# Organic Chemistry
CHpter 1

1.1 Hydrocarbons

Hydrocarbons are organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes, aliphatic and aromatic. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.).
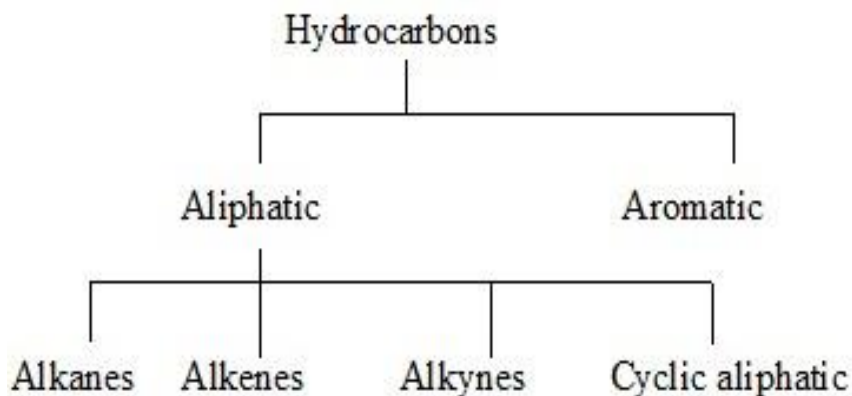

The simplest member of the alkane family and one of the simplest of all organic compounds is methane, CH_4.
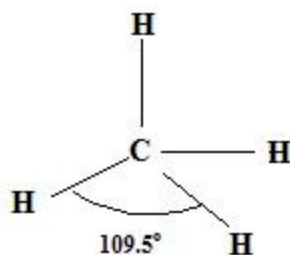
For each of these orbitals to overlap most effectively the spherical *s* orbital of a hydrogen atom, and thus to form the strongest bond, each hydrogen nucleus must be located at a corner of this tetrahedron.

We shall ordinarily write methane with a dash to represent each pair of electrons shared by carbon and hydrogen (I). To focus our attention on individual electrons, we may sometimes indicate a pair of electrons by a pair of dots (II).
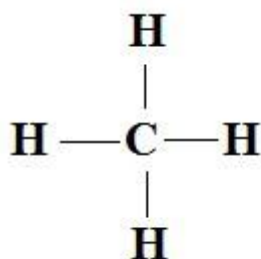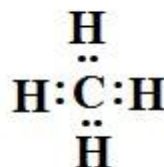
I   II

1.2 Physical Properties of Methane

The unit of such a non-ionic compound, whether solid, liquid, or gas, is the molecule. Because the methane molecule is highly symmetrical, the polarities of the individual carbon-hydrogen bonds cancel out; as a result, the molecule itself is non-polar.

Attraction between such non-polar molecules is limited to van der Waals forces; for such small molecules, these attractive forces must be tiny compared with the enormous forces between, say, sodium and chloride ions. It is not surprising, then, that these attractive forces are easily overcome by thermal energy, so that melting and boiling occur at very low temperature: m.p. -183°C, b.p. -161.5°C. (Compare these values with the corresponding ones for sodium chloride: m.p. 801°C, b.p. 1413°C). As a consequence, methane is a gas at ordinary temperatures.

Methane is colorless and, when liquefied, is less dense than water (relative density 0.4). It is only slightly soluble in water, but very soluble in organic liquids.

1.3 Source of Methane

Methane is an end product of the anaerobic (without air) decay of plants, that is, of the breakdown of certain very complicated molecules. It is the major constituent (up to 97%) of natural gas. It is the dangerous firedamp of the coal mine, and can be seen as marsh gas bubbling to the surface of swamps.

It can be separated very pure from other constituents of natural gas by fractional distillation.
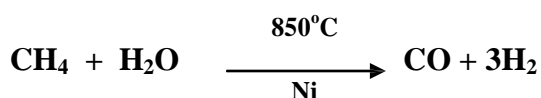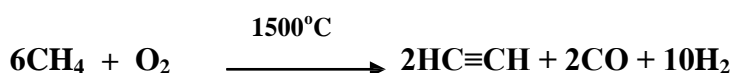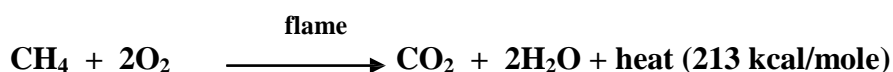
1.4 Reactions of Methane

In its chemical properties as in its physical properties, methane sets the pattern for the alkane family. Typically, it reacts only

with highly reactive substances, or under very vigorous conditions, which, as we shall see. At this point we shall take up only its oxidation: by oxygen, by halogens, and even by water.

1- Oxidation. Heat of Combustion

Combustion to carbon dioxide and water is characteristic of organic compounds; under special conditions it is used to determine their content of carbon and hydrogen.

Combustion of methane is the principal reaction taking place during the burning of natural gas.

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O + \text{heat (213 kcal/mole)}$$

