Al-Mustaqbal University

Department of Medical Laboratory Techniques

Subject: - General Chemistry (1) (2023-2024) lecture (2)

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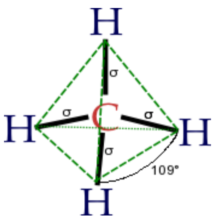
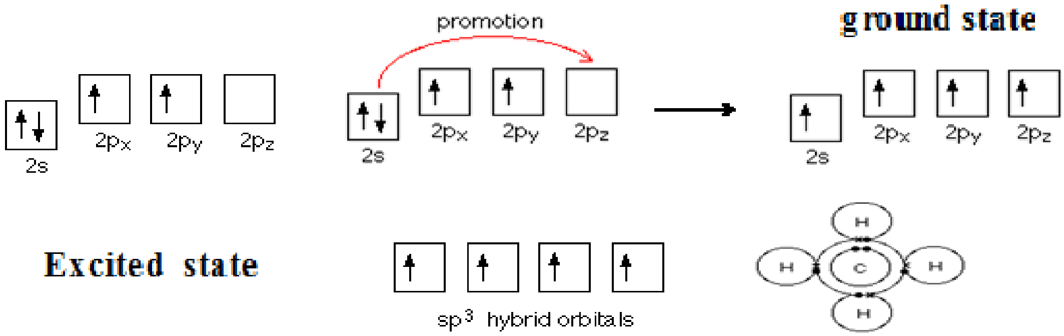
ALKANES

Alkanes - Saturated Hydrocarbons

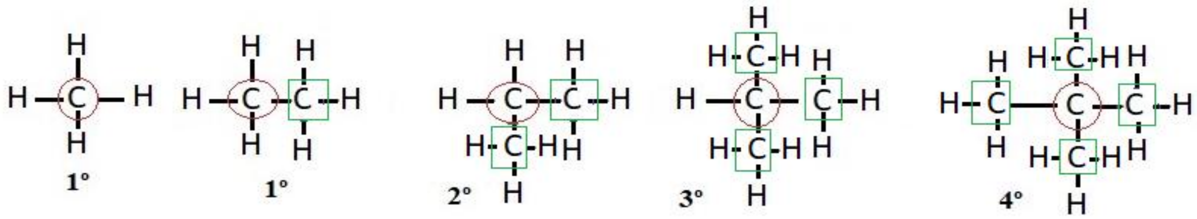
Alkanes, or paraffin's (a still-used historical name for alkanes), are saturated hydrocarbons. They consist only of hydrogen and carbon atoms, all bonds are single bonds. The simplest alkanes is methane, CH_4. Methane molecule has four equivalent carbon-hydrogen bonds arranged tetrahedrally.



The carbon atom is joined to each hydrogen atom by a sigma bond. In methane, the four sp^3 hybride orbitals of carbon atom overlap with s orbital of four hydrogen atom to form four σ C-H bond



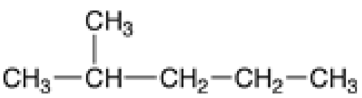
The types of carbon atom are classified to four types deboned on the number of carbon atom attachments with center carbon (1^o, 2^o , 3^o , 4^o).



Saturated hydrocarbons contain only carbon-carbon single bond. Alkanes with carbon chains that are unbranched are sometime called normal alkanes.
Open-chain alkanes (without rings) all have the general formula C_nH_{2n+2}, where n equals the number of carbon atoms.

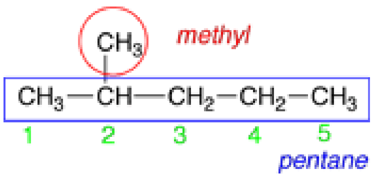
IUPAC System of naming alkanes: -

Although many different types of nomenclature, or naming systems, were employed in the past, today only the International Union of Pure and Applied Chemistry (IUPAC) nomenclature is acceptable for all scientific publications. In this system, a series of rules has been created that is adaptable to all classes of organic compounds. For alkanes, the following rules apply:
1- The ending for all alkanes and cycloalkanes is –ane
2- For alkanes with branched carbon chains, the principal chain is the longest continuous carbon chain. This chain is called the parent chain. For example, the branched chain alkane. Methane , ethane , propane.



the parent chain: $CH_3CH_2CH_2CH_2CH_3$ it has 5 carbon atoms; therefore, it is a derivative of pentane.

