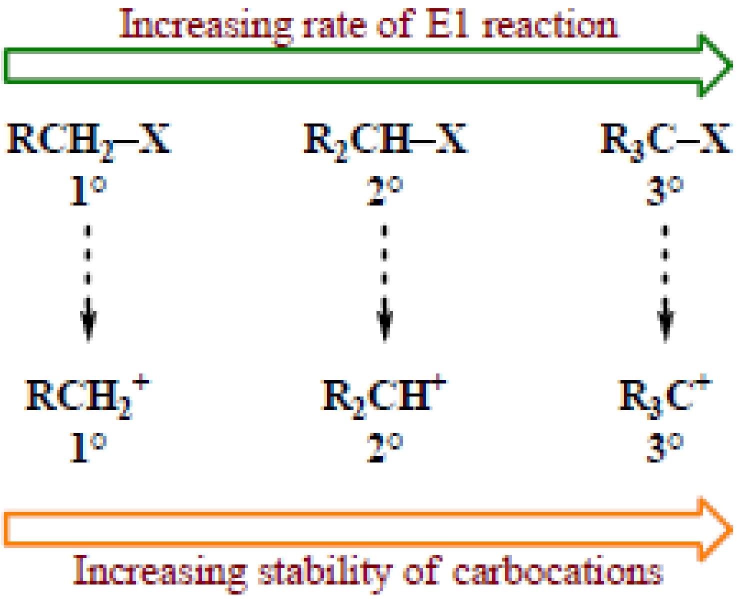


Energy Profile for an E1 Reaction



Factors Affecting the Rate of an E1 Reaction

The rate of an E1 reaction increases as the number of R groups on the carbon with the leaving group increases. The strength of the base usually determines whether a reaction follows the E1 or E2 mechanism. Strong bases like OH^- and OR^- favor E2 reactions, whereas weaker bases like H_2O and ROH favor E1 reactions.

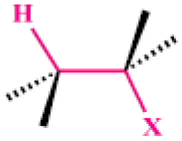


Characteristics of an E1 Reaction

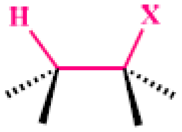
Kinetics	-	First order
Mechanism	-	Two steps
Identity of R group	-	More substituted halides react faster Rate: $R_3CX > R_2CHX > RCH_2X$
Strength of the base	-	Favored by weaker bases such as H_2O and ROH
Leaving group	-	Better leaving group leads to faster reaction rates. Just as in SN1 reactions, the rate determining step involves the C—X bond cleavage
Type of solvent	-	Favored by polar protic solvents, which can stabilize the ionic intermediates

Stereochemistry of the E2 Reaction

The transition state of an E2 reaction consists of four atoms from the substrate (one hydrogen atom, two carbon atoms, and the leaving group, X) aligned in a plane. There are two ways for the C—H and C—X bonds to be coplanar



anti periplanar
H and X are on the opposite side



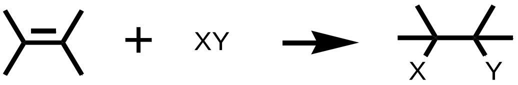
syn periplanar
H and X are on the same side

E2 elimination occurs most often in the anti periplanar geometry. This arrangement allows the molecule to react in the lower energy staggered conformation, and allows the incoming base and leaving group to be further away from each other.

The anti periplanar geometry also allows direct interaction between the bonding electrons of C—H bond and the anti-bonding orbital of the C—X bond

ELECTROPHILIC ADDITION

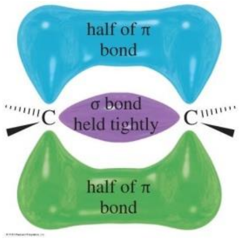
Since σ bonds are stronger than л bonds, double bonds tend to react to convert the double bond into σ bonds

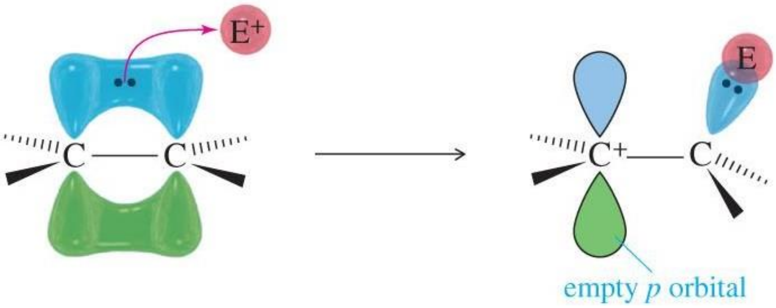


This is an addition reaction. (Other types of reaction have been substitution and elimination).

Addition reactions are typically exothermic.

The л bond is localized above and below the C-C σ bond. The л electrons are relatively far away from the nuclei and are therefore loosely bound.



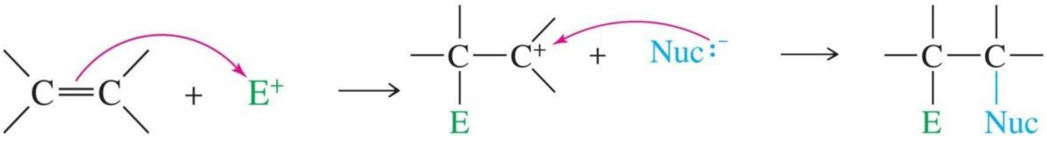


An electrophile will attract those electrons, and can pull them away to form a new bond.

This leaves one carbon with only 3 bonds and a +ve charge (carbocation).

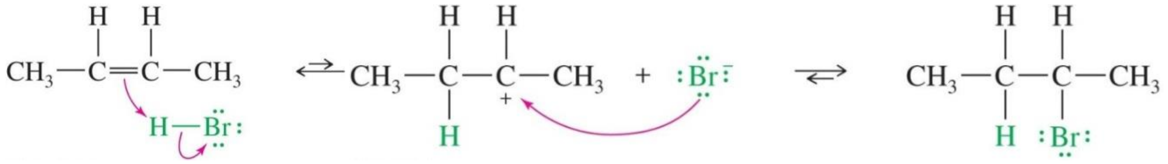
The double bond acts as a nucleophile (attacks the electrophile).

In most cases, the cation produced will react with another nucleophile to produce the final overall electrophilic addition product.



Electrophilic addition is probably the most common reaction of alkenes.

Consider the electrophilic addition of H-Br to but-2-ene:



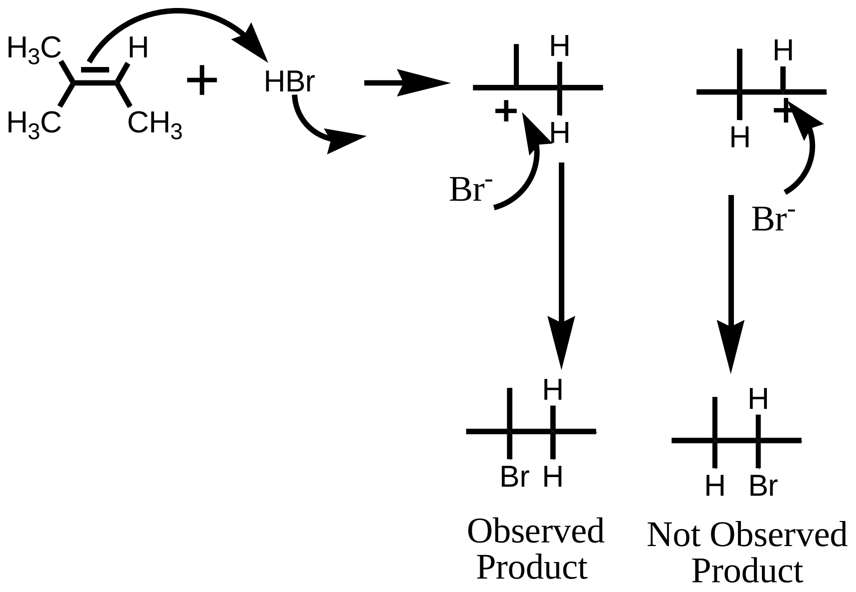
The alkene abstracts a proton from the HBr, and a carbocation and bromide ion are generated.

The bromide ion quickly attacks the cationic center and yields the final product.

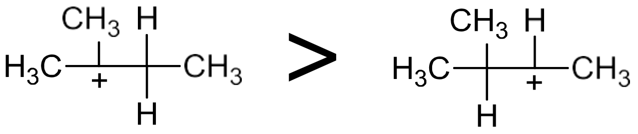
In the final product, H-Br has been added across the double bond.

Orientation of Addition

Consider the addition of H-Br to 2-methylbut-2-ene:



- There are two possible products arising from the two different ways of adding H-Br across the double bond.
- But only one is observed.
- The observed product is the one resulting from the more stable carbocation intermediate.



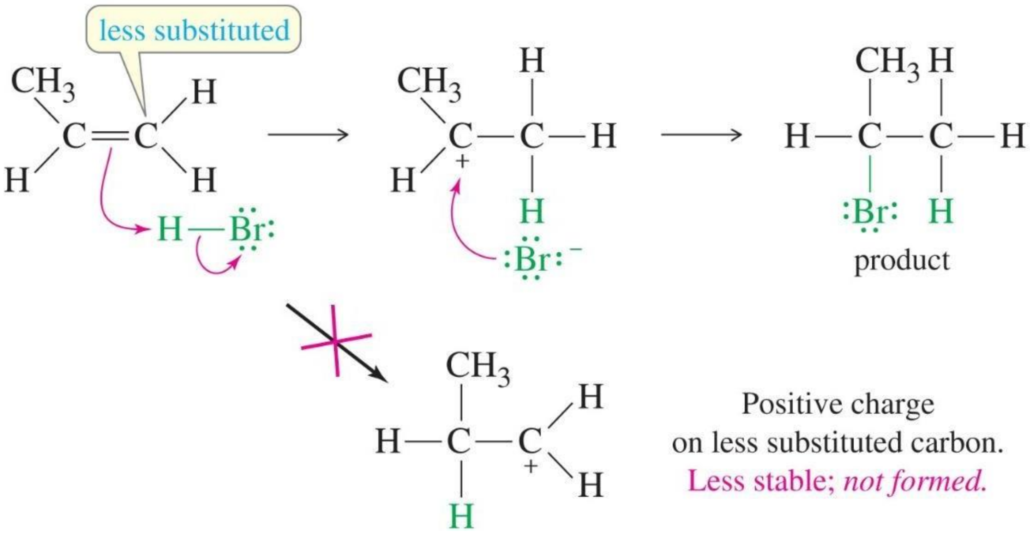
- Tertiary carbocations are more stable than secondary.

- The protonation occurs at the least highly substituted end so that the cation produced is at the most highly substituted end (and therefore more stable).

Markovnikov's Rule: The addition of a proton acid to the double bond of an alkene results in a product with the acid hydrogen bound to the carbon atom that already has the greater number of hydrogens attached.

Reactions that give such products are said to have Markovnikov orientation, and are Markovnikov products.

The electrophilic addition of HBr is said to be regiospecific, since it only gives one orientation of addition.



Positive charge on less substituted carbon. Less stable; *not formed.*

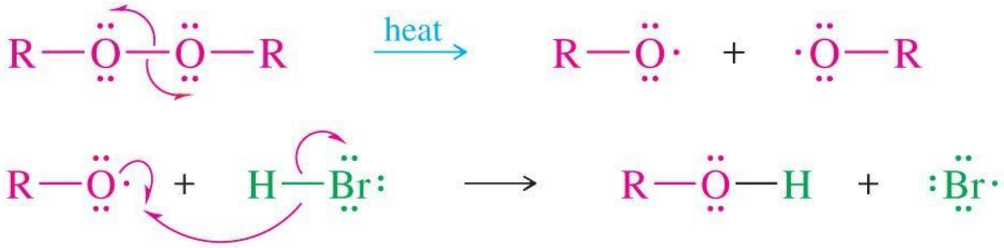
(HCl and HI perform analogous electrophilic addition reactions).

Free Radical addition to Alkenes

It is possible to obtain anti-Markovnikov products when HBr is added to alkenes in the presence of free radical initiators.

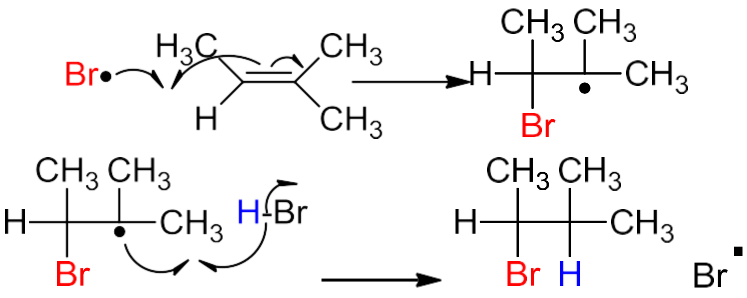
The free radical initiators change the mechanism of addition from electrophilic addition to free radical addition. This change of mechanism gives rise to the opposite regiochemistry.

Initiation:



The oxygen-oxygen bond is weak, and is easily homolytically cleaved to generate two alkoxy radicals, which in turn abstract hydrogen to generate bromine radicals.

Propagation:

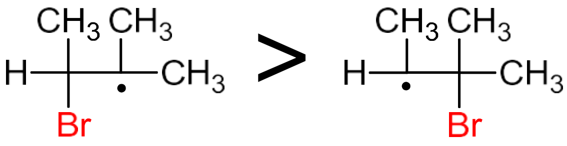


- The bromine radical is electron deficient and electrophilic. The radical adds to the double bond, generating a carbon centered radical.
- This radical then abstracts hydrogen from a molecule of H-Br, giving the product, and another bromine radical. (Chain process).
- The orientation of this reaction is anti Markovnikov.
- The reversal of regiochemistry through the use of peroxides is called the peroxide effect.

To explain the different regiochemistry, we must look at the intermediates:

The electrophile adds to the least substituted end just like before, but this time the electrophile is a bromine radical (not a proton). This generates an intermediate radical.

Tertiary radicals are more stable than secondary radicals. (Radical additions do not proceed with HCl or HI, only HBr).



Addition of Water

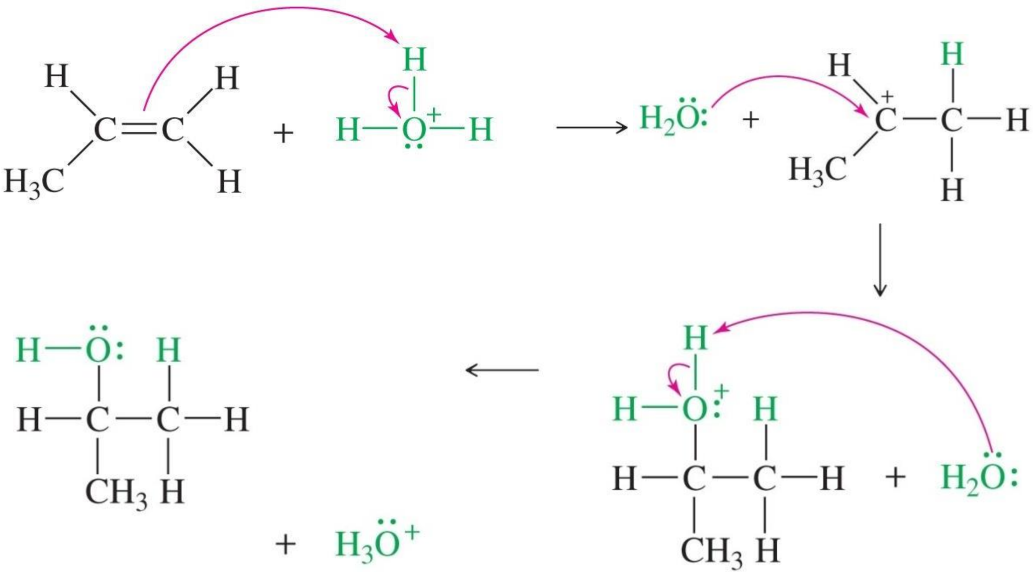
Alkenes can be converted to alcohols.

It is the reverse reaction of the dehydration of alcohols to give alkenes.

The principle of microscopic reversibility states that a forward reaction and a reverse reaction taking place under the same conditions must follow the same reaction pathway in microscopic detail.

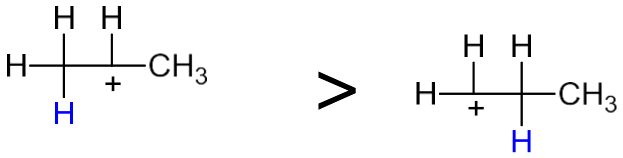
(Logically, it seems sensible that the lowest energy T.S.'s and intermediates for the forward reaction would be the same for the reverse reaction but in the opposite order).

So it is no surprise that the mechanism for hydration of alkenes is identical to that of dehydration of alcohols, but in the reverse order of steps.



- ➢ The first step is the protonation of the double bond to generate a carbocation, which in turn is attacked by water (a nucleophile).
- ➢ The final step is quick proton removal to generate the product.
- ➢ The hydration of alkenes is regiospecific.
- ➢ The orientation is Markovnikov since the proton has added to the least highly substituted end, and the hydroxyl to the most highly substituted end.

The regiochemistry is explained by the intermediate carbocation:



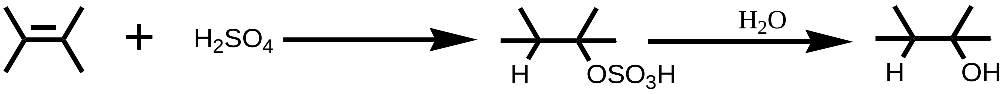
The secondary carbocation is more stable than the primary carbocation.

The reaction of dilute acid to hydrate alkenes is not a fantastic practical route due to insolubility problems, and typically two other indirect approaches are used.

i. Addition of sulfuric acid followed by hydrolysis
ii. Oxymercuration-demercuration

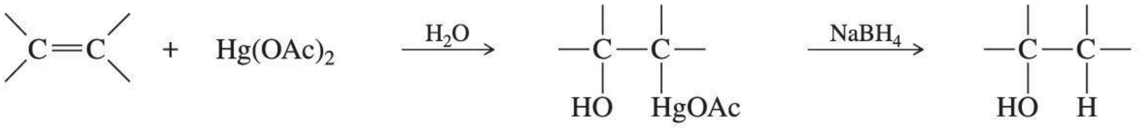
Addition of Sulfuric Acid followed by Hydrolysis

The alkene reacts with conc. sulfuric acid to give an alkyl hydrogen sulfate, which then in turn is hydrolyzed to give the alcohol.



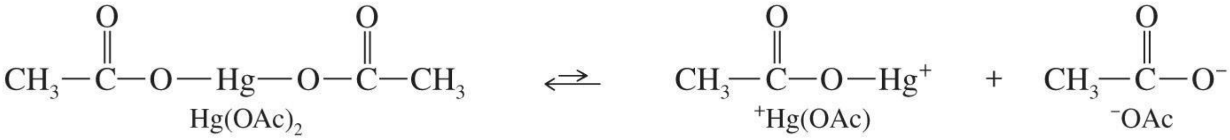
- The formation of the alkyl hydrogen sulfate arises from initial protonation on the double bond, and the intermediate carbocation is trapped by the bisulfate anion. (Markovnikov addition).
- The alkyl hydrogen sulfate can be converted to an alcohol by boiling in water.
- This proceeds usually by SN1 substitution where water is the nucleophile and bisulfate is the leaving group.
- The product has the same regiochemistry as an alcohol formed by direct hydration of the same alkene. (Markovnikov orientation).

This is another alternative for converting alkenes to alcohols with Markovnikov orientation. This method has the advantage of not involving free carbocationic species, and thus removes the possibility of rearrangements.



(Markovnikov orientation)

The reagent is called mercuric acetate, and is usually abbreviated to Hg(OAc)2. In solution it ionizes into acetate ion and a positively charged mercury species which is very electrophilic.



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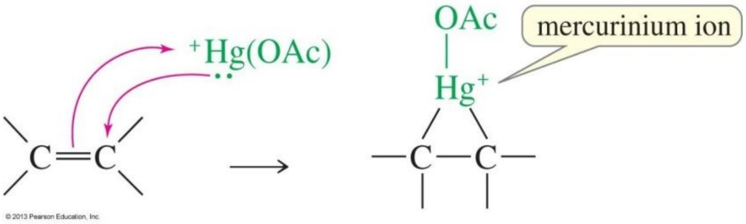
- Oxymercuration is the electrophilic attack of this species on a double bond, giving a 3 membered ring compound called a mercurinium ion.



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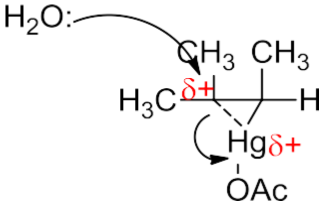
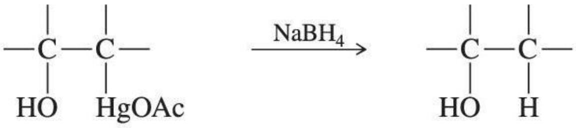
- When water is present, the nucleophilic oxygen will open the mercurinium ring, and generate an organomercurial alcohol.



- Demercuration is the removal of the mercury containing species, which is achieved by reaction with Sodium borohydride, a powerful reducing agent, which replaces the mercury species with a hydrogen atom – giving the desired alcohol.

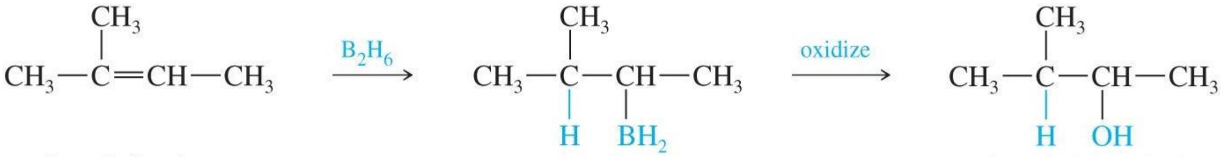


(Markovnikov orientation)

- Oxymercuration-demercuration also gives Markovnikov orientation of the alcohol.

Hydroboration of Alkenes

We have studied three ways of hydrating alkenes to give Markovnikov orientated alcohols.

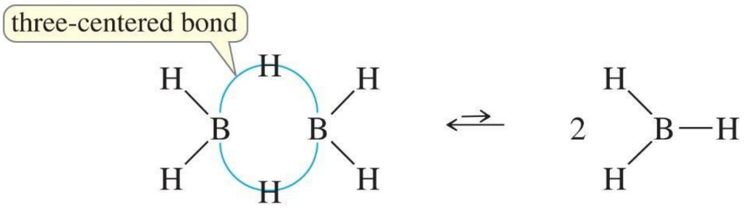


2-methylbut-2-ene

an alkylborane

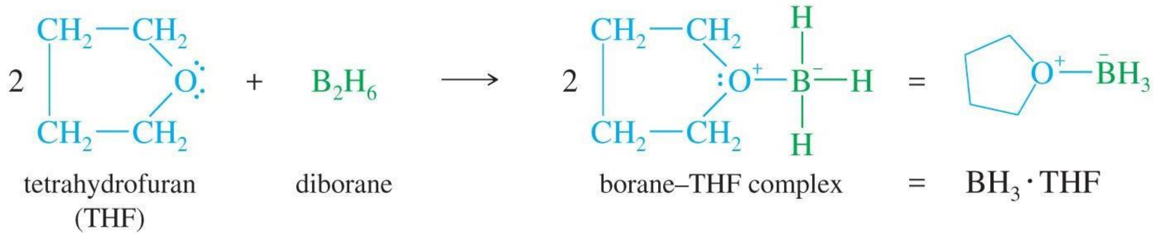
3-methylbutan-2-ol (>90%)

There is also a way to obtain anti-Markovnikov oriented alcohols: hydroboration. Borane adds to alkenes with anti-Markovnikov orientation, and these alkylboranes can then be oxidized to alcohols. Borane is unstable, and exists either as a dimer.



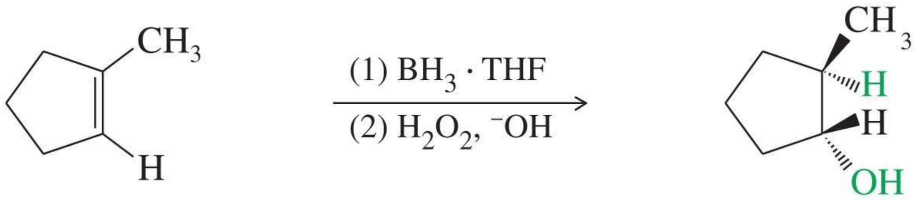
diborane

borane



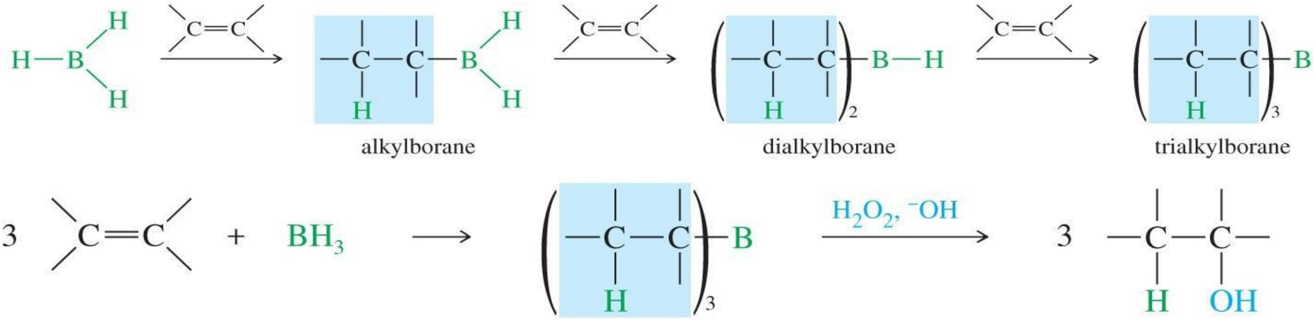
- Borane has only six valence electrons and is very electron deficient. Borane is an electrophilic molecule, and reacts with double bonds in a one step process to generate an alkylborane.
- The boron atom adds to the least highly substituted end of the double bond. This places partial positive charge on the more highly substituted end of the double bond (which is more stable).

Hydroboration also gives syn addition of the boron and hydrogen (and therefore the –OH and –H). This is a stereospecific reaction.



Stoichiometry of the Reaction

In reality, each B-H bond can add across a double bond.



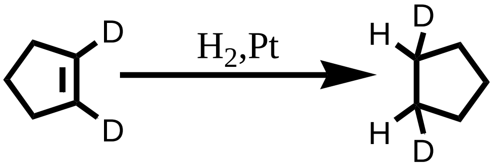
The di- and tri-alkyl boranes behave just as the alkylboranes, but for simplicity they are often written as monoalkylboranes.

Catalytic Hydrogenation

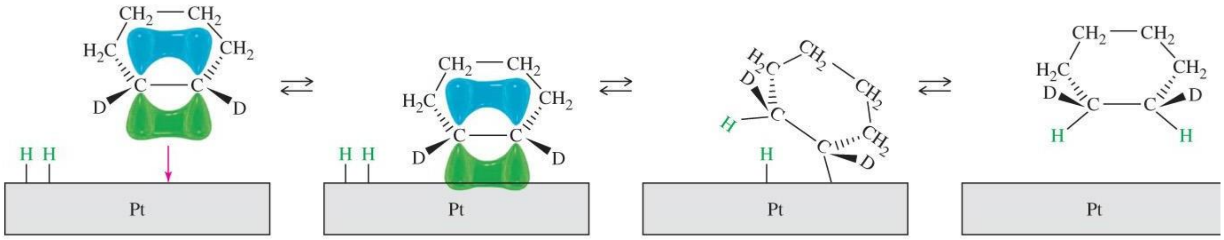
This is the addition of a hydrogen molecule to a compound using a (usually Pt, Pd, Ni) catalyst. When the catalyst is in a different physical state to the other reactants it is called Heterogeneous catalysis (E.g. a solid catalyst with a liquid and a gas).

In contrast a liquid catalyst in a reaction solution is an example of homogeneous catalysis (acid catalyzed alcohol dehydration).

During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add syn to the double bond.



- One face of the л system binds to the catalyst, then the bound hydrogen inserts into the bond, and the product is liberated from the catalyst.



catalyst with hydrogen adsorbed

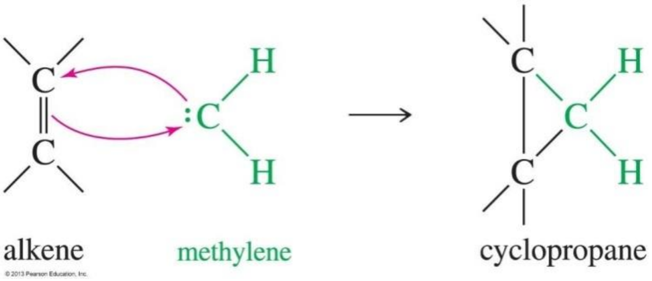
catalyst with hydrogen and alkene adsorbed

hydrogen inserted into C=C

alkane product released from catalyst

Addition of Carbenes

Carbenes are neutral, reactive intermediates with a divalent carbon and a lone pair.

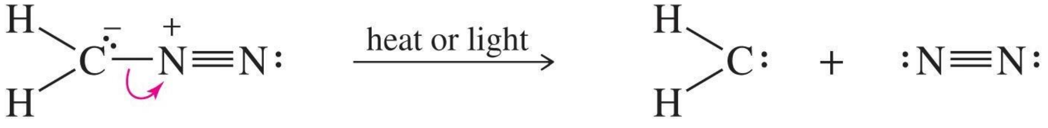


Carbenes are potent electrophiles and react with double bonds to form 3 membered rings (cyclopropanes). There are 3 classical ways to generate carbenes:

1. diazomethane
2. Simmons-Smith Reaction
3. Alpha Elimination from Haloforms

Diazomethane

The heating or photolysis of diazomethane generates a carbene and nitrogen gas.



However, diazomethane is toxic and explosive, and it often forms carbenes that are so reactive that numerous side products are formed.

