

Chapter 4



Saturated Hydrocarbons **"ALKANES"**

Lecture Objectives

After this lecture, the student will be able to:

- ▶ Identify alkanes and the several ways to express alkanes
- ▶ Explain the bonding in alkanes according to VSEPR
- ▶ Explain how hybridization occurs in carbon atom
- ▶ Illustrate the formation of sigma bond in alkanes
- ▶ Explain the physical properties of alkanes
- ▶ Explain the chemical properties of alkanes
- ▶ Illustrate the reactions of alkanes

Saturated Hydrocarbons (Alkanes)

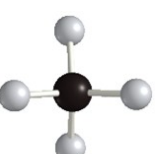
Alkane is a hydrocarbon in which there are only single covalent bonds

With a general formula



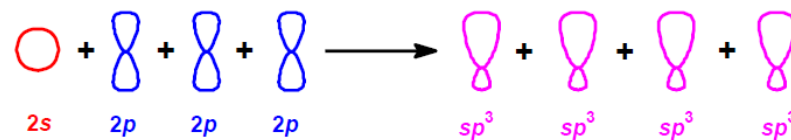
Can be acyclic (open structure) or cyclic (cycloalkanes)

- The simplest alkane is Methane (CH_4), it is the major component of natural gas

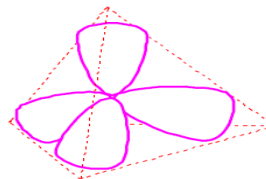


Hybridization

- However, mixing the carbon $2s$ orbital and the 3 carbon $2p$ orbitals gives 4 sp^3 hybrid orbitals:

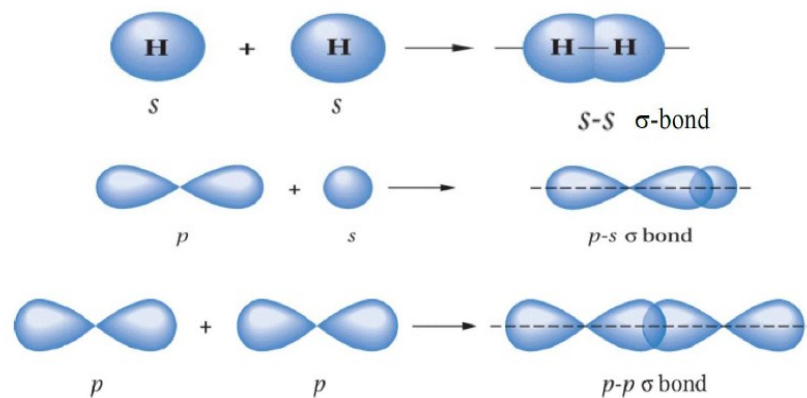


- These 4 sp^3 hybrid orbitals point toward the corners of a tetrahedron:



Orbital View of Bonding: Sigma Bond

- A **sigma (σ) orbital** lies along the axis between two bonded atoms; a pair in a sigma orbital is called a **sigma bond**.



Head to head overlapping

Geometry:

Molecular Orbital Theory:

- ▶ Generate *hybrid orbitals* by “mixing” atomic orbitals in order to achieve the VSEPR geometries
- ▶ The **V**alence **S**hell **E**lectron **P**air **R**epulsion Model

➤ VSEPR theory suggests a tetrahedral structure:



- ▶ Based on the twin concepts that:
 - atoms are surrounded by regions of electron density
 - regions of electron density repel each other

- VSEPR theory suggests a tetrahedral structure:
- But, the atomic orbitals on carbon do not have the correct geometry to give a tetrahedron.

That's why atomic orbitals undergo hybridization

Remember:

- Four electron pairs are organized in a **tetrahedral** arrangement (Alkanes)
Hybridization :sp³, angle 109.5
- Three electron pairs are organized in a **trigonal planar** arrangement (Alkenes)
Hybridization :sp², angle 120
- Two electron pairs in the valence orbital are arranged **linearly** (Alkynes)
Hybridization :sp, angle 180

Carbon Atom Hybridization State Parameters

| Hybridization State | # Of Hybrid Orbitals | # Of 2p Orbitals Left Over | # Of Groups Bonded To Carbon | # Of σ Bonds | # Of π Bonds | Geometry Around Carbon |
|---------------------|----------------------|----------------------------|------------------------------|---------------------|------------------|------------------------|
| sp ³ | 4 | 0 | 4 | 4 | 0 | Tetrahedral |
| sp ² | 3 | 1 | 3 | 3 | 1 | Trigonal Planar |
| sp | 2 | 2 | 2 | 2 | 2 | Linear |

- Petroleum and natural gas are the two most important natural sources of alkanes.
- Natural gas consists mainly of methane (~80%) and ethane (5 – 10%), with lesser amount of some higher alkanes.
- Alkanes are insoluble in water. This is because water molecules are polar, whereas alkanes are non-polar.