$$6CH_4 + O_2 \xrightarrow{1500^oC} 2HC \equiv CH + 2CO + 10H_2$$

$$CH_4 + H_2O \xrightarrow[\text{Ni}]{850^oC} CO + 3H_2$$

2- Halogenation

$$CH_4 \xrightarrow{X_2} CH_3X \xrightarrow[+ HX]{X_2} CH_2X_2 \xrightarrow[+ HX]{X_2} CHX_3 \xrightarrow[+ HX]{X_2} CX_4 \quad \begin{array}{c}\text{Heat or light} \\ \text{required}\end{array}$$
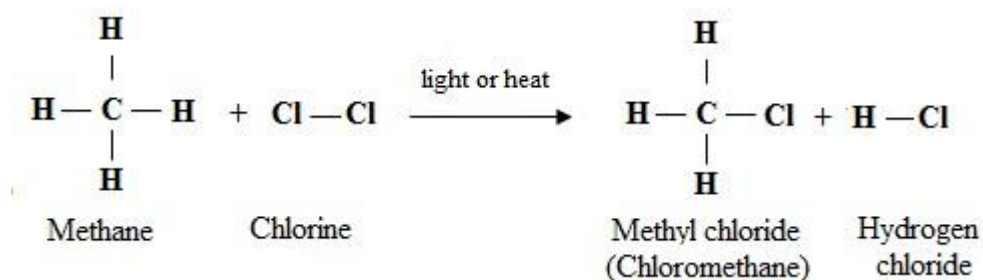
Reactivity of X_2 $F_2 > Cl_2 > Br_2 \; (> I_2)$
                                          Unreactive
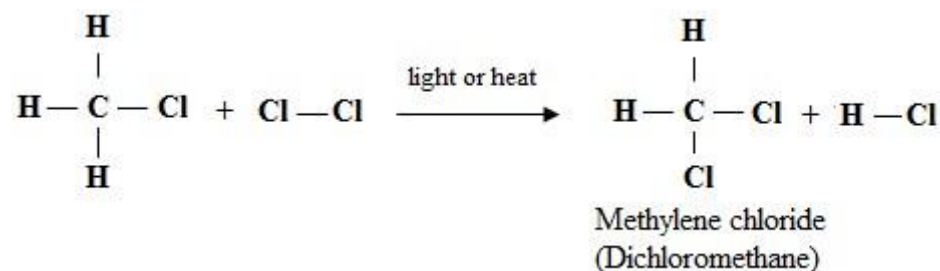
Chlorination: A Substitution Reaction

Under the influence of ultraviolet light or at a temperature of 250-400°C a mixture of the two gases, methane and chlorine, reacts vigorously to yield hydrogen chloride and a compound of formula CH_3Cl. We say that methane has undergone **chlorination**, and we call the product, CH_3Cl *chloromethane* or *methyl chloride* (CH_3 = **methyl**).

Chlorination of methane may yield any one of four organic products, depending upon the stage to which the reaction is carried.

Chlorination is a typical example of a broad class of organic reactions known as *substitution*. A chlorine atom has been substituted for a hydrogen atom of methane, and the hydrogen atom thus replaced is found combined with a second atom of chlorine.

$$
\begin{array}{cccc}
& \text{H} & & \text{H} \\
& | & \text{light or heat} & | \\
\text{H}-\text{C}-\text{H} + \text{Cl}-\text{Cl} & \xrightarrow{\hspace{2cm}} & \text{H}-\text{C}-\text{Cl} + \text{H}-\text{Cl} \\
& | & & | \\
& \text{H} & & \text{H} \\
\text{Methane} & \text{Chlorine} & \text{Methyl chloride} & \text{Hydrogen} \\
& & \text{(Chloromethane)} & \text{chloride}
\end{array}
$$

The methyl chloride can itself undergo further substitution to form more hydrogen chloride and the compound CH_2Cl_2, *dichloromethane* or *methylene chloride* (CH_2 = **methylene**).

$$
\begin{array}{cccc}
& \text{H} & & \text{H} \\
& | & \text{light or heat} & | \\
\text{H}-\text{C}-\text{Cl} + \text{Cl}-\text{Cl} & \xrightarrow{\hspace{2cm}} & \text{H}-\text{C}-\text{Cl} + \text{H}-\text{Cl} \\
& | & & | \\
& \text{H} & & \text{Cl} \\
& & & \text{Methylene chloride} \\
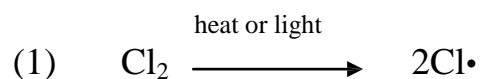& & & \text{(Dichloromethane)}
\end{array}
$$

In a similar way, chlorination may continue to yield $CHCl_3$, *tri chloro methane or chloroform*, and CCl_4, *tetra chloromethane or carbon tetrachloride*.
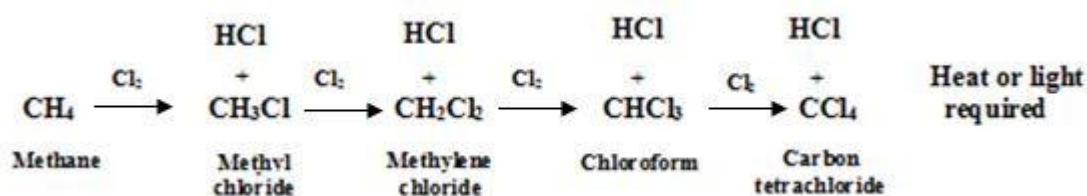

Mechanism: Free radical reaction

The mechanism that is generally accepted is shown in the following equations:

(1) $\quad Cl_2 \xrightarrow{\text{heat or light}} 2Cl\bullet$

(2) $\quad Cl\bullet + CH_4 \longrightarrow HCl + CH_3\bullet$

(3) $\quad CH_3\bullet + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$
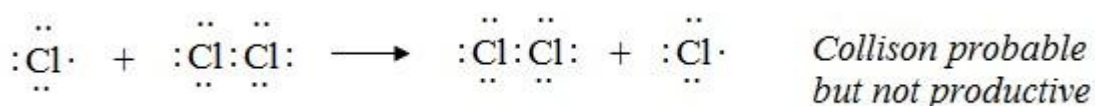
then (2), (3), (2), (3), etc.

