

Chapter 12. Saturated Hydrocarbons

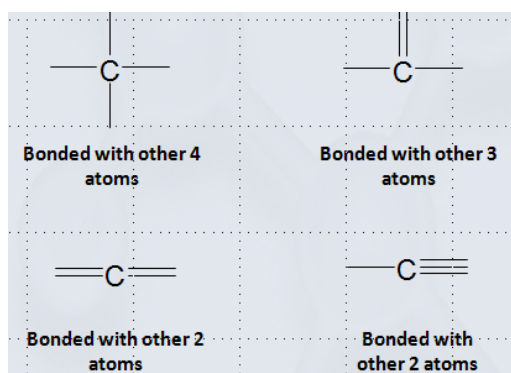
12.1 Organic and Inorganic Compounds

Organic vs. Inorganic

- **Organic chemistry:** Study of hydrocarbons (only carbon and hydrogen atoms) and their various derivatives.
 - Examples: natural gas, petroleum, plastics, rubbers, paper, carbohydrates (sugar, starch), proteins, enzymes, fatty acids, food stuff, drugs, textiles, etc.
- **Inorganic chemistry:** Study of all substances other than hydrocarbons and their derivatives.
 - Examples of inorganic compounds: sulfuric acid, nitric acid, ores and minerals, air, baking powder, caustic soda, table salt, metal alloys (brass, bronze), etc.

12.2 Bonding Characteristics of the Carbon Atom

- C-atom always makes total 4 Bonds
- The sharing of four valence electrons requires the formation of four covalent bonds which are represented by four lines as shown here.



12.3 Hydrocarbons and Hydrocarbon Derivatives

- Hydrocarbon: Compound that contains only carbon and hydrogen atoms.
- Hydrocarbon derivative: Compound that contains carbon and hydrogen and one or more additional elements.
- Saturated hydrocarbon: Hydrocarbon with all carbon–carbon bonds are single bonds.
- Unsaturated hydrocarbon: Hydrocarbon with one or more carbon–carbon multiple bonds (double bonds, triple bonds, or both).

12.4 Alkanes: Acyclic Saturated Hydrocarbons

- **Alkanes:** Open chain (straight or branched) binary compounds of carbon and hydrogen.
- All bonds are single bonds.
- General formula: C_nH_{2n+2} .

12.5 Structural Formulas

Expanded Structural Formula: A two-dimensional structural representation that depicts the bonding of all atoms in a molecule.

Condensed Structural Formula: Structural arrangements of different groupings (a central atom connected with other atoms) in a molecule.

Expanded structural formula			
Condensed structural formula	CH ₄ Methane	CH ₃ —CH ₃ Ethane	CH ₃ —CH ₂ —CH ₃ Propane

Skeletal Structural Formula: Structural arrangement of all bonded carbon atoms without showing the attached hydrogen atoms.

$\text{C}—\text{C}—\text{C}—\text{C}—\text{C}$	means the same as	$\text{CH}_3—\text{CH}_2—\text{CH}_2—\text{CH}_2—\text{CH}_3$
Skeletal structural formula		Condensed structural formula

12.6 Alkane Isomerism

Structural (Constitutional) Isomerism

Compounds having same molecular formula, but different structural arrangements (different connectivity of atoms) are called Isomers, and the phenomenon is known as isomerism.

Space-filling models for the three isomeric C₅H₁₂ alkanes:

(a) Pentane Boiling point = 36.1°C Density = 0.626 g/mL	(b) Isopentane Boiling point = 27.8°C Density = 0.620 g/mL	(c) Neopentane Boiling point = 9.5°C Density = 0.614 g/mL

Number of Isomers Possible for Alkanes of Various Carbon Chain Lengths

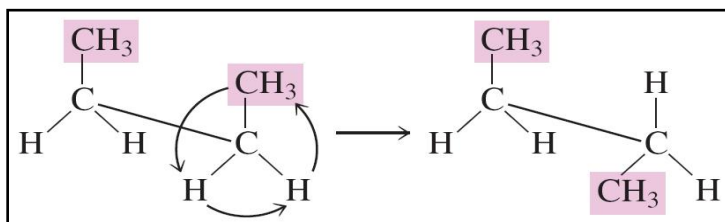
Molecular Formula	Possible Number of Isomers
CH ₄	1
C ₂ H ₆	1
C ₃ H ₈	1
C ₄ H ₁₀	2
C ₅ H ₁₂	3
C ₆ H ₁₄	5
C ₇ H ₁₆	9
C ₈ H ₁₈	18
C ₉ H ₂₀	35
C ₁₀ H ₂₂	75
C ₁₅ H ₃₂	4,347
C ₂₀ H ₄₂	336,319
C ₂₅ H ₅₂	36,797,588
C ₃₀ H ₆₂	4,111,846,763

12.7 Conformations of Alkanes

Conformation: At a given instant, the specific three dimensional spatial arrangement of atoms due to the rotation of C-C single bond in the same molecule.