Intermolecular forces:

- ▶ **Van der Waals interactions (London dispersion forces)**
- ▶ These are instantaneous induced-dipole interactions
- ▶ Important interactions between **nonpolar compounds**
- ▶ Increases with the surface of interaction between molecules, and therefore **London forces increases with molecular weight**

Physical Properties of Alkanes

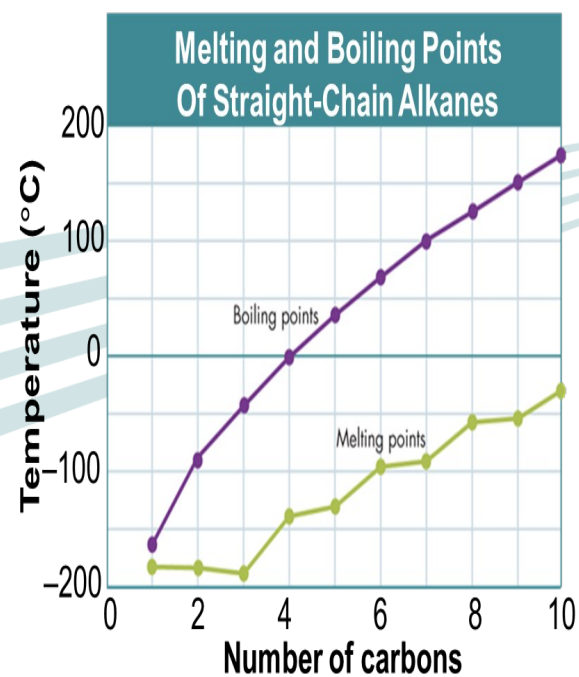
Melting and boiling points:

- **Melting and boiling points increase with increasing molecular weight within a homologous series**

| Compound | Formula | MW (g/mol) | mp (°C) | bp (°C) |
|-------------|--|---------------|---------|---------|
| Methane | CH ₄ | 16 | -182 | -164 |
| Pentane | CH ₃ (CH ₂) ₃ CH ₃ | 72 | -130 | 36 |
| Decane | CH ₃ (CH ₂) ₈ CH ₃ | 142 | -30 | 174 |
| Pentadecane | CH ₃ (CH ₂) ₁₃ CH ₃ | 212 | 10 | 271 |
| Eicosane | CH ₃ (CH ₂) ₁₈ CH ₃ | 282 | 37 | 343 |

Physical Properties of Alkanes

This graph illustrates how the **melting and boiling points** vary with the **number of carbons** in straight-chain alkanes.



Physical Properties of Alkanes

Melting and boiling points:

- Boiling points decrease with chain branching.

| Compound | mp (°C) | bp (°C) |
|---|------------|------------|
| $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_3$ octane | -57 | 127 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH---CH}_2\text{---CH}_3 \\ \\ \text{CH}_3 \end{array}$ 4-methylheptane | -121 | 118 |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{---C---CH}_2\text{---CH---CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ 2,2,4-trimethylpentane | -107 | 99 |

Physical Properties of Alkanes

- ▶ Methane to butane are colorless gases
(propane and butane are easily condensed under pressure and are commonly sold as liquids)
- ▶ Alkanes containing 5 carbons up to about 19 are colorless liquids
(petrol and kerosene are mixtures of liquid alkanes, dye is added to the fluids for safety reasons)
- ▶ Alkanes with more than about 20 carbon atoms are colorless, waxy solids
(paraffin wax is a mixture of solid alkanes)

Physical Properties of Alkanes



VOLATILITY

Due to their low boiling points, lower alkanes are highly volatile.
Volatility refers to the ability of a liquid to change into vapor state.
Among alkanes volatility decreases with increase in chain length.
Among isomeric alkanes more the branching, greater is the volatility

