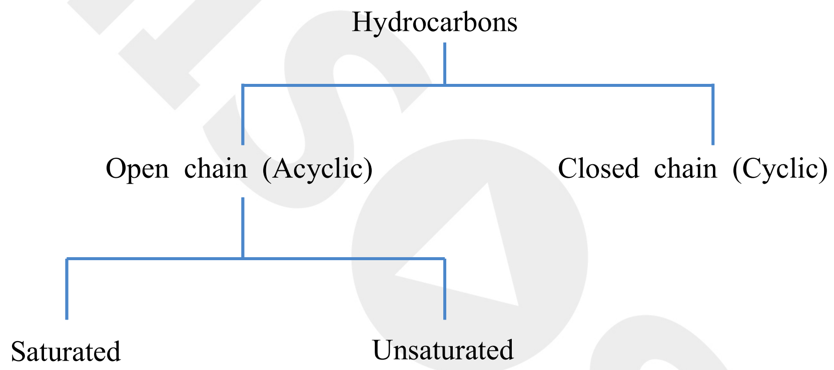
CHEMISTRY

CLASS NOTES FOR CBSE

Chapter 13. Hydrocarbons

01. Introduction

Organic compounds composed of only carbon and hydrogen are called hydrocarbons.



02. Saturated Hydrocarbons

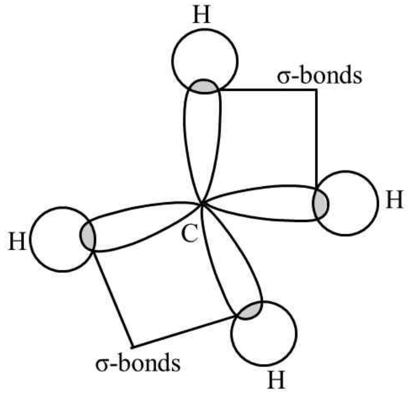
These constitute a homologous series having general formula C_nH_{2n+2} (n may have value 1,2,3,4 ....).
The saturated hydrocarbons are called **paraffins** (Latin: parum= little; affinity= affinity) as they are relatively inert toward chemical reagents. In IUPAC nomenclature, paraffins are termed alkanes. Alkanes have following structural characteristics,

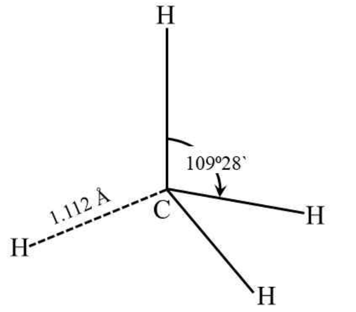
(i) Every carbon atoms is Sp^3 hybridized, its four bonding orbitals are directed toward the four corner of a regular tetrahedron.

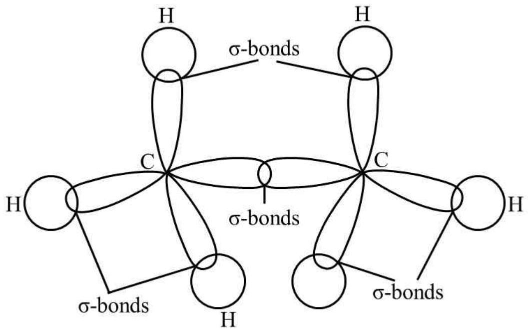
(ii) All the carbon-carbon and caron-hydrogen bonds are strong sigma The carbon-carbon bond is formed form the overlap of Sp^3 orbitals, one form each carbon atom. All carbon-hydrogen bonds result in overlap of Sp^3 hybrid oritals, one form each carbon, atom. All carbon-hydrogen bonds result in overlap of Sp^3 hybrid orbital from carbon and s-orbital form hydrogen.

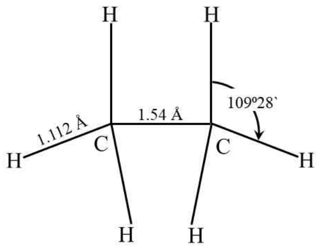
(iii) The bond lengths between carbon-hydrogen are 1.54Å and 1.112Å respectively.

(iv) The bond angles in alkanes are tetrahedral angles having a value of 109.5° (109°28).