Different conformational structures result from C-C single bond rotation, but no breaking of bonds takes place.

Different structural isomers result from different connectivity of atoms, which requires breaking and making of bonds in the same molecule.



12.8 IUPAC Nomenclature of Alkanes

Rules for Naming Stright-Chain Alkanes

Systematic approach for naming alkanes was introduced by the International Union of Pure and Applied Chemistry (IUPAC), and the rules are being updated periodically.

The rules are applied to both types of alkanes:

- **Straight chain** (continuous) alkanes
- **Branched chain** (divided / substituted) alkanes
- Substituent: an atom or group of atoms attached to a chain (or ring) of carbon atoms.
- **Alkyl group**: the group of atoms that would be obtained by removing a hydrogen atom from an alkane.

Rules for Naming Branched-Chain Alkanes

Rule 1: Identify the longest continuous carbon chain and name that chain as the parent

Rule 2: Number the carbon atoms in the parent chain in such a way so that to give the lowest possible number for a substituent (alkyl group).

Rule 3: If only one substituent present, name and locate it by number; then, prefix the number and name to that of the parent carbon chain.

Rule 4: If two or more of the same kind of alkyl group are present in a molecule, indicate the number with a Greek numerical prefix (di-, tri-, tetra-, penta-, and so forth). In addition, a number specifying the location of each identical group must be included. These position numbers, separated by commas, precede the numerical prefix. Numbers are separated from words by hyphens.

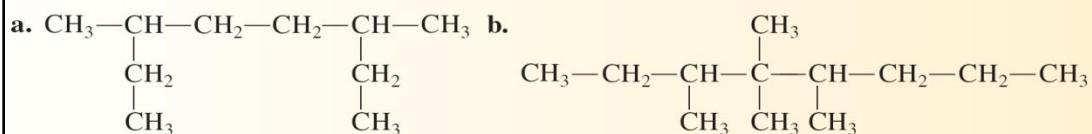
Rule 5: When two kinds of alkyl groups are present on the same carbon chain, number each group separately, and list the names of the alkyl groups in alphabetical order.

Rule 6: Follow IUPAC punctuation rules:

1. Separate numbers from each other by commas.
2. Separate numbers from letters by hyphens.
3. Do not add a hyphen or a space between the last-named substituent and the name of the parent alkane.

Example

Give the IUPAC name for each of the following alkanes.



Answer:

a. 3,6-Dimethyloctane

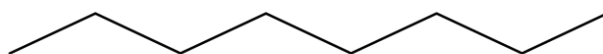
b. 3,4,4,5-Tetramethyloctane

12.9 Line-Angle Structural Formulas for Alkanes

Line-angle (Bond-Angle) structural formula:

- A structural representation in which a line represents a carbon-carbon bond.
- A carbon atom is understood to be present at every point where two lines meet (at the intersection).
- At the ends of each lines.

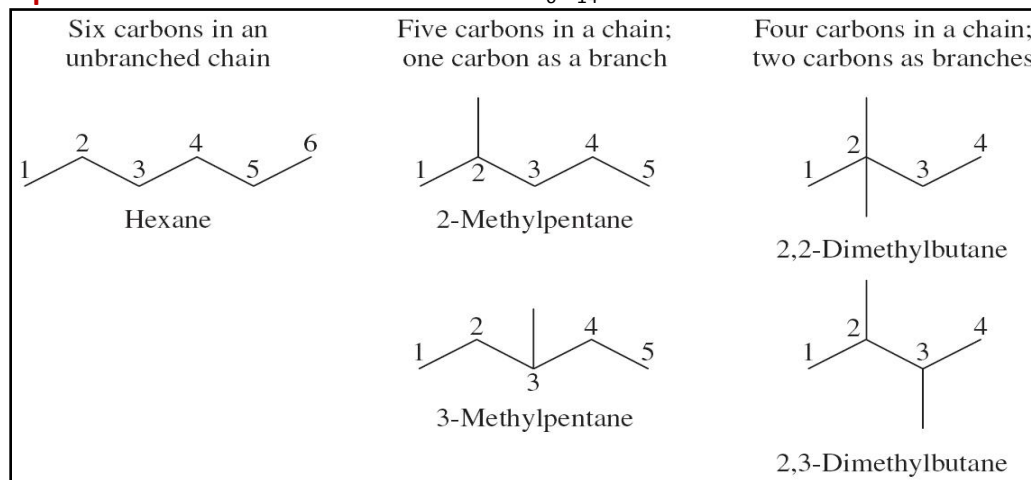
Example:



Octane

Structures of branched-chain alkanes designated using line-angle structural formulas.

