Saturated Hydrocarbons – Alkanes

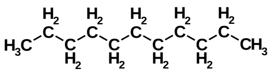
Alkanes are also known as paraffins

- consist only of the elements carbon (C) and hydrogen (H) (i.e., hydrocarbons).
- These atoms are linked together exclusively by single bonds
- Alkanes belong to a homologous series of organic compounds in which the members differ by a constant relative atomic mass of 14.
- An alkyl group is a functional group or side-chain that, like an alkane, consists solely of singly-bonded carbon and hydrogen atoms.

Introduction

- The simplest possible alkane (the parent molecule) is methane, CH_4.
- There is no limit to the number of carbon atoms that can be linked together, the only limitation being that the molecule is acyclic, is saturated, and is a hydrocarbon.
- Saturated hydrocarbons can be linear (general formula $\mathbf{C}_{\boldsymbol{n}}\mathbf{H}_{\mathbf{2}\boldsymbol{n}\mathbf{+2}}$) wherein the carbon atoms are joined in a snake-like structure $\mathbf{C}_{\boldsymbol{n}}\mathbf{H}_{\mathbf{2}\boldsymbol{n}\mathbf{+2}}$.

OR



Homologous series of Alkanes

- A succession of hydrocarbons that differ from each other by one methylene group (—CH_2—) is a **homologous series.**
- For example, the first three alkanes, methane (CH_3—H), ethane ($CH_3\mathbf{CH_2}$—H), and propane ($CH_3\mathbf{CH_2CH_2}$—H), are all members of a homologous series.
- Each compound in a homologous series a homolog.

Homologous series of Alkanes

- branched (general formula $\mathbf{C}_{\boldsymbol{n}}\mathbf{H}_{\mathbf{2}\boldsymbol{n}\mathbf{+2}}$, $\boldsymbol{n}\mathbf{>3}$) wherein the carbon backbone splits off in one or more directions,
- cyclic (general formula $\mathbf{C}_{\boldsymbol{n}}\mathbf{H}_{\mathbf{2}\boldsymbol{n}}$,) wherein the carbon backbone is linked so as to form a loop.
- Saturated oils and waxes are examples of larger alkanes where the number of carbons in the carbon backbone tends to be greater than 10.

Various Alkanes and their properties

No of Carbons	Molecular formula	Name	Condensed structure	Boiling point °C	Melting point °C	Density (g /mL)
1	CH_4	Methane	CH_4	-167.7	-182.5	Gas at RT
2	C_2H_6	Ethane	CH_3CH_2	-88.6	-183.3	Gas at RT
3	C_3H_8	Propane	$CH_3CH_2CH_3$	-42.1	-187.7	Gas at RT
4	C_4H_{10}	Butane	$CH_3(CH_2)_2CH_3$	0.5	-138.3	Gas at RT
5	C_5H_{12}	Pentane	$CH_3(CH_2)_3CH_3$	36.1	129.8	0.5572
6	C_6H_{14}	Hexane	$CH_3(CH_2)_4CH_3$	68.7	-95.3	0.6603
7	C_7H_{16}	Heptane	$CH_3(CH_2)_5CH_3$	98.4	-90.6	0.6837
8	C_8H_{18}	Octane	$CH_3(CH_2)_6CH_3$	127.7	-56.8	0.7026
9	C_9H_{20}	Nonane	$CH_3(CH_2)_7CH_3$	150.8	-53.5	0.7177
10	$C_{10}H_{22}$	Decane	$CH_3(CH_2)_8CH_3$	174.0	-29.7	0.7299

Various Alkanes and their properties

No of Carbons	Molecular formular	Name	Condensed structure	Boiling point °C	Melting point °C	Density (g /mL)
11	$C_{11}H_{24}$	Undecane	$CH_3(CH_2)_9CH_3$	195.8	-25.6	0.7402
12	$C_{12}H_{26}$	Dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	-9.6	0.7487
13	$C_{13}H_{28}$	Tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	-5.5	0.7646
20	$C_{20}H_{42}$	Eicosane	$CH_3(CH_2)_{18}CH_3$	343.0	36.8	0.7886
21	$C_{21}H_{44}$	Heneicosane	$CH_3(CH_2)_{28}CH_3$	449.7	65.8	0.8097