The first step is the breaking of a chlorine molecule into two chlorine atoms. Like the breaking of any bond, this requires energy, *the bond dissociation energy*, in this case 58 kcal/mol as heat or light.
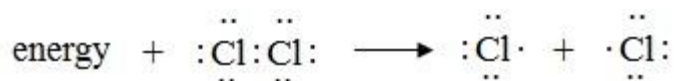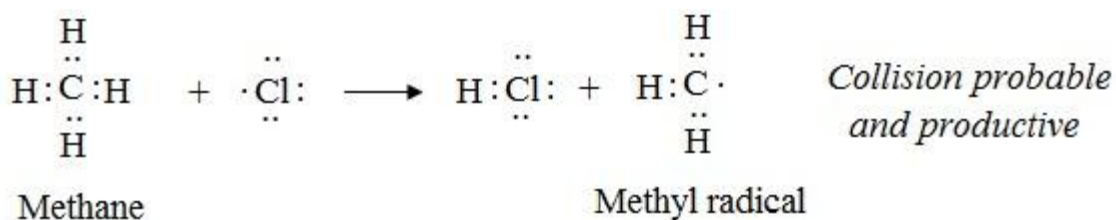

The chlorine molecule undergoes *homolysis. An atom or group of atoms possessing an odd (unpaired) electron is called a* **free radical**.

The free radical is extremely reactive because of its tendency to gain an additional electron and thus have complete octet; from another point of view, energy was supplied to each chlorine atom during the cleavage of the chlorine molecule, and this energy-rich particle tends to lose energy by the formation of a new chemical bond.

To form a new chemical bond, that is, to react, the chlorine atom must collide with some other molecule or atom. What is it most likely to collide with? Obviously, it is most likely to collide with the particles that are present in the highest concentration: chlorine molecules and methane molecules. Collision with another chlorine atom is quite unlikely simply because there are few of these reactive, short-lived particles around at any time. Of the likely collisions, that with a chlorine molecule cause no change; reaction may occur, but it can result only in the exchange of one chlorine atom for another.

$$:\overset{..}{\underset{..}{Cl}}\cdot \ + \ :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \longrightarrow :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \ + \ :\overset{..}{\underset{..}{Cl}}\cdot$$ *Collison probable but not productive*
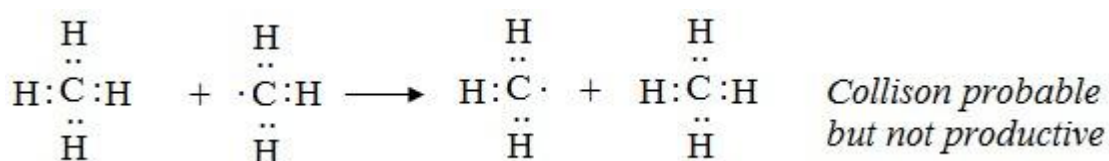
Collision of a chlorine atom with a methane molecule is both *probable* and *productive*. The chlorine atom abstracts a hydrogen atom, with one electron, to form a molecule of a hydrogen chloride:

$$H:\overset{\overset{\textstyle H}{..}}{\underset{\underset{\textstyle H}{..}}{C}}:H \ + \ \cdot\overset{..}{\underset{..}{Cl}}: \longrightarrow H:\overset{..}{\underset{..}{Cl}}: \ + \ H:\overset{\overset{\textstyle H}{..}}{\underset{\underset{\textstyle H}{..}}{C}}\cdot$$ *Collision probable and productive*

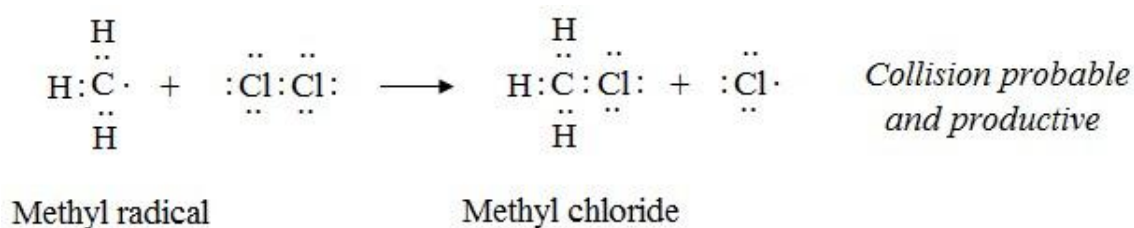Methane   Methyl radical

Now the methyl group is left with an odd, unpaired electron; the carbon atom has only seven electrons in its valence shell. One free radical, the chlorine atom, has been consumed, and a new one, the methyl radical, $CH_3\cdot$, has been formed in its place. This is step (2) in the mechanism.

Now, what is this methyl radical most likely to do? Like the chlorine atom, it is extremely reactive, and for the same reason: the tendency to complete its octet, to lose energy by forming a new bond. Again, collisions with chlorine molecules or methane molecules are probable ones, not collisions with the relatively scarce chlorine atoms or methyl radicals. But collision with a methane molecule could at most result only in the exchange of some methyl radical for another:

$$
\begin{array}{ccccccc}
& H & & H & & H & & H \\
& \ddot{} & & \ddot{} & & \ddot{} & & \ddot{} \\
H:\!C\!:\!H & + & \cdot\dot{C}\!:\!H & \longrightarrow & H:\!C\cdot & + & H:\!C\!:\!H \\
& \ddot{} & & \ddot{} & & \ddot{} & & \ddot{} \\
& H & & H & & H & & H
\end{array}
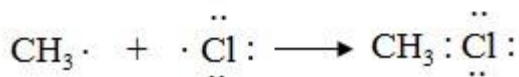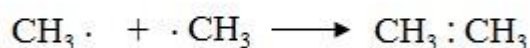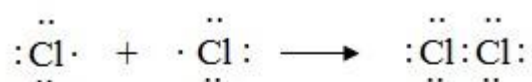$$