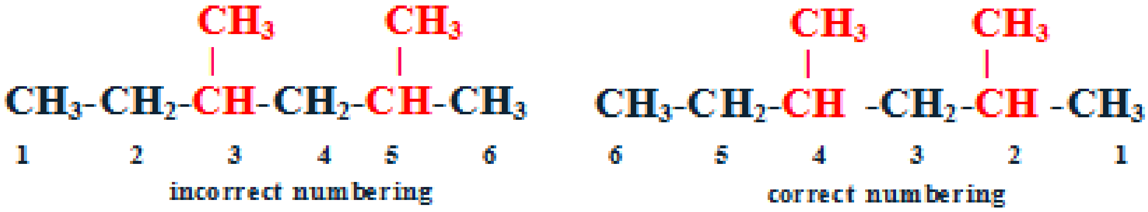
3- The carbon atoms of parent chain are numbered from one end to another giving the lowest number to the first branching point.



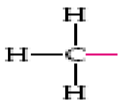
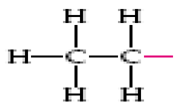
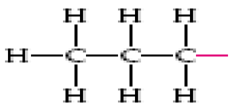
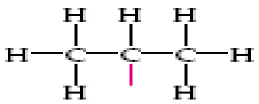
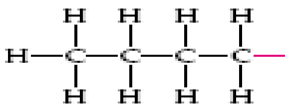
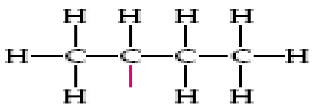
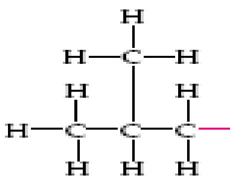
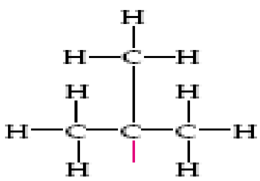
The branch is therefore located on the second carbon.

a- Name each branch attached to the parent chain according to alkyl group. In this case, the branch would be *methyl*.
b- Attach the name of alkyl group to the name of the parent chain as a prefix. Place the location number of the alkyl group in the front of resulting name. In this case, it would be 2- methyl pentane.
4- If there are two or more identical substituents the parent chain from the end that gives the lower number to the substituent closest to the end of the chain. If there are two or more substituent, the number of times they occur

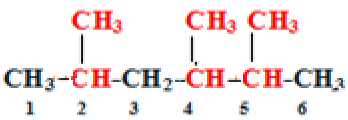
is indicated by the prefixes *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* and so on. A comma is used to separate position number. Of the two possibilities below, we choose the one that numbers the carbon atoms to which the methyl groups are attached as 2 and 4, rather than 3 and 5.



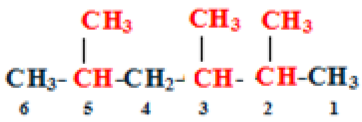
The following table shows the formulas and names of some alkyl groups:

Name	Structural Formula	Condensed Structural
Derived from Methane		
Methyl		CH_3-
Derived from Ethane		
Ethyl		CH_3CH_2-
Derived from Propane		
Propyl		$CH_3CH_2CH_2-$
Isopropyl		CH_3CHCH_3
Derived from Butane		
Butyl		$CH_3CH_2CH_2CH_2-$
Secondary butyl (*sec*-butyl)		$CH_3CHCH_2CH_3$
Derived from Isobutane		
Isobutyl		$CH_3CH(CH_3)CH_2-$
Tertiary butyl (*tert*-butyl)		$CH_3-C(CH_3)-CH_3$

5- If step 4 leads to more than one possibility, number the parent chain, such that the first point of difference has the lowest possible number. Of the two possibilities below, we choose the one that numbers the methyl 3 rather than 4.