Naming Alkanes

1. Determine the number of carbons in the longest continuous carbon chain. This chain is called the **parent hydrocarbon. The name that indicates the number of** carbons in the parent hydrocarbon becomes the alkane's "last name." For example, a parent hydrocarbon with eight carbons would be called *octane.* The longest continuous chain is not always a straight chain; sometimes you have to "turn a corner" to obtain the longest continuous chain.

Naming Alkanes

2. The name of any alkyl substituent that hangs off the parent hydrocarbon is cited before the name of the parent hydrocarbon, together with a number to designate the carbon to which the alkyl substituent is attached. The chain is numbered in the direction that gives the substituent as low a number as possible. The substituent's name and the name of the parent hydrocarbon are joined in one word, and there is a hyphen between the number and the substituent's name.

Naming Alkanes

3. If more than one substituent is attached to the parent hydrocarbon, the chain is numbered in the direction that will result in the lowest possible number in the name of the compound.

- The substituents are listed in alphabetical (not numerical) order, with each substituent getting the appropriate number.

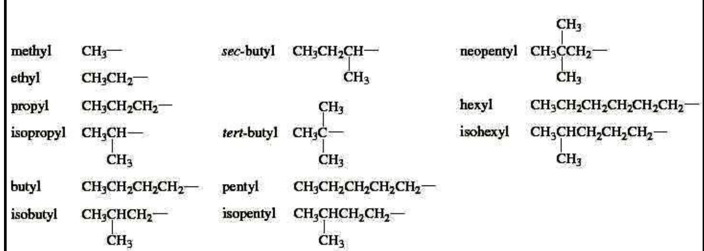
Nomenclature of Alkyl Substituents

- Removing a hydrogen from an alkane results in an **alkyl substituent** (or an alkyl group). Alkyl substituents are named by replacing the "ane" ending of the alkane with "yl."
- The letter "R" is used to indicate any alkyl group.

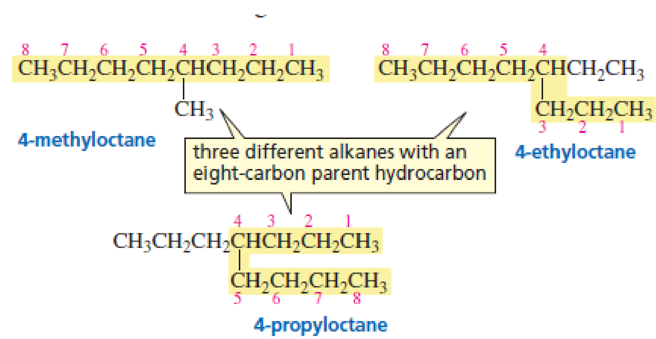
$CH_3—$	$CH_3CH_2—$	$CH_3CH_2CH_2—$	$CH_3CH_2CH_2CH_2—$
a methyl group	an ethyl group	a propyl group	a butyl group

$R—$
any alkyl group

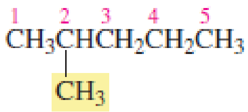
Names of alkyl groups



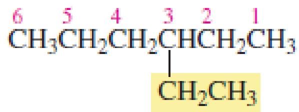
Rule 1: The longest continuous carbon chain



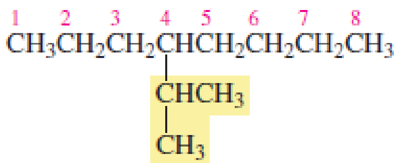
More on rule 2



2-methylpentane

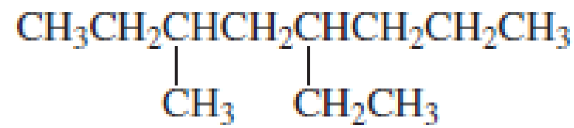


3-ethylhexane



4-isopropyloctane

More on rule 3



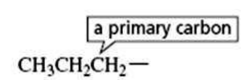
5-ethyl-3-methyloctane
not
4-ethyl-6-methyloctane
because 3 < 4