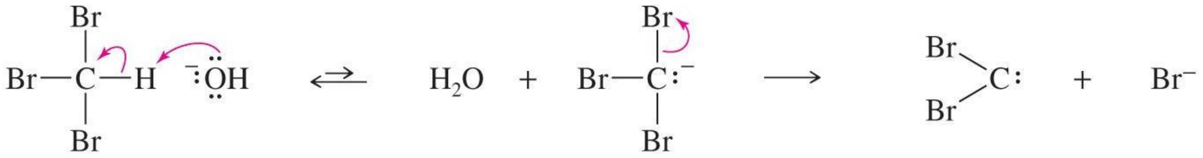
Simmons-Smith Reaction

The reaction of di-iodomethane with zinc metal in the presence of Cu(I) salts generates a carbenoid species ICH_2ZnI. (It behaves like a carbene).

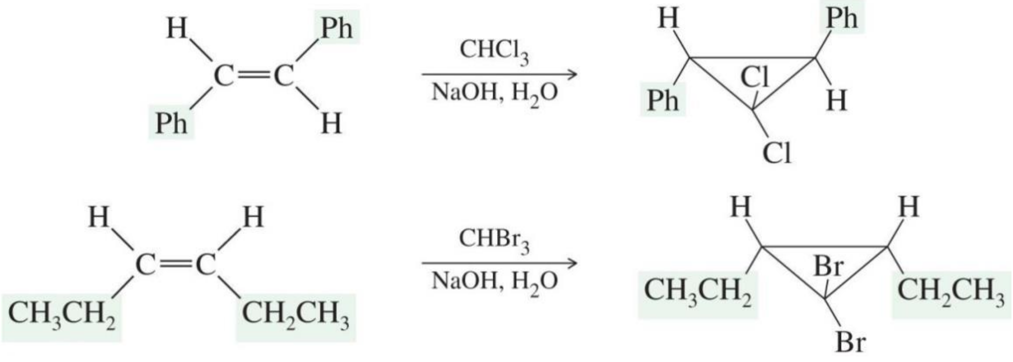
$$CH_2I_2 + Zn(Cu) \rightarrow ICH_2ZnI$$

Alpha Elimination from Haloforms

In the presence of a strong enough base, Bromoform can have its proton removed, and the tribromomethyl anion will eliminate a bromide ion to generate dibromocarbene.

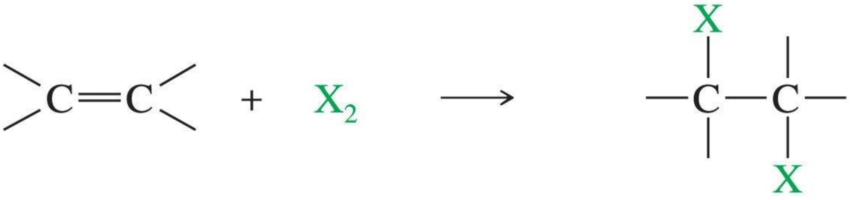


This type of carbene reacts with retention of stereochemistry of the reactants.



Addition of Halogens to Alkenes

Halogens add to alkenes to give vicinal dihalides, normally with anti addition.

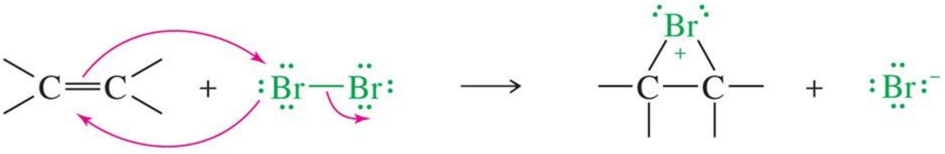


(X_2 = Cl_2, Br_2, sometimes I_2)

usually anti addition

Mechanism

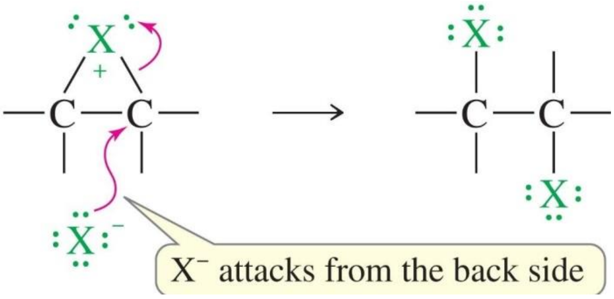
The halogen molecule (X_2) is electrophilic – a nucleophile will attack one end, and displace a halide ion.



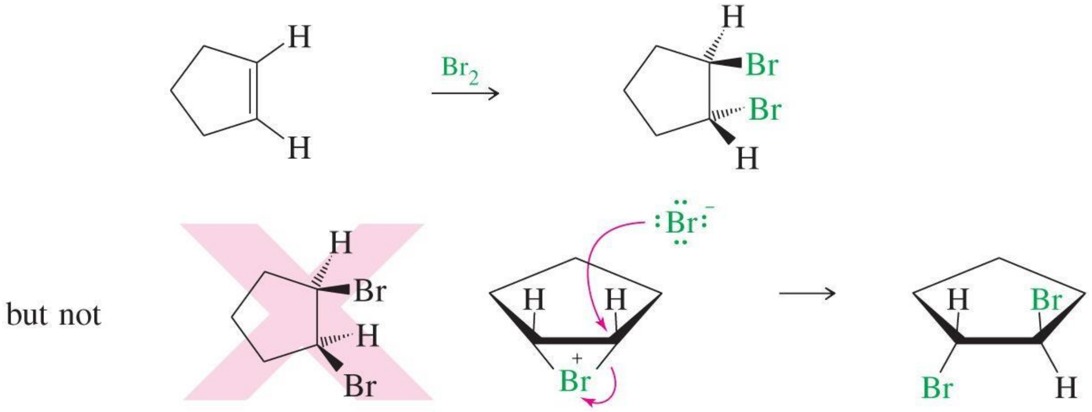
bromonium ion

Typically, a л bond will attack the bromine molecule kicking out bromide ion and generating a bromonium ion. (3 membered positively charged ring containing bromine).

This halonium ring is then opened by back side attack of a nucleophile (often the halide) to give the final anti product.

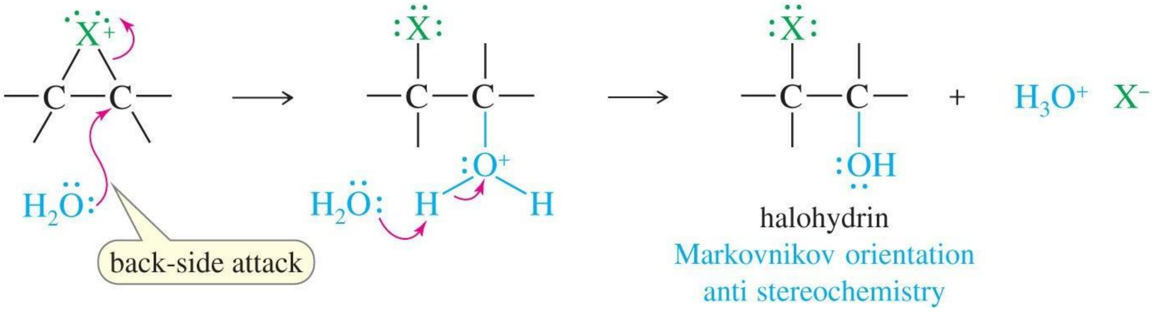


The halogen addition reaction is stereospecific, it gives anti addition.



Halohydrin Formation

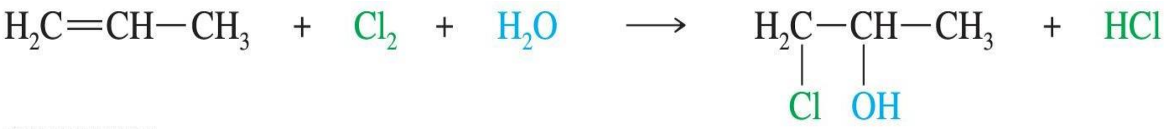
When the halogenation reaction takes place in the presence of a nucleophilic solvent, a nucleophile different from the halide can open the halonium ring. If the reaction is performed in the presence of water, Halohydrins are produced.



.The stereochemistry of the intermediate bromonium ring determines that the final product must be of anti addition, since ring opening must occur via backside attack.

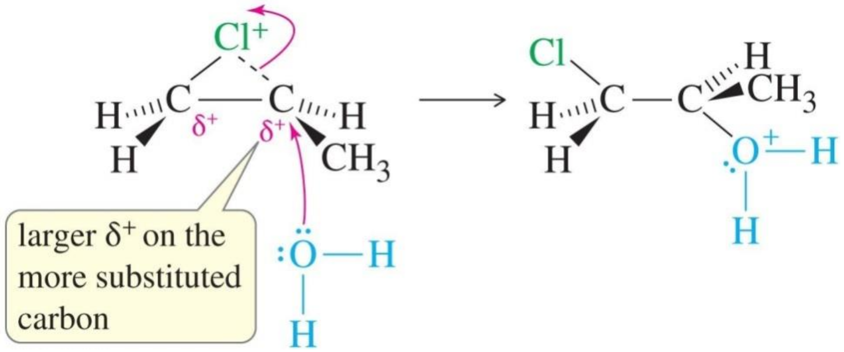
Orientation of Halohydrin Formation

When propene reacts with chlorine water, the major product has the Cl bound to the less highly substituted carbon, and hydroxyl to the most highly substituted carbon.



$$H_2C{=}CH{-}CH_3 + Cl_2 + H_2O \longrightarrow H_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 + HCl$$

In the halonium ring, the halogen is bound to both carbon atoms, which carry some partial positive charge. The more highly substituted carbon can bear more partial positive charge than the less highly substituted carbon.



The nucleophile attacks the site of greatest partial positive charge, which is the more substituted carbon.

Since the electrophile (Cl) is bound to the least highly substituted carbon, and the nucleophile (OH) is bound to the most substituted carbon, this is Markovnikov orientation.

Oxidation of Alkenes

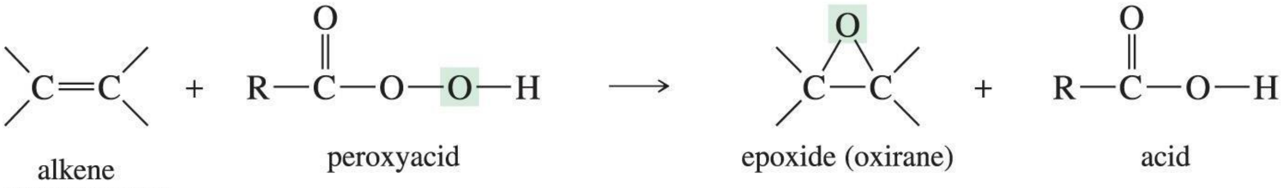
(Addition of hydrogen is termed a chemical reduction.

Addition of halogens across a double bond is called a chemical oxidation). Oxidation is normally the formation of C-O bonds.

There are three common methods for the introduction of oxygen containing functional groups into molecules via alkenes (epoxidation, hydroxylation and oxidative cleavage).

Epoxidation of Alkenes

An epoxide (oxirane) is a three membered ring containing an oxygen. (Heterocyclic version of a cyclopropane).



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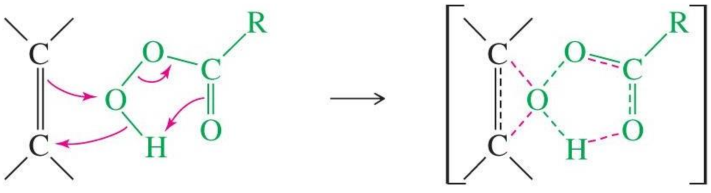
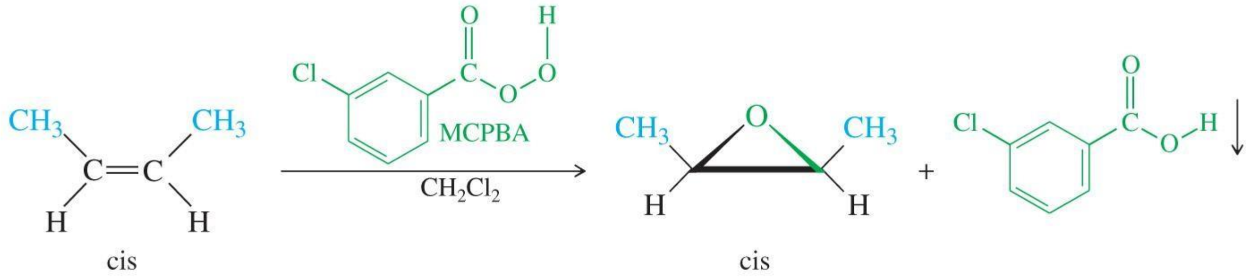
The most common reagent to convert an alkene to an epoxide is a peroxyacid. (Carboxylic acid but with an extra O). It is the oxygen of the OH which is transferred in this oxidation.

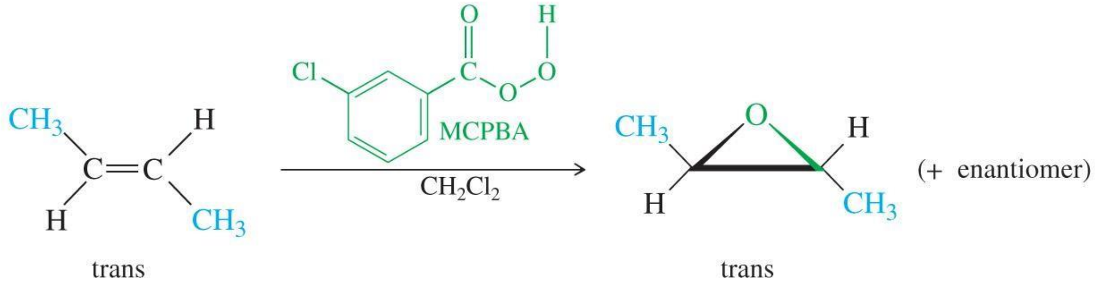
Mechanism

The epoxidation takes place in a concerted one step electrophilic process.



The stereochemistry of the reactant has no time to rearrange in this one step reaction, and so any stereochemistry of the reactant is maintained in the product.

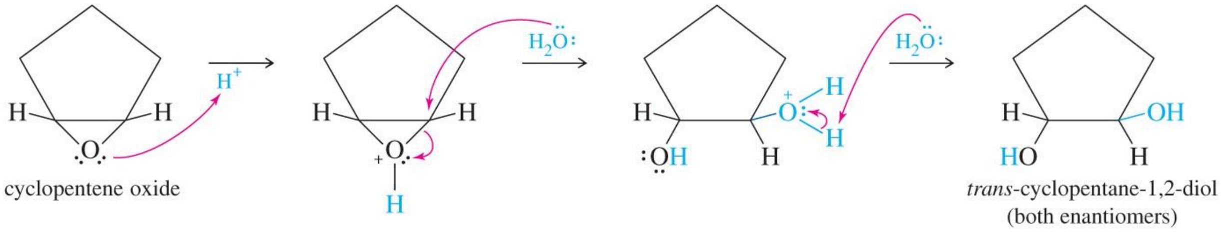




Acid catalyzed Ring Opening

Generally epoxides are stable compounds, but they can be easily ring opened.

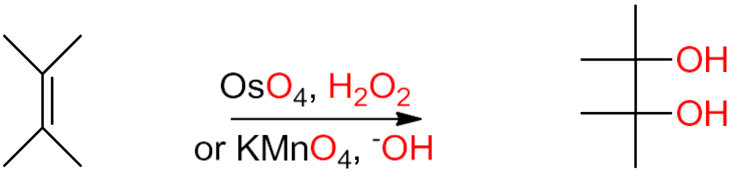
Moderate acids can protonate the ring oxygen (creating a good leaving group) and then any nucleophile can open the ring via back side attack to give anti orientation type products.



Mild acid reacts with epoxides to generate anti 1,2-diols (glycols).

Syn 1,2-Diols (Epoxidation followed by acidic hydrolysis gives anti 1,2-diols).

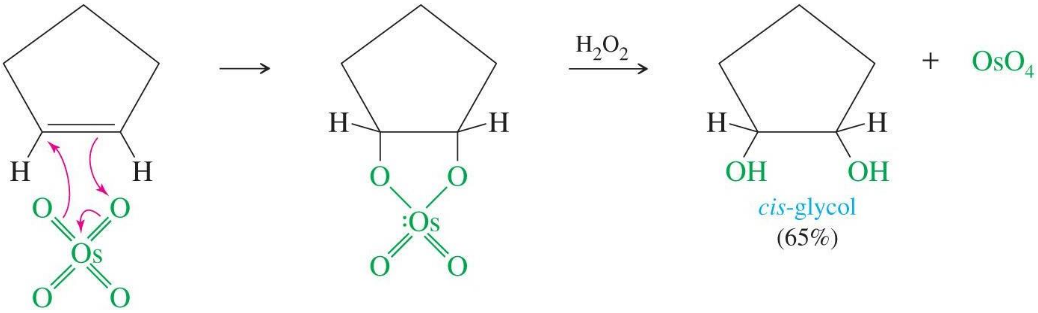
Syn hydroxylation of alkenes gives syn 1,2-diols.



The two most common methods use osmium tetroxide with hydrogen peroxide, or potassium permanganate and hydroxide ion.

Osmium Tetroxide Hydroxylation

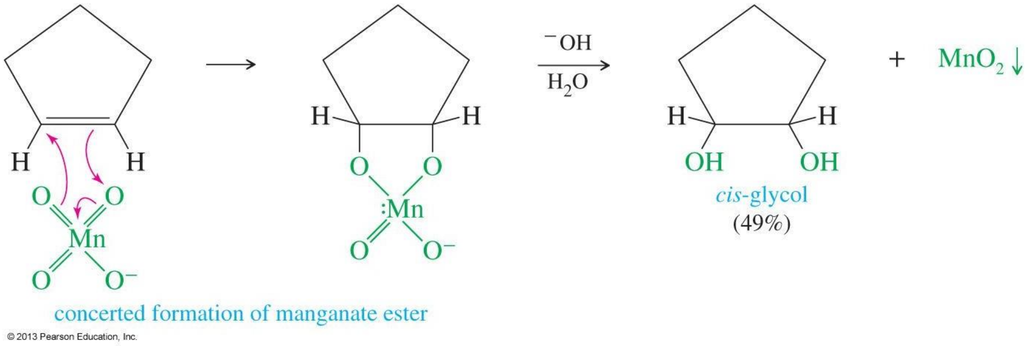
This reaction proceeds via a concerted electrophilic addition generating an osmate ester, which is hydrolyzed to a syn diol by hydrogen peroxide, which also reoxidizes the osmium catalyst.



The two C-O bonds are formed at the same time with the cyclic ester, and the oxygen atoms are added at the same face of the л bond – syn orientation.

Permanganate Hydroxylation

An alkaline, cold solution of potassium permanganate will do exactly the same transformation as osmium tetroxide.

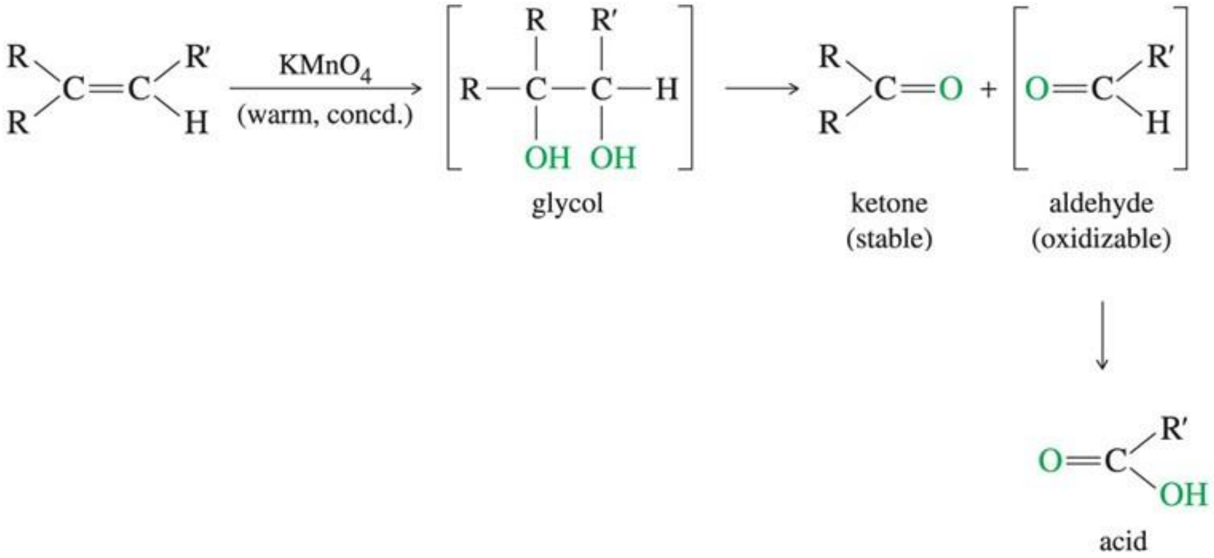


The intermediate cyclic ester again forces syn hydroxylation.

Potassium permanganate is cheaper and less toxic than osmium tetroxide, but gives the product in slightly lower yield.

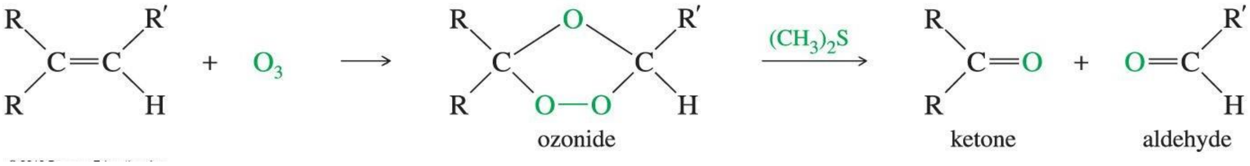
Oxidative Cleavage

If either acid or heat is used with permanganate, cleavage and further oxidation can occur producing ketones and/or aldehydes. The aldehydes further oxidize to carboxylic acids.

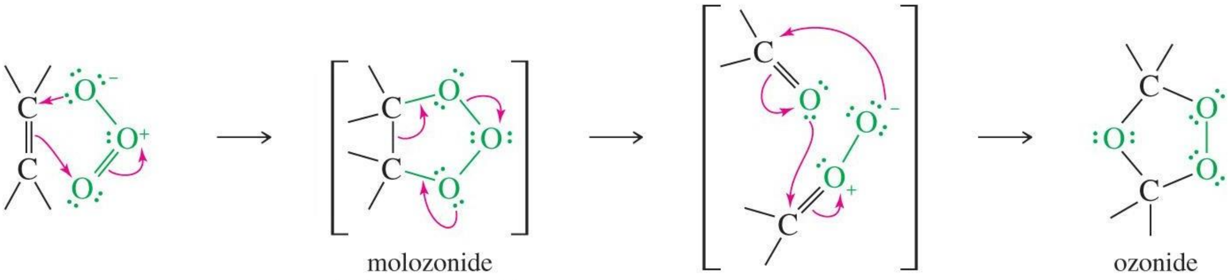


Ozonolysis

Ozone (O_3) also cleaves double bonds, but this milder reagent gives aldehyde and ketones as the products.

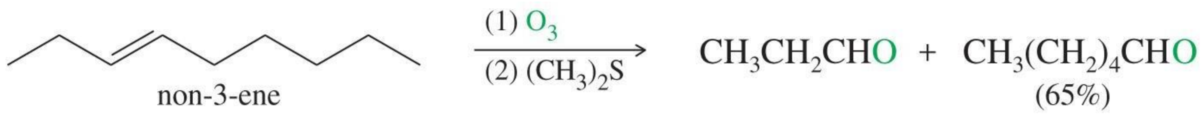


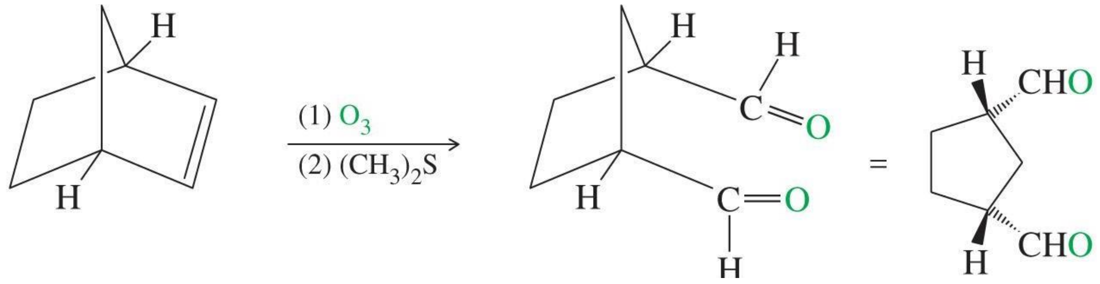
The intermediate ozonide reacts with reducing agents like dimethyl sulfide to produce DMSO and the carbonyl products.



Ozone reacts with the double bond to give an unstable molozonide (primary ozonide) which rearranges to an ozonide.

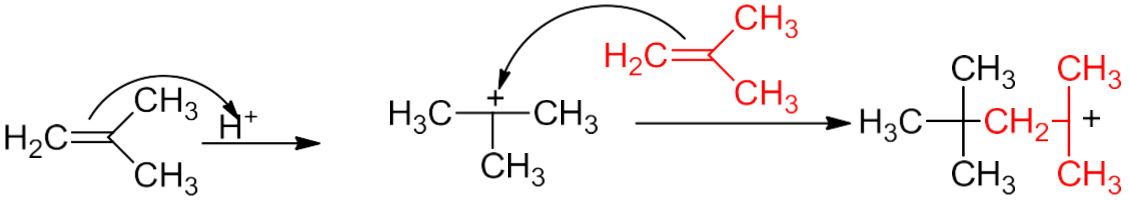
This cleavage reaction is often used to identify the positions of double bonds in alkenes.





Alkenes in the presence of strong acids can be made to polymerize.

An electrophile (H+) adds electrophilically to the double bond, and the carbocation is attacked by another alkene double bond.



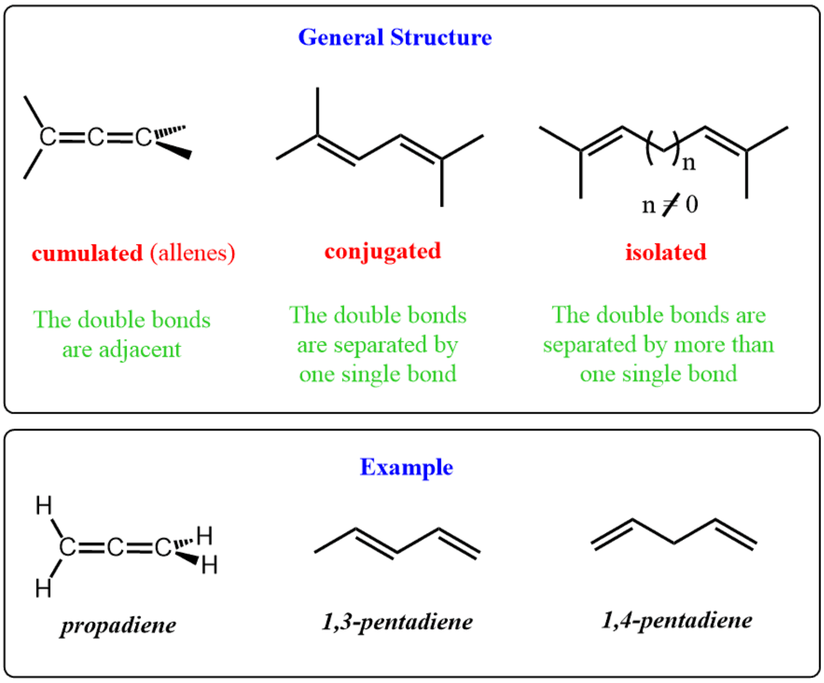
Depending on the reaction conditions either low molecular weight products (dimers trimers, etc) or high molecular products (polymers) are formed.

Alkadienes

Compounds that possess two C=C double bonds. The classification of dienes is based on the proximity of the π bonds.

- When they are adjacent (connected), we have cumulated dienes which are called cumulenes. Allenes is another name used to describe these compounds.
- When separated by one single bond, it is a conjugated diene.
- When the double bonds are separated by more than one single bond, we have an isolated diene.

The Types of Dienes



cumulated (allenes)	conjugated	isolated
The double bonds are adjacent	The double bonds are separated by one single bond	The double bonds are separated by more than one single bond
propadiene	*1,3-pentadiene*	*1,4-pentadiene*

Stability of Conjugated Dienes

The relative stability of isolated and conjugated dienes can be demonstrated by their heats of hydrogenation. For example, the heats of hydrogenation of 1-butene and 1,3-butadiene:


but-1-ene
(1-butene)

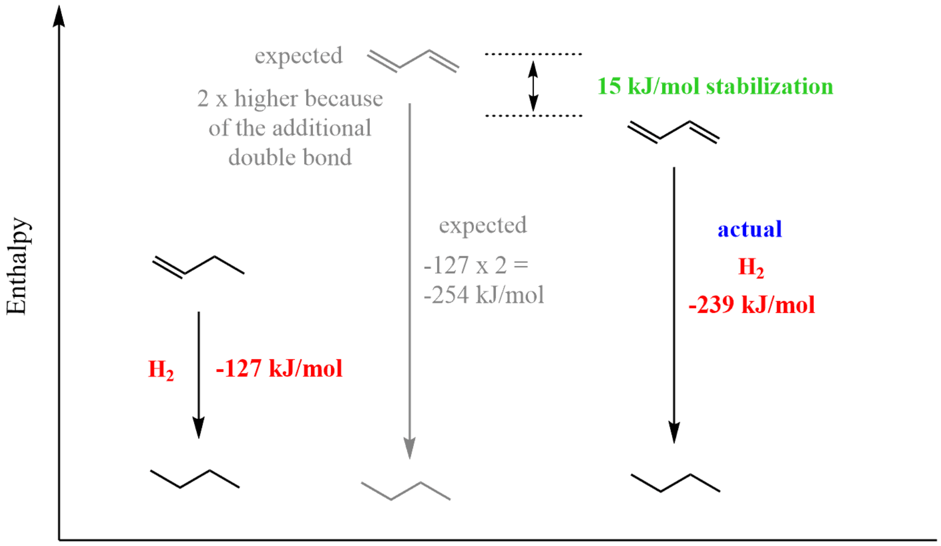

buta-1,3-diene
(1,3-butadiene)

1,3-butadiene has an extra double bond which requires an additional mol of hydrogen to be reduced to butane. In this prospective, 1-butene can be looked at as an intermediate to the final product butane and we can expect that hydrogenation 1,3-butadiene will produce twice the amount of heat as 1-butene would.