Collison probable but not productive

The collision of methyl radical with a chlorine molecule is, then, the important one. The methyl radical abstracts a chlorine atom, with one of the bonding electrons, to form a molecule of methyl chloride:

$$
\begin{array}{ccccccc}
H & & & & H & & \\
\ddot{} & & \ddot{}\ \ \ddot{} & & \ddot{}\ \ \ddot{} & & \ddot{} \\
H:\!C\cdot & + & :\!Cl\!:\!Cl\!: & \longrightarrow & H:\!C\!:\!Cl\!: & + & :\!Cl\cdot \\
\ddot{} & & \ddot{}\ \ \ddot{} & & \ddot{}\ \ \ddot{} & & \ddot{} \\
H & & & & H & &
\end{array}
$$

Collision probable and productive

Methyl radical   Methyl chloride

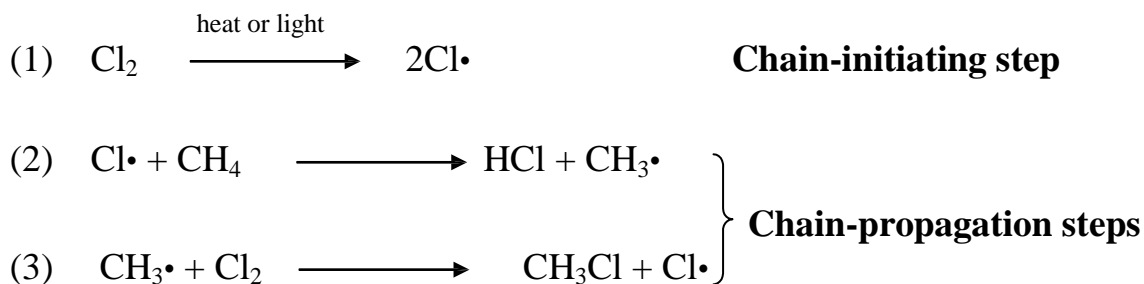The other product is a chlorine atom. This is step (3) in the mechanism.

Here again the consumption of one reactive particle has been accompanied by the formation of another. The new chlorine atom attacks methane to form a methyl radical, which attacks a chlorine molecule to form a chlorine atom, and so the sequence is repeated over and over. Each step produces not only a new reactive particle but also a molecule of product: methyl chloride or hydrogen chloride.

This process cannot, however, go on forever. As saw earlier, union of two short-lived, relatively scarce particles is not likely; but every so often it does happen, and when it does, this particular sequence of reactions stops. Reactive particles are consumed but not generated.

$$:\ddot{C}l\cdot \;+\; \cdot \ddot{C}l: \;\longrightarrow\; :\ddot{C}l:\ddot{C}l:$$

$$CH_3\cdot \;+\; \cdot CH_3 \;\longrightarrow\; CH_3:CH_3$$

$$CH_3\cdot \;+\; \cdot \ddot{C}l: \;\longrightarrow\; CH_3:\ddot{C}l:$$
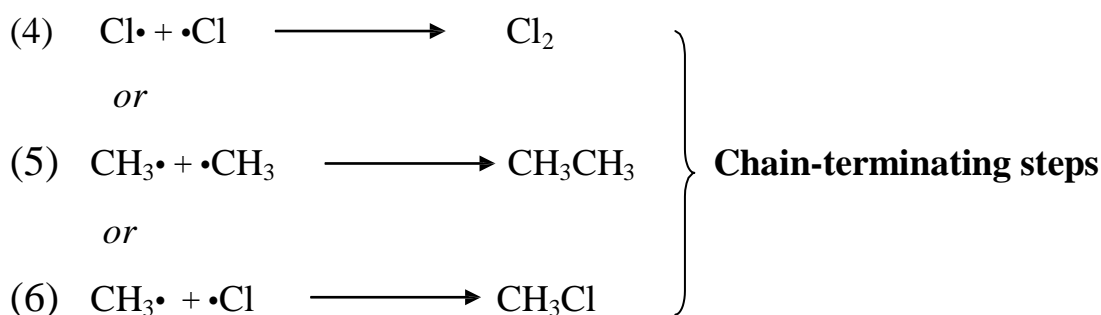
1.5 Chain Reaction

The chlorination of methane is an example of a **chain reaction**, *a reaction that involves a series of steps, each of which generates a reactive substance that brings about the next step.* While chain reactions may vary widely in their details, they all have certain fundamental characteristics in common.

$$\text{(1)} \quad Cl_2 \quad \xrightarrow{\text{heat or light}} \quad 2Cl\bullet \qquad \qquad \textbf{Chain-initiating step}$$

$$\text{(2)} \quad Cl\bullet + CH_4 \quad \longrightarrow \quad HCl + CH_3\bullet$$

$$\text{(3)} \quad CH_3\bullet + Cl_2 \quad \longrightarrow \quad CH_3Cl + Cl\bullet$$

Chain-propagation steps

then (2), (3), (2), (3), etc., until finally:

$$\text{(4)} \quad Cl\bullet + \bullet Cl \quad \longrightarrow \quad Cl_2$$

or

$$\text{(5)} \quad CH_3\bullet + \bullet CH_3 \quad \longrightarrow \quad CH_3CH_3$$

or

$$\text{(6)} \quad CH_3\bullet + \bullet Cl \quad \longrightarrow \quad CH_3Cl$$

Chain-terminating steps

First in the chain of reactions is a **chain-initiating step**, in which energy is absorbed and a reactive particle generated; in the present reaction it is the cleavage of chlorine into atoms (step 1).

There are one or more **chain-propagating steps**, each of which consumes a reactive particle and generates another; here they are the reaction of chlorine atoms with methane (step2), and of methyl radical with chlorine (step 3).

Finally, there are **chain-terminating steps**, in which reactive particles are consumed but not generated; in the chlorination of methane these would involve the union of two of the reactive particles, or the capture of one of them by the walls of the reaction vessel.

1.6 Inhibitors

A small amount of oxygen slows down the reaction for a period of time, which depends upon the amount of oxygen, after which the reaction proceeds normally.

