**Introduction**:
(i) Branched and unbranched aliphatic saturated hydrocarbons are called members of alkane. The structural formula of alkane has only single bonds or all bonds in alkane are only $\sigma$ bonds.
(ii) Alkanes do not react with chemical reagents such as dil. and conc. HCl, dil. & conc. H$_2$SO$_4$, dil. & conc. HNO$_3$, Caustic soda, acidic & basic K$_2$Cr$_2$O$_7$, KMnO$_4$ etc. That is why alkanes are called paraffins. (Parum = little, affins = reactivity).

<table>
<thead>
<tr>
<th>Property</th>
<th>Characteristics of alkane</th>
<th>Property</th>
<th>Characteristics of alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>General formula</td>
<td>$C_nH_{2n+2}$</td>
<td>C–C Bond length</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>C–C Bond energy</td>
<td>82.67 kcal/mole</td>
<td>C–H Bond length</td>
<td>1.112 Å</td>
</tr>
<tr>
<td>C–H Bond energy</td>
<td>98.67 kcal/mole</td>
<td>Hybridisation on C shape</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Bond angle</td>
<td>109.28°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**General Methods of Preparations**:

1. **From alkenes and alkynes (Sabatier and Sandrens reaction) or (By hydrogenation of alkenes and alkynes)**: Alkenes and alkynes on catalytic hydrogenation gives alkanes.

   $\text{R—CH}=\text{CH—R} + \text{H}_2 \xrightarrow{\text{Catalyst}} \text{R—CH}_2\text{CH}_2—\text{R}$

   Alkene

   $\text{R—C}=\text{C—R} + 2\text{H}_2 \xrightarrow{\text{Catalyst}} \text{R—CH}_2\text{CH}_2—\text{R}$

   Alkyne

   **Catalyst**:
   (a) Pd/Pt at ordinary temp. and pressure
   (b) Ni, 200–300 °C (sabatier)
   (c) Raney Nicker at room temp.
   (d) Raney nickel is obtained by boiling Ni/Al with NaOH. Al dissolved & Ni obtained in finally divided state.
   (e) Methane can not be prepared by this method (From unsaturated hydrocarbon).

2. **From alkyl Halides (By reduction)**:

   $\text{R—X} \xrightarrow{2\text{H}} \text{R—H} + \text{HX}$

   **Catalyst**:
   (i) Zn + HCl
   (ii) Zn + CH$_3$ COOH
   (iii) Zn—Cu couple in C$_2$H$_5$OH
   (iv) Red P + HI
   (v) Al + Hg + ethanol

   **Mechanism**:
   $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^0$

   $\text{R}—\text{X} \rightarrow \text{Zn}^{+2} + 2\text{e}^0 \rightarrow \text{R}^+ + \text{X}^0$

   $\text{R}^+ + \text{H}^+ \text{Cl}^- \rightarrow \text{R—H} + \text{Cl}^0$

   $\text{Zn}^{+2} + 2\text{Cl}^- \rightarrow \text{ZnCl}_2$

   Product
Alkyl halides can also be reduced to alkane by H$_2$/Pd or LiAlH$_4$ or H$_2$/Ni.

Reduction is due to the electron transfer from the metal to the substrate (R- X)

If any alkyl halide is asked, the H-atom of any carbon atom of given alkane is removed by halogen atom.

3. **From alkyl halide (By Wurtz reaction):**

A solution of alkyl halide in ether on heating with sodium gives alkane.

\[
R - X + 2Na + X - R \xrightarrow{\text{Dry ether}} R - R + 2NaX
\]

(a) Two moles of alkyl halide treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

\[
2Na + H_2O \rightarrow 2NaOH + H_2
\]

\[
CH_3I + NaOH \rightarrow CH_3OH + NaI
\]

Methanol

(b) Methane cannot be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.

(c) Two different alkyl halides, on wurtz reaction give all possible alkanes.

(d) The separation of mixture in to individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

(e) This reaction generally fails with tertiary alkyl halide.

**Mechanism:** Two mechanism have been proposed for this reaction.

(a) Ionic Mechanism:

\[
2Na \rightarrow 2Na^+ + 2e^-
\]

\[
\delta^+ \quad \delta^- 
\]

\[
R - X \rightarrow R^+ \rightarrow R + X^-
\]

Product

\[
2Na^+ + 2X^- \rightarrow 2NaX
\]

Example : 2C$_2$H$_5$I + 2Na \rightarrow C$_2$H$_5$C$_2$H$_5$ + 2NaI

n-butane

(b) Free radical mechanism :

\[
Na \rightarrow Na^+ + e^-
\]

\[
\delta^+ \quad \delta^-
\]

\[
R \rightarrow R^+ \rightarrow R + X^-
\]

Product

\[
Na^+ + X^- \rightarrow NaX
\]

Free radicals also undergo Disproportionation i.e. one radical gains hydrogen at the expense of the other which loses hydrogen.

\[
H
\]

\[
\xrightarrow{\text{H}}
\]

\[
CH_3 - CH + \xrightarrow{C_2H_4} \rightarrow C_2H_4 + C_2H_4
\]

Ethane Ethylene

This explains the presence of ethylene and ethane in the butane obtained by Wurtz reaction.
**Ex.** If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.

