

# HELIUM

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*See Rare Gases.*

# HERBICIDES

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Herbicides are a class of compounds that allow chemical methods of weed control. This commenced with the introduction of 2,4-dichlorophenoxyacetic acid (2,4-D) in the mid-1940s.

Phenol is the starting material for 2,4-dichlorophenoxyacetic acid via electrophilic aromatic substitution. Chlorination of phenol gives 2,4-dichlorophenol and the sodium salt of this compound is reacted with sodium chloroacetate and acidification gives 2,4-dichlorophenoxyacetic acid.

Another herbicide, 2,4,5-trichlorophenoxyacetic acid, is synthesized by starting with the chlorination of benzene to give 1,2,4,5-tetrachlorobenzene, which reacts with caustic to give 2,4,5-trichlorophenol. Conversion to the sodium salt followed by reaction with sodium chloroacetate and acidification gives 2,4,5-trichlorophenoxyacetic acid. Agent Orange is a 1-to-1 mixture of the butyl esters of 2,4,5-trichlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid.

The bipyridyl herbicide Paraquat is made by reduction of pyridine to radical ions, which couple at the para positions. Oxidation and reaction with methyl bromide gives paraquat. Diquat is formed by dehydrogenation of pyridine and quaternization with ethylene dibromide.

# HEXAMETHYLENEDIAMINE

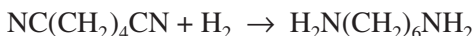
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Hexamethylenediamine (HMDA, boiling point: 204°C, melting point: 41°C) is used in the synthesis of nylon, and it is manufactured from butadiene.

In the process, butadiene first adds one mole of hydrogen cyanide at 60°C with a nickel catalyst via both 1,2 and 1,4 addition to give, respectively, 2-methyl-3-butenitrile and 3-pentenitrile in a 1:2 ratio. Isomerization of the 2-methyl-3-butenitrile to 3-pentenitrile takes place at 150°C. Then more hydrogen cyanide, more catalyst, and a triphenylboron promotor react with 3-pentenitrile to form methylglutaronitrile and mostly adiponitrile. The adiponitrile is formed from 3-pentenitrile probably through isomerization of 3-pentenitrile to 4-pentenitrile and followed by addition of hydrogen cyanide.



Extraction and distillation is necessary to obtain pure adiponitrile. Even then the hexamethylenediamine made by hydrogenation of adiponitrile must also be distilled through seven columns to purify it before polymerization to nylon. Hexamethylenediamine is produced from adiponitrile by hydrogenation.



Evaporation of the reaction product of formaldehyde and ammonia also produces hexamethylenetetramine.

Hexamethylenediamine is used in the production of nylon 6,6 and mainly in making phenol-formaldehyde resins, where it is known as *hexa*. It is also used as a urinary antiseptic (Urotropine) as well as in the rubber industry and for the manufacture of the explosive cyclonite.

# HEXAMETHYLENETETRAMINE

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*See Hexamine.*

# HEXAMINE

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Hexamine [hexamethylenetetramine, methenamine, and urotropine,  $(\text{CH}_2)_6\text{N}_4$ ; melting point:  $280^\circ\text{C}$ ] is a white crystalline solid that decomposes at higher temperatures. Hexamine is soluble in water but only very slightly soluble in alcohol or ether.

Hexamine is manufactured from anhydrous ammonia ( $\text{NH}_3$ ) and a 45% solution of methanol-free formaldehyde ( $\text{HCH}=\text{O}$ ). These raw materials, plus recycle mother liquor, are charged continuously at carefully controlled rates to a high-velocity reactor, since the reaction is exothermic. The reactor effluent is discharged into a vacuum evaporator that also serves to crystallize the product, and the hexamine crystals are washed, dried, and screened. Typically, the yield of hexamine is on the order of 96%.