Oxygen is believed to react with a methyl radical to form a new free radical:

$$CH_3\cdot + O_2 \longrightarrow CH_3\text{-O-O}\cdot$$
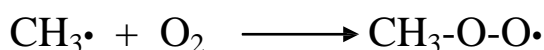
The $CH_3OO\cdot$ radical is much less reactive than the $CH_3\cdot$ radical, and can do little to continue the chain. By combining with a methyl radical, one oxygen molecule breaks a chain, and thus prevents the formation of thousands of molecules of methyl chloride; this, of course, slows down the reaction tremendously. After all the oxygen molecules present have combined with methyl radicals, the reaction is free to proceed at its normal rate.

A substance that slows down or stops a reaction even though present in small amount is called an **inhibitor**. *The period of time during which inhibition lasts, and after which the reaction proceeds normally, is called the inhibition period.*
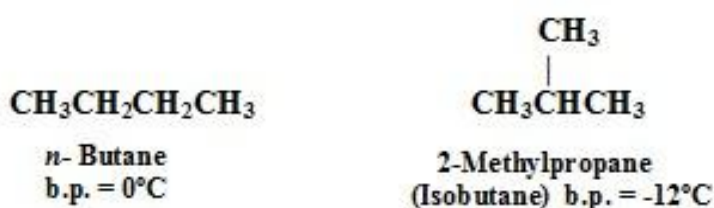
Organic Chemistry

Alkanes

1.7 Introduction

The atoms of the alkane hydrocarbons are joined to one another only through single bonds. The carbon-carbon single bond is of low reactivity. The general formula is $\mathbf{C_nH_{2n+2}}$, where n is the number of carbon atoms. For example, if the molecule contains three carbon atoms, $n = 3$ and $(2n + 2) = 8$, the formula is C_3H_8. If the molecule contains ten carbon atoms, $n = 10$ and $(2n + 2) = 22$, the formula is $C_{10}H_{22}$. Each member of the alkanes series differ from the preceding and the succeeding members by CH_2 atoms, and each carbon atom of an alkane molecule is covalently bonded to for other atoms. The first ten members of this series are listed in Table 3.1.

Table1.1 The first ten member of the alkanes

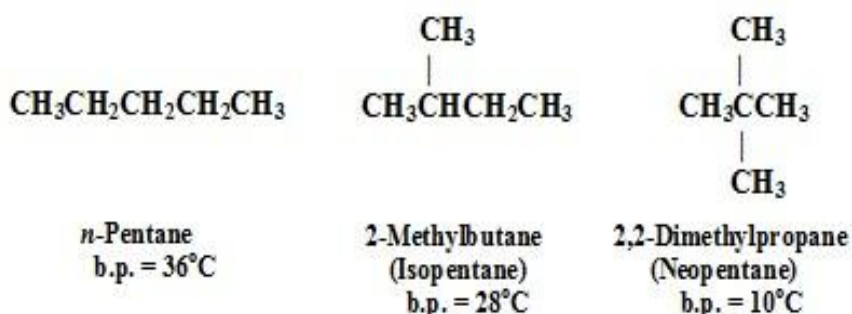| General formula	Structure	Name
CH_4	CH_4	Methane
C_2H_6	CH_3CH_3	Ethane
C_3H_8	$CH_3CH_2CH_3$	Propane
C_4H_{10}	$CH_3(CH_2)_2CH_3$	Butane
C_5H_{12}	$CH_3(CH_2)_3CH_3$	Pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	Hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	Heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	Octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	Nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Decane

1.8 Isomerism in Alkanes

Compounds that have the same molecular formula but different structural formulas were defined as isomers. Isomeric compounds are not possible in the alkanes series until we reach the molecular formula C_4H_{10}. There are two arrangements for the formula C_4H_{10}, and two isomers are known as shown:

$$CH_3CH_2CH_2CH_3$$

n- Butane
b.p. = 0°C

$$\underset{\underset{CH_3}{|}}{CH_3CHCH_3}$$

2-Methylpropane
(Isobutane) b.p. = -12°C

(C_4H_{10} isomers)

They differ both chemically and physically from one another. Experimentally, they can be identified by differences in their melting points, boiling points, densities, solubilities and some other features.

For the formula C_5H_{12}, three isomers have been found, as shown:
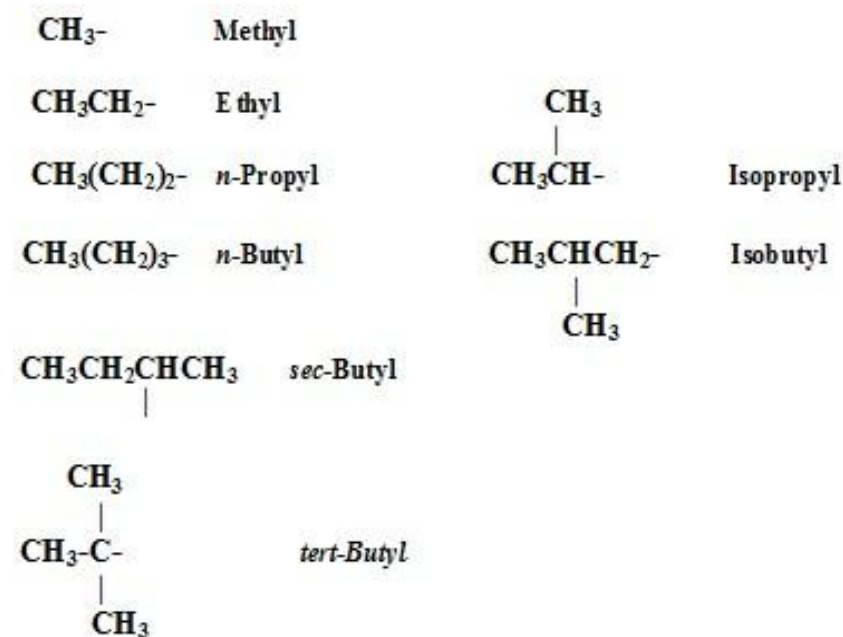
$$CH_3CH_2CH_2CH_2CH_3$$

$$\underset{\underset{CH_3}{|}}{CH_3CHCH_2CH_3}$$

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3CCH_3}}$$

n-Pentane
b.p. = 36°C

2-Methylbutane
(Isopentane)
b.p. = 28°C

2,2-Dimethylpropane
(Neopentane)
b.p. = 10°C

(C_5H_{12} isomers)

The difference in the structure is due to different arrangements of the carbon atoms.