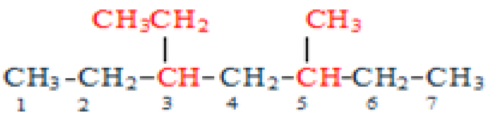


2,4,5-trimethylhexane (incorrect numbering)

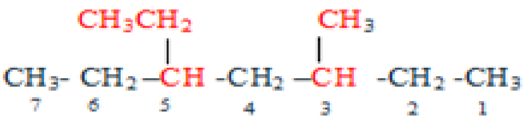


2,3,5-trimethylhexane(correct numbering)

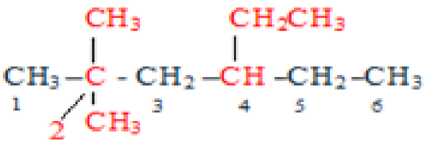
6- If there are two or more different substituent, list them alphabetical order, using the base name (ignore the prefixes). The only prefix which is used when putting the substituents in alphabetical order is iso as in isopropyl or isobutyl. The prefixes sec- and tert- are not used in determining alphabetical order except when compared with each others



3-ethyl-5-methylheptane



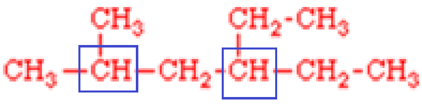
(not 3-methyl-5-methylheptane)



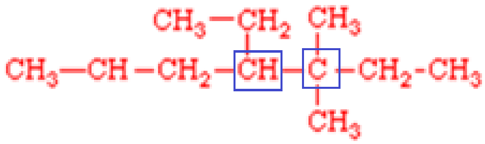
4-ethyl-2,2-dimethylhexane

(not 2,2-dimethyl 4-ehylhexane)

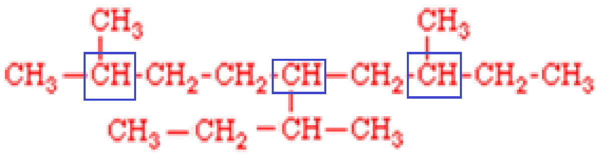
7- There must always be commas between numbers and dashes between numbers and names. Here are some examples:



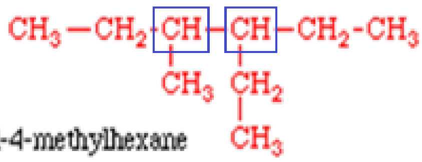
4-ethyl-2-methylhexane



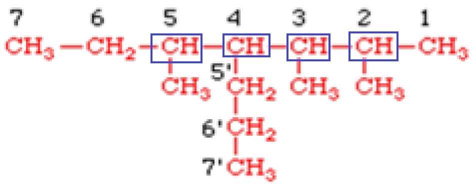
4-ethyl-3,3-dimethylheptane



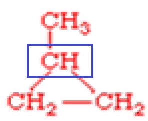
5-sec-butyl-2,7-dimethylnonane



3-ethyl-4-methylhexane



2,3,5-trimethyl-4-propylheptane
(NOT: 2,3-dimethyl-4-sec-butylheptane)