**Sol.** 2, 3-Dimethyl butane.

**Ex.** If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.

**Sol.** n-Butane, 2-Methyl butane and 2, 3-Dimethyl butane.

**Ex.** Which of the following compound can not obtained from wurtz reaction.

(A) ethane  
(B) butane  
(C) isobutane  
(D) hexane

**Sol.** (C) [Hint : In wurtz reaction unsymmetrical alkane can not be obtained.

**Ex.** When ethyl chloride and n-propyl chloride undergoes wurtz reaction which is not obtained.

(A) n–butane  
(B) n–pentane  
(C) n–hexane  
(D) isobutane

**Sol.** (D) \[ \text{C}_2\text{H}_5\text{Cl} + \text{C}_3\text{H}_7\text{Cl} \xrightarrow{\text{Na} \text{ dry ether}} \text{C}_2\text{H}_5\text{C}_2\text{H}_5 + \text{C}_3\text{H}_7\text{C}_3\text{H}_7 + \text{C}_2\text{H}_5\text{C}_3\text{H}_7 \]

4. **Corey-House Synthesis :**

This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R–R’

(i) \[ RX + \text{Li} \xrightarrow{} \text{RLi} + \text{LiX} \]

(ii) \[ 2\text{RLi} + \text{CuX} \xrightarrow{} \text{R}_2\text{CuLi} + \text{LiX} \]

(iii) \[ \text{R}_2\text{CuLi} + \text{R’X} \xrightarrow{(\text{I} \text{or} \text{Z})} \text{R–R’} + \text{RCu} + \text{LiX} \]

**Note :** In Corey-house reaction symmetrical and unsymmetrical alkane both can be formed.

5. **From Frankland Reagent:** If Zn is used in place of Na, the reaction is named as Frankland reaction.

\[ \text{R–X} + 2\text{Zn} + \text{RX} \xrightarrow{} \text{R}_2\text{Zn} + \text{ZnX}_2 \]

Frankland reagent

\[ \text{R}_2\text{Zn} + \text{R–X} \xrightarrow{} \text{R–R} + \text{RZnX} \]

6. **From Carboxylic Acid (By decarboxylation) :** Saturated monocarboxylic acid salt of sodium or potassium on dry distillation with soda lime give alkane.

\[ \text{RCOONa} + \text{NaOH} \xrightarrow{\Delta \text{Cao}} \text{R–H} + \text{Na}_2\text{CO}_3 \]

**Soda Lime**

(a) The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.

(b) Replacement of -COOH by hydrogen is known as decarboxylation.

The alkane formed always contains one carbon atom less than the original acid.

(c) This reaction is employed for stepping down a homologous series.

(d) Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the products.

(e) Decarboxylation of sodium formate gives \( \text{H}_2 \)

\[ \begin{cases} \text{HCOONa} + \text{NaOH (CaO)} \xrightarrow{\Delta} \text{H}_2 + \text{Na}_2\text{CO}_3 \\ \text{CH}_3\text{COONa} + \text{NaOH} + \text{CaO} \xrightarrow{\Delta} \text{CH}_4 + \text{Na}_2\text{CO}_3 \end{cases} \]
Mechanism: Decarboxylation proceeds via the formation of carbanion intermediate as follows.

\[
\begin{align*}
\text{CH}_3\text{C}^\text{O}^- + \text{OH}(\text{NaOH}) \rightleftharpoons \text{CH}_3\text{C}^\text{O}^\text{0} \\
\text{CH}_3\text{C}^\text{O}^\text{0} \rightarrow \text{CH}_3 + \text{H}_2\text{O}
\end{align*}
\]

(a) If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating.

\[
\text{CH}_2\text{COOH} \xrightarrow{\Delta} \text{CH}_3\text{COOH} + \text{CO}_2
\]

(b) \(\text{CH}_4\) can be prepared by \(\text{CH}_3\text{COOH}\).

(c) \(\text{C}_2\text{H}_6\) can be prepared by \(\text{CH}_3\text{CH}_2\text{COOH}\).

(d) \(\text{CH}_3-\text{CH}_2-\text{CH}_3\) can be prepared by Butanoic acid and 2-Methyl propanoic acid.

Ex. How many acids can be taken to obtain isobutane from decarboxylation?

(A) 4  (B) 3  (C) 2  (D) 5

Sol. (C) To obtain isobutane the acids are

(i) \(\text{CH}_3\text{CHCH}_2\text{COOH} \rightarrow \text{CH}_3\text{CHCH}_2\text{H}\)

(ii) \(\text{CH}_3\text{CCH}_3 \rightarrow \text{CH}_3\text{CCH}_3\)

So two acids can be taken.

Reactivity of acid \(\propto\) stability of carbanion

Presence of electron attracting group (–I) in the hydrocarbon part of the fatty acid increases the decarboxylation. If – I is more effective group then weak base may be taken.