However, the experimental data revealed that the heat of hydrogenation for the conjugated diene is less than expected.

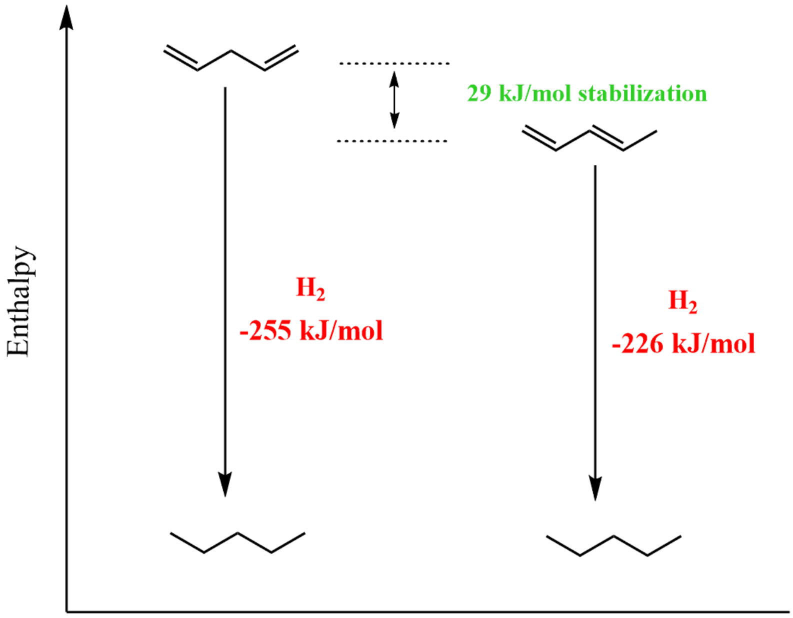
The process is exothermic and smaller value of the hydrogenation indicate that the conjugated diene is more stable than if it was an isolated one. Therefore, we can conclude that conjugated double bonds bring additional stability. In this case, the stabilization associated with the conjugated nature of double bonds is determined to be ∼15 kJ/mol.

This is a general trend for all the conjugated compounds whether they are dienes, trienes or aromatic compounds.



A similar observation is seen when we compare the heats of hydrogenation of 1,4-pentadiene (an isolated diene) and (3E)-1,3-pentadiene (a conjugated diene) to pentane. This time, both molecules have two double bonds. As expected, 1,3-pentadiene has a smaller heat of hydrogenation and therefore, it is lower in energy meaning it is more stable than the isolated 1,4-pentadiene:

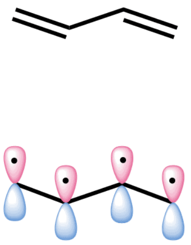
Conjugated Dienes Have Smaller Heats of Hydrogenation
They are More Stable



Why are conjugated dienes more stable than isolated dienes

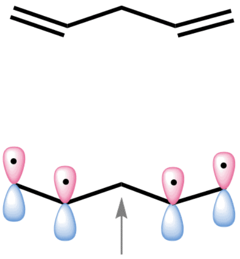
Conjugated dienes are capable of more resonance structures. The overlapping p orbitals on adjacent atoms allow the electrons to be delocalized over the four or more atoms. Keep in mind that to achieve this delocalization, all the p orbitals must be aligned parallelly:

conjugated double bonds



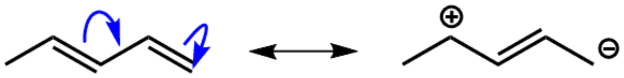
all the electrons are delocalized

isolated double bonds

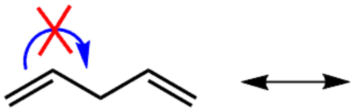


delocalization broken by sp3 carbon

The delocalization breaks when p orbitals are separated by and sp^3-hybridized carbon because it does not have an unhybridized p orbital capable of participating in the electron flow. This is the case with isolated dienes and therefore they are less stable. Resonance structures for 1,4-pentadiene involving the electrons on carbon atoms on both double bonds i.e., they are not delocalized. This delocalization, however, is possible for the conjugated 1,3-pentadiene:

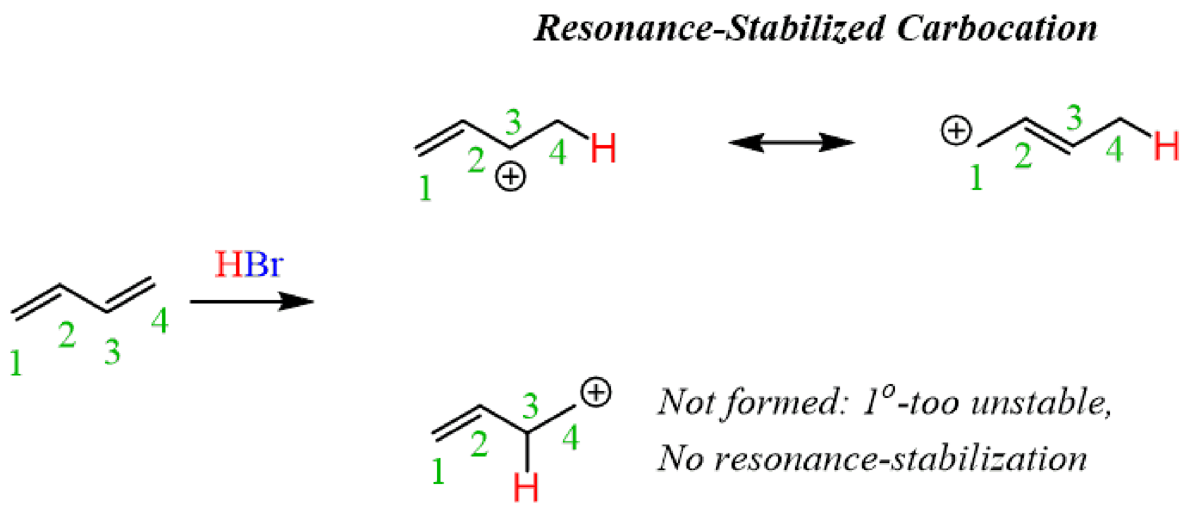


1,3-pentadiene - all the electrons are delocalized



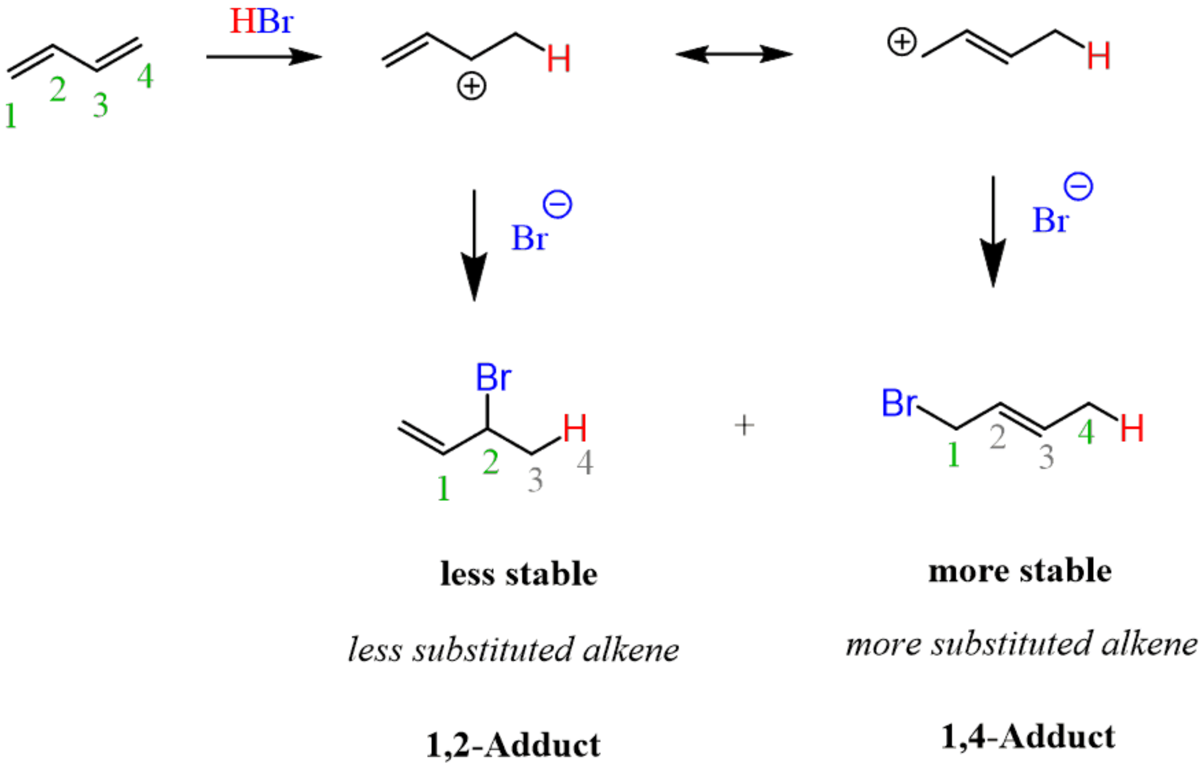
1,4-pentadiene - electrons are not delocalized over the other p orbitals

Electrophilic addition to conjugated dienes - 1, 2 and 1, 4 additions


Resonance-Stabilized Carbocation

Not formed: 1°-too unstable,
No resonance-stabilization

The first one is preferred since it is a secondary carbocation and in addition it is resonance-stabilized. Bromide ion attacks both of the carbocation (the resonance structure). Two alkenes are formed.


less stable

less substituted alkene

1,2-Adduct

more stable

more substituted alkene

1,4-Adduct

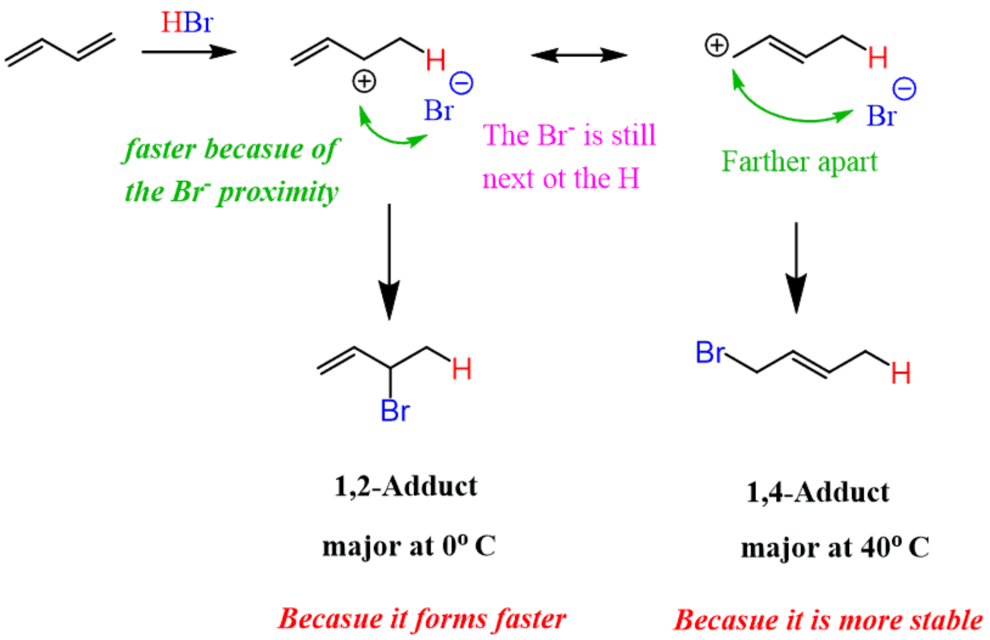
The first alkene less substituted alkene, while the second one is more substituted alkene. Therefore, it is more stable and is expected to be the major product. The more stable product is called a 1,4-adduct and the less stable product is the 1,2-adduct. They are formed by a 1,4- and 1,2-addtion respectively.

The 1,4 adduct is the thermodynamic product of the reaction since it is the more stable product.

The Effect of Temperature

The regiochemistry changes when the reaction is carried out at lower temperatures. The 1,2-addition starts predominating because of the **proximity effect**. The proximity of the Br^- ion to the carbocation right after the protonation of the double bond occurs:

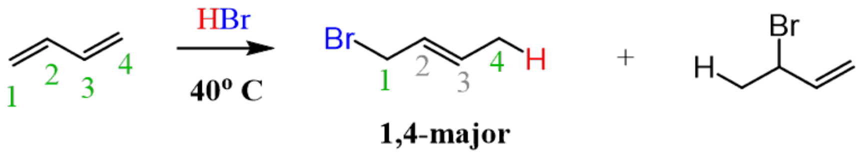
The regiochemistry of Electrophilic Addition to Conjugated Dienes

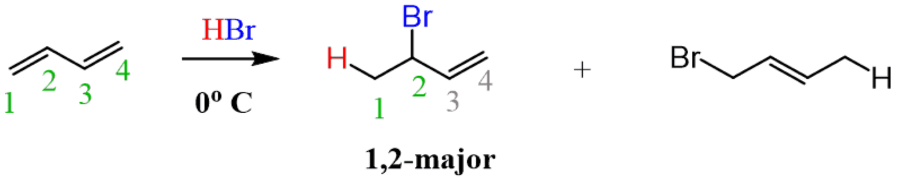


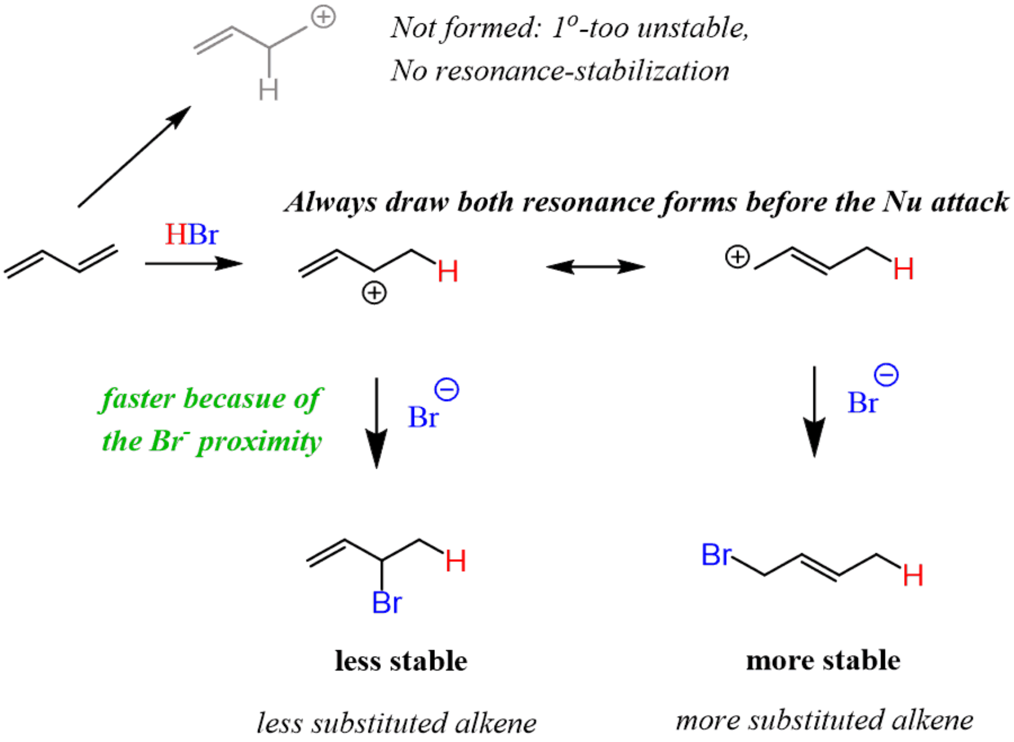
The nucleophilic attack of the Br^- occurs faster as it does not have to wait for the formation of the second resonance structure (remember, however that resonance structures are formalities). Therefore, the **1,2 adduct is the kinetic product** as it forms faster but is less stable. Thereby **the kinetic product is generally favored at lower temperatures** since the molecules do not have sufficient energy to overcome the energy barrier (activation energy) and form the more stable (thermodynamic product).

The summary of the electrophilic addition to conjugated alkenes considering the regiochemistry at low and higher temperatures explained by the corresponding energy diagrams:

Summary of 1,2 and 1,4 Electrophilic Addition to Conjugated Dienes







Not formed: 1°-too unstable,
No resonance-stabilization

Always draw both resonance forms before the Nu attack

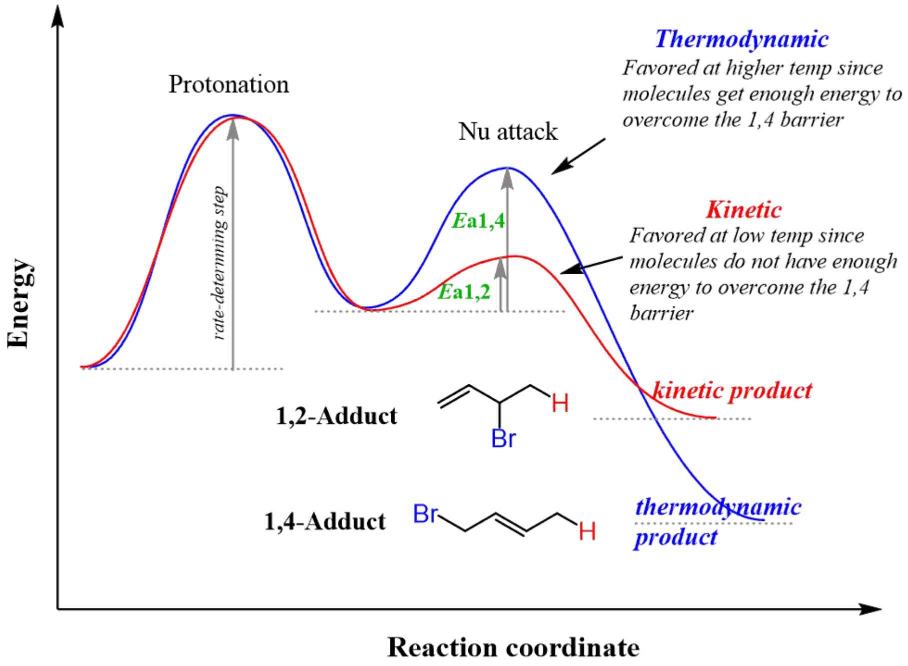
faster becasue of the Br^- proximity

less stable

less substituted alkene

more stable

more substituted alkene



Prediction of All the Products of Electrophilic Additions to Diene

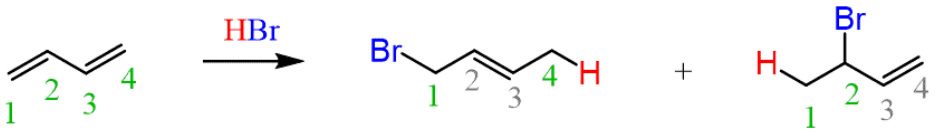
In general, in order to predict the products of an electrophilic addition to a diene, first to identify whether the diene is symmetrical or unsymmetrical.

- If it is **symmetrical, you only need to protonate one of the double bonds** since both double bonds result in the same products.
- If it is **unsymmetrical**, then **you need to consider the protonation of both double bonds.**
- In each case, **you also need to draw both resonance forms** of the resulting carbocation for the nucleophilic attack.
- In addition to this, stereochemistry of the addition reactions to dienes has to consider.

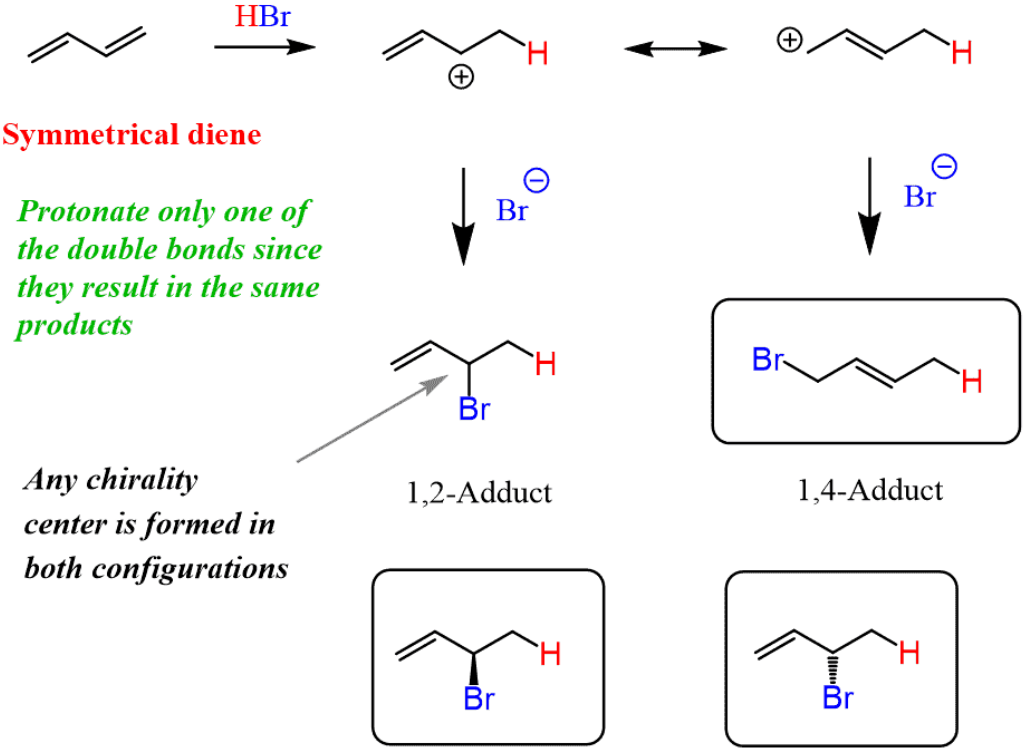
The Stereochemistry of Electrophilic Additions to Symmetric Dienes

Since the addition reaction to the diene goes through formation of a carbocation, the nucleophilic attack occurs from both faces of the sp^2-hybridized carbon and a new chirality center is formed as a racemic mixture.

The Stereochemistry of Electrophilic Additions to Symmetrical Diene is summarized below:



Step 1. *Identify if the diene is symmetrical or unsymmetrical*
If symmetrical *- protonate only one of the double bonds*
If symmetrical *- protonate both double bonds forming the resonance-stabilized carbocation*



Symmetrical diene

Protonate only one of the double bonds since they result in the same products

Any chirality center is formed in both configurations

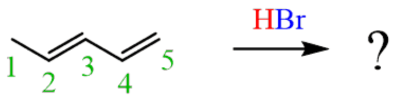
1,2-Adduct

1,4-Adduct

Enantiomers
racemic

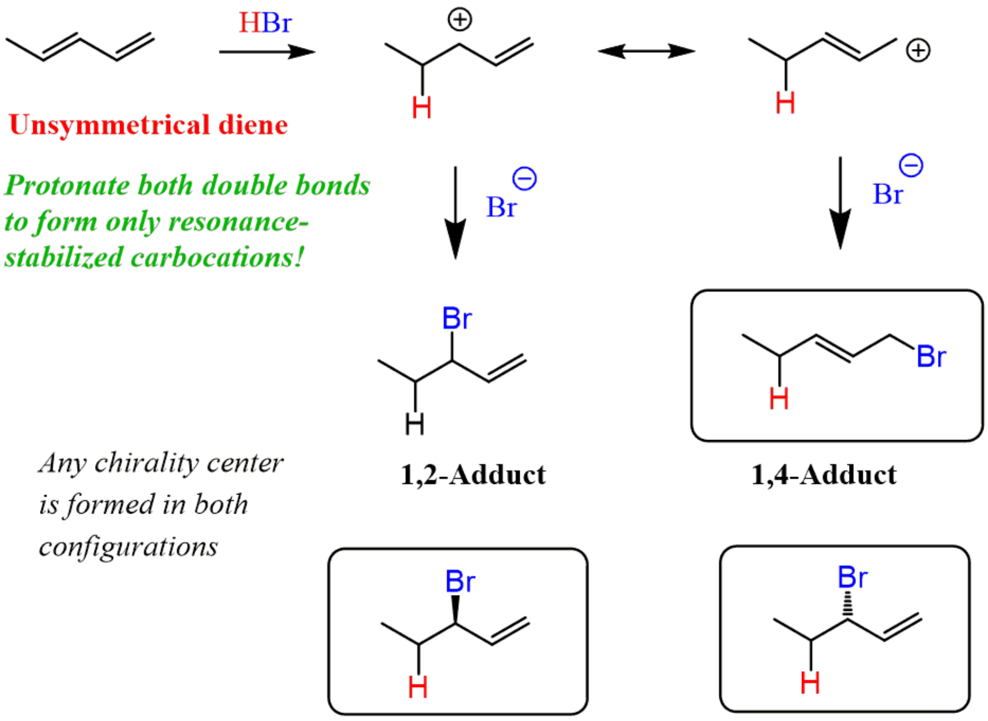
Electrophilic Additions to Unsymmetrical Dienes

It becomes a bit more complicated when the diene is not symmetrical since to consider the protonation of both double bonds. For example, in penta-1,3-diene there are four carbons with a double bond and protonating all of them will lead to a very large number of molecules.



Step 1. *Identify if the diene is symmetrical or unsymmetrical.*
If symmetrical *- protonate only one of the double bonds.*
If symmetrical *- protonate both double bonds forming the resonance-stabilized carbocations.*

Protonation of the first double bond



Unsymmetrical diene

Protonate both double bonds to form only resonance-stabilized carbocations!

Any chirality center is formed in both configurations

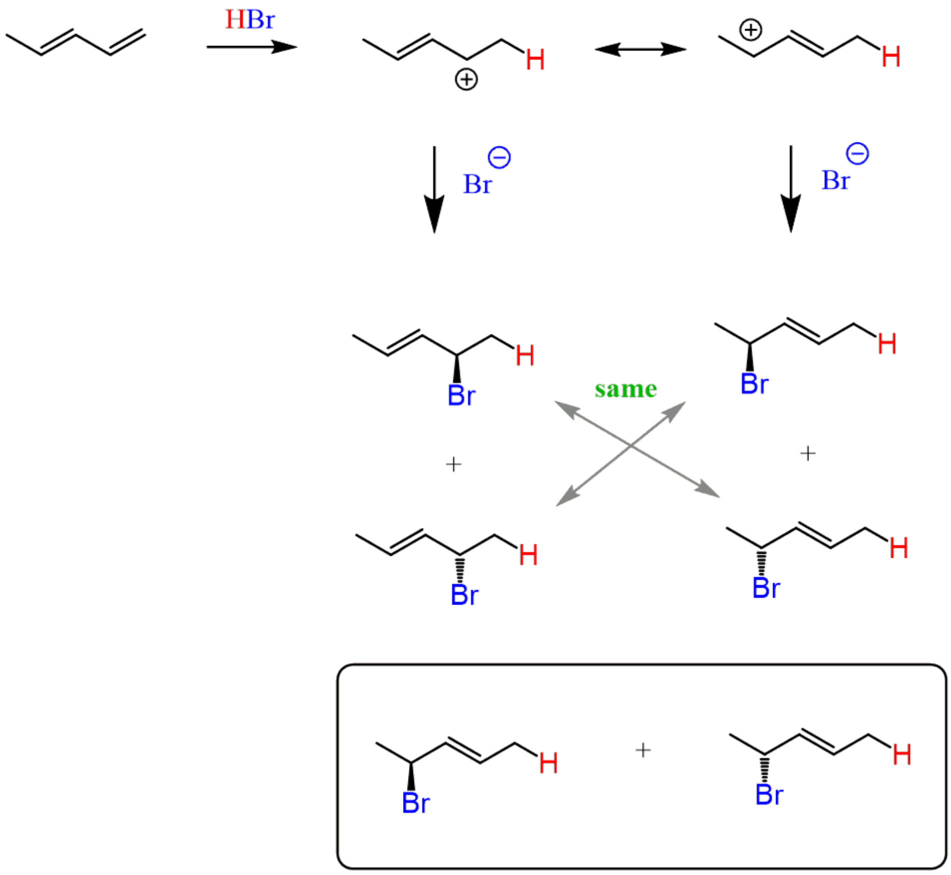
1,2-Adduct

1,4-Adduct

Enantiomers

racemic

Protonation of the second double bond

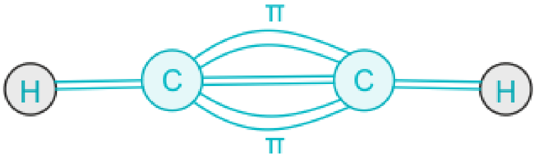


Enantiomers

Alkynes

Alkynes contain four hydrogen atoms less than corresponding alkanes and two hydrogen atoms less than corresponding alkenes and have the general formula C_nH_{2n-2} The aliphatic unsaturated hydrocarbons containing two or three carbon-carbon triple bonds in their structure are called alkadiynes and alkatriynes respectively.

The molecular formula of ethyne is C_2H_2. Each carbon atom in acetylene undergoes sp hybridisation.



Each carbon atom has two sp hybrid orbitals and two unhybridised 2p orbitals. The C-C sigma (σ) bond is formed by axial overlapping of sp hybrid orbitals of two carbon atoms. The remaining sp hybrid orbital of each carbon atom overlaps with the ls orbital of hydrogen atom along the internuclear axis to form two sigma (σ) bonds.

Each carbon atom has two unhybridised 2p orbitals which are perpendicular to each other as well as to the plane of the C-C bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of another carbon atom, which undergo lateral overlap to form two (π) bonds.

