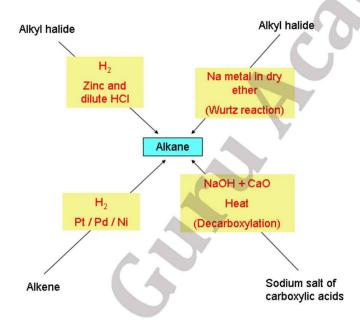
<u>Class XI</u> <u>Chemistry</u> <u>Ch 13: Hydrocarbons</u>

TOP Concepts:

1. Alkanes: General formula: C_nH_{2n+2}

2. Preparation of alkanes:



3. Kolbe's electrolytic method: Alkali metal salts of carboxylic acids undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.

$$^{\circ}$$
 2 CH₃COO Na⁺ + 2H₂O $\xrightarrow{\text{Electrolysis}}$ CH₃ - CH₃ +2 CO₂ + H₂ +2 NaOH

i)
$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-C-O^-+2Na^+$$

At anode:

O

O

II

ii) $2CH_3-C-O^- \xrightarrow{-2e^-} 2CH_3-C-O^- : \longrightarrow 2\dot{C}H_3+2CO_2 \uparrow$

Acetate ion

Acetate

Methyl free free radical radical

iii) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3 \uparrow$

iv) At cathode:

 $H_2O+e^- \rightarrow ^-OH+\dot{H}$
 $2\dot{H} \rightarrow H_2 \uparrow$

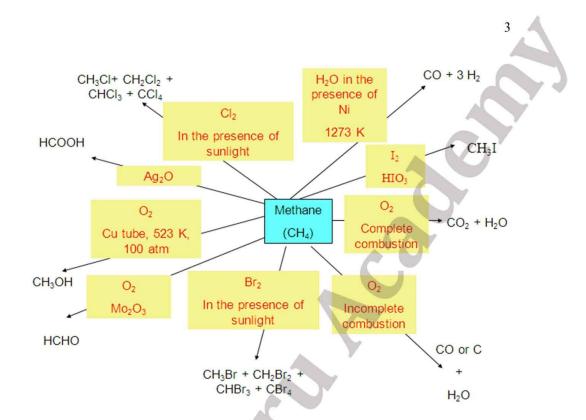
4. Physical properties of alkanes:

- **a. Physical state:** C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. Reason: Hydrocarbons are non- polar because of the covalent nature of C-C and C-H bonds. Thus, they have weak van der Waals forces.
- **b. Boiling points:** Alkanes have low boiling points because they have weak van der Waals forces.

Higher alkanes with higher molecular masses have high boiling points than lower alkanes with low molecular masses. This is because magnitude of van der Waals forces increases with increase in molecular mass or increase in surface area.

Boiling points of branched chain alkanes are lower than the corresponding straight chain alkanes. This is because with branching the molecules become more compact and hence the surface area decreases.

- **c. Melting points:** The alkanes with even number of carbon atoms have higher melting points as compared to the immediately next lower alkane with odd number of carbon atoms. This is because alkanes with even number of carbon atoms have symmetrical structure and hence it results in closer packing in the crystal structure.
- **d. Solubility:** Alkanes are soluble in non- polar solvents and are insoluble in polar solvents since alkanes are non- polar molecules.
- 5. Chemical properties of alkanes:



Aromatization or reforming:

$$\begin{array}{c|c} \operatorname{CH_3} & \operatorname{Cr_2O_3} \text{ or } \operatorname{V_2O_5} \\ \operatorname{CH_2} & \operatorname{CH_2} \\ \operatorname{CH_2} & \operatorname{CH_2} \\ \end{array} \xrightarrow[]{CH_2} & \operatorname{Cr_2O_3} \text{ or } \operatorname{V_2O_5} \\ \end{array} \xrightarrow[]{T73K, 10-20 \text{ atm}} \\ \text{Supported over alumina} \\ \text{Supported over alumina}$$

Isomerisation:

$$\begin{array}{c} \text{CH}_3(\text{CH}_2)_4\text{CH}_3 \xrightarrow{\text{Anhy. AlCl}_3/\text{HCl}} & \text{CH}_3\text{CH}_-(\text{CH}_2)_2 - \text{CH}_3 + \text{CH}_3\text{CH}_2 - \text{CH}_-\text{CH}_2 - \text{CH}_3 \\ n\text{-Hexane} & | & | & | \\ \text{CH}_3 & \text{CH}_3 \\ & 2\text{-Methylpentane} & 3\text{-Methylpentane} \end{array}$$

Pyrolysis or cracking:

A decomposition reaction in which higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. is called pyrolysis or cracking.