Physical Properties of Alkanes

Solubility:

- Solubility - "Like dissolves like"
- Alkanes are nonpolar, hydrophobic
- They are soluble in nonpolar solvents and insoluble in water.

| Compound | MW | bp (°C) | H ₂ O solubility |
|---|-------|---------|-----------------------------|
| <chem>CH3CH2CH2CH2CH2CH3</chem> hexane | 86.18 | 69 | insoluble |
| <chem>ClCH2CH2Cl</chem> 1,2-dichloroethane | 98.96 | 83 | 0.8% |
| <chem>CH3COCH2COCH3</chem> 2,3-butanedione | 86.09 | 88 | 20% |

Physical Properties of Alkanes

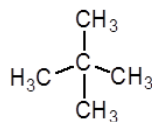
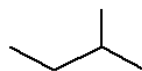
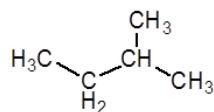
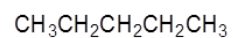
Solubility:

Polar organic compounds are usually soluble in water

| Compound | MW | bp (°C) | H ₂ O solubility |
|--|-------|---------|-----------------------------|
| $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ dimethoxyethane | 90.12 | 83 | ∞ |
| $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 1,4-butanediol | 90.12 | 230 | ∞ |
| $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ putrescine | 88.15 | 158 | ∞ |
| $\text{CH}_3\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_3$ N,N'-dimethylethylenediamine | 88.15 | 119 | ∞ |

QUESTIONS

Name the following compounds



Common name:

IUPAC name:

Chemical Properties of Alkanes

(Reactions):

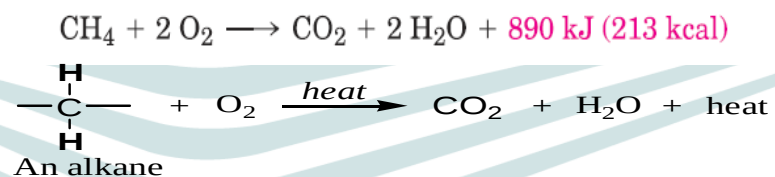
- Alkanes are rather unreactive due to the presence of only C—C and C—H σ -bonds.
- Therefore, they make great nonpolar solvents

Saturated hydrocarbons undergo very few reactions, so they are called **Paraffinic hydrocarbons**.

(Latin *parum*, little; *affinis*, affinity)

1. Combustion (Oxidation):

The reaction of an alkane with O₂ occurs during combustion in an engine or furnace when the alkane is used as a fuel. Carbon dioxide and water are formed as products, and a large amount of heat is released. For example, methane reacts with oxygen according to the equation:



Controlled oxidation under different conditions yield different products like acids, ketones and alcohols.

Oxidation in vapor state occurs via free radicals, eg : alkyl (R°), alkyl peroxy (R00°), alkoxy (R0°)

2. Halogenation (Substitution):

i.e. replacement of hydrogen by halogen, usually chlorine or bromine, giving alkyl chloride or alkyl bromide.

- **Fluorine reacts explosively with alkanes**

It is unsuitable reagent for the preparation of the alkyl fluorides.

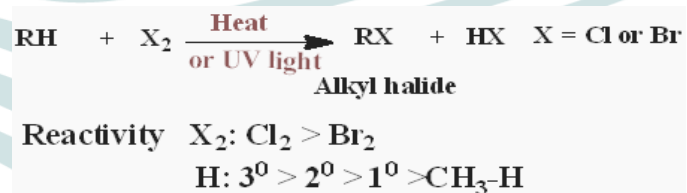
- **Iodine is too unreactive**

It is not used in the halogenation of alkanes.