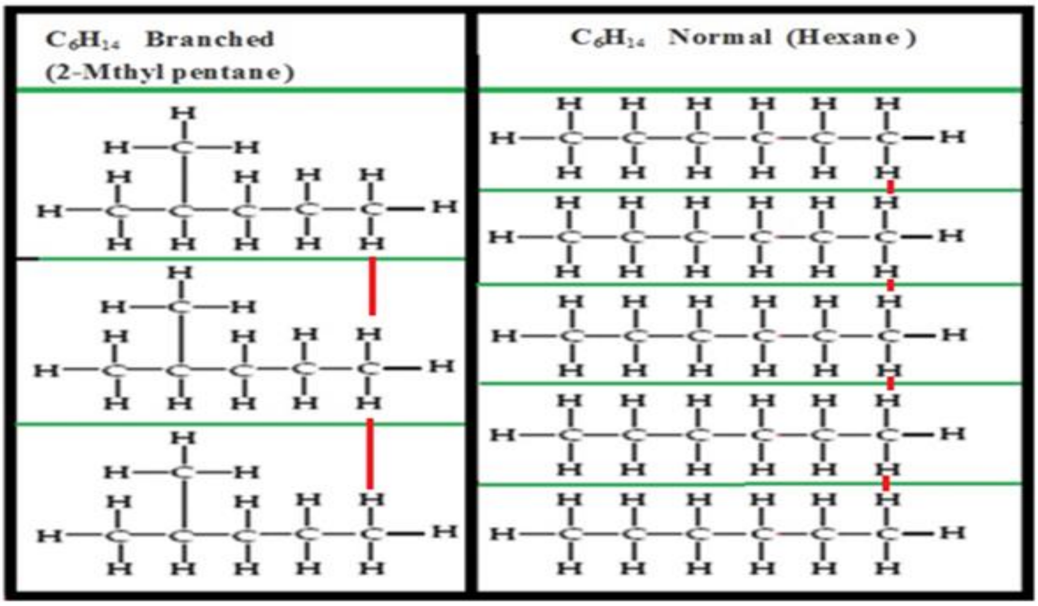
methylcyclopropane

Physical Properties of Alkanes:-

-The attractive forces between the molecules of alkanes are weak. There are only Van der Waals intermolecular forces between alkane molecules.
The alkanes can exist as gases, liquids, or solids at room temperature. The unbranched alkanes methane, ethane, propane, and butane are gases. pentane through hexadecane are liquids; the homologues larger than hexadecane are solids. Solid alkanes are normally soft, with low melting points

Name	State	Formula	MP ^0C	BP ^0C	Density(g/ml)
Methane	Gas	CH_4	-190	-162	0.42
Ethane	Gas	C_2H_6	-183	-89	0.55
Propane	Gas	C_3H_8	-172	-45	0.58
Butane	Gas	C_4H_{10}	-135	-0.5	0.60
Pentane	Liquide	C_5H_{12}	-130	36	0.63
Hexane	Liquide	C_6H_{14}	- 95	69	0.66
Heptane	Liquide	C_7H_{16}	- 91	98	0.68

As the chain length of linear (numbers of carbons) increases the boiling points of the alkanes gradually increase. larger molecules have more surface area, so there is more space for interaction between molecules. Because this makes the molecules harder to separate, you need more heat to boil the liquid to the gas. - Branched alkanes normally exhibit lower boiling points than unbranched alkanes of the same carbon content. For example; n-pentane (CH_3-CH_2-CH_2-CH_2-CH_3) a straight chain alkane has 36^0C b.p., but isopentane $CH_3CH(CH_3)CH_2CH_3$ and neopentane $C(CH_3)_4$ (which are isomers and branched chain carbon atoms) have lower b.p 28 degrees and 10 degree respectively.



This occurs because of the greater van der Waals forces that exist between molecules of the unbranched alkanes.

The unbranched alkanes have greater van der Waals forces of attraction because of their greater surface areas
-Finally, alkanes are almost completely insoluble in water (hydrophobic). This is because, the water molecule is polar, In other hands, alkanes dissolve in most organic solvent

Preparation of Alkanes: -

Alkane **can be prepared by the following methods:**
1- By catalic hydrogenation of unsaturated hydrocarbons (alkenes and alkynes)

$$CH_3\underset{}{\overset{CH_3}{\overset{|}{C}}}H\text{-}CH{=}CH\text{-}CH_3 + H_2 \xrightarrow{Ni} CH_3\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_2CH_3$$

$$R\text{-}C{\equiv}CH + 2H_2 \xrightarrow{Ni} RCH_2CH_3$$

$$CH_3CH_2C{\equiv}CH + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2\text{-}CH_3$$

Methane cannot be prepared by this method because alkenes or alkynes will have two carbons at their lowest level.
2. From alkyl halides via coupling (Wurtz reaction):
When an alkyl halide (usually bromide or iodide) is treated with sodium in dry ether, a symmetrical alkane containing twice the number of carbon atoms of alkyl halide is obtained.

$$RBr + 2Na + R'Br \longrightarrow R\text{-}R' + 2NaBr$$

$$CH_3CH_2\text{-}Br + 2Na + CH_3\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 + 2NaBr$$

3. Reduction of alkyl halides by the use of Grignard reagent:-

Alkyl halides react with magnesium metal in diethyl ether to form alkyl magnesium halides (R-MgX) which are called as Grignard reagents. Grignard reagents are highly reactive and are easily decomposed by water or alcohol to form alkanes

From alkyl halides via Grignard reagent

$$R\text{-}X + Mg \rightarrow R\text{-}MgX \rightarrow R\text{-}H + Mg(OH)X$$

$$CH_3CH_2\text{-}Cl + Mg \longrightarrow CH_3CH_2\text{—}MgCl \xrightarrow{H_2O} CH_3CH_3 + Mg(OH)Cl$$

4- From petroleum and natural gas.