6. Conformations or conformers or rotamers or conformational isomers:

The spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers.

7. Conformations of ethane:

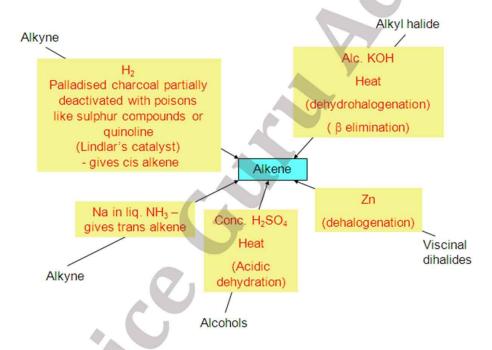
Conformations →	Eclipsed	Staggered	Skew	
	Conformation in which hydrogen atoms attached to two carbons are as closed together as possible	Conformation in which hydrogen atoms are as far apart as possible	Any other intermediate conformation in between eclipsed and sawhorse	
Sawhorse projection	HHH	HHHH		
Newman projection	Н Н Н	Angle of rotation or angle of tortion or dihedral angle H H H H		

8. Geometrical isomers of alkenes:

Trans isomer is non- polar and has zero dipole moment where as cis isomer is polar.

cis isomer has higher boiling points than trans isomer because it is polar. In case of solids, cis isomer has a lower melting point than trans isomer. This is because trans isomer is symmetrical and fits well into the crystal lattice.

9. Preparation of alkenes:



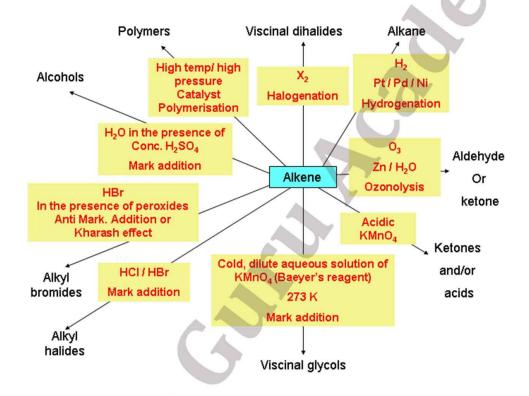
10. Physical properties of alkenes:

- **a. Physical state:** The first three members are gases, the next fourteen are liquids and the higher ones are solids.
- **b. Boiling points:** The boiling points of alkenes increase with the increase in molecular mass.

Boiling points of branched chain alkenes are lower than the corresponding straight chain alkenes. This is because with branching the molecules become more compact and hence the surface area decreases.

c. Solubility: Alkenes are soluble in non- polar solvents and are insoluble in polar solvents.

11. Chemical properties of alkenes:

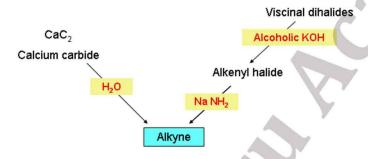


- **12. Test for Unsaturation:** There are two tests to know whether a compound is unsaturated or not:
- **a. Bromine water test:** When an unsaturated compound is reacted with bromine solution in carbon tetrachloride, the reddish orange colour of bromine solution in carbon tetrachloride is discharged.

$$\begin{array}{ccc} \operatorname{CH}_2 = \operatorname{CH}_2 + \operatorname{Br} - \operatorname{Br} & \xrightarrow{\operatorname{CCl}_4} & \operatorname{CH}_2 - \operatorname{CH}_2 \\ \operatorname{Ethene} & & & | & | & | \\ \operatorname{Reddish} & & \operatorname{Br} & \operatorname{Br} \\ \operatorname{orange} & & & 1,2 & \operatorname{Dibromoethane} \\ \end{array}$$

b. Baeyer's reagent test: When an unsaturated compound is reacted with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent, the pink colour of $KMnO_4$ solution is discharged.