Example:

(i) \(\text{R}^\text{CHCH}_2\text{COOH} \xrightarrow{\Delta, \text{NaHCO}_3} \text{R}^\text{CHCH}_2\text{H}\)

(ii) \(\text{R}^\text{NO}_2\text{CHCH}_2\text{COOH} \xrightarrow{\Delta, \text{NaHCO}_3} \text{R}^\text{NO}_2\text{CHCH}_2\text{H}\)
(iii) β-Keto acids are decarboxylated readily simply on heating (soda lime is not required)

\[
R\text{--C--CH}_2\text{COOH} \xrightarrow{\Delta} R\text{--C--CH}_3
\]

Ex. Give reactivity order for decarboxylation?

\[
\begin{align*}
\text{CH}_3\text{--CH}_2\text{--COOH} & \quad \text{CH}_2\text{==CH--COOH} \\
\text{I} & \quad \text{II} \\
\text{CH==C–COOH} & \quad \text{CH==C–COOH} \\
\text{III} & \quad \text{III}
\end{align*}
\]

(A) I > II > III (B) III > II > I (C) III > I > II (D) None is correct

Sol. (B) In decarboxylation intermediates are,

\[
\begin{align*}
\text{CH}_3\text{–CH}_2\Theta & \quad \text{CH}_2\text{==CH}_\Theta & \quad \text{CH==C}_\Theta \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]
The stability order of carbanion – III > II > I
So reactivity order for acid is – III > II > I

7. From carboxylic acid (By Kolbe's process):

Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

\[
2\text{RCOO}^{\ominus} + 2\text{H}_2\text{O} \xrightarrow{\text{Electrolysis}} \text{R} - \text{R} + 2\text{CO}_2 + 2\text{NaOH} + \text{H}_2
\]

Electrolysis of sodium propionate solution give n-butane, ethylene, ethane and ethyl propionate as follows-

\[
2\text{C}_2\text{H}_5 \text{–COONa} \xrightarrow{\text{electro.}} \text{C}_2\text{H}_5 - \text{C}_2\text{H}_5 + 2\text{CO}_2 + 2\text{NaOH} + \text{H}_2
\]

◆ Mechanism : \[\text{C}_2\text{H}_5\text{–COONa} \xrightarrow{\text{electro.} \text{H}_2\text{O}} \text{C}_2\text{H}_5 \text{–COO}^{\ominus} + \text{Na}\] (Ionization)

At Anode :

\[
\text{C}_2\text{H}_5\text{–COO}^{\ominus} \xrightarrow{\ominus} \text{C}_2\text{H}_5 - \text{COO}^{\ominus}
\]

\[
\text{C}_2\text{H}_5\text{–COO}^{\ominus} \xrightarrow{\text{Fragmentation}} \text{C}_2\text{H}_5 + \text{CO}_2
\]

\[
\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \xrightarrow{\text{Product}} \text{C}_2\text{H}_5\text{–C}_2\text{H}_5
\]

An ester is also formed.

\[
\text{C}_2\text{H}_5\text{–COO}^{\ominus} + \text{C}_2\text{H}_5 \xrightarrow{\ominus} \text{C}_2\text{H}_5\text{–COOC}_2\text{H}_5
\]

(minor products)

At cathode :

\[
\text{Na}^{\ominus} + \text{e}^{\ominus} \xrightarrow{\text{Na}} \text{Na} + \text{H}_2 \xrightarrow{\text{NaOH} + \text{H}_2}
\]
(a) Methane cannot be prepared by this method.

(b) Electrolysis of an acid salt gives symmetrical alkane. However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.

\[
\text{R'}\text{COOK} + \text{R''COOK} \xrightarrow{\text{Electrolysis}} (\text{R'}-\text{R''} + \text{R'}-\text{R'} + \text{R''}-\text{R'}) + 2\text{CO}_2 + \text{H}_2 + 2\text{NaOH}
\]

(c) Presence of alkyl groups in \( \alpha \) - position decrease the yield of alkanes.

(d) True aromatic acids do not undergo Kolbe's electrolytic reaction.

(e) Free radical mechanism has been suggested for Kolbe reaction.

(f) At anode alkane (major) and \( \text{CO}_2 \) gas is formed while at cathode \( \text{NaOH} \) and \( \text{H}_2 \) gas is formed.

(g) The concentration of \( \text{NaOH} \) in solution is increased with time so pH of solution is also increased.

8. From alkanol, alkanal, Alkanone and alkanolic acid (By reduction):

The reduction of either of the above in presence of red P and HI gives corresponding alkane.

\[
\text{R—OH} + 2\text{HI} \xrightarrow{\text{Red P} \atop 150 \degree \text{C}} \text{R—H} + \text{H}_2\text{O} + \text{I}_2
\]

\[
\text{R—CHO} + 4\text{HI} \xrightarrow{\text{Red P} \atop 150 \degree \text{C}} \text{RCH}_3 + \text{H}_2\text{O} + 2\text{I}_2
\]

\[
\text{R—CO—R'+4HI} \xrightarrow{\text{Red P} \atop 150 \degree \text{C}} \text{R—CH}_2—\text{R'+H}_2\text{O} + 2\text{I}_2
\]

\[
\text{RCOOH} + 6\text{HI} \xrightarrow{\text{Red P} \atop 150 \degree \text{C}} \text{R—CH}_2—\text{R'+H}_2\text{O} + 3\text{I}_2
\]

