

Two weaker nucleophiles are:

- H_2O (water)
- R-OH (alcohols)

Example

The reaction between bromoethane (alkyl halide) and a hydroxide or cyanide, the products are an alcohol (ethanol) and a nitrile (propanenitrile) respectively:



(Note here that with the nitrile group (a carbon-nitrogen triple bond), the carbon atom is included in the carbon count for carbon chain when naming the compound).

Free radical substitution reaction of methane by a halogen

Three step reaction

- Initiation Cl_2 molecule breaks into Cl^\bullet radicals in presence of UV light
- Propagation: CH_4 molecule loses a H atom to form a CH_3^\bullet Radical
- Halogenation: CH_3^\bullet Radical combines with Cl^\bullet radicals to form a halo alkane; CH_3Cl

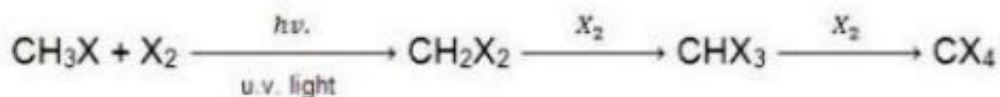
In the presence of excess halogen, all hydrogens on the alkylhalide are replaced by halogen atoms.



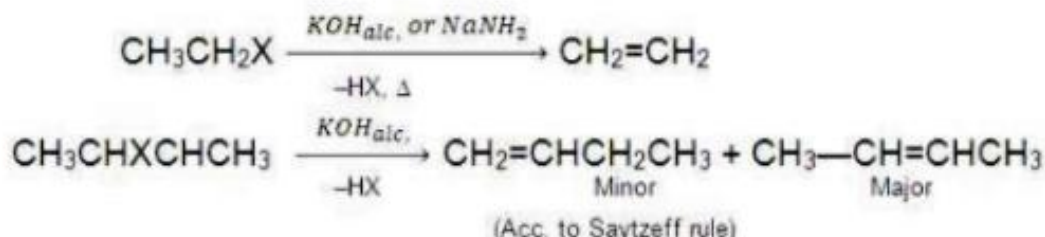
Excess halogen,



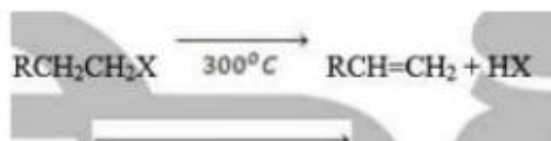
3. Action of halogen:



4. Dehydrohalogenation: elimination of HX by KOH alcoholic.



5. Action of heat on halo alkanes



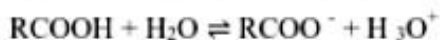
Uses of alkyl halides;

- As alkylating agent i.e. to introduce alkyl group in a molecule.
- Lower members are used as anaesthetic agent, refrigerant and solvents.
- As synthetic reagent.
- Teflon useful for lining frying pans and in the construction of apparatus used in corrosive chemical reactions.
- polyfluorinated alkanes can be used as artificial blood.

CARBOXYLIC ACIDS

Carboxylic acids are weak acids i.e. they do not fully ionise in solution.

Rather an equilibrium is established.



When naming the carboxylic acids, the suffix "oic" replaces the letter "e" at the end of the parent chain name

Eg methanoic acid CHOOH.

FUELS

Petroleum (Latin Petroleum derived from Latin word *petra*= rock and *oleum*= oil or crude oil is a naturally occurring liquid found in formations in the Earth consisting of a complex mixture of hydrocarbons (mostly alkanes) of various lengths.

The approximate length range is C_5H_{12} to $C_{18}H_{38}$.

Any shorter hydrocarbons are considered natural gas or natural gas liquids, while long-chain hydrocarbons are more viscous, and the longest chains are paraffin wax.

Crude oil may also be found in semi-solid form mixed with sand, as in the Athabasca oil sands in Canada, where it may be referred to as crude bitumen.

