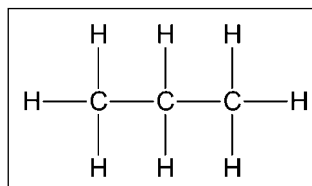


## 75. Propane

**CHEMICAL NAME** = propane  
**CAS NUMBER** = 74-98-6  
**MOLECULAR FORMULA** =  $C_3H_8$   
**MOLAR MASS** = 44.1 g/mol  
**COMPOSITION** = C(81.7%) H(18.3%)  
**MELTING POINT** =  $-187.6^\circ\text{C}$   
**BOILING POINT** =  $-42.1^\circ\text{C}$   
**DENSITY** = 1.30 g/L (vapor density = 1.52, air = 1)



Propane is a colorless, odorless, flammable gas that follows methane and ethane in the alkane series. The root word *prop* comes from the three-carbon acid propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ . Propionic acid comes from the Greek words *protos* meaning first and *pion* meaning fat. It was the smallest acid with fatty acid properties. Propane is the gas used to fuel barbecues and camp stoves giving it the common name bottled gas. It is marketed as liquefied petroleum gas (LPG) or liquefied petroleum; it should be noted that LPG is often a mixture that may contain butane, butylene, and propylene in addition to propane. In addition to cooking, propane can be used as an energy source for space heating, refrigeration, transportation, and heating appliances (clothes dryer). Propane is a \$10 billion industry in the United States, and the United States consumes approximately 15 billion gallons of propane annually.

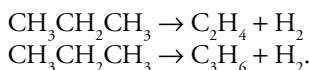
Propane can be stored as liquid in pressurized (approximately 15 atmospheres) storage tanks and/or at cold temperatures and vaporizes to a gas at atmospheric pressure and normal temperatures. This makes it possible to store a large volume of propane as a liquid in a relatively small volume; propane as a vapor occupies 270 times the volume of propane in liquid form. This makes liquid propane an ideal fuel for transport and storage until needed.

Bottled gas was sold as early as 1810 in England, but propane was discovered at the start of the 20th century with the development of the natural gas industry. Problems in natural gas distribution were attributed to condensation of particular fractions of natural gas in pipes. This led to the removal of these higher boiling point gases and a search for applications for these gases. Concurrent with the development of the natural gas industry, society's

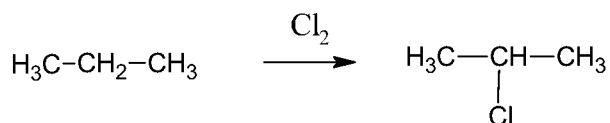
increasing use of automobiles began. Volatile gasoline used in early cars vaporized appreciable amounts of hydrocarbons leading to a continual expense to early car owners. Walter Snelling (1880–1965), a research chemist working for the U.S. Bureau of Mines in 1910, investigated emissions from Ford Model-T gasoline tanks. Snelling developed a still for separating liquid and gaseous fractions of gasoline as he investigated methods to control emissions. Thus Snelling was able to separate propane (and butane) from natural gas. Snelling discovered that propane would condense at moderate pressures and developed a method for bottling liquid propane. By 1912, Snelling and others found that propane could be used as a fuel for cooking and lighting and as a source for cutting torches. Snelling joined with associates to found the American Gasol Company, which was the first commercial provider of propane. A year later, Snelling sold his patent for propane for \$50,000 to Frank Phillips (1873–1950), founder of Phillips Petroleum.

Propane has been used as a transportation fuel since its discovery. It was first used as an automobile fuel in 1913. It follows gasoline and diesel as the third most popular vehicle fuel and today powers more than half a million vehicles in the United States and 6 million worldwide. The widespread use of propane is hampered by the lack of a distribution system, but it has been used to fuel fleets of buses, taxis, and government vehicles. Also, it is heavily used to power equipment such as forklifts. Propane is cleaner burning than gasoline or diesel and has been used to reduce urban air pollution. Compared to gasoline it emits 10–40% of the carbon monoxide, 30–60% of the hydrocarbons, and 60–90% of the carbon dioxide. An advantage of cleaner burning propane is that engine maintenance is improved because of lower engine deposits and fouling. Propane's octane ratings range between 104 and 110. The lower emissions are somewhat compromised by propane's lower energy value; propane has about 75% of the energy content of gasoline when compared by volume. Propane is separated from natural gas and is also produced during petroleum processing. Approximately 53% of the propane produced in the United States comes from the small fraction (less than 5%) found in natural gas and the remainder comes petroleum refining.

Propane's greatest use is not as a fuel but in the petrochemical industry as a feedstock. As an alkane, it undergoes typical alkane reactions of combustion, halogenation, pyrolysis, and oxidation. Pyrolysis or cracking of propane at several hundred degrees Celsius and elevated pressure in combination with metal catalysts result in dehydrogenation. Dehydrogenation is a primary source of ethylene and propylene:



Because propane contains three carbon atoms, halogenation produces two isomers when propane is reacted with a halogen. For example, when propane is chlorinated the chlorine can bond to one of the terminal carbons to produce 1-chloropropane:  $\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CH}_2\text{CH-Cl}$  or the chlorine can bond to the central carbon to give 2-chloropropane:



Propane demonstrates that the carbon atoms have different characteristics in alkanes with more than two carbon atoms. The terminal carbon atoms in propane are bonded to three hydrogen atoms and one carbon atom. A carbon atom bonded to only one other carbon atom is referred to as a primary or  $1^\circ$  carbon. The central carbon atom in propane is bonded to two other carbon atoms and is called a secondary or  $2^\circ$  carbon. A hydrogen atom has the same classification as the carbon atom to which it is attached. Thus the hydrogen atoms attached to the terminal carbon atoms in propane are called primary ( $1^\circ$ ) hydrogens, whereas the central atom has secondary ( $2^\circ$ ) hydrogen. The difference in bonds leads to differences in reactions and properties of different isomers. For example, breaking a primary bond requires more energy than breaking a secondary bond in propane. This makes formation of the isopropyl radical  $\text{CH}_3\text{CHCH}_3\bullet$  easier than the n-propyl radical,  $\text{CH}_3\text{CH}_2\text{CH}_2\bullet$ . Even though the formation of the isopropyl is more favorable energetically, the greater number of primary hydrogen atoms leads to approximately equal amounts of n-propyl and isopropyl radicals formed under similar reaction conditions.

Oxidation of propane can produce various oxygenated compounds under appropriate conditions, but generally alkanes are relatively unreactive compared to other organic groups. Some of the more common oxidation products include methanol ( $\text{CH}_3\text{OH}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), and acetaldehyde ( $\text{C}_2\text{H}_4\text{O}$ ). Propane can be converted to cyclopropane by conversion to 1,3 dichloro-propane using zinc dust and sodium iodide  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{Zn, NaI}}$  cyclopropane.