- Thus C≡C consists of one sigma (σ) bond and two (π) bonds.
- The C≡C bond is stronger than C = C and C-C bond.
- The electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Acetylene is a linear molecule. The H−C≡C bond angle is 180°

Nomenclature of Alkenes

The Nomenclature of Alkenes is done in two ways:

Following rules are used to obtain the IUPAC name of alkynes.

1. Select the longest and continuous chain of carbon atoms containing the carbon-carbon triple bond.
2. Number the carbon atoms from that end that is nearest to the triple bond.
3. Count the number of carbon atoms in the selected chain.
4. The given alkyne is considered as the derivative of the corresponding alkane.
5. The name of the alkyne is derived by replacing the suffix ‘ane’ from the name of parent alkane with ‘yne’.

6. The position of the carbon atom, from which the triple bond starts, is indicated by the lower number.
7. The locant indicating the position of the triple bond is placed immediately before the suffix ‘yne’.
8. The position of the branches (alkyl groups) is indicated by proper numbers.
9. Compounds with more than one triple bond are called diynes, triynes and so forth. Compounds containing both double and triple bonds are called enynes. The numbering of an enyne chain starts from the end nearer to the first multiple bonds, whether double or triple bond. Ties are broken in favour of the double bond.

Methods of Preparation of Alkynes

- ➢ From Calcium Carbide (Industrial Method)

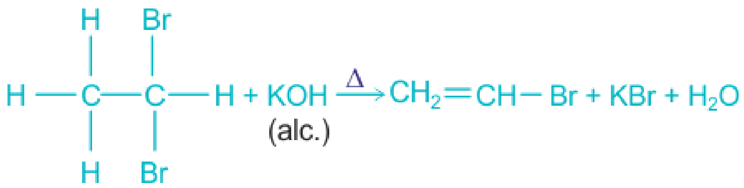
  Calcium carbide reacts with water to give acetylene. Impurities of phosphine (PH_3) and hydrogen sulphide (H_2S) are removed by passing acetylene through copper sulphate solution.

- ➢ From Vicinal And Geminal Dihalide (By Dehydrohalogenation)

  The dihalides in which two halogen atoms are attached to adjacent carbon atoms are called vicinal or alkylene dihalides. The dihalides in which two halogen atoms are attached to the same carbon atoms are called geminal or alkylidene dihalides.

  From Geminal Dihalides

  When ethylene dibromide is boiled with alcoholic caustic potash it gives vinyl bromide which on heating with sodamide gives acetylene.



$$H-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{Br}{C}}-H + \underset{(alc.)}{KOH} \xrightarrow{\Delta} CH_2{=}CH-Br + KBr + H_2O$$

Ethylene dibromide (1,1-Dibromoethane)

Vinyl bromide (Bromoethane)

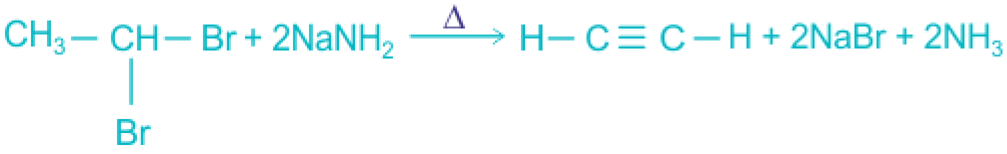
$$CH_2{=}CH-Br + NaNH_2 \xrightarrow{\Delta} H-C\equiv C-H + NaBr + NH_3$$

From vicinal Dihalides

When ethylidene dibromide is boiled with alcoholic caustic potash it gives vinyl bromide which on heating with sodamide gives acetylene.

When ethylene dibromide or ethylidene dibromide is boiled with alcoholic potash, acetylene is formed. But yield is poor because the intermediate compound vinyl bromide is less reactive. Hence bases are stronger than NaOH/KOH, such as $KNH_2/NaNH_2$ are used in the second step.

$$Br-CH_2-CH_2-Br + 2NaNH_2 \xrightarrow{\Delta} H-C\equiv C-H + 2NaBr + 2NH_3$$



$$CH_3-\underset{\underset{Br}{|}}{CH}-Br + 2NaNH_2 \xrightarrow{\Delta} H-C\equiv C-H + 2NaBr + 2NH_3$$

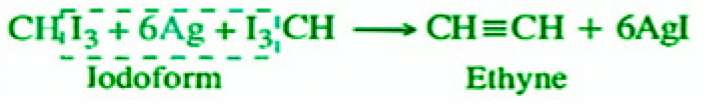
<u>Note:-</u> Alternatively, acetylene can be prepared from ethylene dibromide or ethylidene dibromide on heating with sodamide. It is known as double dehydrohalogenation

- From Tetrahalides (By Dehalogenation)

  When acetylene tetrabromide is heated with zinc in presence of alcohol, acetylene is formed.

- By Dehalogenation of Haloforms:

  When chloroform and iodoform are heated with silver powder, they dehalogenate and yield ethyne.



$$\underbrace{CHI_3 + 6Ag + I_3CH}_{Iodoform} \longrightarrow \underbrace{CH\equiv CH}_{Ethyne} + 6AgI$$

- Synthesis from Carbon and Hydrogen:

  Steam of hydrogen gas may similarly be used to make ethyne by passing it through an electric arc formed between two carbon electrodes. Berthelot synthesis is the name for this method.

$$2C + H_2 \xrightarrow{Electric\ arc} HC \equiv CH$$

<u>Physical Properties of Alkynes</u>

i. Alkynes resemble alkanes and alkenes in their physical properties.

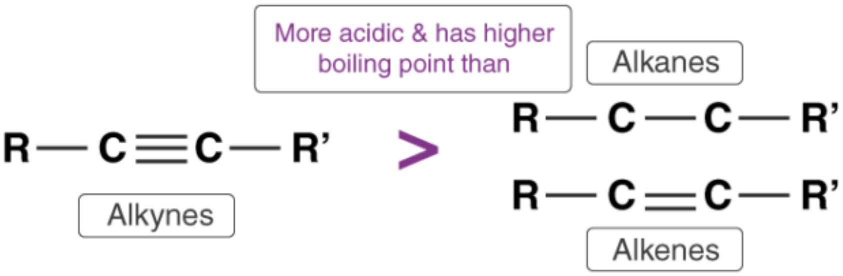
ii. The first three alkynes are gases, the next eight are liquids and the higher ones are solids.

iii. All alkynes, except acetylene, are odourless. Acetylene has a characteristic smell. Generally, they are more polar and have slightly higher boiling points than corresponding alkanes and alkenes. Their melting points and boiling points increase with the increase in molecular mass.

iv. They are less dense than water. They are insoluble in water but quite soluble in organic solvents like ether, benzene, carbon tetrachloride, etc.

v. Acidity of Alkynes

An alkyne molecule contains at least one triple bond between two carbon atoms. For example:- ethyne ($CH\equiv CH$). Ethyne reacts with strong bases such as sodium metal and sodamide ($NaNH_2$) to form sodium acetylide along with the liberation of dihydrogen gas. This reaction of alkynes with bases to liberate dihydrogen gas indicates the acidity of alkynes. $HC \equiv CH + Na \rightarrow HC \equiv C^- Na^+ + 1/2H_2$



Relative Acidity of Alkynes

Acidity of alkynes is due to their ability to lose hydrogen atom to form alkynideions. Thus, alkynes act as Brønsted-Lowry acids. The triple bonded carbon atom in alkynes is "sp" hybridized. Due to the high percentage of "s" character (50%) in alkynes, the "sp" hybridized orbitals of carbon atom in alkynes exhibit high electronegativity. These attract the C-H bond of alkynes to a great extent. Thus, alkyne molecules can easily lose hydrogen atom forming alkynide ions and so the hydrogen atom attached to the triply bonded carbon atom is acidic in nature.

The acidity of alkynes is greater than the acidity of alkanes and alkenes as the carbon atom in alkanes and alkenes are "sp^3" and "sp^2" hybridized respectively. Hence, these molecules contain a smaller percentage of "s" character in comparison to alkynes. Thus, the electronegativity of the carbon atom in these cases is lesser than alkynes. Hence, alkanes and alkenes don't show the reactions with bases to liberate hydrogen gas. It can further be noted that only hydrogen atom attached to a triply bonded carbon atom are acidic not the other hydrogen atoms in the alkyne chain. The general trend in acidity is seen as:

$$HC\equiv CH > H_2C{=}CH_2 > CH_3{-}CH_3$$

$$HC\equiv CH > CH_3{-}C\equiv CH >> CH_3{-}C\equiv C{-}CH_3$$

Chemical properties

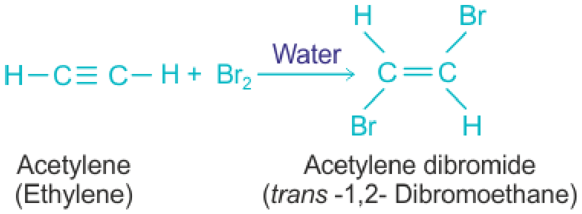
- Formation of Alkanes (Hydrogenation)

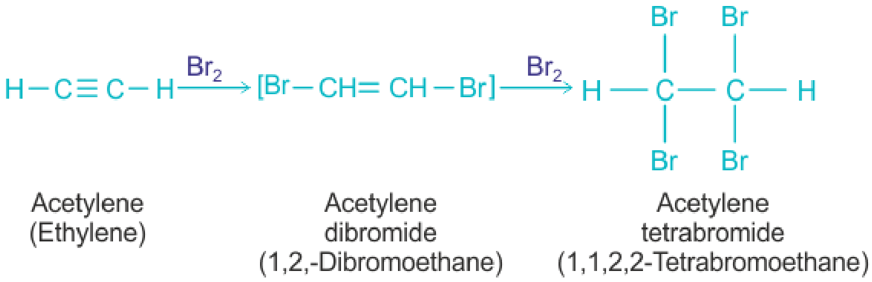
  When acetylene is heated with hydrogen gas in the presence of a catalyst like Raney Nickel, ethane is formed. Hydrogenation may be carried out at room temperature in presence of platinum or palladium. In this reaction, two hydrogen molecules are added across the triple bond in acetylene.

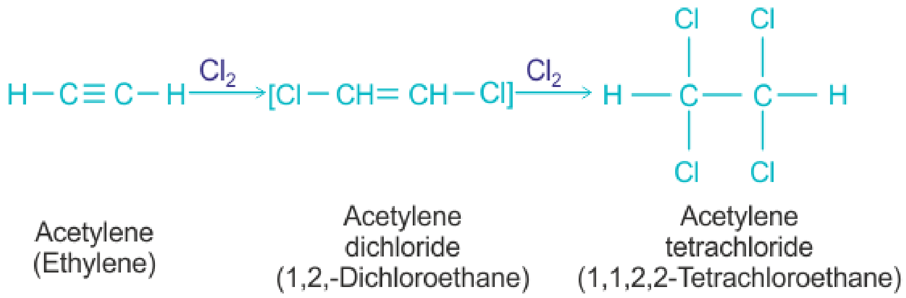
- Formation of Tetrahalides (Halogenation)

  Acetylene reacts with chlorine or bromine even in dark. The reaction is catalysed by light. A dihaloalkene is obtained in the first step, which is then converted into tetrahaloalkane.

  - Iodine adds to acetylene with difficulty.
  - Acetylene reacts with chlorine gas to give acetylene tetrachloride, known as westron. Westron is a non-inflammable liquid and is used as a solvent.
  - Acetylene reacts with dilute bromine water to give acetylene dibromide. Thus, similar to alkenes, alkynes also decolourise bromine water.
    - Acetylene reacts with liquid bromine to give acetylene tetrabromide.



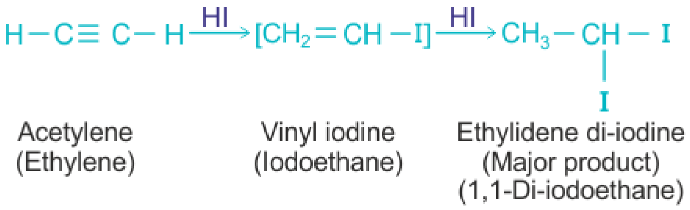


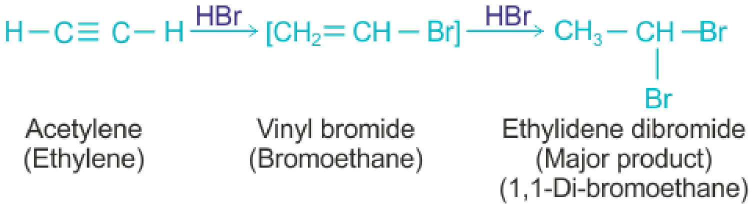


- Formation of Geminal Dihalides (Hydro-halogenation)

  Alkynes react with hydrogen halides to give first vinylic halides and finally geminal dihalides. The order of reactivity of hydrogen halides is HI > HBr > HCl. The addition of hydrogen halide in the second step takes according to Markownikoff's rule.

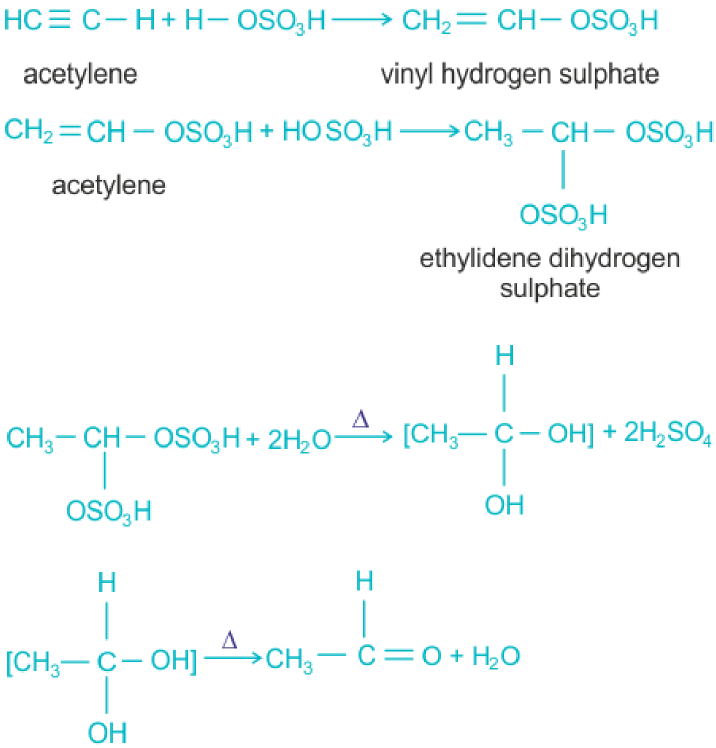
  - Acetylene reacts with hydrogen iodide to give ethylidene di-iodide
  - Acetylene reacts with hydrogen bromide to give ethylidene dibromide.
  - When acetylene is passed through dilute hydrochloric acid in presence of mercuric chloride at 338K, vinyl chloride is obtained. Only one molecule of hydrogen chloride is added.





- Formation of Hydrogen Sulphates (Addition of Sulphuric Acid)

  Acetylene adds two molecules of sulphuric acid to give ethylidene dihydrogen sulphate, which on heating with water gives acetaldehyde.



$$HC\equiv C-H+H-OSO_3H \longrightarrow CH_2=CH-OSO_3H$$

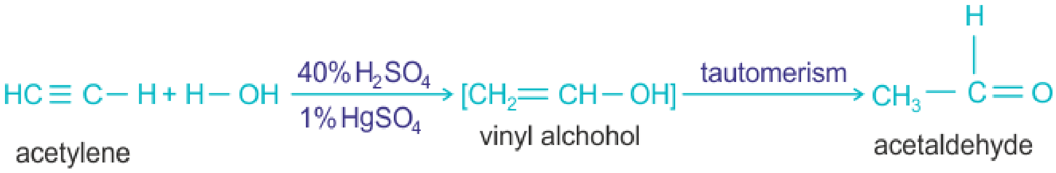
$$CH_2=CH-OSO_3H+HOSO_3H \longrightarrow CH_3-\underset{\displaystyle OSO_3H}{\underset{|}{CH}}-OSO_3H$$

$$CH_3-\underset{\displaystyle OSO_3H}{\underset{|}{CH}}-OSO_3H+2H_2O \xrightarrow{\Delta} [CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-OH]+2H_2SO_4$$

$$[CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-OH] \xrightarrow{\Delta} CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O+H_2O$$

- Formation of Aldehydes/Ketones (Hydration)

  On passing alkynes through warm 40% H_2S0_4 in the presence of 1% mercuric sulphate, aldehydes/ketones are formed.



$$HC\equiv C-H+H-OH \xrightarrow[1\%\,HgSO_4]{40\%\,H_2SO_4} [CH_2=CH-OH] \xrightarrow{\text{tautomerism}} CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O$$

- Ozonolysis

  Acetylene reacts with ozone to give an ozonide, which on boiling with zinc dust and water gives glyoxal. The by-product, hydrogen peroxide is destroyed by zinc dust and further oxidation is avoided.

- Polymerisation

  Acetylene undergoes linear polymerization, under suitable conditions, to give high molecular weight polyene, called polyacetylene or polyethene. It is represented as

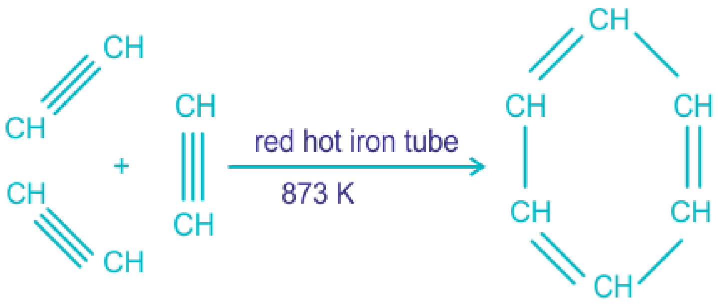
  (−CH=CH−CH=CH−)n

  Thin film of this polymer can be used as electrodes in batteries.

  Polyacetylene films are good conductors of electricity and are lighter and cheaper than metal conductors.

- Formation of Benzene (isomerisation)

When acetylene is passed through red hot iron or quartz tube at 873K, it trimerises to give benzene.



Uses of Alkynes

i. Alkynes are used for a variety of purposes. Following are some of them:

ii. Alkynes are generally used as the starting materials for the manufacture of a large number of organic compounds of industrial importance such as chloroprene, vinyl chloride etc.
iii. Acetylene is used in welding torches.
iv. Alkynes are commonly used to ripen fruits and vegetables artificially.
v. They are used to form polymers
vi. Oxyacetylene flame is used for cutting metals.

IUPAC Rules for Nomenclature

The naming of substituted cycloalkanes follows the same basic steps used in naming alkanes.

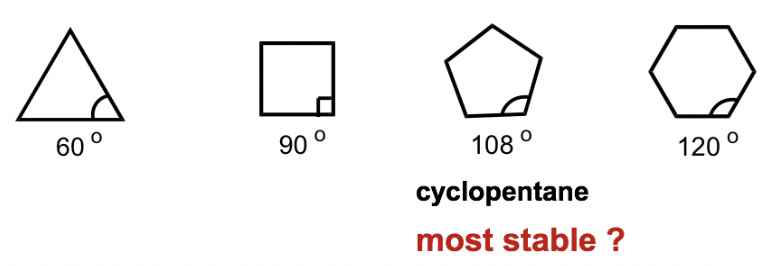
- Determine the parent chain.
- Number the substituents of the ring beginning at one substituent so that the nearest substituent is numbered the lowest possible. If there are multiple choices that are still the same, go to the next substituent and give it the lowest number possible.
- Name the substituents and place them in alphabetical order.

STABILITY OF CYCLOALKANES

structural formula of cycloalkanes

An interesting fact about the cycloalkanes is that they have different relative stabilities, and the stability depends on the size of the ring. It has been observed that cyclic compounds found in nature usually are in 5- or 6-membered rings, and the 3- or 4-membered rings are rather rare.

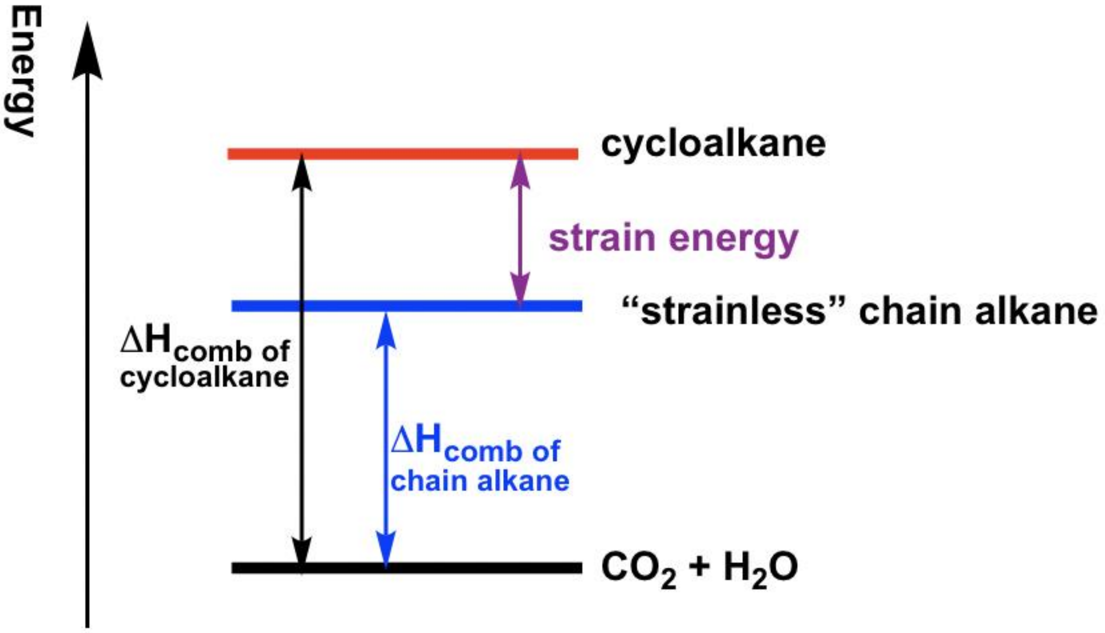
To explain this stability difference, German chemist Adolf von Baeyer proposed the "Bayer Strain Theory". By assuming all the rings are in a *flat* (or planar) shape, Bayer Theory suggests that the difference between the ideal bond angle (which is 109.5° for sp^3 carbon) and the angle in the planer cycloalkane causes the strain, which is called **angle (or ring) strain**. According to the Bayer Theory, cyclopentane would be the most stable because its bond angles, 108°, are closest to the ideal angle of 109.5°. Cyclopropane would be the least stable one since it has the largest angle deviation of 49.5° (60° vs 109.5°). It was also predicted that cyclohexane would be less stable than cyclopentane because of the larger angle deviation (10.5° deviation for cyclohexane vs 1.5° for cyclopentane), and as the number of sides in the cycloalkanes increases beyond six the stability would decrease.



Which cyclo is stable?

However, experimental results show a different trend. It turns out that **cyclohexane** is the most stable ring that is strain-free, and is as stable as an open-chain alkane. Furthermore, cyclic compounds do not become less and less stable as the number of rings increases.

To measure the relative stability of cycloalkanes, the heat of combustion (ΔH_{comb}) for each cycloalkane was measured. The heat of combustion is the amount of heat released when the compounds burns completely with oxygen. The cycloalkanes will be in higher energy levels than corresponding chain alkanes because of strain energy. Therefore, when cycloalkane burns, more heat will be released, so the difference of ΔH_{comb} between cycloalkane vs the "strainless" chain alkane is just the amount of strain energy, as shown below. The larger the difference, the higher the strain energy of the cycloalkane. The strain energy for different cycloalkanes measured by this method are listed in **Table 4.1**.



Combustion reaction: $(CH_2)_n + 3n/2\ O_2 \rightarrow n\ CO_2 + n\ H_2O$ + heat

The relationship between heat of combustion and strain energy

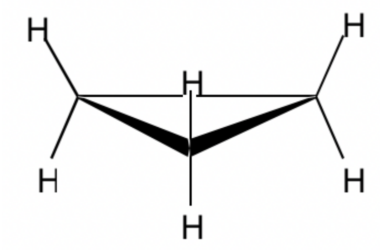
Strain Energies of Cycloalkanes

	cyclopropane	cyclobutane	cyclopentane	cyclohexane
Strain Energy (KJ/mol)	114	110	25	0

The major drawback of the Baeyer Theory was that we must assume that all the rings are flat. The highest stability of cyclohexane from experimental results indicate that the rings may not be in a planar shape. We will have a closer look at the actual shape and conformation of 3-, 4-, 5- and 6-membered cycloalkanes.

CYCLOPROPANE

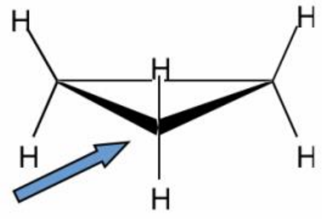
With three carbons for the ring, cyclopropane must be planar.



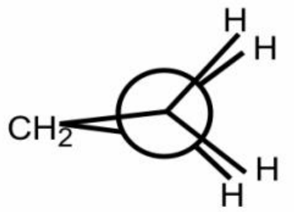
Cyclopropane

The bond angle in cyclopropane is 60°, derived significantly from the optimal angle of 109.5°, so it has very high angle strains. The sp^3-sp^3 orbitals can only overlap partially because of the angle deviation, so the overlapping is not as effective as it should be, and as a result the C-C bond in cyclopropane is relatively weak.

Because of the poor overlapping of sp^3-sp^3orbitals, the bonds formed in cyclopropane resemble the shape of a banana, and are sometimes called banana bonds.
Other than the angle strains, all the adjacent C-H bonds are eclipsed in cyclopropane, therefore the torsional strains are applied as well. Such a strain can be "viewed" more clearly from the Newman projection of cyclopropane.



viewing along the C-C bond with blue arrow to draw the Newman projection



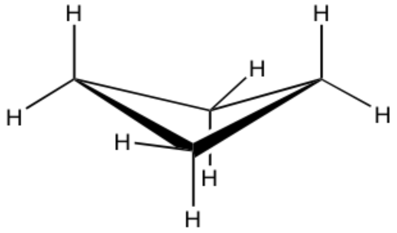
Newman projection of cyclopropane

The Newman projection of cyclopropane might seems weird at first glance. For cyclopropane, there are three carbons, so the CH_2 *group connects with both front and rear carbons of the Newman projection.*

Because of the high level of angle strains and torsional strains, 3-membered rings are unstable. They rarely exist in nature and undergo ring-opening reaction easily to release the strains.

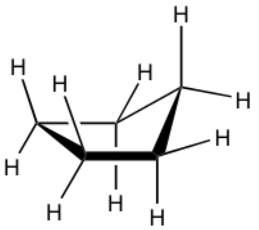
CYCLOBUTANE

Cyclobutane is not planar. The ring puckers (or folds) slightly due to the efforts of releasing some torsional strain. Meanwhile, cyclobutane still has a considerable amount of angle strains as the internal angles become about 88° with the folded shape. Overall, cyclobutane is an unstable structure with rather high level of strains.

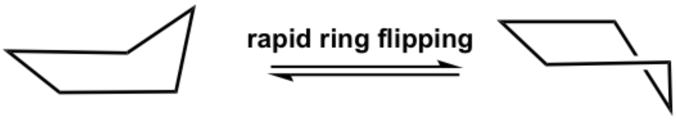


CYCLOPENTANE

Cyclopentane is not planar as well and the total level of strain is lowered quite a lot. It also puckers and adopts a bent conformation where one carbon atom sticks out of the plane of the others, which helps to release the torsional strain by allowing some hydrogen atoms to become almost staggered.



This bent shape of cyclopentane is also called the “envelope” conformation. The envelope conformation can undergo a process called “ring flipping” as a result of C-C bond rotation.



Cyclohexane

It turns out that cyclohexane rings end up adopting a conformation called a chair conformation that reduces both torsional and angle (ring) strain. The conformations of cyclohexane rings are very well-studied and warrant a full discussion on their own. For the time being, we shall simply accept that the conformation adopted by cyclohexane rings represents a beautiful balance that minimizes both torsional and angle strain.

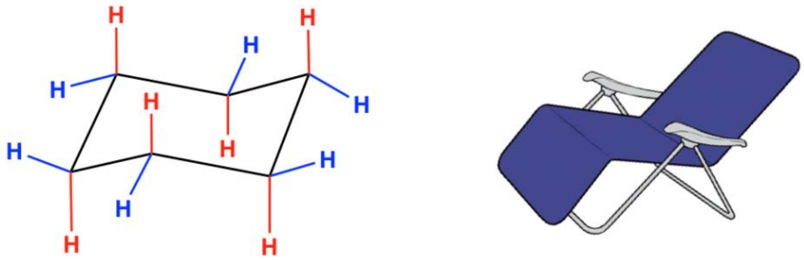
Rings Larger than cyclohexane

Rings larger than six-membered rings tend not to adopt conformations as well-defined as cyclohexane or cyclopentane. As the number of atoms in a ring gets >6, these rings tend to get "floppy" and adopt a large number of less well-defined conformations as the molecules seek to find the lowest energy conformations that minimize both torsional and angle strain as they can.

CONFORMATION ANALYSIS OF CYCLOHEXANE

Chair conformation of cyclohexane

Cyclohexane is the **most stable** cycloalkane. It is strain-free, meaning neither angle strains nor torsional strains apply, and it shows the same stability as chain alkanes. This special stability is due to a unique conformation it adopts. The most stable conformation of cyclohexane is called the "**chair**" **conformation**, since it somewhat resembles a chair.

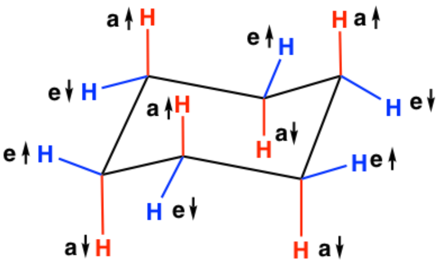


Chair conformation of cyclohexane

In the chair conformation of cyclohexane, all the carbons are at 109.5º bond angles, so no angle strain applies. The hydrogens on adjacent carbons are also arranged in a perfect staggered conformation that makes the ring free of torsional strain as well. This will be illustrated more clearly later when we learn about the Newman projection of the chair conformation.