Petroleum is used mostly, by volume, for producing fuel oil and gasoline (petrol), both important "primary energy" sources.

84% by volume of the hydrocarbons present in petroleum is converted into energy-rich fuels (petroleum-based fuels), including gasoline, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas.

In its naturally occurring form, it may contain other nonmetallic elements such as sulfur, oxygen, and nitrogen.

Crude oil is composed of hundreds of hydrocarbon compounds ranging in size from the smallest, methane, which has only one carbon atom, to large compounds containing 200 or more carbon atoms.

A major portion of these compounds are paraffins, which are straight-chain hydrocarbon compounds such as methane, ethane, and propane.

The remaining hydrocarbon compounds are either cyclic compounds called naphthenes or aromatics.

The products that are normally obtained from crude oil can be grouped as follows.

1. Volatile products
 - Propane LPG (Liquid Petroleum Gas)
 - Butane LPG
 - Light naphtha (C_5 s and C_6)
2. Light distillates

- Gasolines
 - Heavy naphtha
 - Kerosene and jet fuel
3. Middle distillates
 - Diesel fuel
 - Heating oils
 - Gas oils
 4. Fuel oils
 - Marine diesel
 - Bunker fuels (for ships)
 5. Lubricating oils
 - Motor oil
 - Spindle oil
 - Machine oils
 6. Waxes
 - Food and paper coating grade
 - Pharmaceutical grade
 7. Bitumen
 - Asphalt
 - Coke

Products in these groups are produced from distillation processes and treated to meet certain specifications.

These specifications are the result of a compromise between performance capabilities of the product and the treating that must occur to reach these performance characteristics.

It is usually black or dark brown (although it may be yellowish or even greenish) but varies greatly in appearance, depending on its composition.

It has become the world's most important source of energy since the mid- 1950s due to its

- high energy density
- easy transportability
- relative abundance

Petroleum is also the raw material for many chemical products, including

- pharmaceuticals
- solvents
- fertilizers
- pesticides
- plastics

16% not used for energy production is converted into these other materials.

Petroleum is found in porous rock formations in the upper strata of some areas of the Earth's crust.

Known reserves of petroleum are typically estimated at around 1.2 trillion barrels without oil sands, or 3.74 trillion barrels with oil sands.

However, oil production from oil sands is currently limited.

Consumption is currently around 84 million barrels per day, or 3.6 trillion liters per year. Because of reservoir engineering difficulties, recoverable oil reserves are significantly less than total oil-in-place.

At current consumption levels, and assuming that oil will be consumed only from reservoirs, known reserves would be gone around 2039, potentially leading to a global energy crisis.

However, this ignores any new discoveries, rapidly increasing consumption in China & India, using oil sands, using synthetic petroleum, and other factors which may extend or reduce this estimate.

Refining of crude oil

- Crude oil is refined using fractional distillation.
- Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine) which must be removed before refining in order to.
 - i. prevent catalyst poisoning,
 - ii. prevent equipment corrosion,
 - iii. prevent fouling.
- The crude oil is heated and its vaporized components passed into a fractionating column.

- As the components rise up the tower, they start to cool down and will gradually condense back into liquid form.
- They are then tapped off.
- The larger hydrocarbons, with higher boiling points, will condense first and be tapped off near the base of the column e.g. bitumen, wax, grease, fuel oil, diesel, etc.
- The smaller hydrocarbons, with smaller boiling points, will condense later and be tapped off near the top of the column e.g. liquid petroleum gas, kerosene, petrol, etc.
- **Catalytic reforming** is a chemical process used to convert petroleum refinery hydrocarbons, typically having low octane ratings, into high-octane liquid products called **reformates** which are components of high-octane gasoline (also known as high-octane petrol).
- Octane number is a measure of the ignition quality of gas (gasoline or petrol).
- The process re-arranges or re-structures the hydrocarbon molecules in petroleum as well as breaking some of the molecules into smaller molecules.
- The overall effect is that the product reformat contains hydrocarbons with more complex molecular shapes having higher octane values than the hydrocarbons in the in petroleum.
- In so doing, the process separates hydrogen atoms from the hydrocarbon molecules and produces very significant amounts of byproduct hydrogen gas for use in a number of the other processes involved in a modern petroleum refinery.
- Other byproducts are small amounts of methane, ethane, propane, and butanes.

