

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

Alkane is a **hydrocarbon** in which there are only

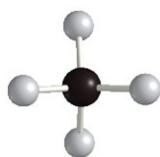
single covalent bonds

With a general formula



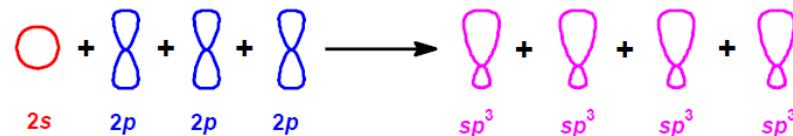
Can be acyclic (open structure) or cyclic
(cycloalkanes)

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

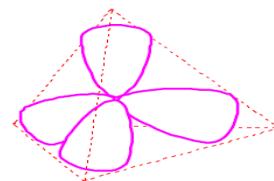


Hybridization

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

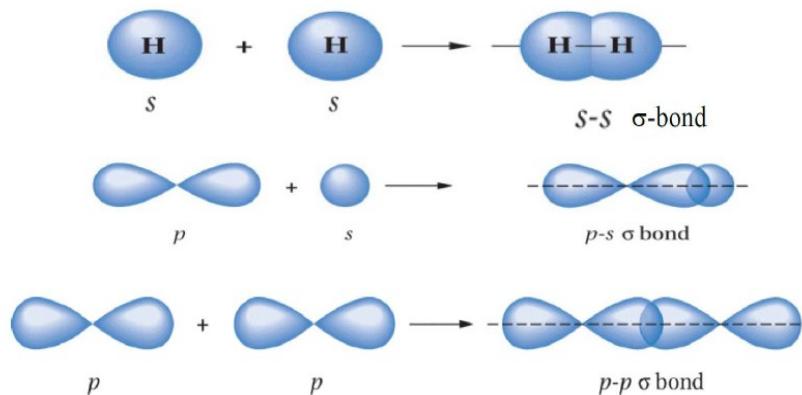


- These $4 sp^3$ hybrid orbitals point toward the corners of a tetrahedron:



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

Molecular Orbital Theory:

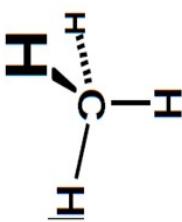
Generate **hybrid orbitals** by “mixing” atomic orbitals in

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Geometry:

➤ 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

Physical Properties of Alkanes

- 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.

Physical Properties of Alkanes

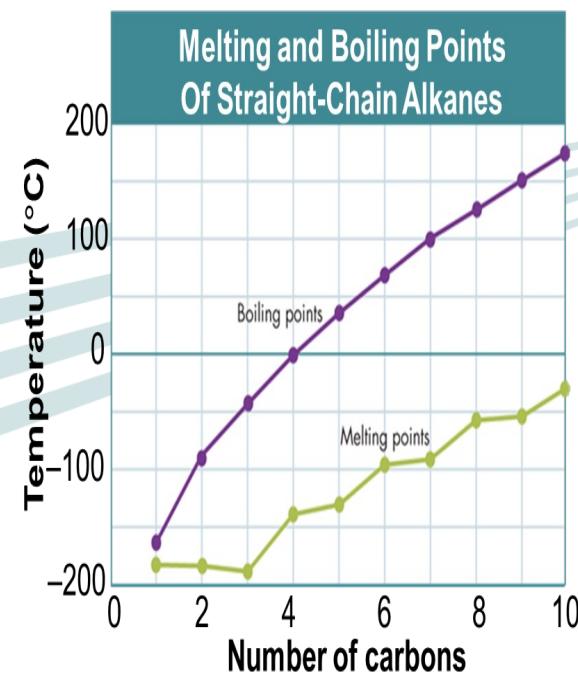
Melting and boiling points:

- **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	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	72	-130	36
Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	142	-30	174
Pentadecane	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$	212	10	271
Eicosane	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$	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)
<chem>CH3CCCCCCCCH3</chem> octane	-57	127
<chem>CH3CCCC(C)CCCH3</chem> 4-methylheptane	-121	118
<chem>CH3C(C)C(C)CCCH3</chem> 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)

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>CH3CCCCCCH3</chem> hexane	86.18	69	insoluble
<chem>ClCCCl</chem> 1,2-dichloroethane	98.96	83	0.8%
<chem>CC(=O)C(=O)CC</chem> 2,3-butanedione	86.09	88	20%

Physical Properties of Alkanes

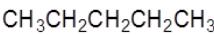
Solubility:

Polar organic compounds are usually soluble in water

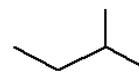
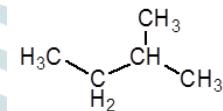
Compound	MW	bp (°C)	H ₂ O solubility
<chem>CH3COCH2CH2OCH3</chem> dimethoxyethane	90.12	83	∞
<chem>OCCCOCCCO</chem> 1,4-butanediol	90.12	230	∞
<chem>NCCCN</chem> putrescine	88.15	158	∞
<chem>NCCN(C)C</chem> N,N'-dimethylethylenediamine	88.15	119	∞

QUESTIONS

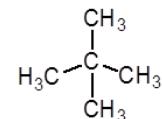
Name the following compounds



Common name:



IUPAC name:



Chemical Properties of Alkanes

(Reactions):

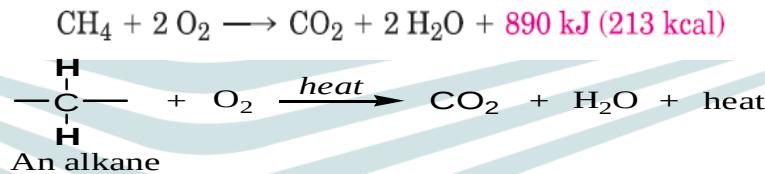
- Alkanes are rather unreactive due to the presence of only C—C and C—H σ -bonds.
- Therefore, they make great nonpolar solvents

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 O_2 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 ($R00^\circ$), alkoxy ($R0^\circ$)

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



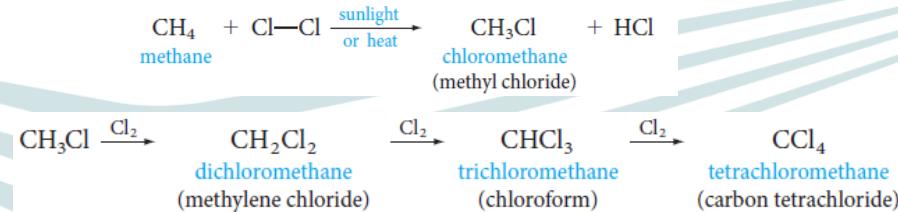
Alkyl halide

Reactivity $\text{X}_2: \text{Cl}_2 > \text{Br}_2$
 $\text{H: } 3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{-H}$

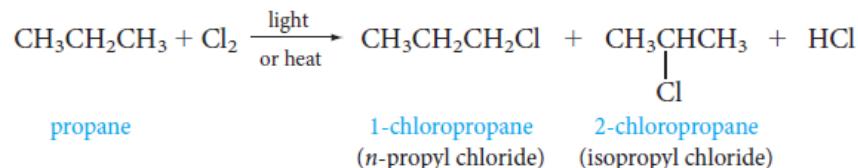
2. Halogenation

(Substitution):

Chlorination of an alkane usually gives a mixture of products

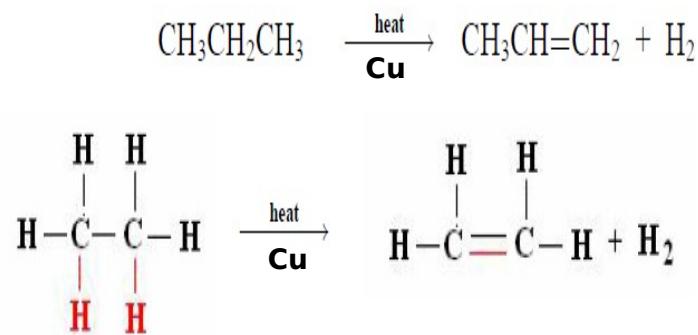


With longer chain alkanes, mixtures of products may be obtained even at the first step. For example, with propane,



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

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



Reactions of Alkanes

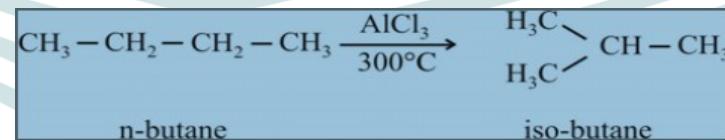
► Other Reactions



❑ Isomerization:

Straight chain alkanes can be isomerized to branched hydrocarbons

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



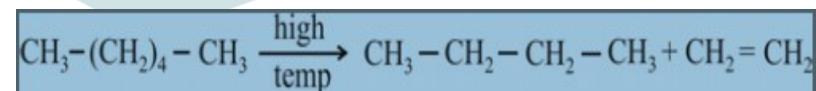
Reactions of Alkanes

► 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



Hexane

Butane

Ethene

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**.