Properties of the chair conformation

In the chair conformation of cyclohexane, the twelve C-H bonds can be divided into two categories based on the orientations, which are ***axial ("a")*** and ***equatorial ("e")***. In the structure below, the six red-coloured bonds are *axial,* and the six blue-coloured bonds are *equatorial*. Axial bonds are vertical and perpendicular to the average plane of the ring, while the equatorial bonds are more "flat" and extend from the perimeter of the ring. For both "*a*" and "*e*", they can either point up ↑(above the ring), or point down ↓(below the ring). The trending of "*a*" and "*e*" bonds in the chair conformation can be summarized as:



- Each carbon has one “*a*”bond and one “*e*”bond; if one bond points up ↑(above the ring), the other has to point down ↓(below the ring)
- For the same type of bonds, the orientation up ↑ and down ↓ alternates from one carbon to the adjacent carbon, meaning if a certain carbon has a ↑, then the adjacent carbon must have a ↓
- For the twelve C-H bonds: 3*a*↑ , 3 *a*↓, 3 *e*↑ , and 3 *e*↓.

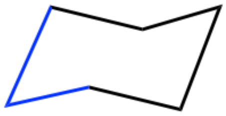
How to draw the chair conformation

It is important to understand and recognize all the bonds in the chair conformation, and you are also expected to be able to draw the conformation correctly and quickly. The procedure is:

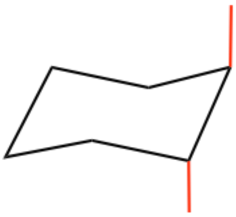
i. Draw two parallel lines of the same length that both point slightly down (if connected, they would form a parallelogram with an internal angle of about 60°/120°).

ii. Connect the right ending points of the two lines with a “V” shape so that the vertex of the V points to the upper right

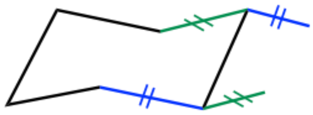
iii. Connect the left starting points of the two lines with another “V” shape so that the vertex of the V points to the bottom left



iv. Add up all of the “a” bonds on each carbon as the **vertical** lines, and follow the alternating trend on adjacent carbons



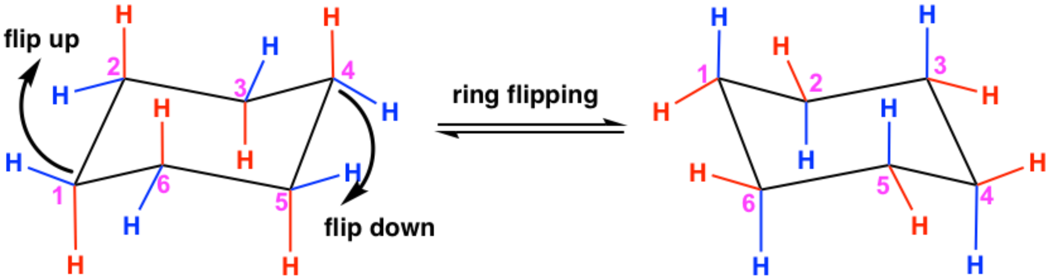
v. Add all of the “e” bonds by following the trend in which on a certain carbon, if an “a” bond points up, then an “e” bond must point down, and vice versa. Also notice that the "e" bond is parallel to the C-C bond which is one bond away, as shown below. The "**green e**" is parallel to the "**green C-C bond"**, and the "**blue e**" is parallel to the "**blue C-C bond".** (It is more challenging to draw "e" bonds, and following the above trend makes it easier).



Ring flipping

When a cyclohexane ring undergoes a chair-chair conformation conversion, this is known as **ring flipping**. Ring flipping comes from C-C bond rotation, but since all of the bonds are limited within the ring, the rotation can only ***partially*** occur, which leads to the ring "flipping". Cyclohexane rapidly interconverts between two stable chair conformations because of the ease of bond rotation. The energy barrier is about 45 kJ/mol, and the thermal energies of the molecules at room temperature are high enough to cause about 1 million interconversions to occur per second.

For cyclohexane, the ring after flipping still appears almost identical to the original ring, but some changes happen on the C-H bonds. Specifically, all the **"a" bonds become "e" bonds**, and all the **"e" bonds become "a" bonds**; however, their relative positions in terms of the ring, up or down, remain the same. The ring flipping is shown in the equation below. Compare the carbon with the <u>same numbering</u> in the two structures to see what happened to the bonds due to ring flipping.



Taking C #1 as an example, you will notice that the red **a**↓ converted to a red **e**↓, and the blue **e**↑ converted to a blue **a**↑ after ring flipping.

Summary of ring flipping for chair conformation:

- ✓ *This is NOT rotation, but ring flipping*
- ✓ *The two structures are conformation isomers (or conformers)*
- ✓ *All "a" bonds become "e" bonds and all "e" bonds become "a" bonds*

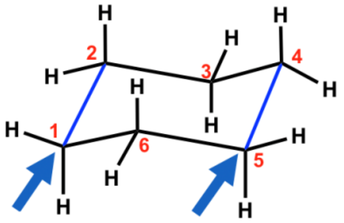
- ✓ *These two conformations are equivalent for the cyclohexane ring itself (without any substituents), with the same energy level.*

A molecular model is very useful for understanding ring flipping.

Newman projection of the chair conformation

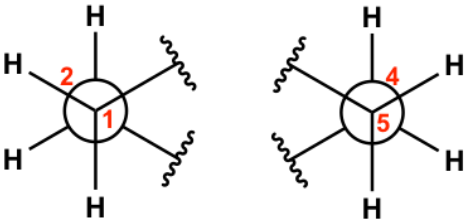
The chair conformation is strain-free, with all the C-H bonds in a staggered position. However, it is not easy to see the staggered conformation in the drawings we have so far, and a Newman projection helps for this purpose.

To draw Newman projections for the chair conformation of cyclohexane, we also need to pick up the C-C bonds to view along, just as we did for alkanes. Since there are a total of six C-C bonds, we will pick two of them, and these two need to be parallel to each other.

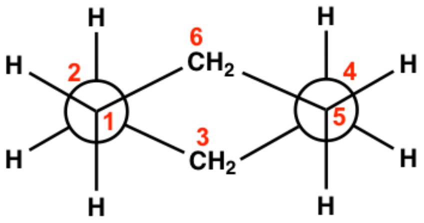


For the chair conformation example here, the two blue parallel C-C bonds, C1-C2 and C5-C4, are chosen for viewing. (There are 3 pairs of parallel bonds in the chair conformation, and any pair can be chosen with the resulting Newman projection looking the same).

For the C1-C2 bond, C1 is the ‘front” carbon and C2 is the “rear” carbon. For the C5-C4 bond, C5 is the ‘front” carbon and C4 is the “rear” carbon. These two bonds will be represented by two “Newman projections” we are familiar with (two circle things), and each represents two carbons, as shown below:



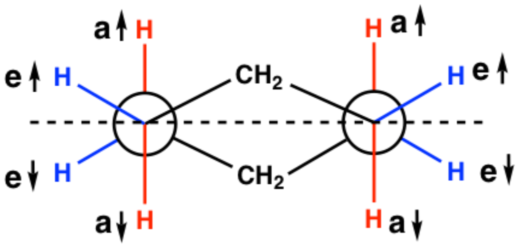
Keep in mind, that there are a total of six carbons in the ring, and the drawing above only shows four of them with C3 and C6 being left out. Additionally, the two “separated” Newman projections above are actually connected to both C3 and C6, so the overall Newman projection of the chair conformation of cyclohexane looks like this:



The *staggered* conformation of hydrogens is clearly shown in the Newman projection here!

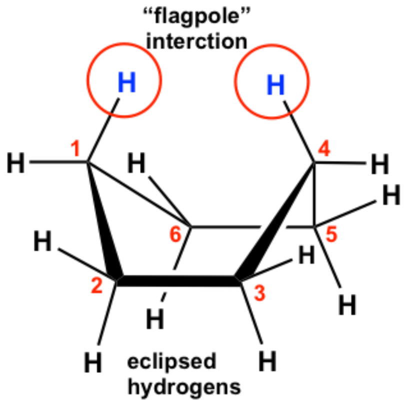
Notes for Newman projections of the chair conformation (refer to the drawing below):

- The “a” or “e” bonds on four carbons (C1, C2, C4 and C5) are shown explicitly, while the bonds on C3 and C6 are just shown as CH$_2$.
- The vertical red C-H bonds are the “a” bonds, and the “flat” blue C-H bonds are the “e” bonds.
- The dashed line in the drawing below can be regarded as the average plane of the ring. Those above the line are the bonds that point up ↑, and those below the line are the bonds that point down ↓.



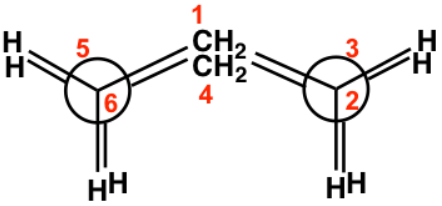
Other conformation of cyclohexane

The chair conformation is the most stable one with the lowest energy, but it is not the only conformation for cyclohexane. During the ring flipping from one chair conformation to another, the ring goes through several other conformations, and we will only briefly discuss the boat conformation here.



Boat conformation of cyclohexane

The boat conformation comes from partial C-C bond rotations (only flipping one carbon up to convert the chair to a boat) of the chair conformation, and all the carbons still have 109.5º bond angles, so there are no angle strains. However, the hydrogens on the base of the boat are all in eclipsed positions, so there are torsional strains. This can be illustrated by the Newman projection below. The Newman projection is drawn by viewing along C6-C5 and C2-C3 bonds of the above boat conformation.

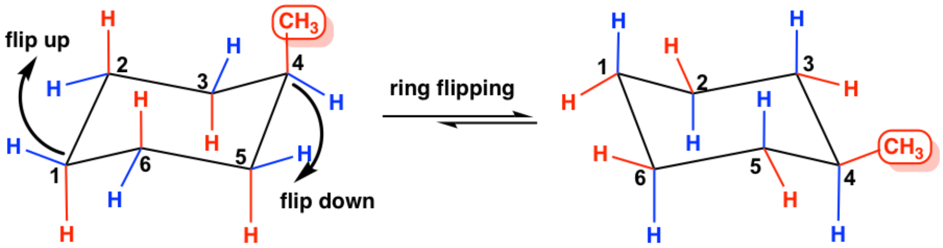


Newman projection of boat conformation

Other than that, the two hydrogen atoms on C1 and C4 are very close to each other and cause steric strain. This is also called the "flagpole" interaction of the boat conformation. The two types of strains make the boat conformation have considerably higher energy (about 30 kJ/mol) than the chair conformation.

Monosubstituted cyclohexane

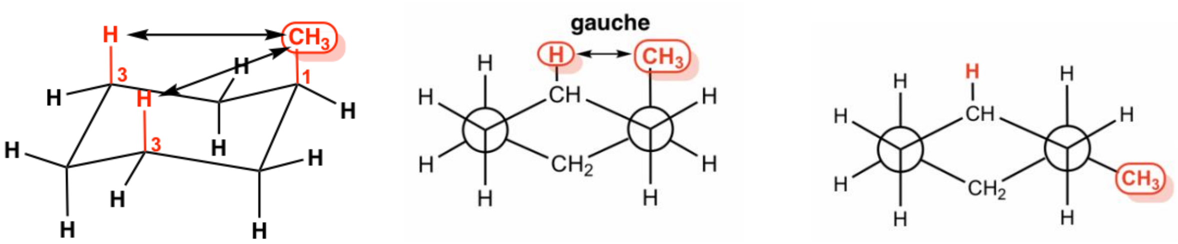
For the cyclohexane ring itself, the two conformers from the ring flipping are equivalent in terms of energy since there are always six hydrogens in the *axial* position and six hydrogens in the *equatorial* position. For substituted cyclohexane, however, the two chair conformations are **not** equivalent anymore. Let's see the example of methylcyclohexane.



(Left one) I, less stable & (Right one) II, more stable

Methylcyclohexane has two chair conformations that are interconvertible through the ring flipping. In conformation **I,** the methyl group occupies an *axial* position, and in conformation **II** the methyl group occupies an *equatorial* position. Studies indicate that the **conformer II** with the *equatorial*-methyl is more stable, with energy of about 7.6 kJ/mol lower than the other conformer.

This difference is due to the "**1,3-diaxal interaction**". In *axial*-methyl conformation, the methyl CH_3 group (regarded as 1st position) is very close to the axial hydrogens that are one carbon away (regarded as 3rd position), and it causes repulsion between the two, which is called the 1,3-diaxal interaction. This type of repulsion is essentially the same as the gauche steric strain because the CH_3 group and the CH are in a gauche position. While for the *equatorial*-methyl conformer, no such strains are applied because the CH_3 group and the CH are in an anti-position. This interaction can be illustrated more clearly by a Newman projection.



1,3-diaxial interaction

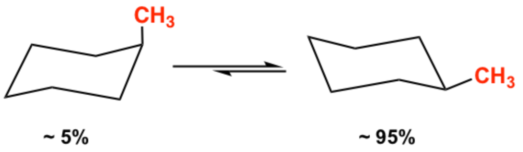
CH₃ group in *axial* position: cause "**1,3-diaxal interaction**", that is the gauche steric strain between CH_3 and CH

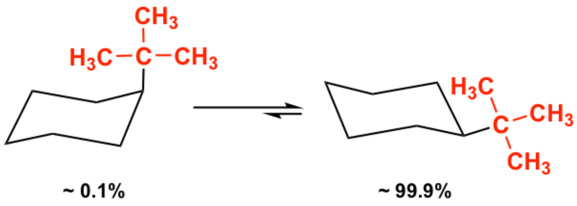
CH_3 group in *equatorial* position: CH_3 and CH are "anti", **no** gauche steric strain applied, **more** stable

For mono-substituted cyclohexane, the equatorial-conformer is more stable than the axial-conformer because of the 1,3-diaxal interaction.

Since the 1,3-diaxal interaction is essentially the steric strain, the larger the size of the substituent, the greater the interaction is. For *t*-butylcyclohexane, the conformation with the *t*-butyl group in the equatorial position is about 21 kJ/mol more stable than the axial conformation.

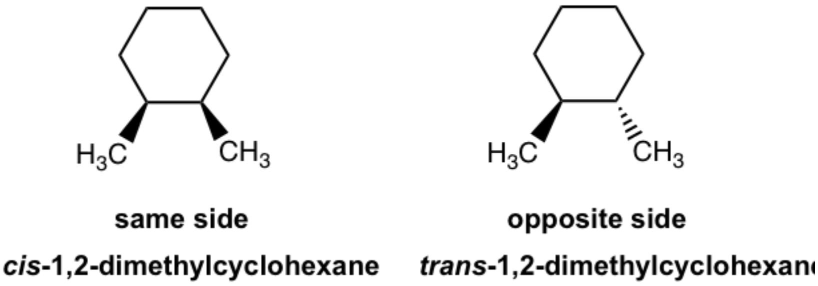
Because of the stability difference between the two chair conformers, the *equatorial* conformation is always the predominant one in the equilibrium mixture. The larger the size of the substituent, the larger the energy difference and the equilibrium constant ***K***, so the equilibrium lies more toward the "equatorial" side. For methylcyclohexane, there is about 95% *equatorial* conformer in the mixture, and the percentage is about 99.9% for t-butylcyclohexane.





Disubstituted cyclohexane

When there are two substituents on different carbons of a cycloalkane, there are two possible relative positions between the two groups – they can be either on the same side or the opposite side of the ring – that are called **geometric isomers**, a type of **stereoisomer**. The isomer with two groups on the same side of the ring is the "*cis*" isomer, and the one with two groups on the opposite side is called the "*trans*" isomer. Because the C-C bond cannot rotate freely due to the restriction of the ring, the two geometric isomers cannot be interconverted.



cis-1,2-dimethylcyclohexane (same side) & trans-1,2-dimethylcyclohexane (opposite side)

So now when considering the conformational isomer, the stereoisomers should be taken into account as well. The general guideline for determining the relative stability of conformers for a certain isomer is:

- The steric effects of all substituents are *cumulative*, and the more substituents in *equatorial* positions, when possible, the more stable the conformation isomer will be.
- For different substituents, the conformer with the *larger* substituent in the *equatorial* positionis more stable.

Let us start with *cis*-1,2-dimethylcyclohexane and compare between the two possible chair conformations:

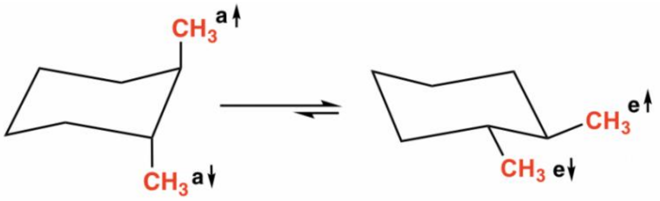
cis-1,2-dimethylcyclohexane **axial-equatorial**

cis-1,2-dimethylcyclohexane **axial-equatorial**

For both conformations, there is one methyl group in *equatorial* and the other methyl group in *axial*, so the two conformers are **equivalent** and have the same energy and stability level.

TRANS-1,2-DIMETHYLCYCLOHEXANE:-

There are also two possible chair conformations:

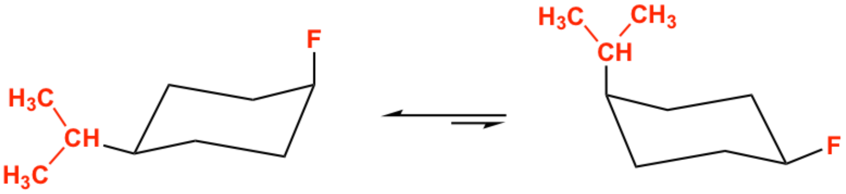


trans-1,2-dimethylcyclohexane **axial-axial, less stable**

trans-1,2-dimethylcyclohexane **equatorial-equatorial, more stable**

In one conformation both methyl groups are *axial*, and in the other conformation both methyl groups are *equatorial*. These two conformers are **not** equivalent, and the di-*equatorial* one is the more stable conformation as we would expect.

cis-1-fluoro-4-isopropylcyclohexane is the structure with two different substituents. Both chair conformations have one *axial* substituent and one *equatorial* substituent. According to the guideline, the conformer with the *larger* substituent in *equatorial* is more stable because if the large group is axial, a stronger steric strain will be generated and it is less stable.



***cis*-1-fluoro-4-isopropylcyclohexane** **large isopropyl group equatorial more stable**

***cis*-1-fluoro-4-isopropylcyclohexane** **less stable**

Benzene and its Derivatives

Chemists have found it useful to divide all organic compounds into two broad classes: aliphatic compounds and aromatic compounds. The original meanings of the words "aliphatic" (fatty) and "aromatic" (fragrant/ pleasant smell).

Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior. Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons.

Benzene:

- A liquid that smells like gasoline; Boils at 80°C & Freezes at 5.5°C
- It was formerly used to decaffeinate coffee and component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers.
- A precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes.
- It is used as a solvent in cleaning and maintaining printing equipment and for adhesivessuch as those used to attach soles to shoes.
- Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

Structure of benzene

History of benzene:

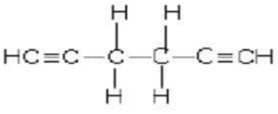
Isolated in 1825 by Michael Faraday who determined C:H ratio to be 1:1 and synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be C_6H_6. He named it benzin later known as benzene. Benzene has the molecular formula C_6H_6.

Arrangement of atoms

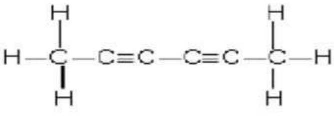
The molecular formula of benzene has been found from analytical data, to be $\mathbf{C_6H_6}$. Relatively higher proportion of carbon and addition of chlorine to benzene molecule indicate it to be an unsaturated compound. Depending on the various facts available, many structures for benzene had been proposed. Some are described below.

Open Chain Structure

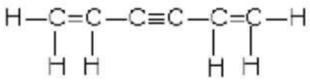
Based upon the tetravalency of carbon, the following open chain structures were proposed for benzene.



(i)



(ii)

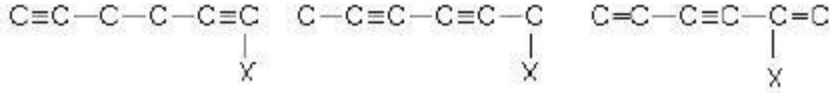


(iii)

Drawbacks of open chain structure:

The open chain structure for benzene was rejected due to thefollowing reasons:

i. Addition reactions usually given by alkenes and alkynes are not given by benzene.
ii. Benzene forms only one kind of mono-substituted product.
iii. An open chain structure however, can form more than one kind of monosubstituted product as shownbelow:



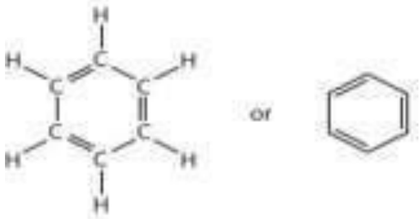
$C\equiv C-C-C-\underset{X}{\underset{|}{C}}\equiv C \quad C-C\equiv C-C\equiv C-\underset{X}{\underset{|}{C}} \quad C=C-C\equiv C-\underset{X}{\underset{|}{C}}=C$

iv. The open chain compounds do, not give reactions such as FriedelCraft reaction, nitration, sulphonation.
v. On reduction with hydrogen in the presence of Ni at 200°C, actually a cyclic compound cyclohexane isobtained.

Kekule's structure

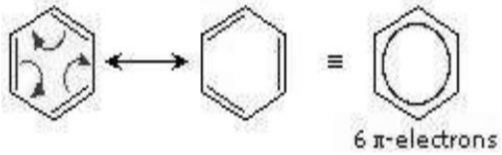
In 1858, August Kekule (of the University of Bonn) had proposed that carbon atoms can join to one another to form chains. Sometimes be closed, to form rings.

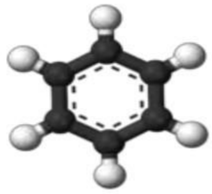
Kekule's structure of benzene was one that we would represent today as



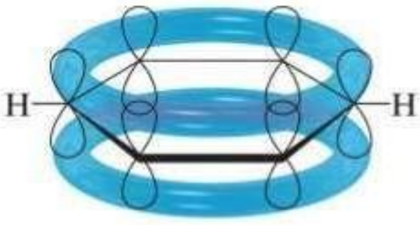
- All the carbon-to-carbon bonds in benzene are equivalent
- The molecule is unusually stable

Chemists often represent benzene as a hexagon with an inscribed circle





- ✓ The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized, or spread out, over all the carbon atoms).
- ✓ Each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it.
- ✓ Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon.
- ✓ The six bond lengths are identical and they are one-and-a half bonds and their length, 1.39 A or 139 picometer (pm), is intermediate between the lengths of single and double bonds (is shorter than typical single-bond lengths, yet longer than typical double-bond lengths).

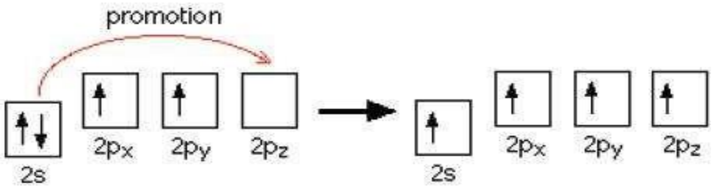


An orbital model for the benzene structure

Building the orbital model

Benzene is built from hydrogen atoms (**$1s^1$**) and carbon atoms (**$1s^2 2s^2 2px^1 2py^1$**). Each carbon atom has to join to three other atoms (one hydrogen and two carbons) and doesn't have enough unpaired electrons to form the required number of bonds, so it needs to promote one of the **$2s^2$** pair into the empty **2pz** orbital.

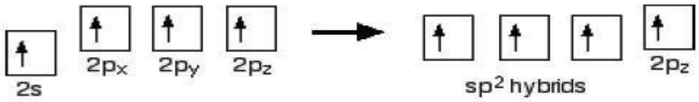
Promotion of an electron



There is only a small energy gap between the **2s** and **2p** orbitals, and an electron is promoted from the **2s** to the empty **2p** to give 4 unpaired electrons. The extra energy released when these electrons are used for bonding more than compensates for the initial input. The carbon atom is now said to be in an excited state.

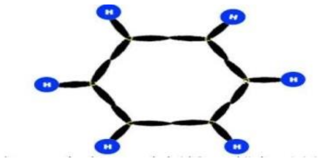
Hybridisation

Because each carbon is only joining to three other atoms, when the carbon atoms hybridise their outer orbitals before forming bonds, they only need to hybridise *three* of the orbitals rather than all four. They use the **2s** electron and two of the 2p electrons, but leave the other **2p** electron unchanged.

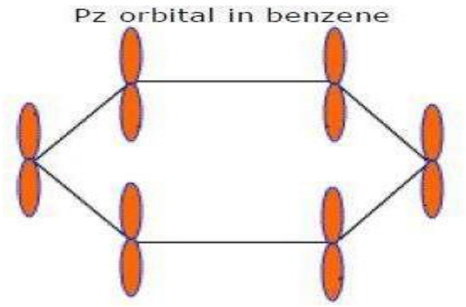


- ✓ The new orbitals formed are called **sp2** *hybrids*, because they are made by an **s** orbital and two **p** orbitals reorganizing themselves.
- ✓ The three **sp^2** hybrid orbitals arrange themselves as far apart as possible which is at 120° to eachother in a plane. The remaining **p** orbital is at right angles to them.
- ✓ Each carbon atom now looks like the diagram on the right. This is all exactly the same as happens in ethene.
- ✓ The difference in benzene is that each carbon atom is joined to two other similar carbon atoms instead of just one. Each carbon atom uses the **sp^2** hybrids to form sigma bonds with two other carbons andone hydrogen atom.

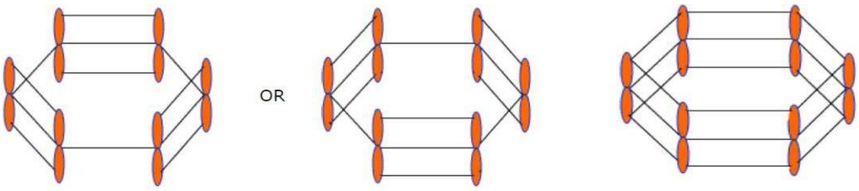
The next diagram shows the sigma bonds formed, but for the moment leaves the **p** orbitals alone.



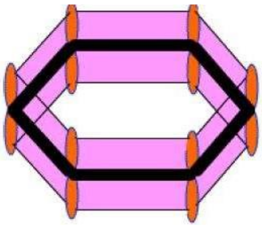
Since sigma bond results from the overlap of above said planar orbital, all **H** and **C** atoms are in the same plane and their generate a hexagonal ring of **C** atoms.



Each **C** atom in benzene also has an unhybrid **2pz** orbital containing one electron. These **2pz** orbital are perpendicular to the plane of sigma bonds.



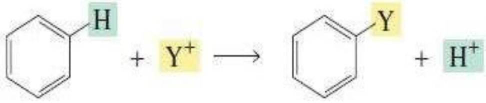
Actually these **2pz** orbital produce a **π (pi)** molecular orbital containing six electrons. One half of this **π (pi)** molecular orbital lies above the plane of hexagonal ring and remaining half below the ring like a sandwich.



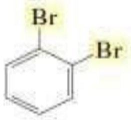
The overlap of these **2pz** orbital results in the formation of a fully delocalized **π (pi)** bond, which extends all over the six **C** atoms of benzene nucleus. The molecular orbital approach clearly indicates that these six electrons could be found anywhere in highly delocalized manner. As a result of delocalization, a stronger **π (pi)** bond and a more stable benzene molecule is obtained which undergo substitution reactions more frequently than addition reactions.

- Benzene is a flat molecule, with every carbon and hydrogen lying in the same plane thesebonds are designated as a sigma (σ) bonds.
- Each sp^2 hybridized C in the ring has an unhybridized *p* orbital perpendicular to the ringwhich overlaps around the ring.
- The six pi (π) electrons are delocalized over the six carbons.

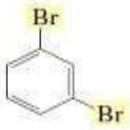
Benzene yields only one monosubstitution product, C_6H_5Y. Only one bromobenzene, C_6H_5Br, is obtained when one hydrogen atom is replaced by bromine; similarly, only one chlorobenzene, C_6H_5C1, or one nitrobenzene, $C_6H_5NO_2$, etc., has ever been made. This fact places a severe limitation on the structure of benzene: each hydrogen must be exactly equivalent to every other hydrogen, since the replacement of any one of them yields the same product.



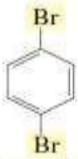
Benzene yields three isomeric disubstitution products, $C_6H_4Y_2$ or C_6H_4YZ. e.g. like only three isomeric dibromobenzenes, $C_6H_4Br_2$, three chloronitrobenzenes, $C_6H_4ClNO_2$, etc. This fact further limits our choice of a structure to Kekule's structure of benzene compare to any other structures with the molecular formula C_6H_6.



1,2-dibromobenzene
ortho-dibromobenzene
o-dibromobenzene



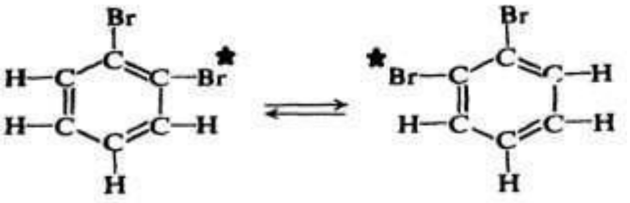
1,3-dibromobenzene
meta-dibromobenzene
m-dibromobenzene



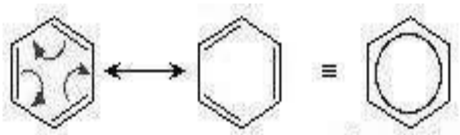
1,4-dibromobenzene
para-dibromobenzene
p-dibromobenzene

The relative positions of two substituents on a benzene ring can be indicated either by numbers or by the prefixes ortho, meta, and para. Adjacent substituents are called ortho, substituents separated by one carbon are called meta, and substituents located opposite one another are designated para. Often, only their abbreviations (o, m, p) are used in naming compounds.