Primary, Secondary & Tertiary Carbons

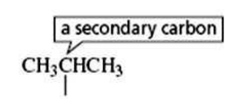
- A **primary carbon** is a carbon that is bonded to only one other carbon.
- A **secondary carbon** is a carbon that is bonded to two other carbons. An isopropyl group is obtained when a hydrogen is removed from the *secondary carbon* of propane.
- A **tertiary carbon** is a carbon that is bonded to three other carbons.

Nomenclature of Alkyl Substituents

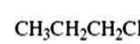
- Two alkyl groups—a propyl group and an isopropyl group—contain three carbon atoms.
- A propyl group is obtained when a hydrogen is removed from a *primary carbon* of propane.



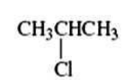
a propyl group



an isopropyl group



propyl chloride



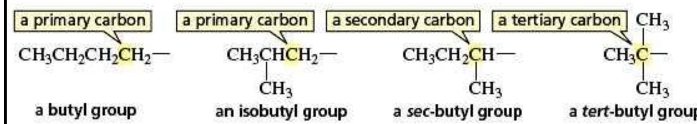
isopropyl chloride

Nomenclature of Alkyl Substituents

- There are four alkyl groups that contain four carbon atoms.
- The butyl and isobutyl groups have a hydrogen removed from a primary carbon.
- A *sec*-butyl group has a hydrogen removed from a secondary carbon (*sec*-, often abbreviated *s*-, stands for secondary).
- A *tert*-butyl group has a hydrogen removed from a tertiary carbon (*tert*-, sometimes abbreviated *t*-, stands for tertiary).

17

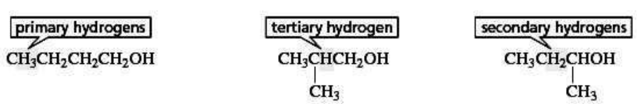
Primary, secondary and tertiary carbon atoms



18

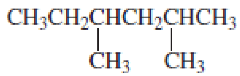
Primary, Secondary & Tertiary Hydrogens

- Like the carbons, the hydrogens in a molecule are also referred to as primary, secondary, and tertiary.
- **Primary hydrogens** are attached to primary carbons, **secondary hydrogens** to secondary carbons, and **tertiary hydrogens** to tertiary carbons.

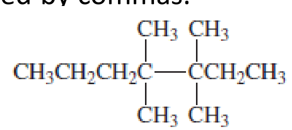


Nomenclature rules ....

- If two or more substituents are the same, the prefixes “di,” “tri,” and “tetra” are used to indicate how many identical substituents the compound has. The numbers indicating the locations of the identical substituents are listed together, separated by commas.



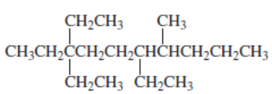
2,4-dimethylhexane



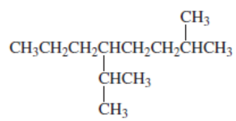
3,3,4,4-tetramethylheptane

20

- The prefixes di, tri, tetra, *sec, and tert are ignored in alphabetizing substituent* groups, but the prefixes iso, neo, and cyclo are not ignored.



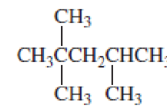
3,3,6-triethyl-7-methyldecane



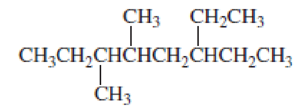
5-isopropyl-2-methyloctane

Naming Alkanes

4. When both directions lead to the same lowest number for one of the substituents, the direction is chosen that gives the lowest possible number to one of the remaining substituents.