1.9 Alkyl Groups

Any branch consisting of only carbon and hydrogen and only single bond is called **alkyl group**. The general formula for an alkyl group is C_nH_{2n+1}, since it contains one less hydrogen than the parent alkane, C_nH_{2n+2}.

CH_3- Methyl

CH_3CH_2- Ethyl

$CH_3(CH_2)_2-$ *n*-Propyl

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{CH}-\quad\text{Isopropyl}$$

$CH_3(CH_2)_3-$ *n*-Butyl

$$CH_3CHCH_2-\quad\text{Isobutyl}$$
$$\underset{CH_3}{|}$$

$$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}CH_3\quad\text{sec-Butyl}$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\quad\text{tert-Butyl}$$

Beyond butyl the number of groups becomes so great that it is impracticable to designate them all by various prefixes. Even though limited, this system is so useful for the small groups just described.

However large the group concerned, the prefix *n-* is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon.
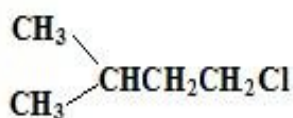
$$CH_3CH_2CH_2CH_2CH_2Cl \qquad CH_3(CH_2)_4CH_2Cl$$
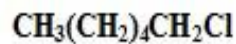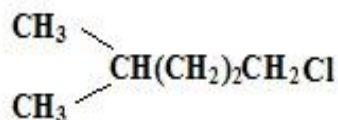
n-Pentyl chloride   *n*-Hexyl chloride

The prefix *iso-* is used to designate any alkyl group (of six carbons or fewer) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain.

Isopentyl chloride   Isohexyl chloride

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply.

1.10 Nomenclature

A.Common names:

The prefixes *n-*, *iso-*,and *neo-* are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required. However, the prefix *n-* has been retained for any alkane, no matter how large, in which all carbon form a continuous chain with no branching:
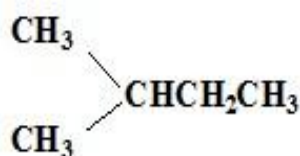
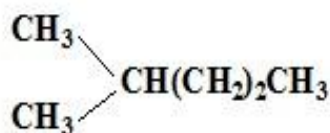$$CH_3CH_2CH_2CH_2CH_3 \qquad CH_3(CH_2)_4CH_3$$
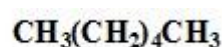
n-Pentane   *n*-Hexane

An *isoalkane* is a compound of six carbons or fewer in which all carbons except one from a continuous chain and that one carbon is attached to the next-to-end carbon:

In naming any other of the higher alkanes, we make use of the IUPAC system.

B. (UPAC system):

Essentially the rules of the IUPAC system (International Union of Pure and Applied Chemistry) are:

1- Use the ending (*–ane*) for all alkanes.

2- Attach a prefix to this, to specify the number of carbon atoms in the longest continuous chain in the molecule. The prefixes through C-10 are:

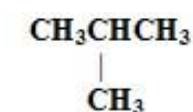|			
Meth-	1C	Hex-	6C
Eth-	2C	Hept-	7C
Prop-	3C	Oct-	8C
But-	4C	Non-	9C
Pent-	5C	Dec-	10C

3- Pick the longest continuous chain in a branched chain alkane as the basis for the name.

4- To specify which carbon atom of the parent chain holds a branch, number the parent chain from whichever end of its chain reaches the first branch with the lower number.

5- Determine the correct name for each branch or any other group or atom such as a halogen atom.

6- If the same group occurs more than ones as a side chain, indicate this by the prefix di-, tri-, tetra-, etc., to show how many of these groups are, and indicate by various numbers the positions of each group.

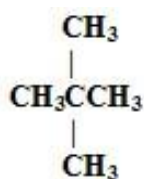7- If there are several different groups attached to the parent chain, name them in alphabetical order.

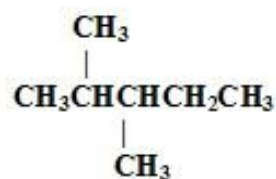CH_3CHCH_3
|
CH_3

Methylpropane
(Isobutane)

$CH_3(CH_2)_3CH_3$

Pentane
(*n*-Pentane)

CH_3
$\diagdown$
$\quad CH(CH_2)_2CH_3$
$\diagup$
CH_3

2-Methylpentane
(Isohexane)

CH_3
$\diagdown$
$\quad CHCH_2CH_3$
$\diagup$
CH_3

(Isopentane)

$$CH_3$$
$$|$$
$$CH_3CCH_3$$
$$|$$
$$CH_3$$

Dimethylpropane
(Neopentane)

$$CH_3$$
$$|$$
$$CH_3CHCHCH_2CH_3$$
$$|$$
$$CH_3$$

2,3-Dimethylpentane

$$CH_3CHCH_3$$
$$|$$
$$CH_3$$

Methylpropane
(Isobutane)