- **Halogenation of alkanes take place at high temperatures or under the influence of ultraviolet light (UV).**

2. Halogenation (Substitution):

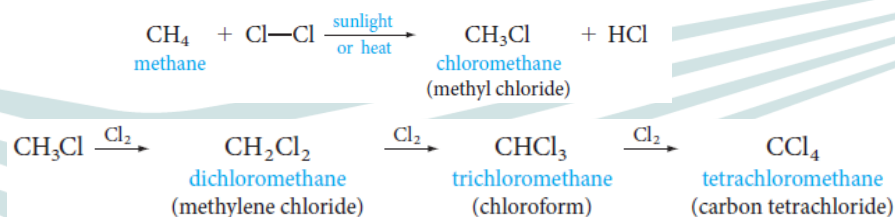
The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed



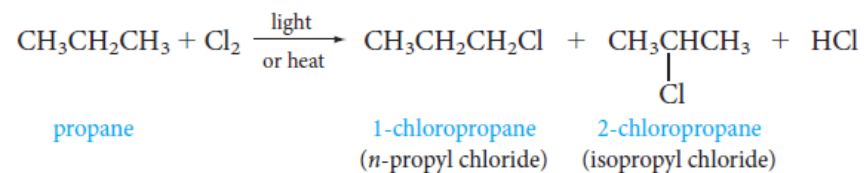
2. Halogenation

(Substitution):

Chlorination of an alkane usually gives a mixture of products

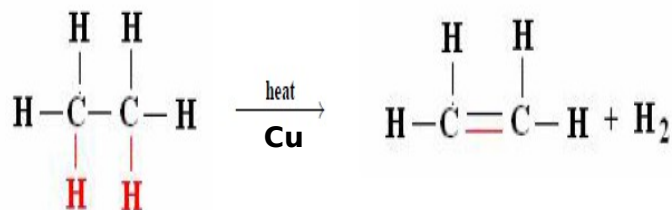
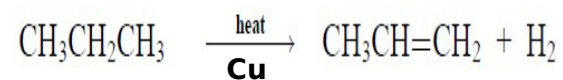


➤ With longer chain alkanes, mixtures of products may be obtained even at the first step. For example, with propane,



► **3. Dehydrogenation (Elimination Reaction):**

- In these reactions *hydrogen is lost* from an alkane upon heating to form an *alkene*.



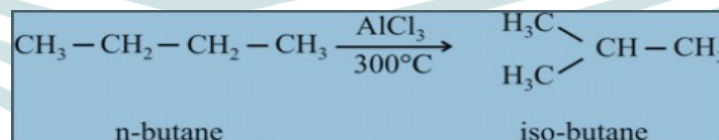
Reactions of Alkanes

► Other Reactions

□ Isomerization:

Straight chain alkanes can be isomerized to branched hydrocarbons

by heating in AlCl_3 at 300°C . eg: n butane to iso butane



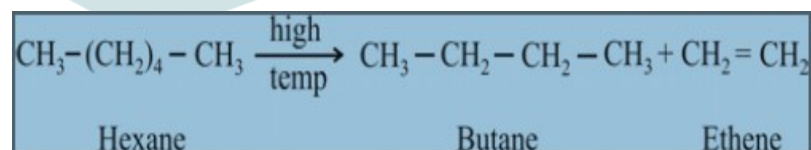
Reactions of Alkanes

► Other Reactions

□ Pyrolysis/Cracking:

Thermal decomposition of alkanes is called pyrolysis.

When alkanes are heated to a high temperature, both C-H and C-C bonds rupture. In absence of oxygen resulting radicals may combine to form new alkanes or abstract H from another radical center to form alkene



Just to remember (Summary)

Test your Self

- What is the **molecular formula of Alkanes**
- What is the **type of hybridization of Alkanes**
- What is the **type of bond between the C-H in alkanes**
- What is the **type of bond between C-C in alkanes**
- What is **the suggested structure of alkane according to the VSEPR theory**
- What is **the suggested angle in Alkane according to the VSEPR theory**
- How does the molecular weight, structure, and type of bonds affect the melting and boiling points of Alkanes
- The State of Alkanes (gas, liquid, and solid) depends on **???????**
- Alkanes are hydrophobic and soluble in nonpolar or polar**???**

Chemical Properties of Alkanes

Summary

- ▶ Alkanes are relatively **unreactive**
- ▶ Alkanes **do not react** with strong acids, bases, oxidizing agents (oxidants) or reducing agents (reductants)
- ▶ Alkanes **combust** (**react rapidly with oxygen**) releasing energy, which makes alkanes useful as fuels.
- ▶ Alkanes undergo **free radical substitution reaction with halogens** such chlorine gas and bromine in the presence of **ultraviolet light or heat**.
- ▶ Alkanes undergo **Elimination** reactions to produce **alkenes**.