In the above reaction \( \text{I}_2 \) is formed which acts as reducing agent and may reduce alkane and form alkyl halide. So red P is added in the reaction to remove \( \text{I}_2 \) formed in the reaction.

\[
\text{R—CH}_3 + \text{I}_2 \xRightarrow{2\text{P} + 3\text{I}_2} \text{R—CH}_2—\text{I} + \text{HI}
\]

9. From alkanones (By Clemmensen's method):

Carbonyl compound (Preferably ketones) may also be reduced with Zinc amalgam and concentrated HCl (Zn—Hg/HCl), this reaction is called Clemmensen reduction.

\[
\text{R—CO—R'+4H} \xrightarrow{\text{Zn/Hg} \atop \text{con.HCl}} \text{R—CH}_2—\text{R'+H}_2\text{O}
\]

\( \text{CH}_4, \text{CH}_3—\text{CH}_3, \text{isobutane and neopentane} \) are not obtained from Ketones because these alkane do not contain \( \text{CH}_2 \) group.

10. From alkanols and alkanones (By Wolf Kishner reaction):

\[
\text{C}==\text{O} + \text{NH}_2\text{NH}_2 \xrightarrow{\text{Hydrazine}} \text{C}==\text{N.NH}_2 \xrightarrow{\text{Glycol/KOH} \atop \Delta} \text{CH}_2 + \text{N}_2
\]

☐ From G.R.:

(a) Formation of alkanes with same number of C atoms: With same number of C-atoms as G.R. react with compound containing active hydrogen alkanes is obtained.

\[
\text{R—MgX} + \text{H—O—H} \rightarrow \text{R—H} + \text{Mg(OH)}_2 \text{X}
\]

\[
+ \text{R—O—H} \rightarrow \text{R—H} + \text{Mg(OR)}_2 \text{X}
\]

\[
+ \text{R—NH—H} \rightarrow \text{R—H} + \text{Mg(NHR)}_2 \text{X}
\]

This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

(b) G.R. react with alkyl halide to give higher alkanes:

\[
\text{RMgX} + \text{R'}—\text{X} \rightarrow \text{R—R'} + \text{MgX}_2
\]
Ex. Which of the following does not give alkane with $R-\text{Mg}-X$.
(A) Ph—OH  (B) Cl—NH$_2$  (C) CH$_3$COOH  (D) HCl

Sol. (B)

[Hint : Except Cl—NH$_2$ all have active hydrogen, but Cl—NH$_2$ when reacts with $R-\text{Mg}-X$ the product is $R-NH_2$.]

From metal carbide (By hydrolysis):

Only CH$_4$ can be obtained by the hydrolysis of Be or Al carbides

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \xrightarrow{\Delta} 4\text{Al(OH)}_3 + 3\text{CH}_4$$

$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{Be(OH)}_2 + \text{CH}_4$$

11. Physical Properties:

(i) C$_1$ to C$_4$ gases, Neopentane also gas but n-pentane and isopentane are low B.P. liquids.

(ii) Next members C$_5$ to C$_{17}$ are Colourless liquids and above C$_{17}$ are Waxy solids.

(iii) Density: The density of alkanes increases with increase in molecular weight and becomes constant at 0.8 g/mL. Thus all alkanes are lighter than water.

(iv) Solubility: Alkanes being non polar and thus insoluble in water but soluble in non-polar solvents

Example: $\text{C}_6\text{H}_6$, CCl$_4$, ether etc.

- The solubility of alkanes decreases with increase in molecular weight
- Liquid alkanes are themselves good non-polar solvents.

(v) Boiling point $\propto$ molecular weight (for n-alkanes)

:: Vanderwaals force of attraction $\propto$ molecular weight $\propto$ surface area of molecule.

i.e. boiling point Pentane < hexane < heptane

Also boiling point $\propto \frac{1}{\text{number of side chain}}$

because the shape approaches to spherical which results in decrease in Vanderwaals forces (as surface area decreases)

Thus boiling point n-Pentane > Isopentane > neopentane

(vi) Melting Point: M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their alkanes of odd number of carbon atoms.

The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.

\[
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{Odd number of carbon}
\end{array}
\quad < 
\quad \begin{array}{c}
\text{C} \quad \text{C} \\
\text{Even number of carbon}
\end{array}
\]

Ex. Alkanes are inert in nature, why?

Sol. Alkanes are quite inert substances with highly stable nature. Their inactiveness has been explained as:

(i) Alkanes have all the C—C and C—H bonds being stronger $\sigma$ bonds and are not influenced by acid, oxidants under ordinary conditions.