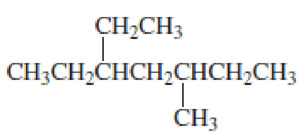


2,2,4-trimethylpentane
not
2,4,4-trimethylpentane
because 2 < 4



6-ethyl-3,4-dimethyloctane
not
3-ethyl-5,6-dimethyloctane
because 4 < 5

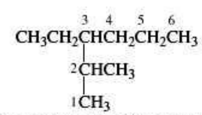
- 5. If the same substituent numbers are obtained in both directions, the first group cited receives the lower number.



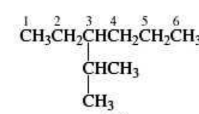
3-ethyl-5-methylheptane
not
5-ethyl-3-methylheptane

Naming Alkanes

6. If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greatest number of substituents.



3-ethyl-2-methylhexane (two substituents)



not
3-isopropylhexane (one substituent)

Physical properties

- Alkanes experience inter-molecular van der Waals forces. Stronger inter-molecular van der Waals forces give rise to greater boiling points of alkanes.
- There are two determinants for the strength of the van der Waals forces:
  - the number of electrons surrounding the molecule, which increases with the alkane's molecular weight
  - the surface area of the molecule

25

Physical properties

- Under standard conditions, from CH_4 to C_4H_{10} alkanes are gaseous; from C_5H_{12} to $C_{17}H_{36}$ they are liquids; and after $C_{18}H_{38}$ they are solids.
- As the boiling point of alkanes is primarily determined by weight, it should not be a surprise that the boiling point has almost a linear relationship with the size (molecular weight) of the molecule.
- As a rule of thumb, the boiling point rises 20 - 30 °C for each carbon added to the chain; this rule applies to other homologous series

26

Properties of Alkanes

- Alkanes are not very reactive and have little biological activity.
- Alkanes can be viewed as a molecular scaffold upon which can be hung the interesting biologically-active/reactive portions (functional groups) of the molecule.
- Alkanes do not conduct electricity, nor are they substantially polarized by an electric field. For this reason they do not form hydrogen bonds and are insoluble in polar solvents such as water.

27

Properties of Alkanes

- Alkanes are said to be hydrophobic in that they repel water
- Their solubility in nonpolar solvents is relatively good, a property that is called lipophilicity. Different alkanes are, for example, miscible in all proportions among themselves.
- The density of the alkanes usually increases with increasing number of carbon atoms, but remains less than that of water. Hence, alkanes form the upper layer in an alkane-water mixture.

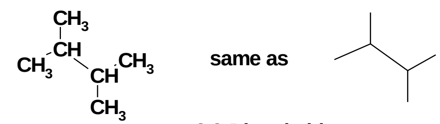
28

Properties of Alkanes…

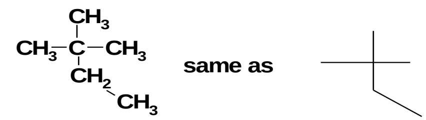
- A straight-chain alkane will have a boiling point higher than a branched-chain alkane due to the greater surface area in contact, thus the greater van der Waals forces, between adjacent molecules.
- For example, compare isobutane and n-butane, which boil at -12 °C and 0 °C respectively.

Properties of Alkanes…

- 2,2-dimethylbutane and 2,3-dimethylbutane boil at 50 °C and 58 °C, respectively.



2,3-Dimethyl-butane



2,2-Dimethyl-butane

Properties of Alkanes…

- For the latter case, two molecules 2,3-dimethylbutane can "lock" into each other better than the cross-shaped 2,2-dimethylbutane, hence the greater van der Waals forces, resulting in higher boiling point.

Applications of Alkanes

- The first four alkanes are used mainly for heating and cooking purposes, and in some countries for electricity generation. Methane and ethane are the main components of natural gas; they are normally stored as gases under pressure.
- It is, however, easier to transport them as liquids: This requires both compression and cooling of the gas.