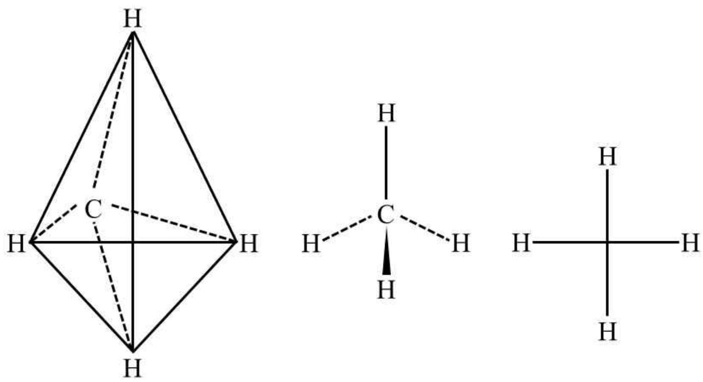








The structure of methane molecule can be represented by (a), (b) and (c). Fig. (a) is the **tetrahedral structure** of methane in which.



(a) (b) (c)

Structure Isomerism in alkanes

Alkanes exhibit chain isomerism. The first three members, *viz*., methane, ethane and propane do not exhibit isomerism as they can be represented by only one structural formula.
Butane has two chain isomers.

$CH_3CH_2CH_2CH_3$
n-Butane

$$\begin{array}{c} \quad\;\; CH_3 \\ \quad\;\; | \\ CH_3—CH—CH_3 \end{array}$$
(2-Methylpropane)

With increase in the number of carbon atoms in the molecule, the number of chain isomers also increases.

Alkane	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	$C_{10}H_{22}$
No. of possible isomers	3	5	9	18	75

Greater the branching greater the stability; so increasing order of stability is:
n-pentane < iso-pentane < neo-pentane;

Preparation of Alkanes

(i) From unsaturated hydrocarbons

$$\underset{\text{Ethane}}{CH_2 = CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3$$

$$\underset{\text{Propane}}{CH_3 - CH = CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3 - CH_2 - CH_3}$$

$$\underset{\text{Propane}}{CH_3 - C \equiv C - H} + 2H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3 - CH_2 - CH_3}$$

(ii) From alkyl halides

(a) Reduction :

$$\underset{\text{Chloromethane}}{CH_3 - Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Methane}}{CH_4} + HCl$$

$$\underset{\text{Chloroethane}}{C_2H_5 - Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Ethane}}{C_2H_6} + HCl$$

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow{Zn,\ H^+} CH_3CH_2CH_3 + HCl$$

(b) Wurtz reaction :

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaBr$$

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} \underset{\text{n-Butane}}{C_2H_5 - C_2H_5}$$

$$2CH_3–CH_2–Br+4Na+2Br–CH_3 \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3+CH_3CH_2CH_3+CH_3CH_3+4NaBr$$

(iii) From carboxylic acids

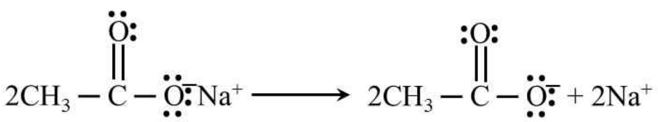
(a) By decarboxylation of carboxylic acids :

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(b) Kolbe's electrolytic method :

$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2CO_2 + H_2 + 2NaOH$$

Mechanism : The reaction follows a free-radical mechanism :



At anode :

(a) $$\underset{\text{Acetate ion}}{2CH_3-\overset{\overset{\Large :\ddot{O}:}{||}}{C}-\ddot{\underset{..}{O}}:^-} \xrightarrow{-2e^-} \underset{\text{Acetate free radical}}{2CH_3-\overset{\overset{\Large \ddot{O}:}{||}}{C}-\ddot{\underset{..}{O}}^\bullet} \longrightarrow \underset{\text{Methyl free radical}}{2\dot{C}H_3} + 2CO_2\uparrow$$

(b) $CH_3^\bullet + CH_3^\bullet \longrightarrow CH_3-CH_3$

At cathode :

(a) $2H_2O + 2e^- \longrightarrow 2OH^- + 2H^\bullet$

$2H^\bullet \longrightarrow H_2$

(b) $2Na^+ + 2OH^- \longrightarrow 2NaOH$

This method is applicable for the preparation of symmetrical alkanes only and not suitable for the preparation of methane. In Kolbe's electrolytic methods the alkane obtained is always a higher alkane due to the formation of carbon-carbon (C—C) bond restricting the formation of methane by this process.

Properties of Alkanes

Physical Properties :

(i) **State :** Due to the weak vander Waal's forces, the first four members C_1 to C_4 i.e. methane, ethane, propane and butane are gases. Form C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They all are colourless and odourless.