Although used to some extent in medicine as an internal antiseptic, the primary use of hexamine is in the manufacture of synthetic resins where the compound is a substitute for formalin (aqueous solution of paraformaldehyde) and its sodium hydroxide catalyst. Hexamine is also used as an accelerator for rubber.

# HEXANES

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Hexane isomers ( $C_6H_{14}$ ) are produced by two-tower distillation of straight-run gasoline that has been distilled from crude oil or natural gas liquids.

Hexanes are mostly used in gasoline. They are also used as a solvent and as a medium for various polymerization reactions.

# HEXYLRESORCINOL

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Hexylresorcinol (1,3-dihydroxy-4-hexylbenzene) is an odorless solid that has marked germicidal properties and is used as an antiseptic, commonly employed in a dilution of 1:1000.

In the manufacture of hexylresorcinol, resorcinol and caproic acid are heated with a condensing agent, such as zinc chloride, and the intermediate ketone derivative is formed, which is purified by vacuum distillation. After reduction with zinc amalgam and hydrochloric acid, impure hexylresorcinol is formed, which can be purified by vacuum distillation.

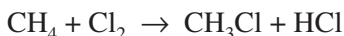
# HYDROCHLORIC ACID

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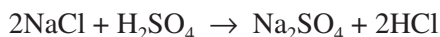
Hydrogen chloride (HCl, boiling point:  $-35^{\circ}\text{C}$ ) is a colorless, poisonous gas with a pungent odor. Aqueous solutions of hydrogen chloride are known as *hydrochloric acid* or, if the hydrogen chloride in solution is of the commercial grade, as *muriatic acid*. Hydrochloric acid typically contains 24 to 36% by weight hydrogen chloride.

Hydrochloric acid is obtained from four major sources:

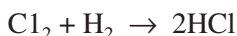
1. As a by-product in the chlorination of both aromatic and aliphatic hydrocarbons or from the thermal degradation of organic chlorine compounds,



2. From reacting sodium chloride (salt) and sulfuric acid,



3. From the combustion of hydrogen and chlorine,



4. From Hargreaves-type operations,



The reaction between hydrogen and chlorine is highly exothermic and spontaneously goes to completion as soon as it is initiated. The equilibrium mixture contains about 4% by volume free chlorine. As the gases are cooled, the free chlorine and free hydrogen combine rapidly so that when  $200^{\circ}\text{C}$  is reached, the gas is almost pure hydrogen chloride. By carefully controlling the operating conditions, a gas containing 99% hydrogen chloride can be produced and it can be further purified by absorbing it in water in a tantalum or impervious or impregnated graphite absorber. The aqueous



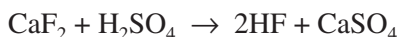
solution is stripped of hydrogen chloride under slight pressure, giving strong gaseous hydrogen chloride that is dehydrated to 99.5% hydrogen chloride by cooling it to  $-12^{\circ}\text{C}$ . Large amounts of anhydrous hydrogen chloride are needed for preparing methyl chloride, ethyl chloride, vinyl chloride, and other such compounds.

Hydrochloric acid is replacing sulfuric acid in some applications such as metal pickling, which is the cleaning of metal surfaces by acid etching. It leaves a cleaner surface than sulfuric acid, reacts more slowly, and can be recycled more easily. It is used in chemical manufacture especially for phenol and certain dyes and plastics. In oil well drilling, it increases the permeability of limestone by acidifying the drilling process.

# HYDROFLUORIC ACID

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Hydrofluoric acid (melting point:  $-83.1^{\circ}\text{C}$ , boiling point:  $19.5^{\circ}\text{C}$ ) is produced by treating fluorspar ( $\text{CaF}_2$ ) with 20% oleum and heating it with sulfuric acid in a horizontal rotating drum.



Hydrofluoric acid is used for manufacture of fluorocarbons, including fluoropolymers, chlorofluorocarbons; chemical intermediates including fluoroborates, surfactants, herbicides, and electronic chemicals; aqueous hydrofluoric acid; petroleum alkylation; and uranium processing.