Industries that use petroleum as a raw material

- Pharmaceutical industries
- Solvents manufacturing industries
- Fertilizer manufacturing industries
- Pesticide manufacturing industries
- Plastic manufacturing industries

POLYMERIZATION

A polymer is large molecule (macromolecule) built up by repetitive bonding (covalent) of smaller molecules (monomers).

Polymers are formed by linking monomers through chemical reaction called polymerization.

Homopolymers: are formed from identical monomers



Copolymers: are formed from nonidentical monomers



Types of polymers

Natural: synthesized by organisms e.g. natural rubber, natural silk, cellulose, proteins, starch etc.

Synthetic: man-made e.g. polyethylene, polypropylene, poly-styrene, polybutadiene, nylon poly-amides, polycarbonates, phenolics, amino resins, epoxy resins etc.

Addition polymers: are formed by combining monomers across double or triple bonds e.g. Polyethylene and other polyolefins, Polystyrene and related vinyl polymers etc.

Condensation polymers: are formed by reactions involving loss of small groups e.g. Polyesters and polyamides, polycarbonates, phenol (urea, melamine) – formaldehyde resins, epoxy resins etc.

Crystalline (crystallinity, $\geq 50\%$) e.g. Polyethylene (HDPE and LDPE), polypropylene (isotactic), stretched nylon polyamides, polyoxymethylene etc. cellulose (cotton) fibre.

Amorphous (crystallinity, $\geq 50\%$) e.g. Natural rubber and most synthetic rubbers, N-alkylated(>15% alkylation) nylon polyamides, poly (methacrylates and acrylates) poly (vinyl acetate), polystyrene etc.



A **thermoplastic**, or **thermosoftening plastic**, is a polymer that becomes pliable or moldable above a specific temperature, and returns to a solid state upon cooling.

Thermosetting polymer forms irreversible chemical bonds during heating.

Thermosets often do not melt, but break down and do not reform upon cooling.

Monomer	Polymer
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<p>Ethylene</p> $\text{CH}_2 = \text{CH}_2$	<p>Polyethylene</p> $-(\text{CH}_2-\text{CH}_2)_n-$
<p>Propylene</p> $\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{CH}_3 \end{array}$	<p>polypropylene</p> $\left[\begin{array}{cc} & \\ \text{CH}_3 & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
<p>Acrylonitrile</p> $\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{CN} \end{array}$	<p>Polyacrylonitrile</p>
<p>Styrene</p> $\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	<p>Polystyrene</p>

Monomer(s)	Polymer		
$\text{CH}_2=\text{CH}_2$ (ethene) (or ethylene)	$-\text{CH}_2-\text{CH}_2-$	Polyethylene (PE)	Most common polymer. Used in bags, wire insulation, and squeeze bottles
$\text{CH}_2=\text{CH}$ $\quad $ CH_3 (1-propene) (or propylene)	$-\text{CH}_2-\text{CH}-$ $\quad $ CH_3	Polypropylene (PP)	Fibers, indoor-outdoor carpets, bottles
$\text{CH}_2=\text{CH}$ $\quad $  (styrene)	$-\text{CH}_2-\text{CH}-$ $\quad $ 	Polystyrene (PS)	Styrofoam, molded objects such as tableware (forks, knives and spoons), trays, videocassette cases
$\text{CH}_2=\text{CH}$ $\quad $ Cl (vinyl chloride)	$-\text{CH}_2-\text{CH}-$ $\quad $ Cl	Poly(vinyl chloride) (PVC)	Clear food wrap, bottles, floor covering, synthetic leather, water and drain pipe
$\text{CF}_2=\text{CF}_2$ (tetrafluoroethene)	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoroethylene (Teflon)	Nonstick surfaces, plumbing tape, chemical resistant containers and films