(ii) **Solubility :** Alkanes are non-polar or weakly polar compounds so these are soluble in non-polar solvents (benzene, ether, chloroform, carbontetrachloride etc.) and are insoluble in polar solvents (water etc.).

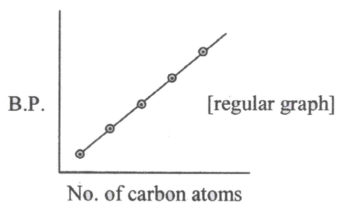
(iii) **Boiling point :** For homologues B.P. $\propto$ Molecular weight

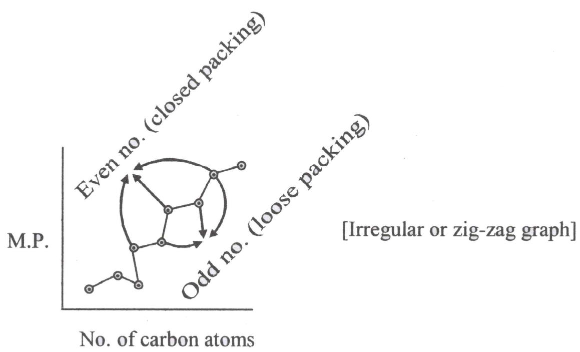
because Mol. wt. $\uparrow$= Surface area $\uparrow$= Intermolecular Vander wall's interaction $\uparrow$= B.P.$\uparrow$

For isomers $\text{B.P.} \propto \dfrac{1}{\text{No. of branches}}$

because Branches $\uparrow$ = Spherical shape $\uparrow$ = Surface area $\downarrow$ = B.P. $\downarrow$

(iv) **Melting point :** The melting point of alkanes depends upon molecular weight as well as packing in crystal lattice.





$\boxed{\uparrow \text{M.P. (odd to even)} > \uparrow \text{M.P. (even to odd)}}$

03. Chemical Reactions of Alkanes

(i) **Substitution reactions**

Alkanes, because of having only C—C and C—H sigma bonds undergo only substitution reactions. Some important substitution reactions of alkanes are discussed below.

(a) **Halogenation of Alkanes :**

Halogenation of an alkane is carried out by treating it with a suitable halogen in presence of ultraviolet light or by heating the reaction mixture to 520–670 K.

The order of reactivity of different halogens in these reactions is :

$$F_2 > Cl_2 > Br_2 > I_2$$

- **Chlorination :**

  During chlorination of methane, all the four hydrogen atoms are replaced one by one to form a mixture of products. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[\text{520-670 K}]{h\nu \text{ or}} \underset{\substack{\text{Chloromethane} \\ \textit{(Methyl chloride)}}}{CH_3Cl} + HCl$$

$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow[\text{520-670 K}]{h\nu \text{ or}} \underset{\substack{\text{Dichloromethane} \\ \textit{(Methylene chloride)}}}{CH_2Cl_2} + HCl$$

$$\underset{\text{Dichloromethane}}{CH_2Cl_2} + Cl_2 \xrightarrow[\text{520-670 K}]{h\nu \text{ or}} \underset{\substack{\text{Trichloromethane} \\ \textit{(Chloroform)}}}{CHCl_3} + HCl$$

$$\underset{\text{Trichloromethane}}{CHCl_3} + Cl_2 \xrightarrow[\text{520-670 K}]{h\nu \text{ or}} \underset{\substack{\text{Tetrachloromethane} \\ \textit{(Carbon tetrachloride)}}}{CCl_4} + HCl$$

Mechanism of halogenation:

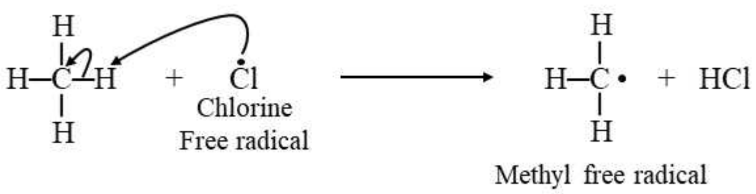
Halogenation of alkanes occurs by a *free radical mechanism*. Each free radical reaction consists of three steps :

(i) **Chain initiation :**

When a mixture of CH_4 and Cl_2 is hearted to 520-670 K in dark or is subjected to UV light at room temperature, Cl2 absorbs energy and undergoes homolytic fission producing chlorine free radicals.

$$Cl{-}Cl \xrightarrow[\text{Homolytic fission}]{\text{520-670 K or UV light}} \underset{\text{Chlorine free radical}}{2\,\dot{C}l}$$

(ii) **Chain propagation :**



(a)