However, that two 1,2-dibromo isomers differing in the positions of bromine relative to the double bonds, should be possible:



On the other hand, it is believed by some that Kekule had unthinkingly anticipated our present concept of *delocalized electrons*, and drew two pictures (as shown above). The currently accepted structure did not arise from the discovery of new facts about benzene, but is the result of an extension or modification of the structural theory; this extension is the concept of resonance.



6 π-electrons

OR

I

II

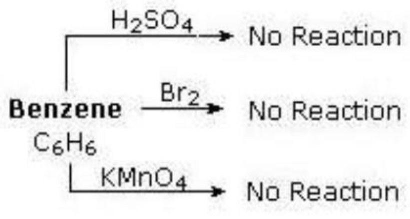
Resonance: structures that differ only in the arrangement of electrons. Benzene is a hybrid of I and II. Since; I and II are exactly equivalent, and hence of exactly the same stability, they make equal contributions to the hybrid.

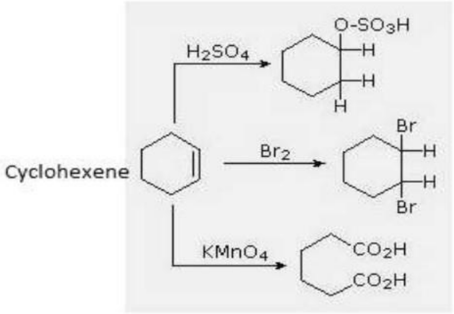
Stability:

The most striking evidence to unusual stability of benzene ring is found in the chemical reactions of benzene & the heat released in a hydrogenation reaction of one mole of an unsaturatedcompound.

Benzene undergoes substitution rather than addition.

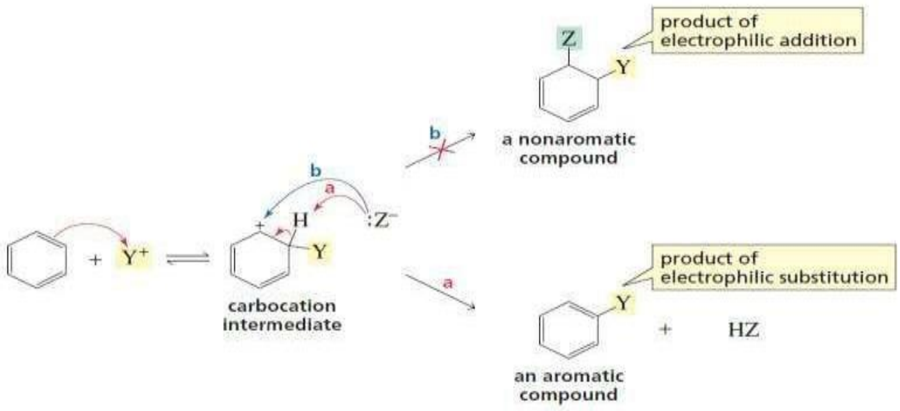
Example: cyclohexene an alkene undergoes rapid addition reaction, under same conditions were benzene reacts either not at all or very slowly and this exhibited a high degree of unusual chemical stability of benzene compared with known alkenes and cycloalkenes (aliphatic compounds).





Example: In addition reaction an alkene reacts with an electrophile, thereby forming a carbocation intermediate. In the second step of an electrophilic addition reaction, the carbocation reacts with a nucleophile to form an addition product.

If the carbocation intermediate formed from the reaction of benzene with an electrophile were to react similarly with a nucleophile (depicted as event b in Figure below), the addition product would not be aromatic. If, however, the carbocation loses a proton from the site of electrophilic attack (depicted as event a in Figure below), the aromaticity of the benzene ring is restored. Because the aromatic product is much more stable than the nonaromatic addition product, the overall reaction is an electrophilic substitution reaction rather than an electrophilic addition reaction. In the substitution reaction, an electrophile substitutes for one of the hydrogens attached to the benzene



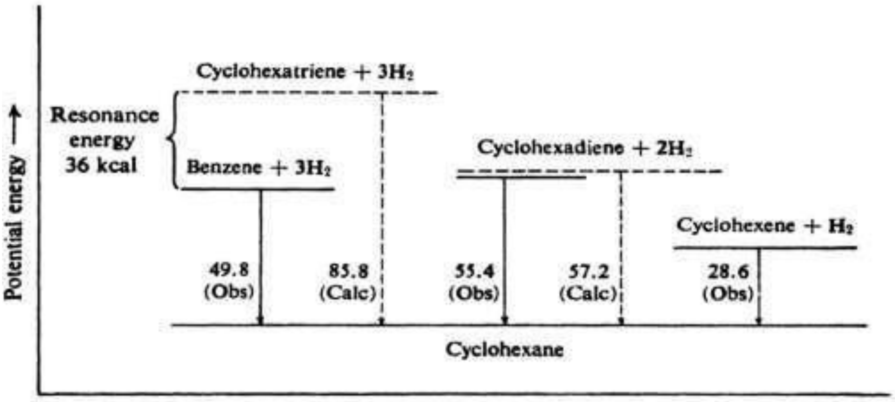
In place of addition reactions, benzene readily undergoes a new set of reactions, all involving substitution. The most important are Halogenation, Nitration, Sulfonation, Friedel–Crafts acylation & Friedel–Crafts alkylation.

In an electrophilic aromatic substitution reaction, an electrophile is put on a ring carbon, and the H^+ comes off the same ring carbon.

Heat of hydrogenation (resonance energy) and combustion.

The heat released in a hydrogenation reaction of one mole of an unsaturated (doublebonded) compound is called the **heat of hydrogenation**.

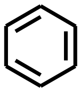
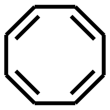
A quantitative data which show how much more stable is benzene. Cyclohexene has a heat of hydrogenation of 28.6 kcal and cyclohexadiene has one about twice that (55.4 kcal). We expected cyclohexatriene (i.e. in imagine that benzene contains three double bonds in it) to have a heat of hydrogenation about three times as large as cyclohexene, that is, about 85.8 kcal. Actually the value for benzene (49.8 kcal) is 36 kcal less than this expected amount.



Aromatic character: The Huckel 4n + 2 rule

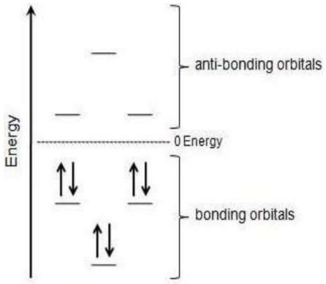
In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has 4n+2 π (*Pi*) electrons, it is considered aromatic. This rule would come to be knownas Hückel's Rule.

Criteria for Aromaticity & Anti-Aromaticity:

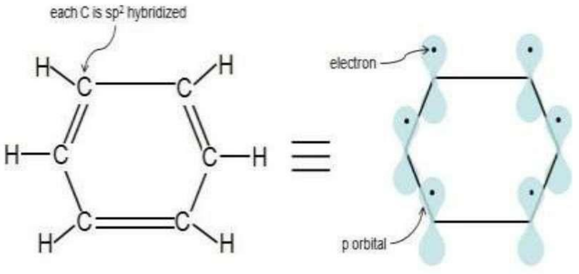
Aromatic	**Anti-aromatic**	**Non-aromatic**
The molecule is cyclic (a ring of atoms)	The molecule is cyclic (a ring of atoms)	Fails any one of the criteria on the left or everything else
The molecule is planar or flat (all atoms in the molecule lie in the same plane)	The molecule is planar or flat (all atoms in the molecule lie in the same plane)	
The molecule is fully conjugated (p orbitals at every atom in the ring)	The molecule is fully conjugated (p orbitals at every atom in the ring)	
The molecule has 4n+2 π electrons (n=0 or any positive integer)	The molecule has 4nπ Electrons	
Unusually stable	Unusually stable	
 Benzene	 Cyclobutadiene	 Cyclooctatetraene
Resonance energy (heat of hydrogenation energy) 36 kcal/mol	Only stable below -100◦C	

- ➢ According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons.
- ➢ With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n) leaving all bonding orbitals filled and no anti-bonding orbitals occupied.
- ➢ This gives a total of 4n+2 π electrons.

- In benzene, each double bond (π bond) always contributes 2 π electrons. Benzene has 3double bonds, so it has 6 π electrons.
- Its first 2 π electrons fill the lowest energy orbital, and 4 π electrons remaining fill in theorbitals of the succeeding energy level.
- Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitalshave any electrons.



molecular orbital diagram for benzene



benzene has 6 π electrons

To apply the 4n+2 rule, first count the number of π electrons in the molecule. Then, set this number equal to 4n+2 and solve for n. If is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons: 4n+2=6; 4n=4; n=1 For benzene, we find that n=1, which is a positive integer, so the rule is met. Benzene is aromatic compound.

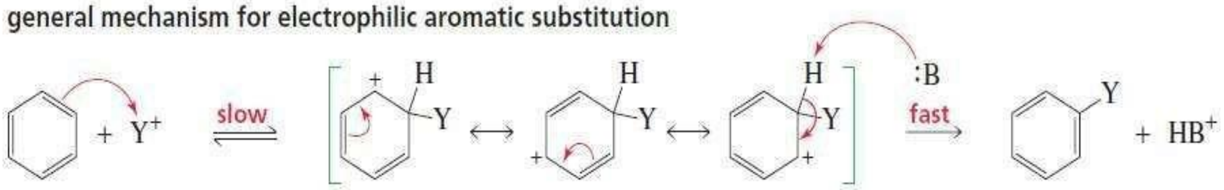
Reactions of Benzene:

Benzene readily undergoes a new set of reactions, all involving substitution i.e. Electrophilic Aromatic Substitution Reactions. It involves the reaction of an electrophile with an aromatic compound, were electrophile substitutes for a hydrogen of an aromatic compound.

General Mechanism for Electrophilic Aromatic Substitution Reactions:

- Similar to alkenes, benzene (aromatics) has a cloud of π electrons available to attack electrophiles (the aromatic ring is nucleophilic)
- The resulting carbocation is stabilized by resonance and is called: Sigma complex
- These reactions are greatly facilitated by addition of Lewis acid catalyst.
- Key bonds formed C-Y and key bonds broken C-H
- Electron donating substituents increase the rate of substitution reaction by activating thebenzene ring to electrophilic attack
- Electron withdrawing substituents decrease the rate of substation reaction by deactivatingthe benzene ring to electrophilic attack.

general mechanism for electrophilic aromatic substitution



The general mechanism can be applied to the following reactions and the only difference will be the nature of the electrophile, and how it is formed.

Halogenation: Bromine (Br), Chlorine (Cl), or Iodine (I) substitutes for a hydrogen (Lewis acid: $AlCl_3/FeCl_3/AlBr_3/FeBr_3$, etc.)

Nitration: A nitro (NO_2) group substitutes for a hydrogen (acid: H_2SO_4).

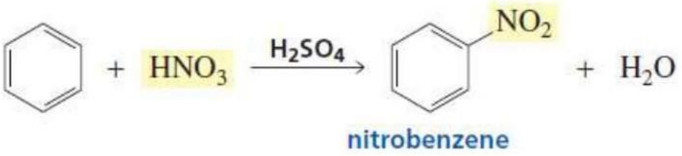
Sulfonation: A sulfonic acid (SO_3H) group substitutes for a hydrogen (acid: H_2SO_4).

Friedel–Crafts acylation: An acyl (R-C=O) group substitutes for a hydrogen (Lewis acid: ($AlCl_3/FeCl_3$).

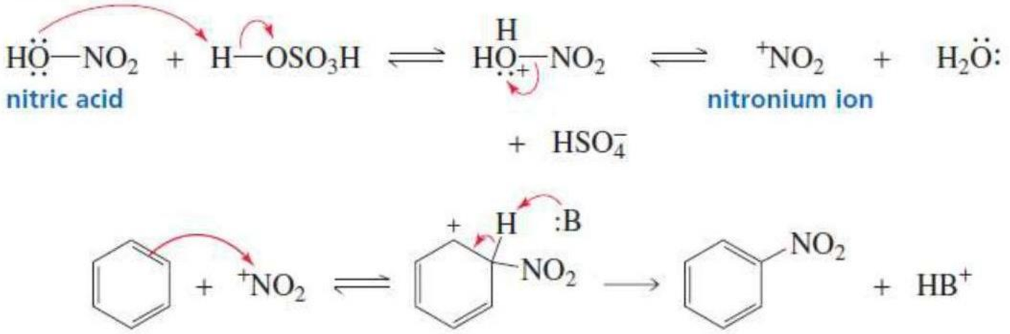
Friedel–Crafts alkylation: an alkyl (R) group substitutes for a hydrogen (Lewis acid: ($AlCl_3/FeCl_3$).

Nitration of Benzene: Nitration of benzene with nitric acid requires sulfuric acid as a catalyst.

Electrophile: $O=\overset{+}{N}=O$ nitronium ion

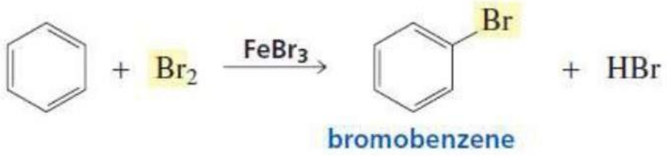


mechanism for nitration

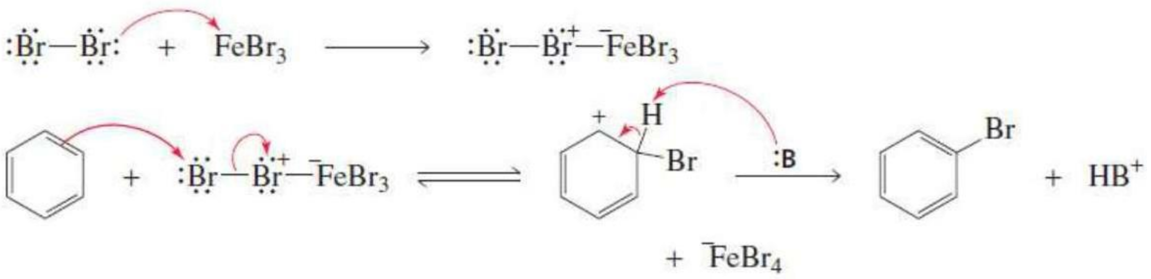


Halogenation of Benzene: The bromination or chlorination of benzene requires a Lewis acid such as ferric bromide or ferric chloride. Recall that a Lewis acid is a compound that accepts a share in a pair of electrons.

Bromination: Electrophile Br^+



mechanism for bromination



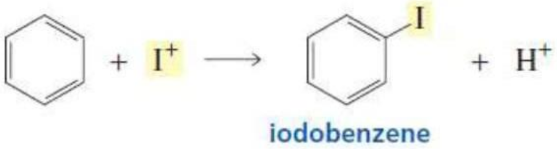
$$\bar{F}eBr_4 + HB^+ \longrightarrow HBr + FeBr_3 + :B$$

Iodination: For iodination, iodine is simply oxidized with nitric acid (HNO3) to liberate the I+, which is then used as the electrophile.

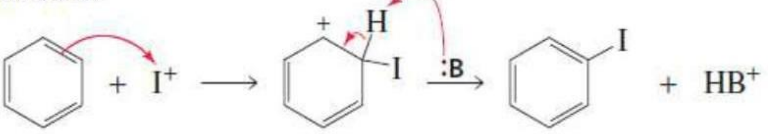
$$H^+ + HNO_3 + \tfrac{1}{2} I_2 \rightarrow I^+ + NO_2 + H_2O$$

or

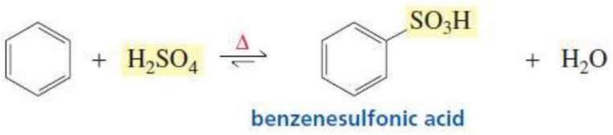
$$I_2 \xrightarrow{\text{oxidizing agent}} 2\,I^+$$



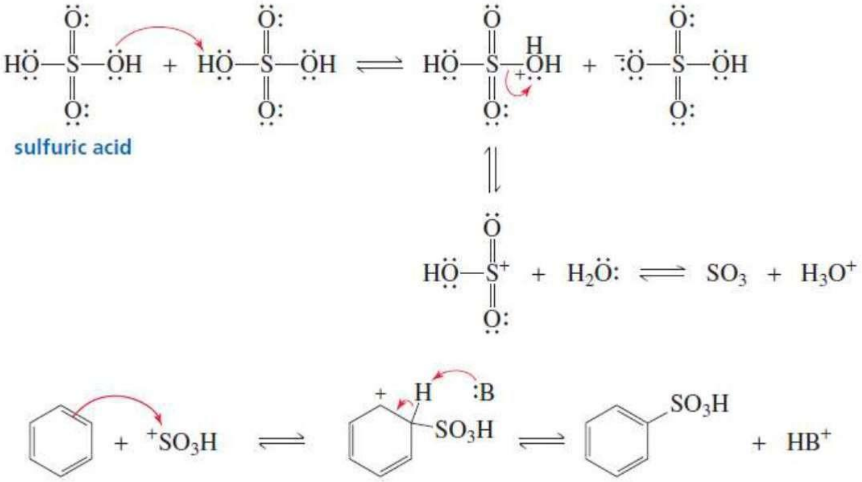
mechanism for iodination



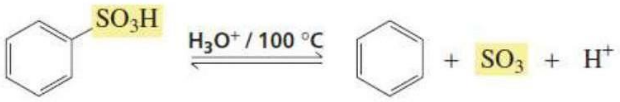
Sulfonation of Benzene: Fuming sulfuric acid (a solution of in sulfuric acid) or concentrated sulfuric acid is used to sulfonate aromatic rings. Electrophile: HSO_3^+



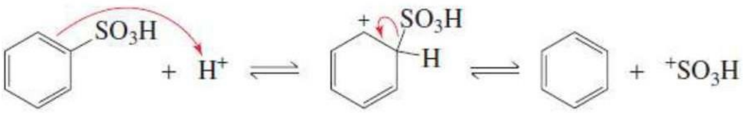
mechanism for sulfonation



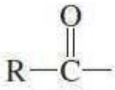
Sulfonation of benzene is a reversible reaction. If benzenesulfonic acid is heated in dilute acid, the reaction proceeds in the reverse direction.



mechanism for desulfonation

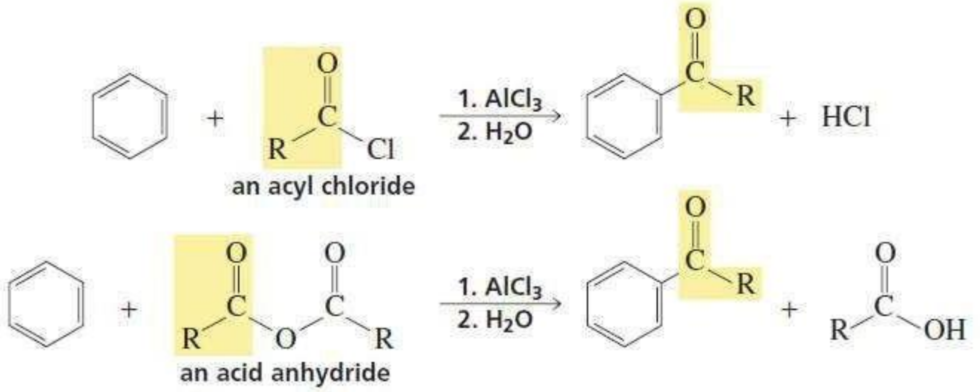


Friedel–Crafts Acylation: Friedel–Crafts acylation places an acyl group on a benzene ring.



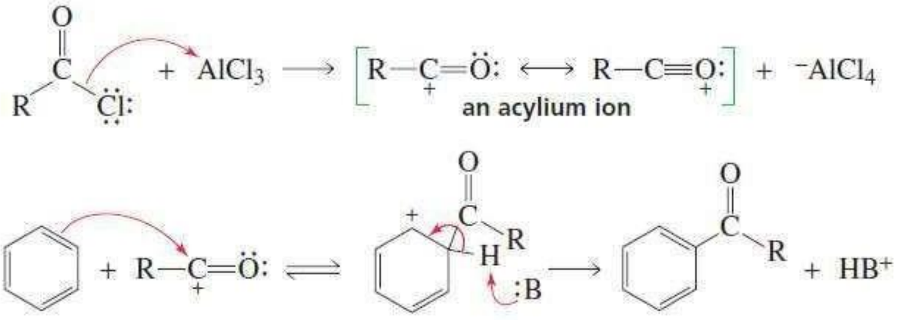
an acyl group

Either an acyl halide or an acid anhydride can be used for Friedel–Crafts acylation.



An acylium ion is the electrophile required for a Friedel–Crafts acylation reaction. This ion is formed by the reaction of an acyl chloride or an acid anhydride with $AlCl_3$

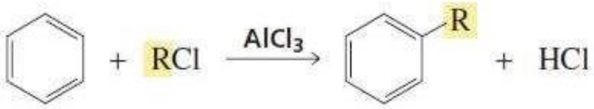
mechanism for Friedel–Crafts acylation



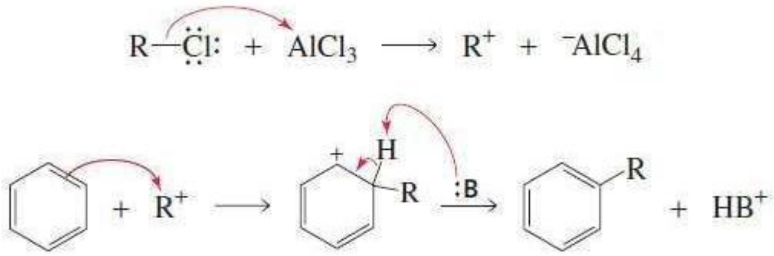
LIMITATIONS of Friedel-Crafts acylation:

- Acylation can only be used to give ketones. This is because HCOCl decomposes to COand HCl under the reaction conditions.
- Deactivated benzenes are not reactive to Friedel-Crafts conditions, the benzene needs tobe as or more reactive than a mono-halobenzene.
- The Lewis acid catalyst AlCl3 often complexes to aryl amines making them very unreactive.
- Amines and alcohols can give competing N or O acylations rather than the require ringacylation

Friedel–Crafts alkylation: Friedel–Crafts alkylation places an alkyl group on a benzene ring. $R-$ **an alkyl group**

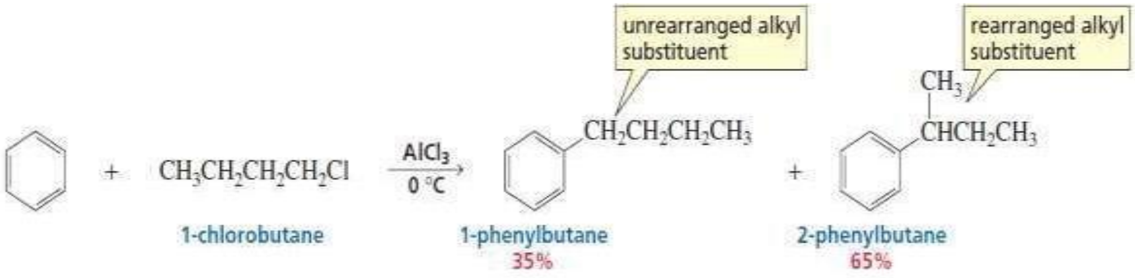


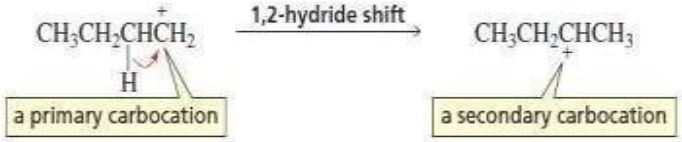
A carbocation is formed from the reaction of an alkyl halide with $AlCl_3$, Alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides can all be used. Vinyl halides and aryl halides cannot be used because their carbocations are too unstable to be formed.



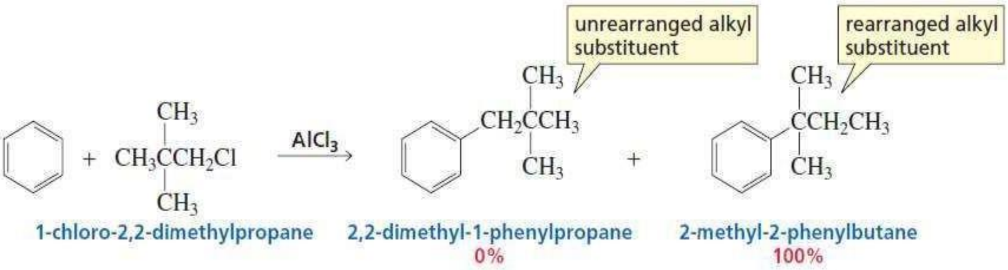
- An alkyl-substituted benzene is more reactive than benzene. Therefore, to prevent further alkylation of the alkyl-substituted benzene, a large excess of benzene is used in Friedel– Crafts alkylation reactions.
- A carbocation will rearrange if rearrangement leads to a more stable carbocation.
- When the carbocation can rearrange in a Friedel–Crafts alkylation reaction, the major product will be the product with the rearranged alkyl group on the benzene ring.

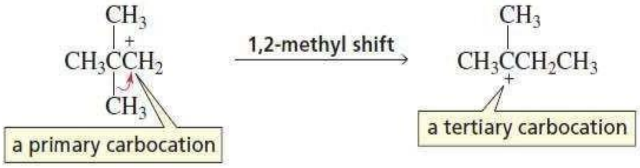
Example: less stable primary carbocation to stable secondary carbocation



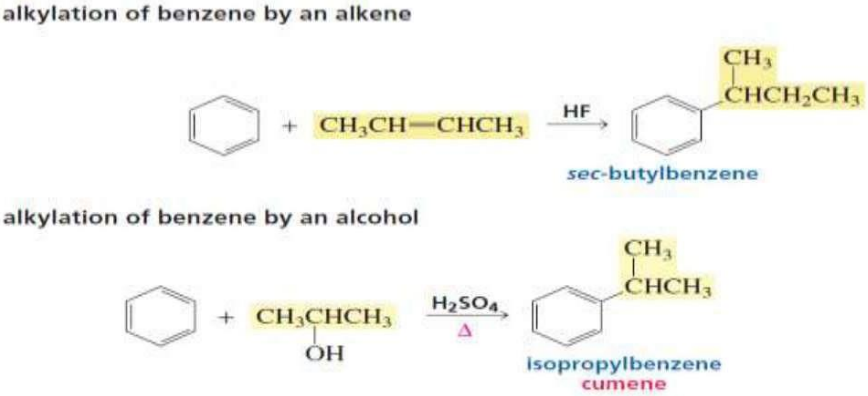


Example: less stable primary carbocation to stable tertiary carbocation



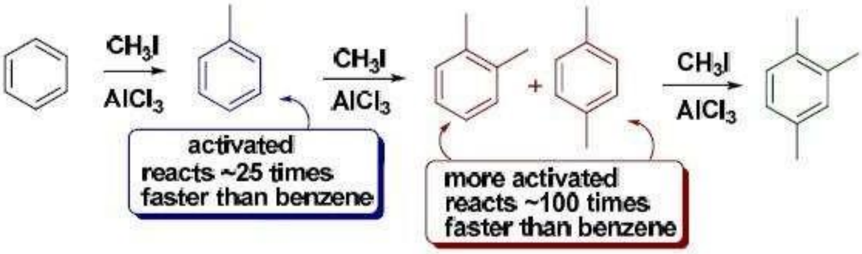


Any other carbocation source can be used in the presence of an aromatic ring to give Friedel Crafts substitution products.



LIMITATIONS to the Friedel-Crafts Alkylation:

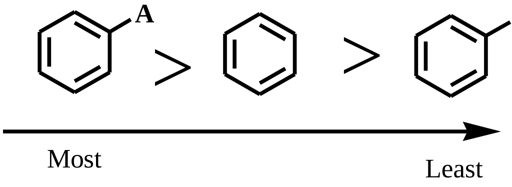
- Works only with benzene and activated derivatives; Vinyl or aryl halides do not react (their intermediate carbocations are too unstable).
- The Lewis acid catalyst $AlCl_3$ often complexes to aryl amines making them very unreactive.
- Poly-alkylation is often the result since the alkylation product is more reactive than the original compound (Note: This can usually be controlled with an excess of the benzene). For example:



Effect of Substituents on Reactivity and Orientation of Mono Substituted Benzene Compounds towards Electrophilic Substitution Reaction

The reactions of substituted benzenes are similar to those of benzene, but can take place faster or slower than benzene depending on the substitution pattern.

The substituent can either increase or decrease the rate of the reaction depending on its nature.



- ✓ Activating (**A**) if the benzene ring it is attached to is more reactive than benzene i.e. one that provides more electrons (electron donating groups) to the aromatic system
- ✓ Deactivating (**D**) if the ring it is attached to is less reactive than benzene i.e. one that pullselectrons away from the aromatic system.
- ✓ Substituent(s) direct the incoming electrophile to a specific location.

As shown in **Table 1**, nearly all groups fall into one of two glasses: activating and ortho, para directing, or deactivating and meta-directing. The halogens are in a class by themselves, being deactivating but ortho, para-directing.

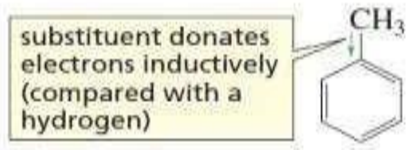
The Effect of Substituents on Reactivity

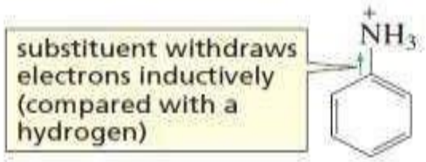
There are two ways substituents can donate electrons into a benzene ring: inductive electron donation and electron donation by resonance. There are also two ways substituents can withdraw electrons from a benzene ring: inductive electron withdrawal and electron withdrawal by resonance.