Example: The five constitutional isomers of C_6H_{14} .



12.10 Classification of Carbon Atoms

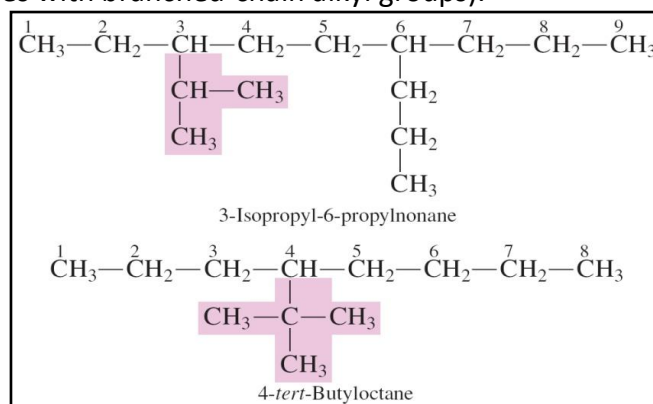
Based on the skeletal structure of the C-atom in a hydrocarbon chain, each C-atom can be classified as follows:

- **Primary:** If bonded with only one C- atom
- **Secondary:** If bonded with other 2 C- atoms
- **Tertiary:** If bonded with other 3 C-atoms
- **Quaternary:** If bonded with other 4 C- atoms

12.11 Branched-Chain Alkyl Groups

Continuous chain alkyl groups: The simplest type of alkyl group with continuous chain of carbon atoms.

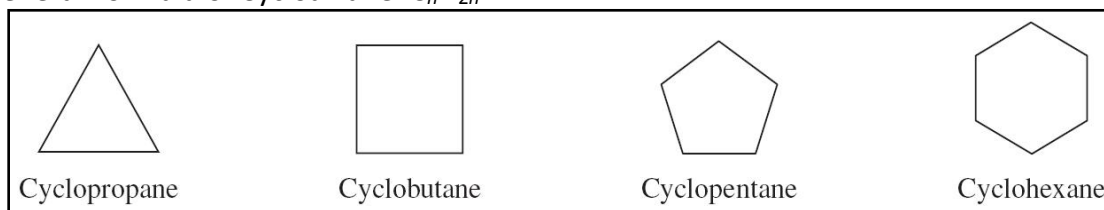
Branched-chain alkyl groups: Alkyl groups are added to the continuous parent chain of carbon atoms (Alkenes with branched-chain alkyl groups).



12.12 Cycloalkanes

Cycloalkanes are alkanes that contain a ring of three or more carbons.

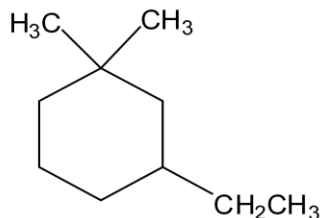
General Formula of Cycloalkane: C_nH_{2n}



12.13 IUPAC Nomenclature for Cycloalkanes

- Count the number of carbons in the ring, and name the parent cyclic chain (just like an alkane).
- Add the prefix *cyclo* to the IUPAC name of the unbranched alkane, e.g., Cyclopentane
- Name any alkyl groups on the ring in the usual way
- Numbering conventions used in locating substituents on the ring:
 - If there is just one ring substituent, it is not necessary to locate it by number.
 - When two ring substituents are present, the carbon atoms in the ring are numbered beginning with the substituent of higher alphabetical priority and proceeding in the direction (clockwise or counterclockwise) that gives the other substituent the lower number.

When three or more ring substituents are present, ring numbering begins at the substituent that leads to the lowest set of location numbers. When two or more equivalent numbering sets exist, alphabetical priority among substituents determines the set used



3-Ethyl-1,1-dimethylcyclohexane

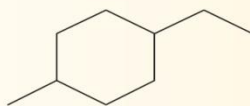
Example

Assign IUPAC names to each of the following cycloalkanes.

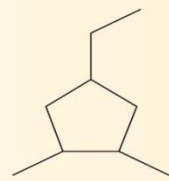
a.



b.



c.



Answers:

- Methylcyclopropane**
- 1-Ethyl-4-methylcyclohexane**
- 4-Ethyl-1,2 dimethylcyclopentane**

12.14 Isomerism in Cycloalkanes

Cycloalkanes also exhibit stereoisomerism.

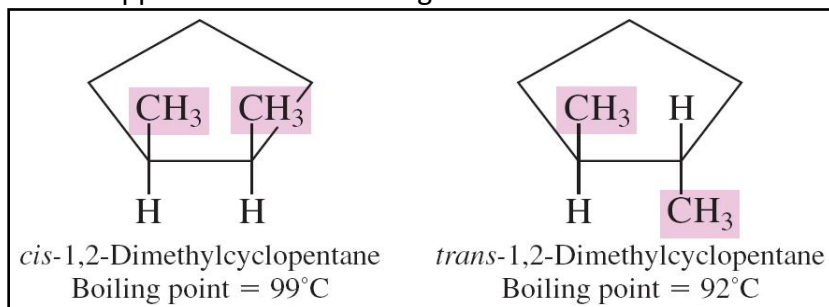
- Stereoisomers have the same molecular and structural formulas but different orientations of atoms in space.
- Several forms of stereoisomerism exist.