$\begin{array}{c} \text{CO}_2\text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CH}_3 \\ \text{(methyl methacrylate)} \end{array}$	$\begin{array}{c} \text{CO}_2\text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	Poly(methyl methacrylate) (Lucite, Plexiglas)	1.1) Addition polymers (continued) Glass replacement, paints, and household products
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{CN} \\ \text{(acrylonitrile)} \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CN} \end{array}$	Polyacrylonitrile (Acrlan, Orlon, Creslan)	Fibers used in knit shirts, sweaters, blankets, and carpets
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{OOCCH}_3 \\ \text{(vinyl acetate)} \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{OOCCH}_3 \end{array}$	Poly(vinyl acetate) (PVA)	Adhesives, Elmer's glue, paints, textile coatings, and chewing gum
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{(2-methyl-1,3-butadiene)} \\ \text{(or isoprene)} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$	Polyisoprene Natural rubber	Rubber bands, gloves, tires, conveyor belts, and household materials
$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{(2-chloro-1,3-butadiene)} \\ \text{(or chloroprene)} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$	Polychloroprene (neoprene rubber)	Oil and gasoline resistant rubber
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_5 \\ \text{(styrene)} \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_5 \end{array}$	Styrene butadiene rubber (SBR) (copolymer)	Non bounce rubber used in tires

Uses of addition polymers

- polyethene is used in plastic bags and in crates
- polypropene is used in plastic tubing
- polychloroethene (polyvinylchloride) is used in waterproof clothing and records
- polyphenylethene (polystyrene) is used in packaging
- Polyethene: packaging
- Polyvinyl chloride: packaging
- Nylon: clothing
- Polystyrene: clothing, mattress

CARBOHYDRATES

Monosaccharides and disaccharides

Monosaccharides

Are the simplest sugars (single sugars).

Can be used for fuel.

Can be linear or cyclic.

Can be converted into other organic molecules.

Can be combined into polymers.

Examples of monosaccharides: Glucose.

Disaccharides

Double sugars

Consist of two monosaccharides

Are joined by a glycosidic linkage

Remember simple sugars are put together to form disaccharides by the process of dehydration synthesis (condensation reaction)

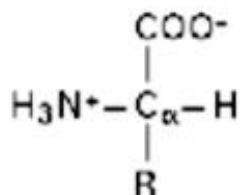
Example: fructose, sucrose

PROTEINS

A protein is a chain of amino acids linked together by peptide bonds (covalent bond between the -COO^- group of one amino acid and the -NH_3^+ -group of the next one (-CO-NH- ; H_2O is set free when the bond is created).

There are 20 proteinogenic amino acids.

The general structure of an amino acid is as follows.



R is the side chain (also called residue)

The amino acid has a carboxyl-group (-COO^-) and an amino group (-NH_3^+).

Classification of Proteins

Proteins can be classified by their functions and by their structure (and their physical properties and enzymatic mechanisms).

Examples for classification by function:

- hydrogenase: catalyses the formation of hydrogen or the reversible oxidation of hydrogen
- dehydrogenase: removes hydrogen from a molecule
- acetylase: creates acetate esters
- kinase: transfers a phosphate group from a high-energy donor molecule (e.g. ATP) to a substrate
- phosphatase: hydrolyses phosphate esters
- oxidoreductase: catalyses a redox (oxidation-reduction) reaction
- polymerase: creates a new DNA or RNA strand using an existing DNA or RNA strand as template
- isomerase: converts one isomeric form of a molecule to another

LIPIDS

A class of biological molecules (i.e., are of biological origin) defined by low solubility in water and high solubility in non-polar solvents (such as chloroform)

They are largely hydrocarbon in composition, thus represent highly reduced forms of carbon, and upon oxidation in metabolism, yield large amounts of energy.

Examples of lipids:

- fats and oils,
- certain vitamins & hormones,
- most non-protein membrane components.