Reactions of Alkanes: -

The alkanes are the least reactive organic compounds. A mong the few reaction that alkanes undergo are their reaction with oxygen and halogens.

1-OxidationReaction:-

In the presence of excess oxygen and spark, alkanes burn to form carbon dioxide, water and a large quantity of energy released:

$$CH_3\text{-}CH_2\text{-}CH_3 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O + Heat$$

If insufficient oxygen is available, partial oxidation of alkanes occur to form carbon monoxide or even elemental carbon:

$$2CH_4 + 3O_2 \longrightarrow 2\,CO + 4H_2O$$

$$2CH_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 4H_2O$$

2- Halogenation Reactions: -

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine *or* iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple substitution reaction in which a C-H bond is broken and a new C-X bond is formed. The reactivity of the halogens decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$. The chlorination of methane provides a simple example of this reaction.

Methane and chlorine substitution reactions happen in which hydrogen atom in the methane are placed one at a time by chlorine atoms. You end up with a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloro-methane.

$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$ chloromethane

$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$ dichloromethane

$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$ trichloromethane

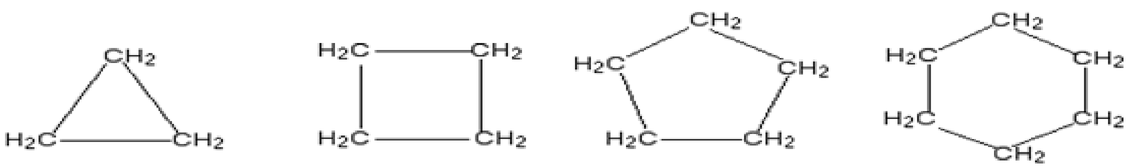
$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$ tetrachloromethane

The relative amounts of the various products depend on the proportion of the two reactants used. In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.

Cycloalkanes

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring, and are also saturated, meaning that all the carbons atoms that makes up the ring are single bonded to other atoms (no double or triple bonds). They have the general formula C_nH_{2n}.

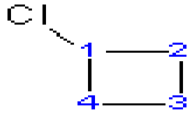
***The cycloalkanes are named by adding the prefix cyclo- to the name of the straight chain hydrocarbon containing the same number of carbon atoms**



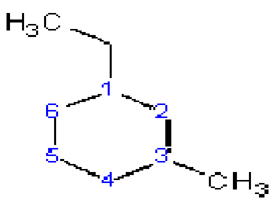
cyclopropane cyclobutane cyclopentane cyclohexane

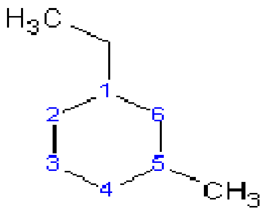
***When there is only one substituent on the parent chain, indicating the number of the carbon atoms with the substituent is not necessary.**

(1-chlorocyclobutane or cholorocyclobutane is acceptable)



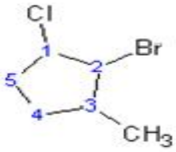
***If there is more than one substituent, the direction of numbering of substituent around the ring is chosen to give the lowest possible number.**



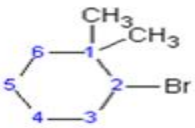


1-Ethyl-3-methylcyclohexane and Not 1-ethyl-5-methylcyclohexane

***When naming the cycloalkane, substituents must be placed by alphabetical order.**

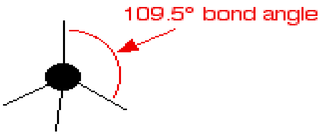


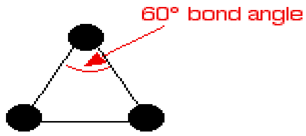
2-Bromo-1-chloro3-methylcyclopentane



2-bromo-1,1-dimethylcyclohexane

Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones - especially cyclopropane. Cyclopropane is much more reactive than you would expect. The reason has to do with the bond angles in the ring. Normally, when carbon forms four single bonds, the bond angles are about 109.5°. In cyclopropane, they are 60°.





With the electron pairs this close together, there is a lot of repulsion between the bonding pairs joining the carbon atoms. That makes the bonds easier to break.