*See Fluorine.*

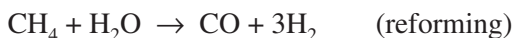
# HYDROGEN

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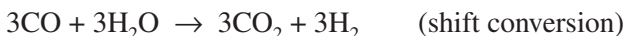
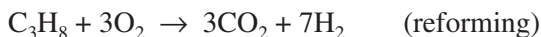
Hydrogen (boiling point:  $-252.8^{\circ}\text{C}$ ) is primarily manufactured by steam-reforming natural gas ( $\text{CH}_4$ ) or hydrocarbons ( $\text{C}_n\text{H}_{2n+2}$ ).

A variety of low-molecular-weight hydrocarbons can be used as feedstock in the steam-reforming process. The reaction occurs in two separate steps: reforming and shift conversion.

Methane:

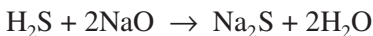


Propane:



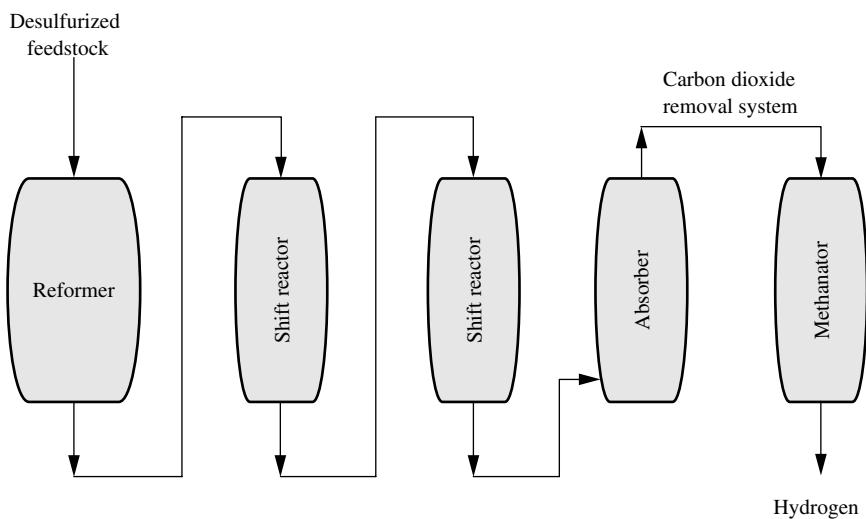
The reforming step makes a hydrogen–carbon monoxide mixture (*synthesis gas*) that is used to produce a variety of other chemicals.

In the steam-reforming process (Fig. 1), the hydrocarbon feedstock is first desulfurized by heating to  $370^{\circ}\text{C}$  in the presence of a metallic oxide catalyst that converts the organosulfur compounds to hydrogen sulfide. Elemental sulfur can also be removed with activated carbon absorption. A caustic soda scrubber removes the hydrogen sulfide by salt formation in the basic aqueous solution.



Steam is added and the mixture is heated in the furnace at 760 to  $980^{\circ}\text{C}$  and 600 psi over a nickel catalyst. When higher-molecular-weight hydrocarbons are the feedstock, potassium oxide is used along with nickel to avoid larger amounts of carbon formation.

There are primary and secondary furnaces in some plants. Air can be added to the secondary reformers. Oxygen reacts with some of the hydrocarbon feedstock to keep the temperature high. The nitrogen of the air is



**FIGURE 1** Hydrogen production by steam reforming hydrocarbon feedstocks.

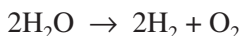
utilized when it, along with the hydrogen formed, reacts in the ammonia synthesizer. More steam is added and the mixture enters the shift converter, where iron or chromic oxide catalysts at 425°C further react the gas to hydrogen and carbon dioxide.