Role of lipids:

- They store energy and protect and insulate internal organs. In human bodies they are stored as fat cells and in animal bodies as starch.
- They are found in nerve fibers and hormones as steroids, which act as chemical messengers.

- Because they are not soluble in water, a major function of lipids is to build the cell membranes that separate the internal contents of cells from the surrounding aqueous environment.

Lipids are divided into the four groups:

- Simple lipids (waxes, fats and oils).
- Complex lipids (glycerophospholipids).
- Steroid (Cholesterol and steroid hormones).
- Prostaglandins.

HARD AND SOFT WATER

The main causes of water hardness are dissolved compounds, particularly compounds of calcium and magnesium.

Calcium (Ca^{2+}) ions and magnesium (Mg^{2+}) ions that have been leached from minerals in the ground result in "**water hardness**".

These ions do not pose any health threat, but they can engage in reactions that leave insoluble mineral deposits, such as scum rings on bathtubs and cooking vessels, or scale on industrial boilers, which decrease the boilers' efficiency.

These deposits can make hard water unsuitable for many uses.

Advantages of hard water

- Good source of calcium for strong bones and teeth
- Most prefer the taste of hard water

Disadvantages of hard water

- Lime scale blocks pipes and reduces efficiency of kettles, washing machines.
- Wastes soap and leaves a scum which can be difficult to remove from clothing.

Methods of softening hard water

The process of removing Ca^{2+} and Mg^{2+} from the water is known as water softening.

The common methods of softening hard water include

I. Precipitation using lime ($\text{Ca}(\text{OH})_2$)



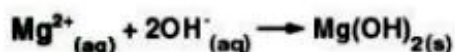
from water from lime precipitate

Notice that Ca^{2+} appears on both sides of equation.

The calcium ion from lime does not actually participate in the reaction to generate insoluble $\text{Mg}(\text{OH})_2$.

Hence, this ion is called a **spectator ion** and can be omitted from the equation.

We can write the overall reaction as the **net ionic equation**:



ii. **Precipitation using soda ash (Na_2CO_3)**



from water from lime from soda ash precipitate

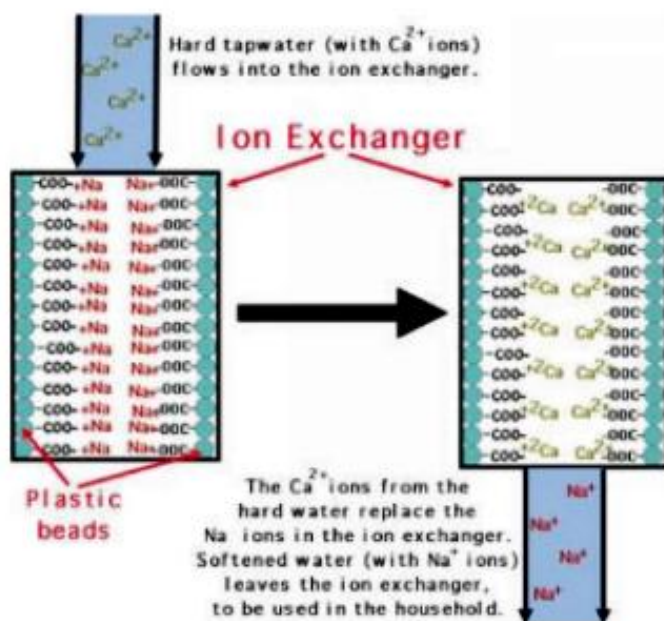
Bicarbonate (HCO_3^-) remaining in the water is nontoxic and does not negatively affect the flavor of the water.

- iii. **Distillation**: It is effective but expensive due to energy consumption.
- iv. **Ion-exchange** devices consist of a bed of plastic (polymer) beads covalently bound to anion groups, such as $-\text{COO}^-$.

The negative charge of these anions is balanced by Na^+ cations attached to them.