(ii) The C—C bond is completely non polar and C—H is weak polar. Thus polar species i.e. electrophiles or nucleophiles are unable to attack these bonds under ordinary conditions.
12. Chemical Properties:

- **Oxidation**:
  - **Complete oxidation or combustion**: Burn readily with non-luminous flame in presence of air or oxygen to give CO₂ and water with evolution of heat. Therefore, alkanes are used as fuels.

\[
C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O + Q; \quad (\Delta H = -\text{ve})
\]

- **Incomplete oxidation**: In limited supply of air gives carbon black and CO.

\[
2\text{CH}_4 + 3O_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O} \\
\text{CH}_4 + O_2 \rightarrow \text{C} + 2\text{H}_2\text{O}
\]

   C-black (used in printing)

- **Catalytic oxidation**:
  1. Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

\[
2\text{CH}_4 + O_2 \xrightarrow{\text{Red hot Cu or Fe tube}} 2\text{CH}_3\text{OH} \\
\text{CH}_4 + O_2 \xrightarrow{\text{MnO}_3} \text{HCHO} + \text{H}_2\text{O}
\]

  (ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

\[
\text{CH}_3(\text{CH}_2)_n\text{CH}_3 \xrightarrow{\text{CH}_3\text{COO}_2\text{Mn}} \text{CH}_3(\text{CH}_2)_n\text{COOH}
\]

  (iii) Tertiary alkanes are oxidized to give tertiary alcohols by KMnO₄.

- **Substitution Reactions**: Substitution reaction in alkanes shows free radical mechanism. They give following substitution reaction.

  (a) **Halogenation**: Replacement of H-atom by halogen atom

\[
\text{R—H} + X_2 \rightarrow \text{R—X} + \text{HX}
\]

Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temp.

The reactivity order for halogens shows the order: \(\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2\)

Reactivity order of hydrogen atom in alkane is: \(\text{Tertiary C—H} > \text{Sec. C—H} > \text{primary C—H}\)

(i) **Fluorination**: Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F₂ diluted with an inert gas (like N₂).

By the action of HgF₂ on bromo or iodo derivatives.

\[
\text{C}_2\text{H}_5\text{I} + \text{HgF}_2 \rightarrow \text{C}_2\text{H}_5\text{F} + \text{HgI}_2
\]
(ii) **Chlorination** :

\[
\begin{align*}
\text{CH}_4 & \xrightarrow{\text{Cl}_2} \text{CH}_3\text{Cl} \xrightarrow{\text{Cl}_2} \text{CH}_2\text{Cl}_2 \xrightarrow{\text{Cl}_2} \text{CHCl}_3 \xrightarrow{\text{Cl}_2} \text{CCl}_4
\end{align*}
\]

The monochloro derivative of alkane is obtained by taking alkane in large excess. When chlorine is in excess, a mixture of mono, di, tri, tetra and perchloro derivatives is obtained.

\[
\text{Explosively CH}_4 + \text{Cl}_2 \rightarrow \text{C} + \text{HCl}
\]

**Mechanism** for \( \text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{UV}} \text{CH}_3\text{Cl} + \text{HCl} \)

**Step I**  
**Chain initiation step** :  
\( \text{Cl}:\text{Cl} \xrightarrow{\text{Cl}^* + \text{Cl}^*} \)

**Step II**  
**Chain propagation step** :

\[
\text{Cl}^* + \text{H} \cdot \text{CH}_3 \rightarrow \text{HCl} + \text{CH}_3
\]

Methane  
Methyl radical

**Step III**  
**Chain termination step** :

\[
\text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2, \quad \text{CH}_3^* + \text{Cl} \rightarrow \text{CH}_3\text{Cl}, \quad \text{CH}_3^* + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3
\]

A \( \cdot\text{Cl} \) can also attack \( \text{CH}_3\text{Cl} \) to form chloromethyl (\( \cdot\text{CH}_2\text{Cl} \)) free radical. This free radical participates further in the chain reaction to yield methylene chloride (dichloromethane).

Similarly, chloroform and \( \text{CCl}_4 \) are obtained by further chain reaction.

(iii) **Bromination** : \( \text{Br}_2 \) reacts with alkanes in a similar manner but less vigorously.

(iv) **Iodination** : Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the \( \text{CH}_3\text{I} \) to \( \text{CH}_4 \).

Iodination may be carried out in the presence of an oxidising agent such as \( \text{HIO}_3, \text{HIO}_4, \text{HNO}_3, \text{HgO} \) etc. Which destroy HI,

\[
\text{CH}_4 + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{HI}
\]

\[
5\text{HI} + \text{HIO}_3 \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}
\]

Iodination is very slow because energy of activation of the reaction is very large

\[
\text{CH}_4 + \text{I}^* \rightarrow \text{HI} + \cdot\text{CH}_3
\]

**Note** :

Halogenation is inhibited in presence of oxygen because oxygen reacts with alkyl free radicals to form less reactive peroxy alkyl radical \( \cdot\text{R–O–O}^* \) which can not propagate the chain.

**Reactivity selectivity Principle** :

(i) **Probability factor** : The factor is based on the number of each kind of H atom in the molecule.

For example is \( \text{CH}_3–\text{CH}_2–\text{CH}_2–\text{CH}_3 \) there are six equivalent 1 H's and four equivalent 2 H's.