Di-substituted Cycloalkanes exhibit Cis-Trans isomerism.

- Cis–trans isomers have the same molecular and structural formulas but different spatial orientations of atoms due to the restricted rotation about bonds.

Cis- is a prefix that means “on the same side.” In cis-1,2-dimethylcyclopentane, the two methyl groups are on the same side of the ring.

Trans- is a prefix that means “across from.” In trans-1,2-dimethylcyclopentane, the two methyl groups are on opposite sides of the ring.



12.15 Sources of Alkanes and Cycloalkanes

Natural Gas and Petroleum

Natural Gas:

- 50 - 90% Methane
- 1 - 10% Ethane
- Up to 8% Higher Alkanes (mostly Propane and Butanes)

Petroleum (crude oil):

- Complex mixture of acyclic and cyclic hydrocarbons
-

Petroleum Refining

Refining: Isolation of soil, sand, sulfur, etc., from the crude oil and physical separation of the hydrocarbons mixture into several fractions.

Fractional Distillation: Process of separating different components from a mixture based on their boiling points.

12.16 Physical Properties of Alkanes and Cycloalkanes

Solubility and Density

Solubility: Follows the rule 'like dissolves like'

- Soluble in non-polar solvents e.g., in hexanes
- Insoluble in polar solvents e.g., water, alcohol
- Application: protective wax coating on fruits to prevent loss of water as well as from fungi or bacterial strain etc.

Density: Lighter than water

- Densities of alkanes and cycloalkanes range from
- 0.6 – 0.8 g/mL (water density at 4 degree C = 1.0 g/mL)
- Practical illustration: quick spreading of oil spills in water.
- Fire caused by floating oil can not be extinguished by water.

Boiling Points

The boiling points increase with an increase in the number of carbon atom in chain length or ring size.

Branching in carbon chain lowers the boiling point of an alkane.

Cycloalkanes have higher boiling points than their noncyclic counterparts with the same number of c-atoms

12.17 Chemical Properties of Alkanes and Cycloalkanes

Vigorous reaction with oxygen (usually from air)

Accompanied by the evolution of heat and light

Always an exothermic process

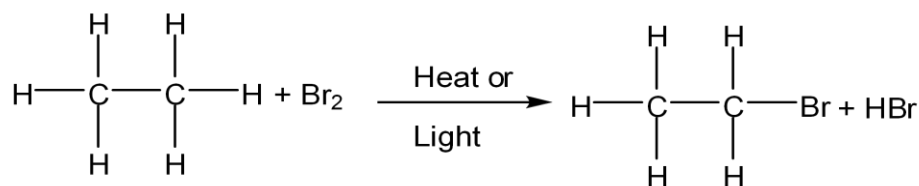
The final products of any complete combustion of hydrocarbons are:

- Carbon dioxide and Water (vapor)
- $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{Energy}$
- $2\text{C}_6\text{H}_{14} + 19\text{O}_2 \rightarrow 12\text{CO}_2 + 14\text{H}_2\text{O} + \text{Energy}$
- Incomplete / partial combustion results in a mixture of carbon dioxide and carbon monoxide with water (g)

Halogenation

Direct reaction with halogens (chlorine, bromine, iodine)

Substitution of one or more H-atoms of hydrocarbons by halogen atoms (substitution reaction of alkanes)



12.18 Nomenclature and Properties of Halogenated Alkanes

Halogenated Alkanes: Derivatives alkanes in which one or more hydrogen atoms are substituted by halogen atoms.

Halogenated cycloalkanes: Cycloalkane derivatives in which one or more hydrogen atoms are substituted by halogen atoms

These derivatives are named as:

- Haloalkanes or Halocycloalkanes (IUPAC naming)
- Alkyl Halides or Cycloalkyl halides (common naming)

IUPAC Rules

Follow the same rules for naming alkanes / cycloalkanes

Lowest locant number is given to the top priority group.

Alkyl and halogen substituents have the same ranking.

If 2 or more different substituents are present, the alphabetical order determines their priority.

IUPAC (one word)
haloalkane
chloromethane
Common (two words)
alkyl halide
methyl chloride

Physical Properties of halogenated alkanes

Density: Many halogen derivatives are heavier than water.

Polarity: They are mostly polar compounds (if unsymmetrical).

Boiling Points: Generally higher than parent hydrocarbons.