Inductive Electron Donation and Withdrawal

- ✓ It is a permanent effect
- ✓ It operates on sigma bonded electrons
- ✓ Electron shift take place towards more electro negative atom

If a substituent that is bonded to a benzene ring is less electron withdrawing than a hydrogen, the electrons in the sigma bond that attaches the substituent to the benzene ring will move toward the ring more readily. Such a substituent donates electrons inductively compared with a hydrogen.

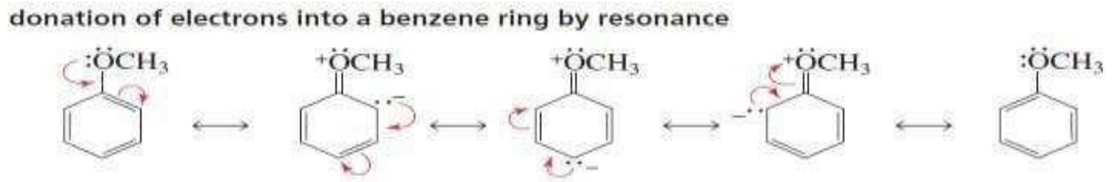




If a substituent is more electron withdrawing than a hydrogen, it will withdraw the sigma electrons away from the benzene ring more strongly than will a hydrogen. Withdrawal of electrons through a sigma bond is called inductive electron withdrawal. The NH_3^+ group is a substituent that withdraws electrons inductively because it is more electronegative than a hydrogen.

Resonance Electron Donation and Withdrawal

If a substituent has a lone pair on the atom that is directly attached to the benzene ring, the lone pair can be delocalized into the ring; these substituents are said to donate electrons by resonance. Substituents such as OH, OR, and Cl donate electrons by resonance.



If a substituent is attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the pi electrons of the ring can be delocalized onto the substituent; these substituents are said to withdraw electrons by resonance. Substituents such as C=O, C≡N, O=N-O (NO_2) and withdraw electrons by resonance.

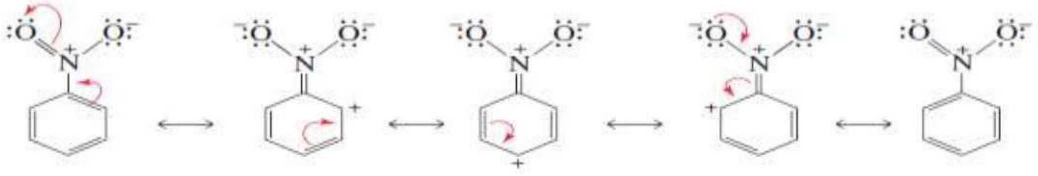
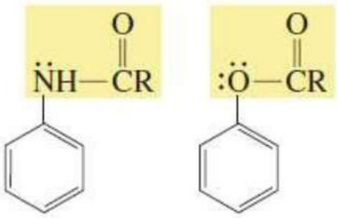


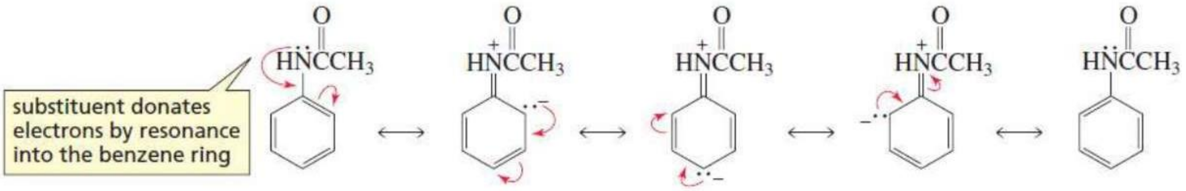
Table 1 Effect of substituents

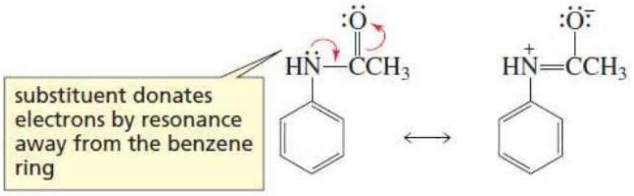
Activating		Deactivating	
Strong	$-NH_2$, (-NH, $-NR_2$), -OH	*m-* Directors	$-NO_2$, $-N(CH_3)_2$, -CN, -COOH, $-S0_3H$, -CHO, -COR
Moderate	-OR, $-NHCOCH_3$	*o, p* directors	-F, -Cl, -Br, -I
weak	$-C_6H$,$-CH_3$, -R		

Note: The **moderately activating substituents** also donate electrons into the ring by resonance and withdraw electrons from the ring inductively. These substituents are less effective at donating electrons into the ring by resonance because, unlike the strongly activating substituents that donate electrons by resonance only into the ring, the moderately activating substituents can donate electrons by resonance in two competing directions: into the ring and away from the ring.

moderately activating substituents

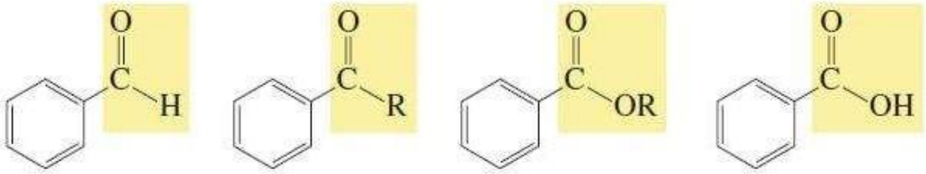



substituent donates electrons by resonance into the benzene ring

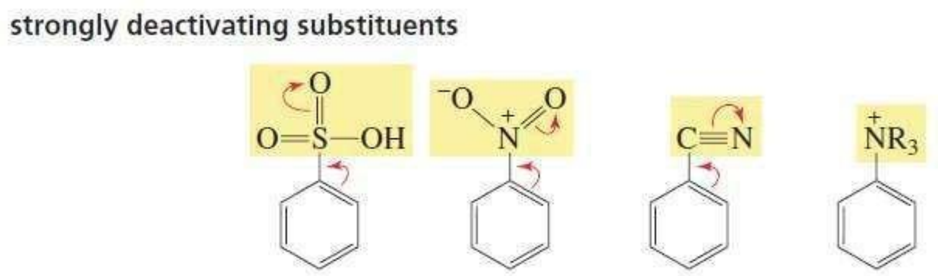

substituent donates electrons by resonance away from the benzene ring

The moderately deactivating substituents all have carbonyl groups directly attached to the benzene ring. Carbonyl groups withdraw electrons both inductively and by resonance.

moderately deactivating substituents



The strongly deactivating substituents are powerful electron withdrawers. Except for the ammonium ions (NH_3^+, NH_2R^+, NHR_2^+ and NR_3^+), these substituents withdraw electrons both inductively and by resonance. The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electrons inductively.

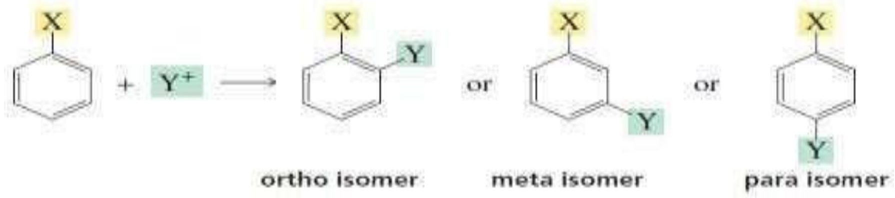


strongly deactivating substituents

The Effect of Substituents on Orientation

When substituted benzene undergoes an electrophilic substitution reaction, The substituent already attached to the benzene ring determines the location of the new substituent.

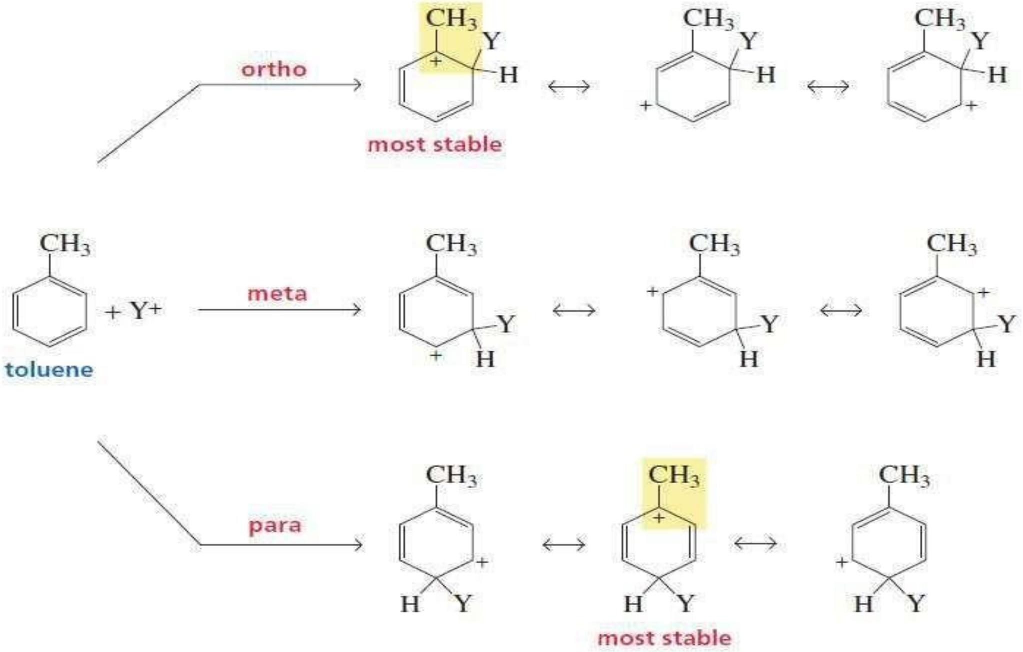
All activating substituents and the weakly deactivating halogens are ortho–para directors, and all substituents that are more deactivating than the halogens are meta directors. Thus, the substituents can be divided into three groups:



The above classification is based on the stability of the carbocation intermediate that is formed in the rate-determining step.

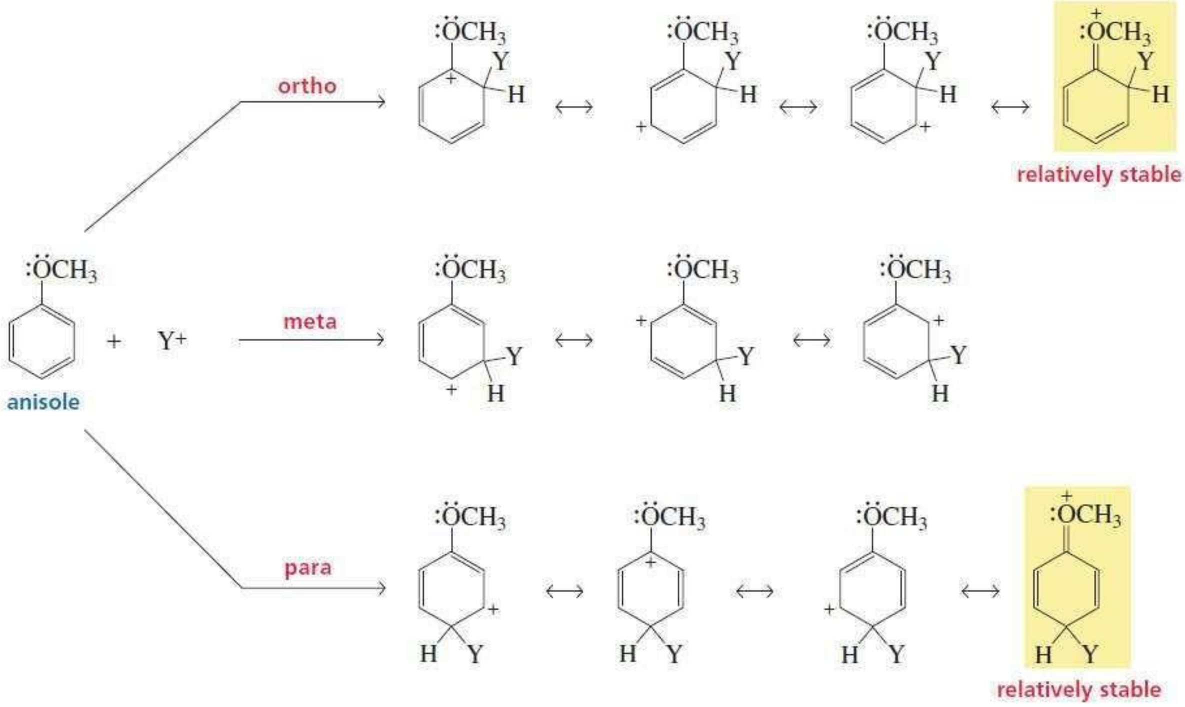
Example:

If a substituent donates electrons inductively like a methyl group, for example in Toulene, the substituent is attached directly to the positively charged carbon, which the substituent can stabilize by inductive electron donation. These relatively stable resonance contributors are obtained only when the incoming group is directed to an ortho or para position.



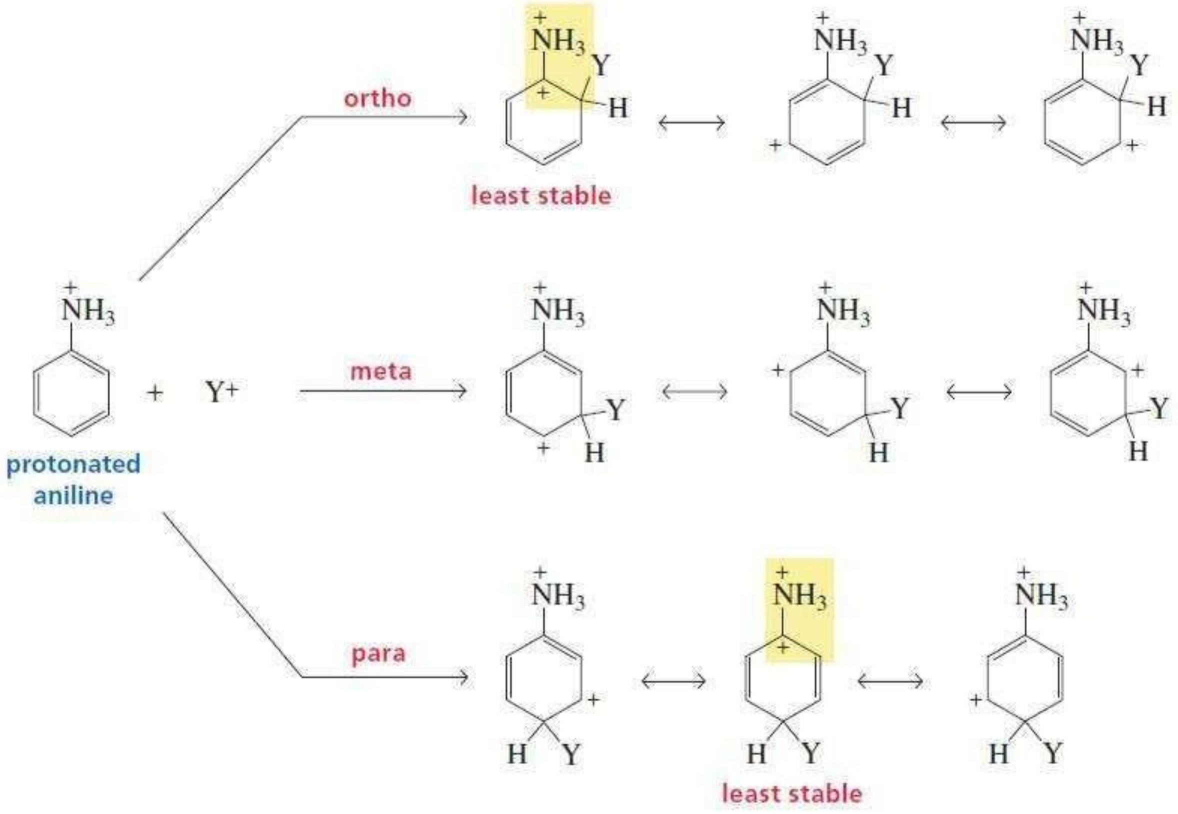
Example:

If a substituent donates electrons by resonance, like a methoxy group, for example in Anisole, the carbocations formed by putting the incoming electrophile on the ortho and para positions have a fourth resonance contributor. This is an especially stable resonance contributor because it is the only one whose atoms (except for hydrogen) all have complete octets. Therefore, all substituents that donate electrons by resonance are ortho–para directors.



Example:

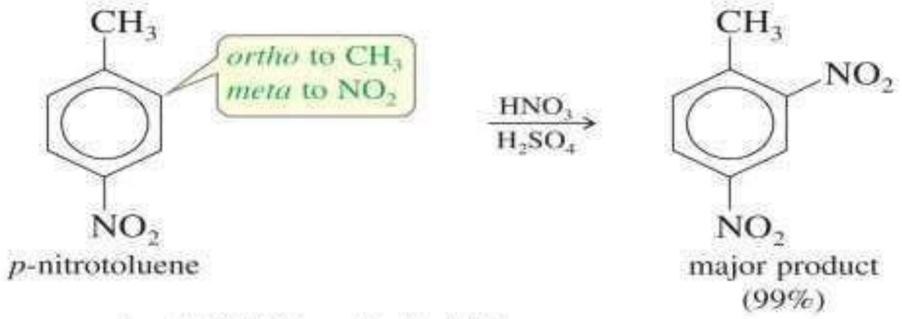
Substituents with a positive charge or a partial positive charge on the atom attached to the benzene ring, withdraw electrons inductively from the benzene ring, and most withdraw electrons by resonance as well. For all such substituents, the indicated resonance contributors in Figure below are the least stable because they have a positive charge on each of two adjacent atoms, so the most stable carbocation is formed when the incoming electrophile is directed to the meta position. Thus, all substituents that withdraw electrons (except for the halogens, which are ortho–para directors because they donate electrons by resonance) are meta directors.

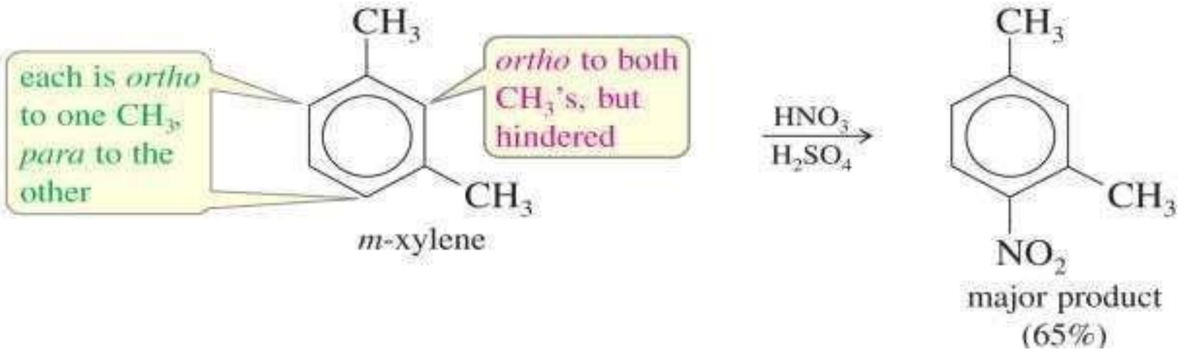


Effect of Multiple Substituents on Electrophilic Aromatic Substitution

When 2 substituents are already on the ring

- ✓ the stronger activator usually predominates.
- ✓ Steric factors will also play a role in determining the structure of the new product.



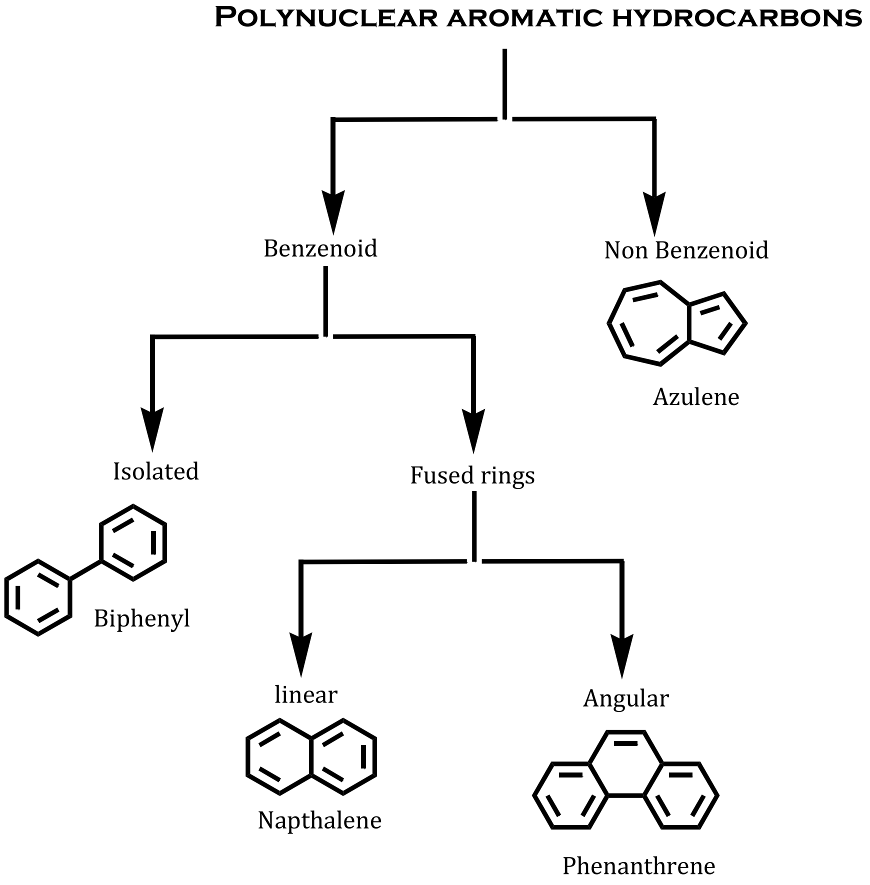


POLYNUCLEARHYDROCARBONS:-

A polynuclear aromatic hydrocarbon is a hydrocarbon made up of fused aromatic ring molecules. These rings share one or more sides and contain delocalized electrons.

Polynuclearhydrocarbons are organic molecules rich in fossil fuels, such as coal and petroleum. They are formed from a variety of natural (forest fires, by burning wood whilefood is cooked at a high temperature, grilled, or smoked and volcanic eruptions) and environmental pollutant reactions (chemicals are released in cigarette smoke and from burning waste).

CLASSIFICATION:



Properties

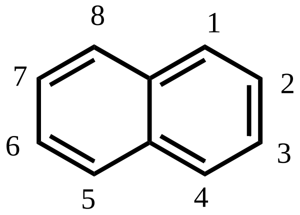
Polynuclear aromatic hydrocarbons are lipophilic, nonpolar molecules, insoluble in water. 2-, 3-, and 4-ring polynuclearhydrocarbons are sufficiently volatile to exist in the gas phases, while larger molecules exist as solids. Pure solid polynuclearhydrocarbons may be colourless, white, pale yellow, or pale green.

Health Effects

- ✓ Polynuclear aromatic hydrocarbons are extremely important because they are associated with genetic damage and diseases leading to increased problems over time.
- ✓ PAHs are toxic to aquatic life. In addition to toxicity, these compounds are often mutagenic, carcinogenic, and teratogenic.
- ✓ Prenatal exposure to these chemicals is associated with lowered IQ and childhood asthma.
- ✓ People get exposed to PAHs from breathing contaminated air, eating food that contains the compounds, and from skin contact.

Napthalene:

Naphthalene (C10H8) is an aromatic hydrocarbon in which two benzene rings are fused in ortho positions. For the purposes of naming its derivatives, the positions are indicated by figures.



Isolation from coal-tar:

Napthalene is the largest single component of coal-tar about 6-10 percent. The hydrocarbon was first noticed as a deposit in the condensers during the distillation of naphtha fraction and hence its name. It is obtained by cooling the middle oil fraction around 160-230°C, where upon naphthalene crystallizes out. The crude crystals are removed by centrifuging.

These are melted and then treated successively with concentrated sulphuric acid to remove phenols. Finally the naphthalene is sublimed to give the pure product.

Properties:

Physical:-

✓ Naphthalene is a white solid which crystallises in shining plates.

✓ It's m.p.-80°C and b.p.- 218°C, having a strong odour.

✓ It is very volatile and sublimes readily on warming. Naphthalene is insoluble in water, but dissolves easily in organic solvents, particularly in ether and benzene.

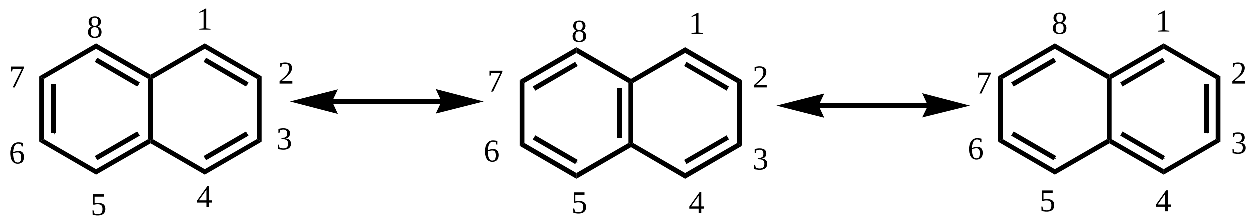
Chemical:-

✓ The reactions of naphthalene are essentially the same as those of benzene. It undergoes substitution readily and forms addition products.

✓ However it is somewhat less aromatic than benzene. Thus the double bonds in naphthalene exhibit in part the reactivity of alkenes and it forms addition compounds more readily than does benzene. As soon as one of the ring is fully saturated by addition of hydrogen or halogen.

Resonance structure of naphthalene:

X-ray diffraction studies show that, unlike benzene, all carbon –carbon bonds in naphthalene are not of the same length. In particular the C1-C2 bond is considerably shorter (1.36A°) than the C2-C3 bond (1.40A°). This difference can be understood if we examine the three resonance forms given above. Notice that the C1-C2 bond is double in two structures (A and B) and single in only one (C); whereas the C2-C3 bond is single in two structures (A and B) and double in only one (C). Therefore, expect the C1-C2 bond to have more double-bond character (shorter bond length), and the C2-C3 bond to have more single-bond character (longer bond length).

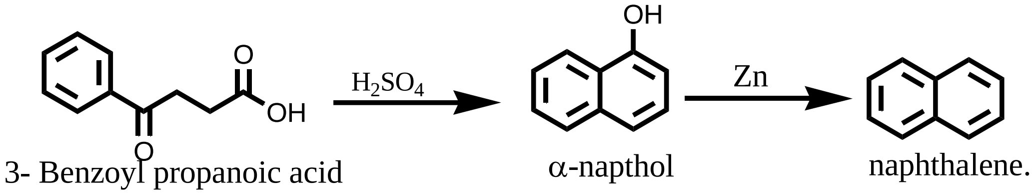


The resonance energy of naphthalene is about 61 kcal/mole. This value is less than twice the amount of a single benzene ring (36 kcal/mole). As a result, naphthalene is somewhat less aromatic (more reactive) than benzene.

Preparation of Napthalene:

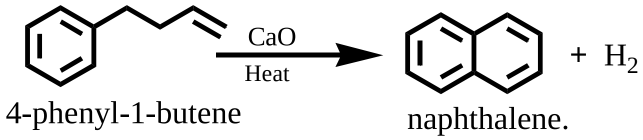
- From 3-Benzoyl propanoic acid:

  When 3-benzoyl propanoicacid is heated with sulphuric acid, α-napthol is formed, which on distillation with zinc dust forms naphthalene.



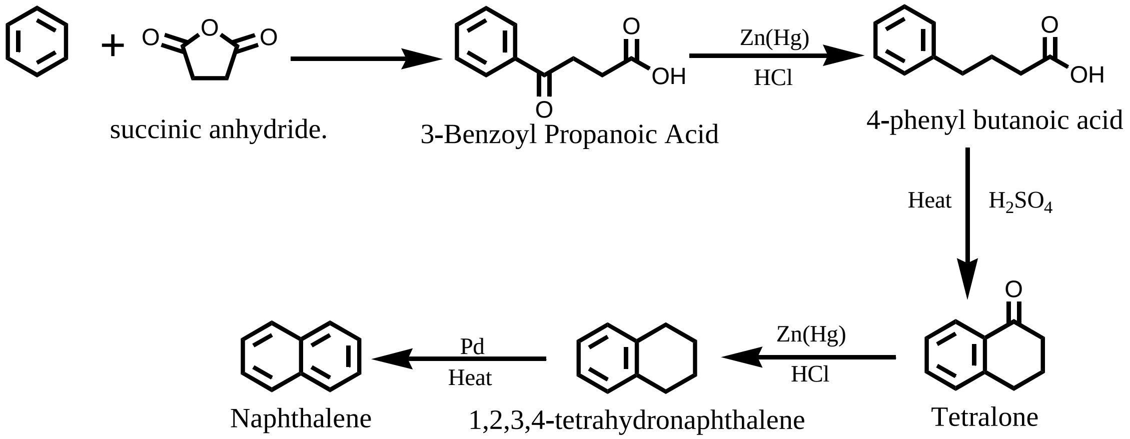
- From 4-phenyl-1-butene:

  When 4-phenyl-1-butene is passed over red hot calcium oxide naphthalene is formed.



- Haworth synthesis:

  It involves five steps.