The probability of abstracting 1 H's to 2 H's is 6 to 4. i.e., 3 to 2.
Reactivity of halogen free radical: the more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br radical is more selective and less influenced by the probability factor (Reactivity selectivity principle).

Reactivity of alkanes (ease of abstration of 'H' atoms): Since the rate determining step in halogenations is abstraction of hydrogen by a halogen atom be the formation of alkyl radical, halogenation of alkanes follows order of stability of free radical is $3° > 2° > 1° > CH_3$.

Reactivity ratio of H atom for Chlorination
$1° : 2° : 3° H = 1 : 3.8 : 5$

Reactivity ratio of H atom for bromination
$1° : 82° : 1600$

The above order of stability of radicals is due to the ease of their formation from the corresponding alkane which in turn is due to difference in the value of $\Delta H$.

Reactivity of any H-atom $\propto$ number of H atoms of that kind × reactivity of that H.

Thus the amount of energy required to form the various classes of radicals decreases in the order $CH_3 > 1° > 2° > 3° (\Delta H_1 > \Delta H_2 > \Delta H_3 > \Delta H_4)$. Therefore, it easiest to form $3°$ radical and it is most difficult to form $CH_3$. We can also interpret this in an alternative way the case of abstraction of H atoms from hydrocarbon follows the sequence $3° > 2° > 1° CH_4$ which should also be the case of formation of free radicals.

The above order of stability is in accordance with the stability of free radicals on the basis of delocalization of odd electron. Order of stability of free radical is:
Allyl, benzyl $> 3° > 2° > 1° >$ methyl, vinyl.

**Ex.** What is the percentage of products obtained from monobromination of isobutane?

**Sol.**

<table>
<thead>
<tr>
<th>Product (I)</th>
<th>No. of primary H</th>
<th>reactivity of primary H</th>
<th>$\Delta H_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product (II)</td>
<td>No. of tertiary H</td>
<td>reactivity of tertiary H</td>
<td>$\Delta H_3$</td>
</tr>
</tbody>
</table>

% of product (I) = $\frac{9}{1600+9} \times 100 = 0.56\%$

% of product (II) = $\frac{1600}{1600+9} \times 100 = 99.44\%$

**(b) Nitration:** (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with $-NO_2$ group.
At ordinary temperature, alkanes do not react with HNO$_3$. But reacts with vapours of Conc. HNO$_3$ at 450 °C.

$$R - H + HO - NO_2 \xrightarrow{400-500^\circ C} R - NO_2 + H_2O$$

Since the reaction is carried at high temp. the C–C bonds of alkanes break during the reaction and a mixture of nitroalkanes is formed.

**Example**: $CH_3-CH_3 + HNO_3 \xrightarrow{450^\circ C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Nitro propane</td>
<td>25%</td>
</tr>
<tr>
<td>2-Nitro propane</td>
<td>40%</td>
</tr>
<tr>
<td>Nitro ethane</td>
<td>10%</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>25%</td>
</tr>
</tbody>
</table>

**Mechanism**: (Free Radical substitution)

Step – I

$$HO - NO_2 \xrightarrow{\Delta} OH + NO_2$$

$$R \cdot H + \cdot OH \rightarrow R + H_2O$$

Step – II

$$R + HO - NO_2 \rightarrow R - NO_2 + OH$$

(Product)

Step – III

$$R + NO_2 \rightarrow R - NO_2$$

$$R + OH \rightarrow R - OH$$ (minor)

$$OH + NO_2 \rightarrow HONO_2$$

(c) **Sulphonation**: Replacement of H atom of alkane by –SO$_3$H is known sulphonation.

Alkane react with fuming H$_2$SO$_4$ or oleum (H$_2$S$_2$O$_7$).

The branched lower alkanes and higher alkanes react to give alkane sulphonic acid.

**Example**:

$$CH_3-CH_3 + HO-\text{SO}_3\text{H} \rightarrow CH_3CH_2\text{SO}_3\text{H} + H_2O$$

2-Methyl propane 2-methyl propane–2-sulphonic acid

The reactivity order for sulphonation is tert. H > Sec. H > prim. H

**Mechanism**: (Free Radical substitution)

$$\text{HOSO}_3\text{H} \xrightarrow{400^\circ C} \text{HO}^* + \text{SO}_3\text{H}$$

$$\text{C}_6\text{H}_{13}H + \cdot OH \rightarrow \cdot \text{C}_6\text{H}_{13} + H_2O$$

$$\cdot \text{C}_6\text{H}_{13} + \cdot \text{SO}_3\text{H} \rightarrow \text{C}_6\text{H}_{13}\text{SO}_3\text{H}$$
Lower members such as propane, butane, pentane etc. react with \( \text{SO}_3 \) in vapourphase to form sulphonic acids.

\[
\text{C}_3\text{H}_8 + \text{SO}_3 \rightarrow \text{C}_3\text{H}_7 - \text{SO}_3\text{H}
\]

(d) **Chlorosulphonation (Reed reaction)**: Reaction with a mixture of \( \text{SO}_2 \) and \( \text{Cl}_2 \) at ordinary temp. in the presence of UV light is called chlorosulphonation.