Some shift converters have high- and low-temperature sections, the high-temperature section converting most of the carbon monoxide to carbon dioxide. Cooling to 38°C is followed by carbon dioxide absorption with monoethanolamine ( $\text{HOCH}_2\text{CH}_2\text{NH}_2$ ). The carbon dioxide (an important by-product) is desorbed by heating the monoethanolamine and reversing this reaction.



Alternatively, hot carbonate solutions can replace the monoethanolamine. A methanator converts the last traces of carbon dioxide to methane, a less interfering contaminant in hydrogen used for ammonia manufacture.

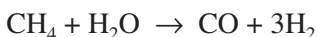
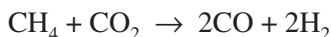
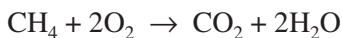
Hydrogen is also produced by an electrolytic process that produces high-purity hydrogen and consists of passing direct current through an aqueous solution of alkali, and decomposing the water.



A typical commercial cell electrolyzes a 15% sodium hydroxide ( $\text{NaOH}$ ) solution, uses an iron cathode and a nickel-plated-iron anode, has

an asbestos diaphragm separating the electrode compartments, and operates at temperatures from 60 to 70°C. The nickel plating of the anode reduces the oxygen overvoltage.

Partial oxidation processes rank next to steam-hydrocarbon processes in the amount of hydrogen made. They can use natural gas, refinery gas, or other hydrocarbon gas mixtures as feedstocks, but their chief advantage is that they can also accept liquid hydrocarbon feedstocks such as gas oil, diesel oil, and even heavy fuel oil. All processes employ noncatalytic partial combustion of the hydrocarbon feed with oxygen in the presence of steam in a combustion chamber at flame temperatures between 1300 and 1500°C. For example, with methane as the principal component of the feedstock:



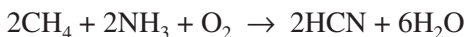
The overall process is a net producer of heat; for efficient operation, heat recovery (using waste heat boilers) is important.

Most of the hydrogen is generated on site for use by various industries, particularly the petroleum industry. Other uses include ammonia production, metallurgical industries to reduce the oxides of metals to the free metals, methanol production, and hydrogen chloride manufacture.

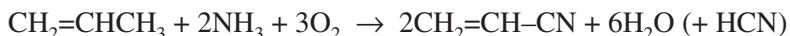
# HYDROGEN CYANIDE

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Hydrogen cyanide (melting point:  $-14^{\circ}\text{C}$ , boiling point:  $26^{\circ}\text{C}$ ) is manufactured by the reaction of natural gas (methane), ammonia, and air over a platinum or platinum-rhodium catalyst at elevated temperature (the Andrussov process).



Hydrogen cyanide is also available as a by-product from acrylonitrile manufacture by ammoxidation.



Hydrogen cyanide is used for the production of methyl methacrylate, adiponitrile, cyanuric chloride, and chelating agents.

*See Methane.*

# **HYDROGEN PEROXIDE**

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Hydrogen peroxide is the most widely used peroxide compound. Originally, it was produced by the reaction of barium peroxide and sulfuric acid but this process and use have been superseded.

The most important method of making hydrogen peroxide is by reduction of anthraquinone to the hydroquinone, followed by reoxidation to anthraquinone by oxygen and formation of the peroxide.

The hydrogen peroxide is extracted with water and concentrated, and the quinone is recycled for reversion to the hydroquinone. A second organic process uses isopropyl alcohol, which is oxidized at moderate temperatures and pressures to hydrogen peroxide and acetone. After distillation of the acetone and unreacted alcohol, the residual hydrogen peroxide is concentrated.

Hydrogen peroxide applications include commercial bleaching dye oxidation, the manufacture of organic and peroxide chemicals. Hydrogen peroxide is also used in pulp and paper chemical synthesis, textiles, and environmental control, including municipal and industrial water treatment.