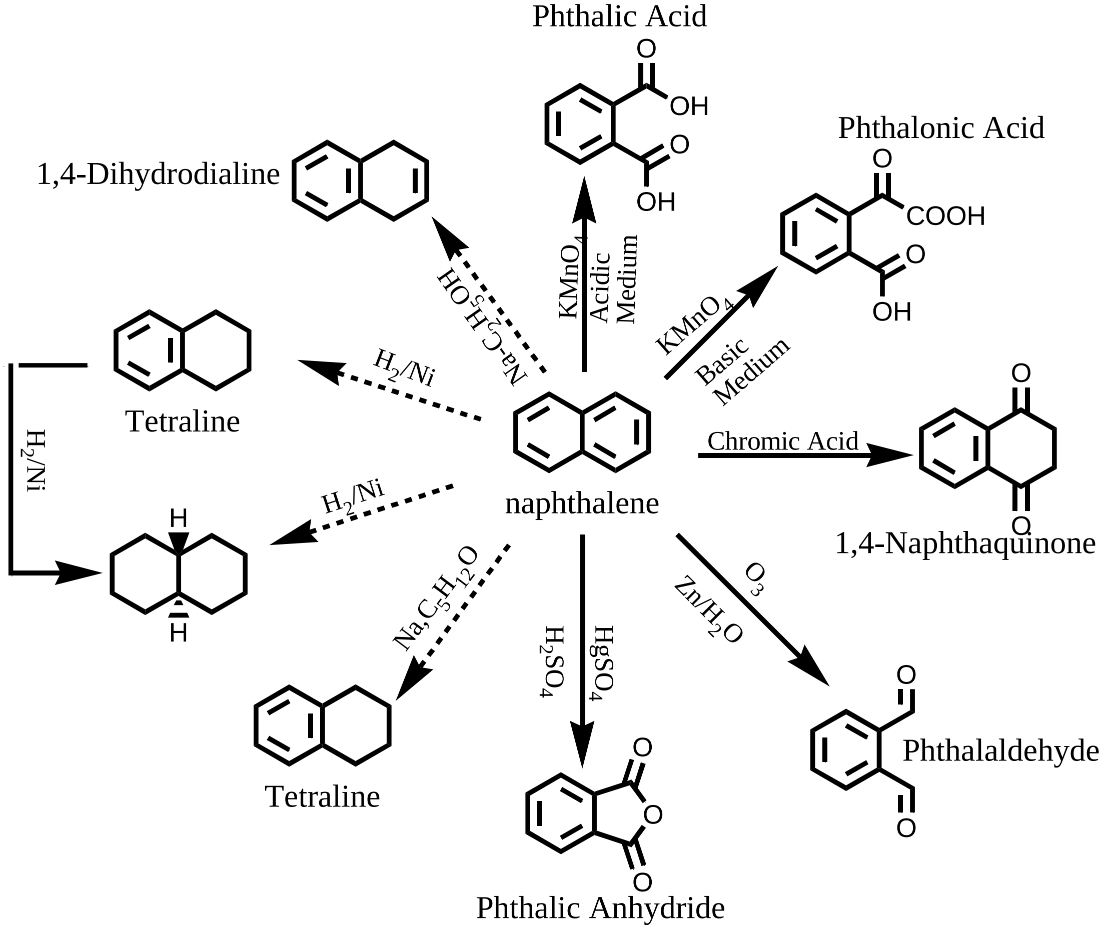
  - ✓ Step I: Formation of 3-benzoyl propanoic acid by the treatment of benzene with succinic anhydride.
  - ✓ Step II: 3-benzoyl propanoic acid is treated with amalgamated zinc to produce 4-phenyl butanoic acid.
  - ✓ Step III: 4- phenyl butanoic acid is heated with conc. Sulphuric acid to form Tetralone (ring closer reaction).

- ✓ Step IV: Tetralone is again heated with amalgamated zinc and HCl to give tetraline.
- ✓ Step V: Tetraline is heated with palladium to yield naphthalene.

Reactions of Naphthalene:

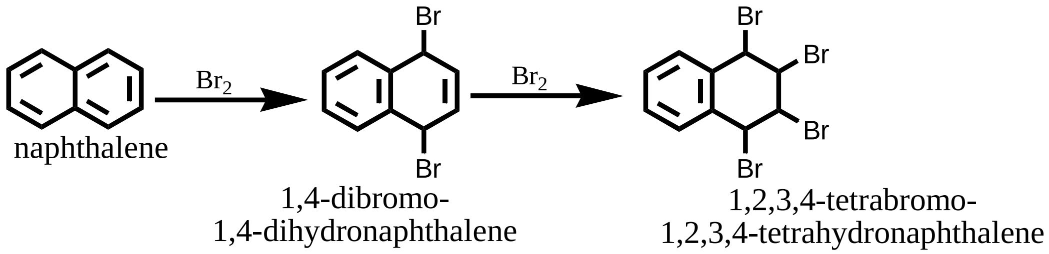
Naphthalene is more reactive than benzene. It undergoes several reactions like oxidation, reduction, addition, nitration, halogenations, acylation etc.

Oxidation and reduction of Naphthalene:



Addition Reaction:

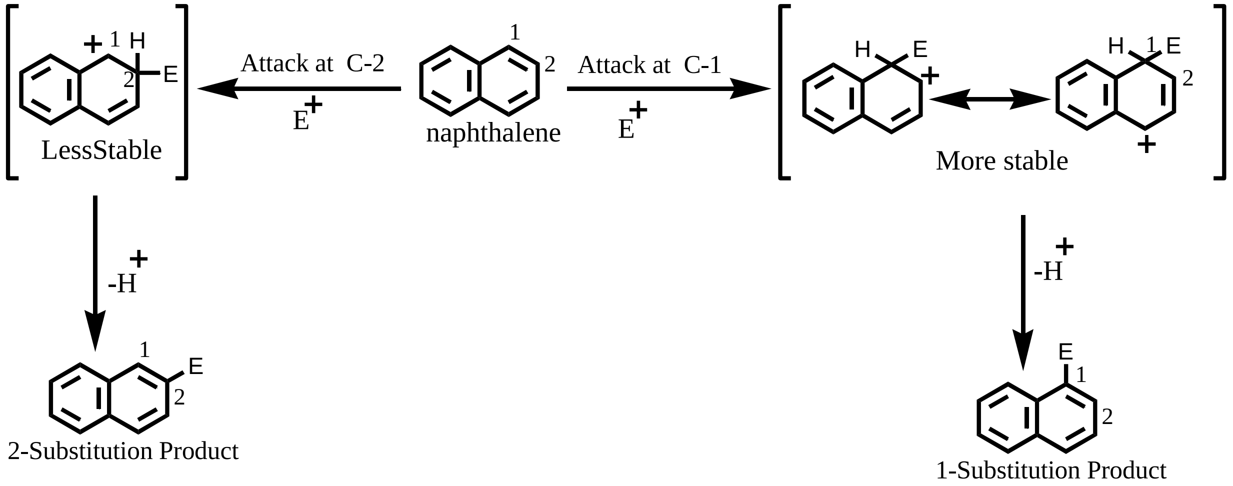
Addition of bromine or chlorine to naphthalene gives naphthalene dibromide or naphthalene dichloride. Further addition of bromine or chlorine results in formation of naphthalene tetra bromide or naphthalene tetra chloride.



Electrophilic substitution reactions:

Naphthalene, like benzene, undergoes electrophilic substitution reactions. Substitution occurs primarily at C1(α-position). This can be understood if we examine the intermediate carbonium ion. Two resonance forms can be written for the intermediate carbonium ion obtained from the attack at C-1(without involving the other ring), whereas only such form is possible for substitution at C-2.E+in the following equations represents an electrophile.

Consequently the former intermediate is more stable and the product with a substituent at C-1 predominates. Substitution at C-2 (ß-position) occurs only when the reactions are carried at higher temperatures or when bulkier solvents are used.



- Nitration reaction:

  Naphthalene nitrates with a mixture of nitric acid and sulphuric acid at low temperature to form mainly the α-nitronaphthalene.

- Halogention reaction:

  Naphthalene in presence of iron catalyst reacts with halogen to form α-substituted naphthalene.

- Sulphonation:

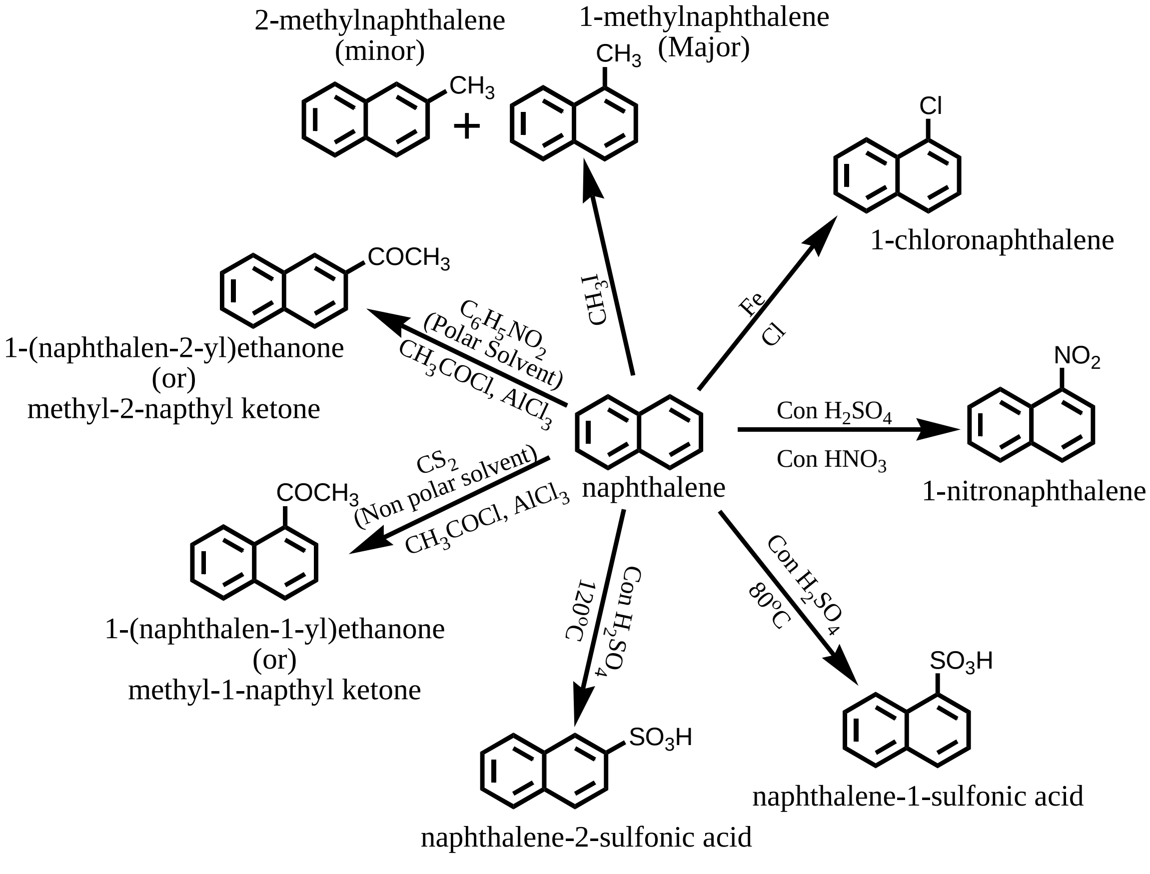
  Sulphonation of Napthalene at low temperature (80°C) produces naphthalene-1-sulfonic acid while at higher temperature (120°C) it produces naphthalene -2-sulfonic acid.

- Friedel-craft acylation:

  Naphthalene undergoes Friedel-crafts reaction with acetyl chloride to form the α or β products depending on the conditions

- Friedel craft alkylation

  Friedel craft alkylation at low temperature is carried out for naphthalene, which reacting with iodomethane to produce 1-methyl naphthalene as major product and 2-methylnaphthalene as minor product.

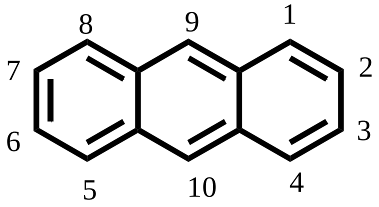


Uses of Napthalene:

- ✓ Production of Napthols.
- ✓ Production of Dyes.
- ✓ Preparing of beta blocker drugs.
- ✓ To synthesize synthetic dyes.
- ✓ Usefull insecticide.
- ✓ Veterinary medicine – dusting powder.
- ✓ Polyethylene naphthalene to prepare plastic bottles.
- ✓ Naphthalene sulfonic acids are used to prepare plasticizers, natural rubbers etc.
- ✓ Naphthalene drugs to cure cough, urine infection, eye trouble etc.

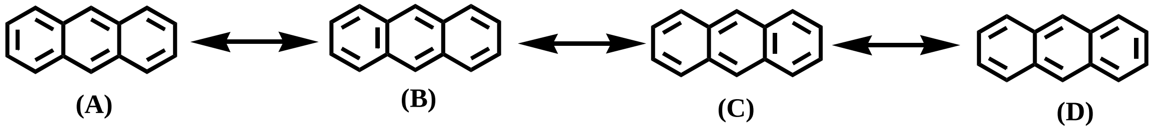
Anthracene

Anthracene is present is coal-tar to the extent of 0.3 to 3.5 perecent hence its name Greek anthrac meaning coal. on distillation of tar, it passes over in the high boiling fractions anthracene oil. The molecule of anthracene is made of three benzene nuclei fused in ortho positions. It is a colorless solid polycyclic aromatic hydrocarbon



Resonance structure of anthracene:

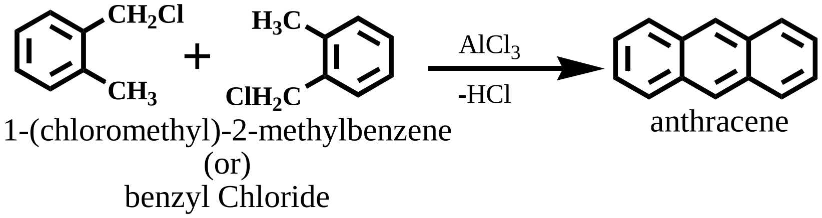
x-ray diffraction studies show that, like naphthalene ,all carbon bonds in anthracene are not of the same length. In particular, the C1-C2 bond is considerably shorter (1.37A°) than the (C2-C3)bond (1.42A°). This difference in bond lengths can be understood if we examine the four resonance forms given above. Notice that the C1-C2 bond is double in three structures(A,B and C), and single in only one (D); whereas the C2-C3 bond is single in three structures(A,B and C) and double in only one (D). We would, therefore, expect the C1-C2 bond to have more double-bond character (shorter bond length), and the C2-C3 bond to have more single-bond character (longer bond length). The resonance energy of anthracene is 84 kcal/mole. This averages to 28 kcal/mole per ring, which is substantially lower than that of benzene (36 kcal/mole).As a result, anthracene is much less aromatic than benzene and behaves more like an unsaturated aliphatic hydrocarbon.



Preparation of Anthracene:

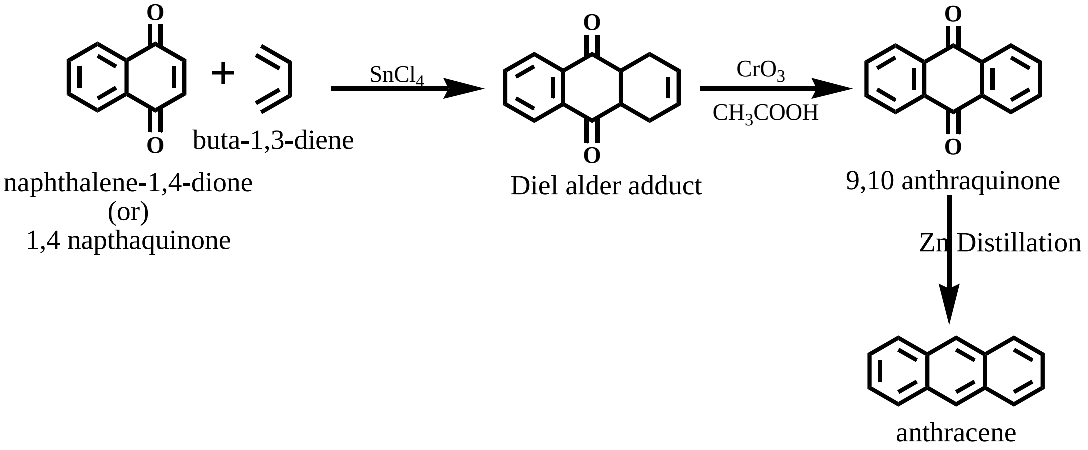
- By Friedel-Craft Reaction:

  Two molecules of benzyl chloride is condensed in presence of $AlCl_3$ to produce Anthracene.



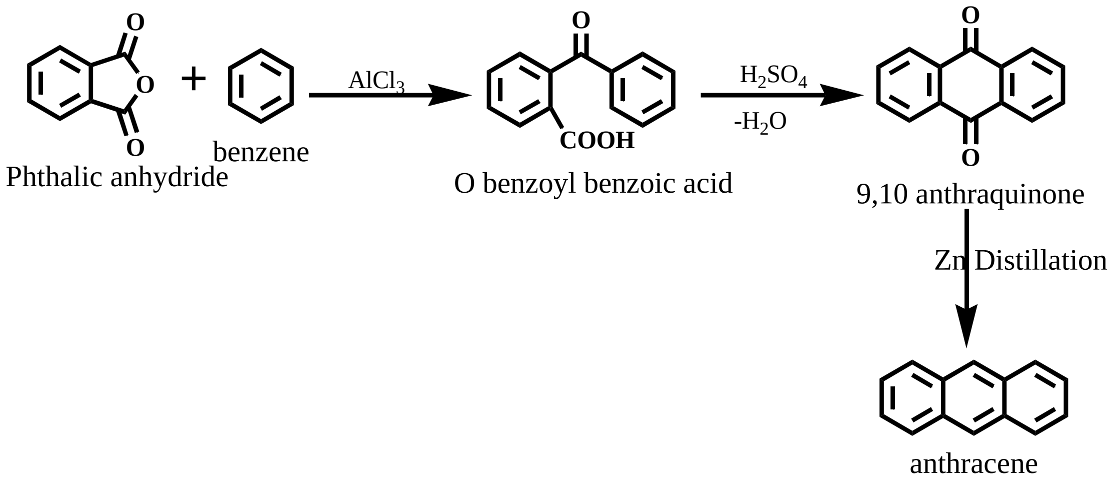
- By Diel-Alder Reaction:

  This involves the reaction of 1, 4 napthaquinone with 1, 3 butadiene further oxidized with CrO_3 to form 9, 10 anthraquinone, which on distillation (Zn) produce anthracene.



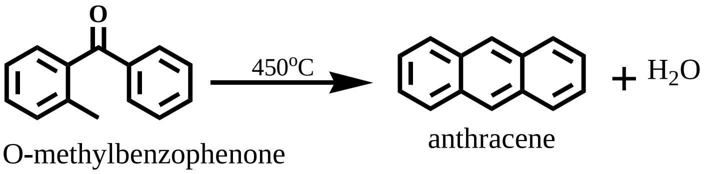
- By Haworth Synthesis:

  Benezene on reaction with phthalic anhydride in presence of $AlCl_3$ produces O-Benzoyl benzoic acid, futher it is heated with conc. H_2SO_4 to give 9.10-anthraquinone. On distillation of 9,10-anthraquinone with zinc dust will produce anthracene.



- Elbs Reaction:

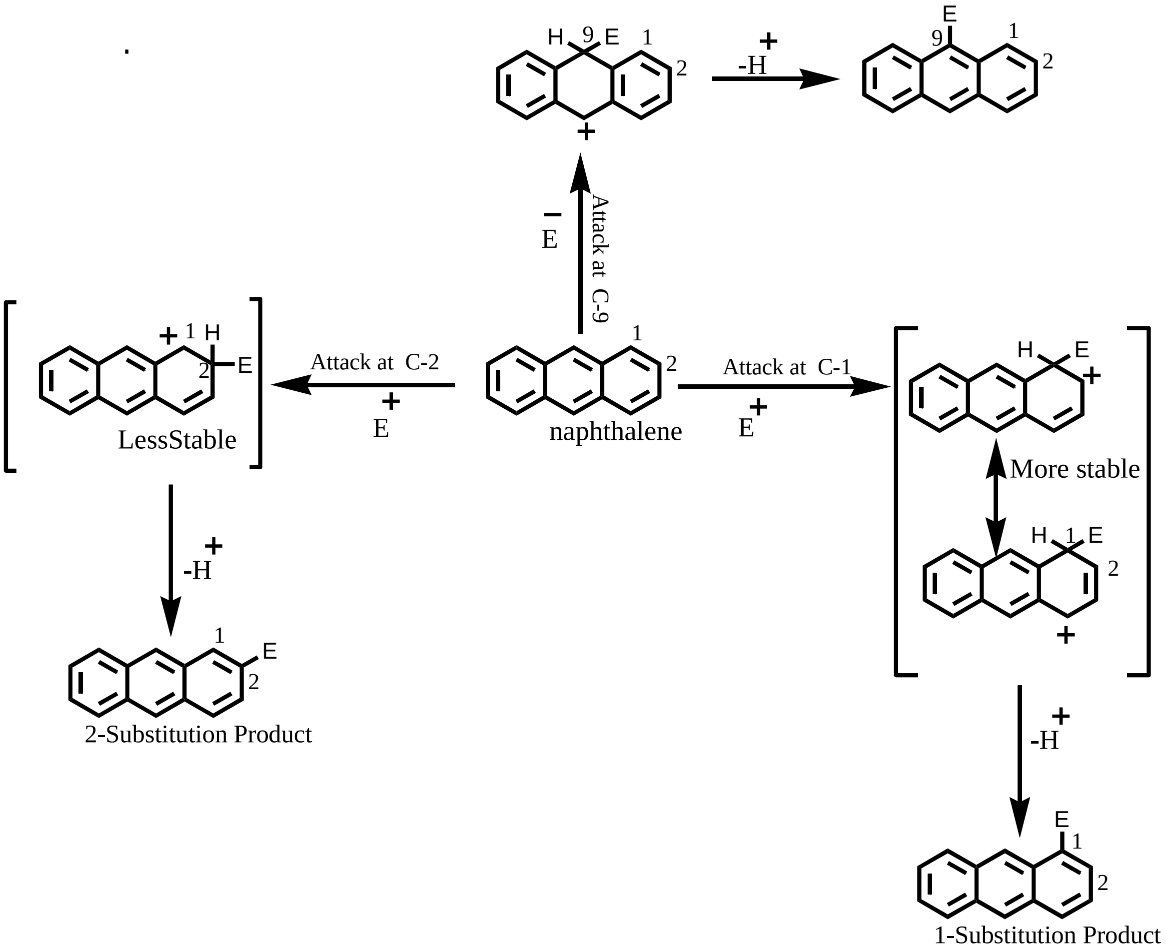
Pyrolysis of O-methylbenzophenone at 450°C can produce anthracene.



Properties of anthracene:

Anthracene is a colorless solid. It melts at 218°C and boils at 340°C.Anthracene is insoluble in water, but dissolves in benzene. It shows a strong blue fluorescence when exposed to ultraviolet light. This fluorescent property of anthracene is used in criminal detection work, since a small amount of finely powder anthracene on clothing, skin, money, etc. is not detected under ordinary light but easily noticed when exposed to ultraviolet light.

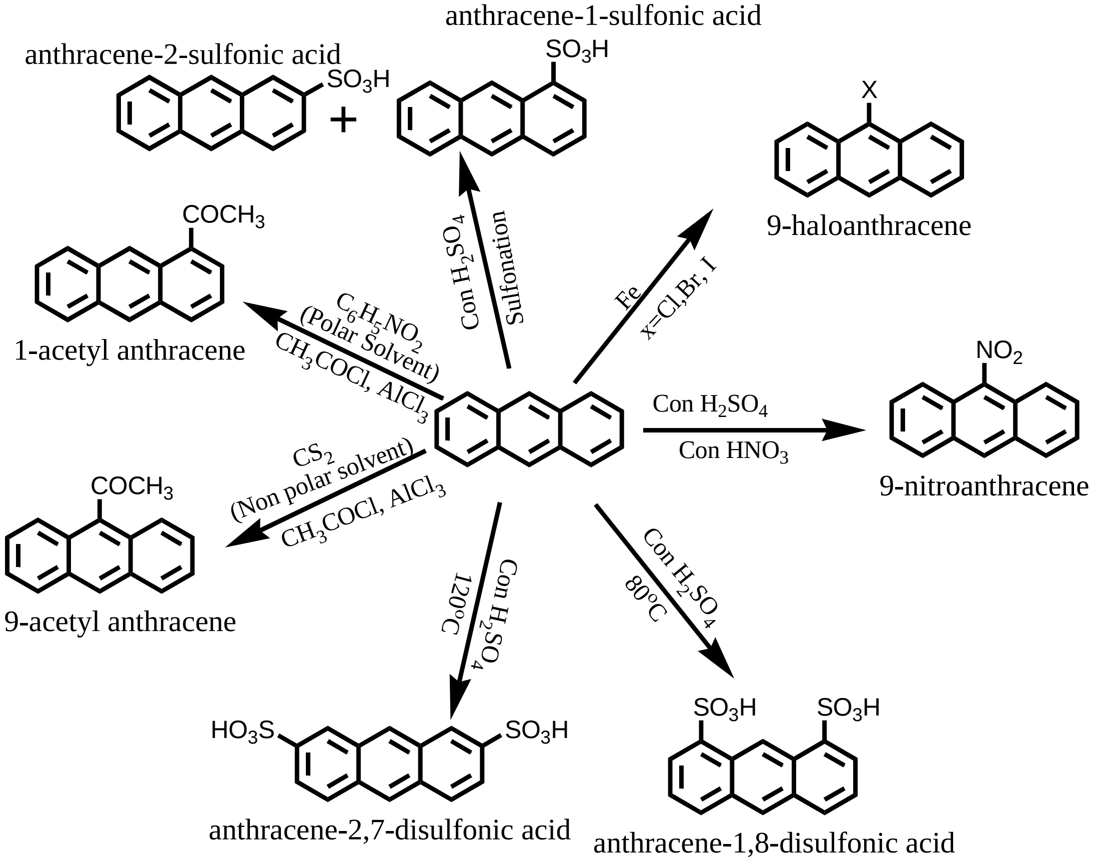
Chemical anthracene undergoes addition and electrophilic substitution reactions. These reactions preferentially occur at the C-9 and C-10 positions. This can be understood if we examine the intermediate carbonium ions obtained from attack at C-1, C-2, and C-9 (all other positions are equivalent to either 1 or 2 or 9 by symmetry). E^+ in the following equations represents an electrophile.



Attack at C-9 yields a carbonium ion intermediate in which two benzene rings are retained; where as attack C-1 or C-2 yields an intermediate in which a naphthalene system is retained. The former intermediate is more stable and its formation favoured because the resonance energy of two benzene rings (2 * 36 =72 kcal) exceeds that of naphthalene (61kcal).

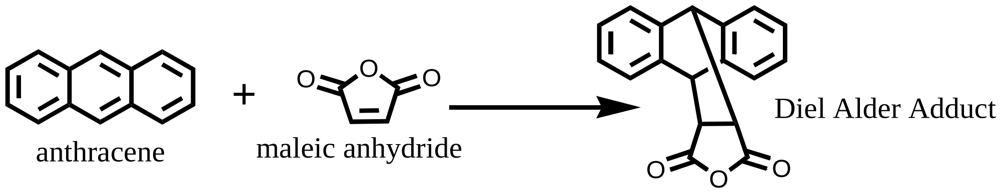
Reactions of Anthracene:

i. Electrophillic substitution reactions:



ii. Diels-Alder Reactions:

Anthracene undergoes Diels-Alder reaction at 9, 10 positions and form endo anthracene maleic anhydride.

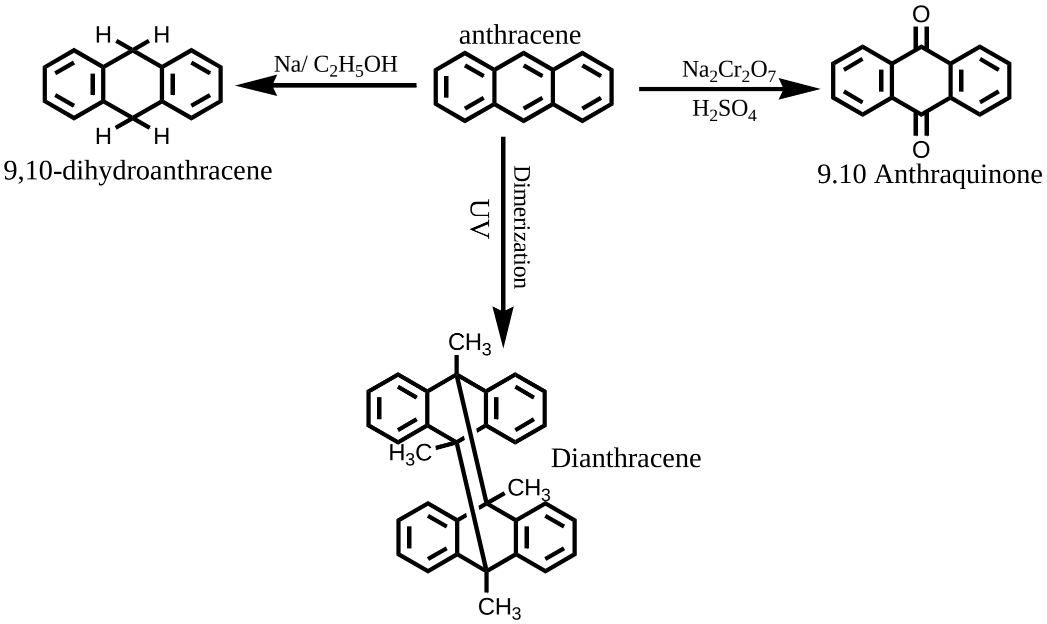


iii. Oxidation and reduction:

Anthracene undergoes oxidation with sodium dichromate and sulfuric acid to form 9, 10 anthraquinone and on reduction with sodium and ethyl alcohol produces 9, 10 dihydroanthracene.

iv. Dimerization:

Dimerization of anthracene in UV light produces dianthracene.



Uses of anthracene:

- Anthracene glycosides are oxygenated derivatives of pharmacological importance that are used as laxatives or catharatics, antineoplasticagent, polycystic kidney. eg:- Emodin
- It has anti-inflamatory, antibacterial, antifungal andantiproliferative activity. eg:-Chrysophanol, Aloe-emodin
- As natural dyes.
- Hepatoprotective,nephroprotective, antioxidant. Eg:- Rhein