\[
\text{C}_3\text{H}_8 + \text{SO}_2 + \text{Cl}_2 \xrightarrow{\text{UV}} \text{C}_3\text{H}_7\text{SO}_2\text{Cl} + \text{HCl}
\]

Propane sulphonyl Chloride

Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.

\[
\text{C}_3\text{H}_7\text{SO}_2\text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{C}_3\text{H}_7\text{SO}_3\text{H} + \text{HCl}
\]

propane sulphonic acid

\[
\text{C}_3\text{H}_7\text{SO}_3\text{H} + \text{NaCl} \rightarrow \text{C}_3\text{H}_7\text{SO}_3\text{Na} + \text{HCl}
\]

Sodium salt of sulphonic acid (used as detergent)

**Isomerization** :

Unbranched chain alkanes on heating with \( \text{AlCl}_3 + \text{HCl} / 200^\circ\text{C} \) are converted into branched chain alkanes

\[
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{AlCl}_3 + \text{HCl}} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3
\]

n-butane \hspace{1cm} Isobutane

Branched chain alkanes converted to more branched alkane.

\[
\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{AlCl}_3 + \text{HCl}} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\]

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

**Pyrolysis or Cracking or thermal decomposition** :

When alkanes are heated to 500-700\(^\circ\text{C}\) they are decomposed into lower hydrocarbon. This decomposition is called pyrolysis. In petroleum industry it is also termed as cracking. Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

**Example** : \( \text{CH}_4 \xrightarrow{1000^\circ\text{C}} \text{C} + \text{H}_2 \)

\[
\text{CH}_3 - \text{CH}_3 \xrightarrow{500^\circ\text{C} \ \text{absence of air}} \text{CH}_2 = \text{CH}_2 + \text{H}_2
\]

\[
\text{CH}_3\text{CH}_3\text{CH}_3 \xrightarrow{\text{Cracking}} \text{CH}_3\text{CH} = \text{CH}_2 + \text{CH}_4 \text{CH} = \text{CH}_2 + \text{H}_2
\]

n-Butane \xrightarrow{\text{Cracking}} 1-Butene + 2-Butene + Ethane + Ethene + Propene + \( \text{CH}_4 + \text{H}_2 \)

The mechanism of pyrolysis occurs via free radicals.
Hydroforming or dehydrogenation or cyclisation or catalytic reforming or aromatization:

Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on Al₂O₃ support at 500°C aromatic hydrocarbons are formed.

\[
\text{n-hexane} \xrightarrow{\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3 \atop 500^\circ\text{C}} \text{benzene} + 4\text{H}_2
\]

\[
\text{CH}_3(\text{CH}_2)_5 - \text{CH}_3 \xrightarrow{\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3 \atop 500^\circ\text{C}} \text{benzene} + 4\text{H}_2
\]

n-heptane        Toluene

\[
\text{CH}_3(\text{CH}_2)_6 - \text{CH}_3 \xrightarrow{\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3 \atop 500^\circ\text{C}} \text{o-xylene}
\]

n-octane        o-xylene

It provides an excellent method of passing from aliphatic to aromatic series.

Chlorinolysis:

\[
\text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{300-400}^\circ\text{C, Pressure}} \text{C}_2\text{Cl}_6 + \text{CCl}_4 + \text{HCl}
\]

(s)        (l)        (g)
Ex. 1 Which of the following reactions can be employed for getting unsymmetrical alkanes in good yield?
(A) Wurtz reaction  (B) Corey–House reaction  
(C) Both  (D) None of these  Ans.(B)
Sol. Wurtz reaction is suitable for symmetrical alkanes
Ex. 2 Sodium propionate on decarboxylation with sodalime gives
(A) Propane  (B) Ethane  (C) Butane  (D) Pentane  Ans.(B)
Sol. Decarboxylation with soda lime results in the formation of alkane with one carbon less than the starting compounds
Ex. 3 Which of the following alkanes cannot be produced by Kolbe electrolysis of sodium or potassium salts of carboxylic acids?
(A) Methane  (B) Ethane  (C) Butane  (D) Hexane  Ans.(A)
Sol. In Kolbe electrolysis, the alkane is formed by union of two alkyl groups. The alkane formed has, thus, two or more carbon atoms.
Ex. 4 The homolytic fission of hydrocarbon results in the formation of -
(A) Free radicals  (B) Carbocations  
(C) Carbanions  (D) Carbenes.  Ans.(A)
Sol. Homolytic fission results in the formation of free radicals.
Ex. 5 n-Heptane when heated to a temperature of about 800 K under high pressure in the presence of Cr₂O₃/Al₂O₃ catalyst gives -
(A) 1-heptene  (B) 2-Methylhexane  (C) Toluene  (D) Xylene.  Ans.(C)
Sol. \(\text{CH}_3-(\text{CH}_2)₅-\text{CH}_3 \xrightarrow{\cdot 4\text{H}_2} \text{CH}_3\) 
Ex. 6 The reaction conditions leading to the best yield of \(\text{C}_2\text{H}_5\text{Cl}\) are -
(A) \(\text{C}_2\text{H}_6\) (excess) + \(\text{Cl}_2\) \xrightarrow{\text{UV light}} \(\text{B) C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{room temperature}}\)
(C) \(\text{C}_2\text{H}_6 + \text{Cl}_2\) (excess) \xrightarrow{\text{UV light}}  (D) \(\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}\)  Ans.(D)
Sol. \(\text{C}_2\text{H}_6\) should be used in excess, otherwise polychlorination will take place
Ex. 7 Number of isomer which can be theoretically obtained on monochlorination of 2-methylbutane is -
(A) 1  (B) 2  (C) 3  (D) 4  Ans.(D)
Sol. \(\text{CH}_3\) – \(\text{CH} - \text{CH}_2 - \text{CH}_3\)
Ex. 8 Complete oxidation of ethane yields -
(A) Ethanol  (B) Ethanoic acid  (C) Ethanal  (D) \(\text{CO}_2\) and \(\text{H}_2\text{O}\)  Ans.(D)
Sol. \(2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}\)
Ex. 9 In iso-pentane, the H atom that can be most easily substituted is on -