$$CH_3$$
$$|$$
$$CH_3CHCH_2CCH_3$$
$$|\qquad|$$
$$CH_3\quad CH_3$$

2,2,4-Trimethylpentane

$$CH_3\ CH_2CH_3$$
$$|\quad|$$
$$CH_3-CH-C-CH_2-CH_2-CH_3$$
$$|$$
$$CH_3$$
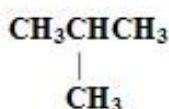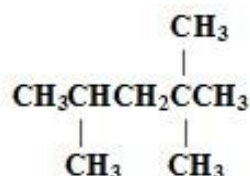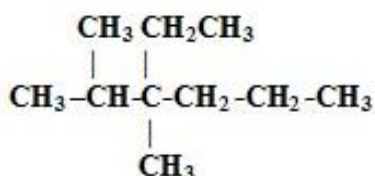
3-Ethyl-2,3-dimethylhexane

$$CH_3$$
$$|$$
$$CH_2$$
$$|$$
$$CH_3-CH_2-CH_2-CH-\ CH-\ C-\ CH_2-CH_3$$
$$|\qquad|\quad\ |$$
$$CH\quad CH_3\ CH_2$$
$$\diagup\ \diagdown\qquad\quad |$$
$$CH_3\ \ CH_3\qquad CH_3$$
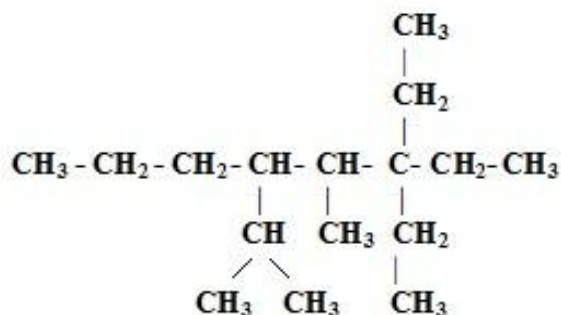
3,3-Diethyl-5-isopropyl-4-methyloctane

The alkyl halides which appear so often in the alkane chemistry are named *haloalkanes*; that is, halogen is simply treated as a side chain. We first name the alkane as though no halogen were present, and then add *fluoro, chloro, bromo,* or *iodo*, together with any needed number and prefixes.

$$CH_3Cl$$

Chloromethane
(Methyl chloride)

$$CH_3CH_2Br$$

Bromoethane
(Ethyl bromide)

$$CH_3CHCH_3$$
$$|$$
$$Cl$$

2-Chloropropane
(Isopropyl chloride)

$$CH_3CH_2CH_2CH_2Cl$$

1-Chlorobutane
(Butyl chloride)

$$CH_3CH_2CHCH_3$$
$$|$$
$$Br$$

2-Bromobutane

$$CH_3$$
$$|$$
$$CH_3-C-Cl$$
$$|$$
$$CH_3$$

2-Chloro-2-methylpropane

$$CH_3$$
$$|$$
$$CH_3CH_2CCHCH_3$$
$$|\ |$$
$$Cl\ Cl$$

2,3-Dichloro-3-methylpentane

$$Cl_2CH - CHCl_2$$

1,1,2,2-Tetrachloroethane

$$CH_3$$
$$|$$
$$CH_3CHCH_2I$$

1-Iodo-2-methylpropane

$$CH_3$$
$$|$$
$$CH_3-C-CH_3$$
$$|$$
$$F$$

2-Fluro-2-methylpropane

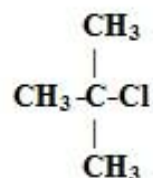$$Br\ NO_2$$
$$|\ \ |$$
$$CH_3CHCHCH_3$$

2-Bromo-3-nitrobutane

$$NO_2$$
$$|$$
$$BrCH_2CH_2CHCH_3$$

1-Bromo-3-nitrobutane

The names shown beneath the structural formulas are systematic names. Those shown in parentheses are common names.

1.11 Physical Properties of Alkanes:

The alkane molecule is held together entirely by covalent bonds, which either join two atoms of the same kind and hence are non-polar, or join atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar. The forces holding non-polar molecules are limited to van der Waals forces, they are weak and of very short range. They act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule and hence the larger its surface area the stronger the intermolecular forces.

The boiling points and the melting points of the alkanes rise as the number of the carbons increases. That is because boiling and melting require overcoming the intermolecular forces of liquid and a solid; the boiling point and melting points rise because these intermolecular forces increase as the molecules get larger.

The branching, lower the boiling points because with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the

result that the intermolecular forces become weaker and are overcome at a lower temperature.
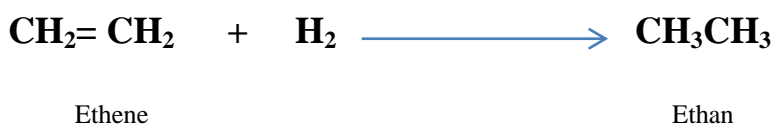
In agreement with the rule of thumb, "like dissolves like", alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as a solvent, the liquid alkanes dissolves compounds of low polarity and do not dissolve compounds of high polarity.

The relative density increases with size of the alkanes, and all alkanes are less dense than water. In general, to be denser than water a compound must contain a heavy atom like Br or I, or several atoms like Cl.

1.12 Preparation of Alkanes:

1- Hydrogenation of alkenes

Hydrogenation is the most useful method for preparing alkanes. It is the addition of H_2 to a multiple bond.

$$C_nH_{2n} \xrightarrow{\text{H}_2 + \text{Pt,Pd or Ni}} C_nH_{2n+2}$$

Alkene   **Alkane**

$$CH_2= CH_2 \quad + \quad H_2 \longrightarrow CH_3CH_3$$

Ethene   Ethan

$$CH_3CH=CH_2 + H_2 \longrightarrow CH_3CH_2CH_3$$

Propene   Propane
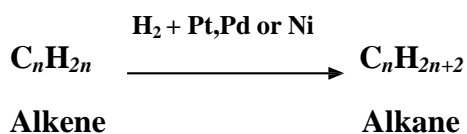
2-Reduction of alkyl halides:

(a) Hydrolysis of Grignard reagent:

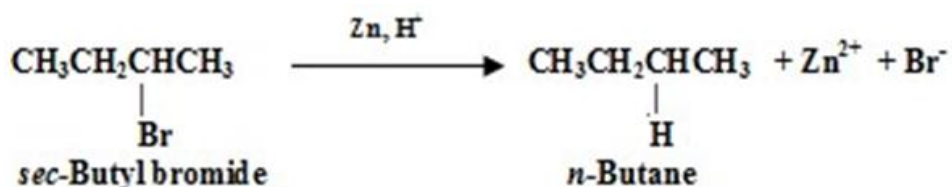When a solution of an alkyl halide in dry ethyl ether, is allowed to stand over turnings of metallic magnesium, the resulting solution is known as a Grignard reagent. The reaction with water gives an alkane.

$$R-X + Mg \longrightarrow \underset{\substack{\text{Grignard}\\\text{Reagent}}}{R-Mg\,X} \xrightarrow{H_2O} R-H + Mg(OH)X$$

(b) Reduction by metal and acid:

Reduction of an alkyl halide with metal and acid, involves the replacement of a halogen atom by a hydrogen atom. The product is an alkane.

$$R-X + Zn + H^+ \longrightarrow R-H + Zn^{2+} + X^-$$

$$CH_3CH_2X + Zn + H^+ \longrightarrow CH_3CH_3 + Zn^{2+} + X^-$$

$$\underset{\substack{|\\Br\\sec\text{-Butyl bromide}}}{CH_3CH_2CHCH_3} \xrightarrow{Zn,\ H^+} \underset{\substack{|\\H\\n\text{-Butane}}}{CH_3CH_2CHCH_3} + Zn^{2+} + Br^-$$

1.13 Reactions of Alkanes:

Alkanes are generally not considered to be very reactive substance. However, under suitable conditions they are do react.

1- Halogenation

2- Oxidation

1- Halogenation

Alkanes react with the halogens (except iodine) to form substitution products.

$$-\overset{|}{\underset{|}{C}}-H \;+\; X_2 \quad\xrightarrow[\text{or light}]{250\text{-}400^\circ}\quad -\overset{|}{\underset{|}{C}}-X \;+\;HX$$

Usually a mixture

Reactivity X_2: $Cl_2 > Br_2$

H_2: $3^\circ > 2^\circ > 1^\circ > 2^\circ \; CH_3\text{-}H$

$$CH_3CH_3 \;+\; \xrightarrow[\text{light, 25}^\circ C]{Cl_2} CH_3CH_2\text{-}Cl$$
Ethane   Chloroethane
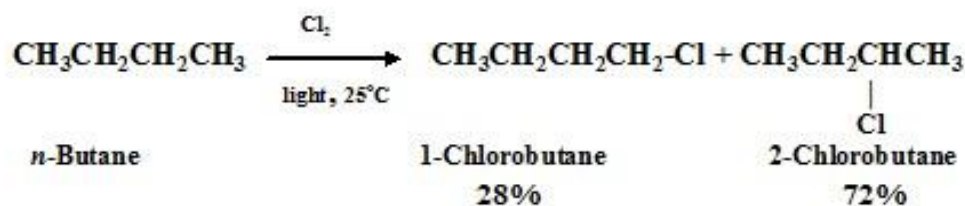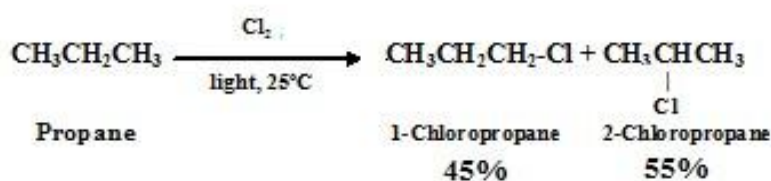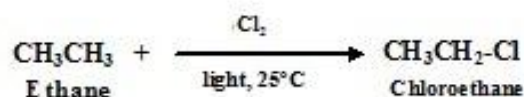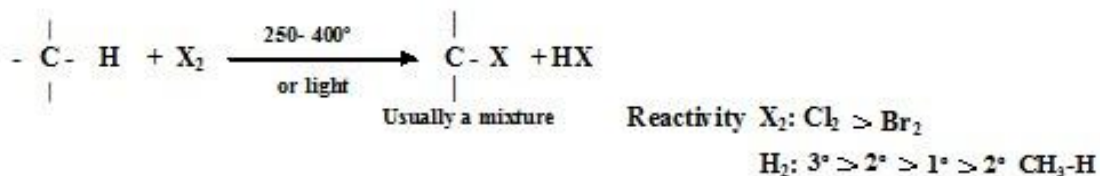
$$CH_3CH_2CH_3 \xrightarrow[\text{light, 25}^\circ C]{Cl_2} CH_3CH_2CH_2\text{-}Cl \;+\; CH_3\underset{\underset{Cl}{|}}{CH}CH_3$$

Propane   1-Chloropropane   2-Chloropropane

                                45%   55%

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, 25}^\circ C]{Cl_2} CH_3CH_2CH_2CH_2\text{-}Cl \;+\; CH_3CH_2\underset{\underset{Cl}{|}}{CH}CH_3$$

n-Butane   1-Chlorobutane   2-Chlorobutane

                                28%   72%

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow[250\text{-}400^\circ C]{Cl_2} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Cl \;+\; CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

Isobutane   Isobutyl chloride   *tert*-Butyl chloride

                                64%   36%

2- Oxidation (Combustion)

Although alkanes are resistant to attack by oxidizing agents generally, they all undergo combustion in air or oxygen, the products of complete oxidation being carbon dioxide and water.

$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} n\ CO_2 + (n+1)\ H_2O$$

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow{\text{flame}} 5CO_2 +$$