Applications of Alkanes

- Propane and butane can be liquefied at fairly low pressures, and are well known as liquified petroleum gas (LPG).
- Propane, for example, is used in the propane gas burner, butane in disposable cigarette lighters.
- The two alkanes are used as propellants in aerosol sprays.

33

Applications of Alkanes

- From pentane to octane the alkanes are reasonably volatile liquids.
- They are used as fuels in internal combustion engines, as they vaporise easily on entry into the combustion chamber without forming droplets, which would impair the uniformity of the combustion.

34

Applications of Alkanes

- Branched-chain alkanes are preferred, as they are much less prone to premature ignition, which causes knocking, than their straight-chain homologues.
- This propensity to premature ignition is measured by the octane rating of the fuel, where 2,2,4-trimethylpentane (*isooctane*) has an arbitrary value of 100, and heptane has a value of zero.

35

Applications of Alkanes

- Alkanes from hexadecane upwards form the most important components of fuel oil and lubricating oil.
- In latter function, they work at the same time as anti-corrosive agents, as their hydrophobic nature means that water cannot reach the metal surface. Many solid alkanes find use as paraffin wax, for example, in candles.
- This should not be confused however with true wax, which consists primarily of esters.

36

Applications of Alkanes

- Alkanes with a chain length of approximately 35 or more carbon atoms are found in bitumen, used, for example, in road surfacing.
- However, the higher alkanes have little value and are usually split into lower alkanes by cracking.
- Some synthetic polymers such as polyethylene and polypropylene are alkanes with chains containing hundreds of thousands of carbon atoms. These materials are used in innumerable applications, and billions of kilograms of these materials are made and used each year.
- Apart from their use as fuels, the middle alkanes are also good solvents for non-polar substances.

37

Give examples of 5 saturated hydrocarbons with an everyday application?

- 1) Methane, CH_4 is a natural gas and is used in home heating.
- 2) Butane, C_4H_{10} is also used in heating but is also used in refrigeration
- 3)Pentane, C_5H_{12} is used in the production of polystyrene foam
- 4) Hexane, C6H14 is the solvent used in most glues
- 5)Octane, C8H18 is the main ingredeint in gasoline

38

Hazards of Alkanes

- Methane is explosive when mixed with air (1 – 8% CH_4) and is a strong greenhouse gas: Other lower alkanes can also form explosive mixtures with air. The lighter liquid alkanes are highly flammable, although this risk decreases with the length of the carbon chain.
- Pentane, hexane, heptane, and octane are classed as *dangerous for the environment* and *harmful*.
- The straight-chain isomer of hexane is a neurotoxin.

39

Cycloalkanes

- These are types of alkanes which have one or more rings of carbon atoms in the chemical structure of their molecules.
- Cycloalkanes are classified into small, common, medium, and large cycloalkanes, where cyclopropane and cyclobutane are the small ones, cyclopentane, cyclohexane, cycloheptane are the common ones, cyclooctane through cyclotridecane are the medium ones, and the rest are the larger ones

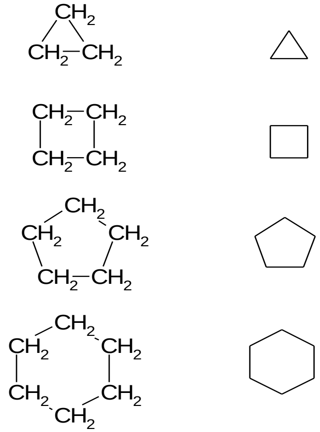
40

Properties of CycloAlkanes

- Cycloalkanes are similar to alkanes in their general physical properties, but they have higher boiling points, melting points, and densities than alkanes. This is due to stronger London forces because the ring shape allows for a larger area of contact.
- Cycloalkanes exhibit almost the same degree of unreactivity as alkanes, due to their containing only unreactive C-C and C-H bonds; however, the ring strain can cause cycloalkanes to be more reactive.

41

Nomenclature of Cycloalkanes



Cyclopropane

Cyclobutane

Cyclopentane

Cyclohexane

42