\[
\begin{array}{c}
1 \\
\downarrow \\
CH_3-CH-CH_2-CH-CH_3
\end{array}
\]

(A) C-1  (B) C-2  (C) C-3  (D) C-4  \text{ Ans. (B)}

Sol. Ease of substitution of various types of H atoms is \(3^0 > 2^0 > 1^0\).

Ex. 10 8 c.c. of gaseous hydrocarbon requires 40 c.c. of \(O_2\) for complete combustion. Identify hydrocarbon.

Sol. Volume of hydrocarbon = 8 c.c.; Volume of \(O_2\) = 40 c.c.

Formula No. 1, \[\frac{8}{40} = \frac{2}{3n+1}\] (For alkane)

\[\frac{1}{5} = \frac{2}{3n+1}\] or \(3n + 1 = 10\) or \(3n = 10 - 1 = 9\) \(\therefore n = 3\)

The value of \(n\) comes in whole number from 1st formula it means hydrocarbon is Alkane and it is of 3C atom.

\(\therefore\) Hydrocarbon is \(C_3H_8\) (Propane)

Ex. 11 10 mL of a mixture of \(CH_4\) and \(C_3H_8\) requires 41 mL of oxygen for complete combustion. What is the volume of \(CH_4\) and \(C_3H_8\) in the mixture.

Sol. Suppose the volume of \(CH_4\) in \((CH_4 + C_3H_8)\) mix = \(x\) c.c.

\(=\) Volume of \(C_3H_8\) will be = \(10 - x\) c.c.

For \(CH_4\) \(2CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O\)

\(\therefore\) 1 Vol. of \(CH_4\) requires 2 vol. of \(O_2\) for complete combustion

\(\therefore\) \(x\) c.c. of \(CH_4\), 2x c.c. of \(O_2\)

For \(C_3H_8\) \(C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O\)

\(\therefore\) 1 volume of \(C_3H_8\) requires 5 ml of \(O_2\) for complete combustion

\(\therefore\) \((10 - x)\) c.c. of \(C_3H_8\) requires \(5(10 - x)\) c.c. of \(O_2\)

Total Volume of \(O_2\) = \(2x + 5(10 - x)\) it is equivalent to 41

(according to question)

\(\therefore\) \(2x + 5(10 - x) = 41\)

\(\therefore\) \(x = 3\) c.c.

\text{Volume of CH}_4 \text{ is 3 c.c. and volume of C}_3H_8 \text{ is 7 c.c.}

Ex. 12 If 5 g \(C_2H_5I\) reacts with Na (Metallic) in presence of ether, and the yield is 60% then how many grams of n-butane will you get.

Sol. \(2C_2H_5I + 2Na \rightarrow C_4H_{10} + 2NaI\)

Molecular weight of \(2C_2H_5I = 24 + 5 + 127 = 156\)

Molecular weight of \(C_4H_{10} = 48 + 10 = 58\)

Two molecule of \(C_2H_5I\) are taking part in above reaction.
\[
\begin{align*}
\therefore & \quad \text{We get } 58 \text{ g of } C_4H_{10} \text{ from } 2 \times 156 \text{ g of } C_2H_5I \\
\therefore & \quad \text{We get } \frac{58}{2 \times 156} \text{ g } C_4H_{10} \text{ from } 1 \text{ g of } C_2H_5I \\
\therefore & \quad \text{We get } \frac{58 \times 5}{2 \times 156} \text{ g } C_4H_{10} \text{ from } 5 \text{ g of } C_2H_5I \\
\end{align*}
\]

yield is 60%

So the quantity of \( C_4H_{10} \) will be \( \frac{58 \times 5}{2 \times 156} \times \frac{60}{100} \text{ g} = 0.55 \text{ g} \)

**Ex.13** The density of one hydrocarbon at N.T.P. is 1.964 g/litre. Identify the hydrocarbon.

**Sol.**

Molecular weight of Hydrocarbon

= density of 1 lit. x 22.4 = 1.964 x 22.4 = 44

So Molecular weight of hydrocarbon = 44

So the hydrocarbon is \( C_3H_8 \) (Propane).