When hard water containing Ca^{2+} and Mg^{2+} is passed through the ion exchanger, the Ca^{2+} and Mg^{2+} ions are more attracted to the anion groups than the Na^+ ions.

Hence, they replace the Na^+ ions on the beads, and so the Na^+ ions (which do not form scummy residues) go into the water in place of the Ca^{2+} and Mg^{2+} .



When hard water passes through the ion exchanger, the calcium ions from the water replace the sodium ions in the ion exchanger.

The softened water, containing sodium ions in place of calcium ions, can be collected for household use.

Unfortunately, many people with high blood pressure or other health problems must restrict their intake of sodium.

Because water softened by this type of ion exchange contains many sodium ions, people with limited sodium intakes should avoid drinking water that has been softened this way.

SOAPS, NON-SOAPY DETERGENTS

Soaps are generally referred to as sodium stearate or potassium stearate

The following represent their general structure



Preparation of soaps

Soaps are prepared by saponification which is an esterification reaction between an alkali such as KOH and NaOH and a long chain fatty acid obtained from animal fat or vegetable oils.



or

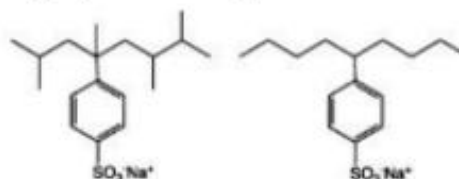


Examples of acids include:

Stearic acid $R = \text{C}_{17}\text{H}_{35}\text{OOH}$

Synthetic detergents are generally referred to as sodium alkylbenzene sulfonates.

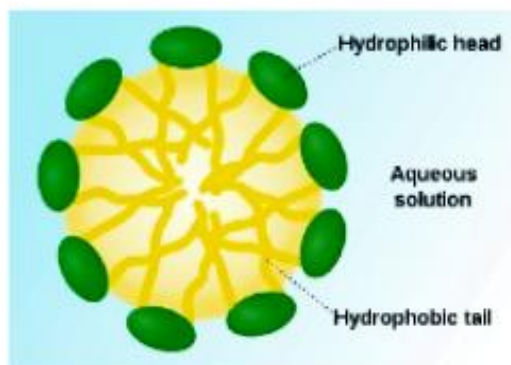
The following represent their general structure



Detergents are prepared by sulfonation reaction between long chain triglycerides (fatty acids) with conc sulphuric acid and NaOH.

Cleansing action of soaps and detergents

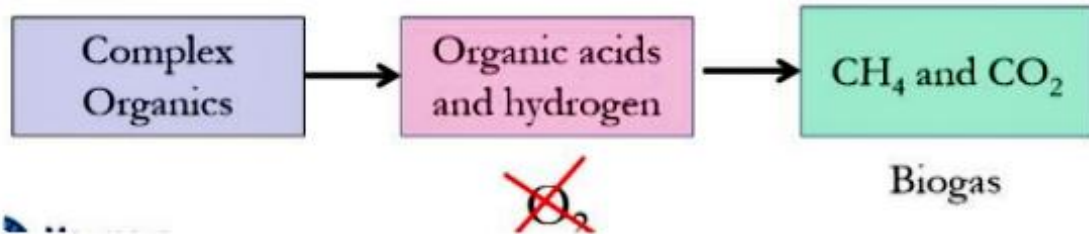
- The hydrophobic tails 'burrow' into the droplet of oil or grease.
- The hydrophilic heads are left to face the surrounding water.
- This results in the formation of a ball-like structure (a micelle).
- The non-polar substances, such as oil or grease, are held inside the ball and suspended in water, to be washed away.



The structure of a micelle

Anaerobic and aerobic digestion

Anaerobic digestion/treatment is a natural process in which a variety of different species of microorganisms including bacteria convert organic wastes through a variety of intermediates into methane gas in the absence of oxygen.



Aerobic digestion/treatment is a natural process in which a microorganisms including bacteria decompose organic wastes through a variety of intermediates in the presence of oxygen.