13. Preparation of alkynes:



14. Physical properties of alkynes:

a. Solubility: Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.

b. Melting and boiling point:

The melting and boiling points of the members of the alkyne family are slightly higher as compared to those of corresponding alkanes and alkenes. This is because alkynes have a linear structure and therefore their molecules are more closely packed as compared to alkanes and alkenes. The magnitude of attractive forces among them is higher and therefore, the melting and boiling points are also higher.

The melting point, boiling point and density of alkynes increase with increase in molar mass. This is because magnitude of van der Waals forces increases with increase in molecular mass or increase in surface area.

15. Acidic nature of alkynes: Hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. Example:

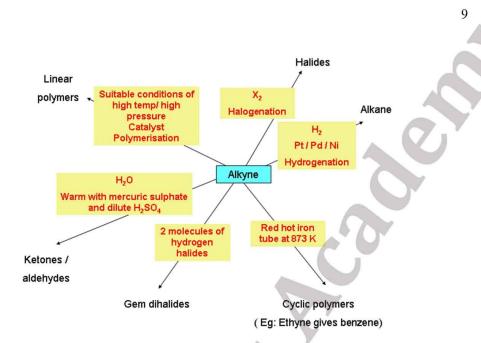
$$HC \equiv CH + Na \longrightarrow HC \underset{ethynide}{\equiv} C^-Na^+ + \frac{1}{2}H_2$$

$$HC \equiv C^{-}Na^{+} + Na \longrightarrow Na^{+}C^{-}_{\substack{\text{disodlum} \\ \text{ethynide}}} = C^{-}Na^{+} + \frac{1}{2}H_{2}$$

Reason:

	Alkyne	Alkene	Alkane
Hybridisation of carbon to which H atom is attached	sp	sp ²	sp ³
Percentage s character of carbon	50% (maximum)	66.6 %	25% (minimum)
Electronegativity of carbon atom	Highest	Less than alkyne and more than alkane	lowest
Extent of attraction of hydrogen atoms of C-H bonds towards C	Highest	Less than alkyne and more than alkane	lowest
Ease of liberation of H atoms as protons	Highest	Less than alkyne and more than alkane	lowest
Acidic character	Highest	Less than alkyne and more than alkane	lowest

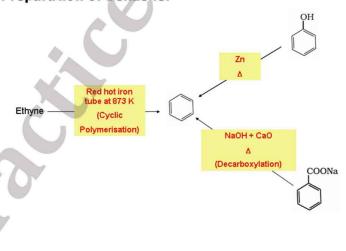
16. Chemical properties of alkynes:



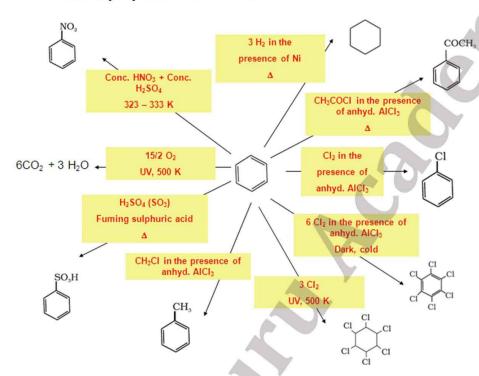
17. Conditions for aromaticity:

- a. Planarity: The ring should be planar. In simple words, all the carbons of the ring should be sp² hybridised.
- b. Complete delocalisation of the π electrons in the ring: The π electrons should be completely delocalized. In simple words, in the ring alternate single and double bonds should exist.
- c. Hückel Rule: Presence of $(4n + 2) \pi$ electrons in the ring where n is an integer (n = 0, 1, 2, ...)

18. Preparation of benzene:



19. Chemical properties of benzene:



20. Directive influence of a functional group in monosubstituted benzene:

a. Ortho para directing groups: Groups which direct the incoming group to *ortho* and *para* positions.

Activating groups: Groups which increase the electron density on ortho and para positions of the benzene ring.

Example: -NH₂, -NHR, -NHCOCH₃, -OCH₃, -CH₃, -C₂H₅,

Deactivating groups: Groups which decrease the electron density on ortho and para positions of the benzene ring.

Example: -X

Halogens are moderately deactivating groups because they have strong – I effect (electron withdrawing effect). Due to this the overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on o- and p- positions is greater than that at the m-position. Hence, they are also o- and p- directing groups.

b. Meta directing groups: The groups which direct the incoming group to *meta* position.

Example: $-NO_2$, -CN, -CHO, -COR, -COOH, -COOR, $-SO_3H$