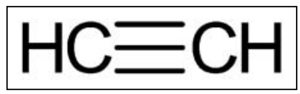
3. Acetylene



CHEMICAL NAME = ethyne
CAS NUMBER = 74–86–2
MOLECULAR FORMULA = C_2H_2
MOLAR MASS = 26.0 g/mol
COMPOSITION = C(92.3%) H(7.7%)
MELTING POINT = −80.8°C
BOILING POINT = −80.8 (sublimes)
DENSITY = 1.17 g/L (vapor density = 0.91, air = 1)

Acetylene, which is the simplest alkyne hydrocarbon, exists as a colorless, flammable, unstable gas with a distinctive pleasant odor (acetylene prepared from calcium carbide has a garlic smell resulting from traces of phosphine produced in this process). The term *acetylenes* is used generically in the petroleum industry to denote chemicals based on the carbon-carbon triple bond. Acetylene was discovered in 1836 by Edmund Davy (1785–1857) who produced the gas while trying to make potassium metal from potassium carbide (K_2C_2). In 1859, Marcel Morren in France produced acetylene by running an electric arc between carbon electrodes in the presence of hydrogen. Morren called the gas produced carbonized hydrogen. Three years later, Pierre Eugène-Marcelin Berthelot (1827–1907) repeated Morren's experiment and identified carbonized hydrogen as acetylene.

A method for the commercial production of acetylene was discovered accidentally in 1892 by Thomas Willson (1860–1915). Willson was experimenting on aluminum production at his company in Spray, North Carolina. He was attempting to produce calcium in order to reduce aluminum in aluminum oxide, Al_2O_3. Willson combined coal tar and quicklime in an electric furnace and, instead of producing metallic calcium, he produced a brittle gray substance. The substance was calcium carbide, CaC_2, which when reacted with water, produced acetylene. Willson's work led to the establishment of a number of acetylene plants in the United States and Europe during the next decade.

The triple bond in acetylene results in a high energy content that is released when acetylene is burned. After Willson's discovery of a method to produce commercial quantities of acetylene, Henry-Louis Le Châtelier (1850–1936) found that burning acetylene and oxygen in approximately equal volumes produced a flame hotter than any other gas. Flame temperatures between 3,000°C and 3,300°C were possible using acetylene and pure oxygen, which was high enough to cut steel. The hot flame from acetylene is due not so much from its heat of combustion, which is comparable to other hydrocarbons, but from the nature of the flame produced by acetylene. Acetylene burns quickly when combined with pure oxygen, producing a flame with a tight concentrated inner cone. The transfer of energy from the flame occurs in a very small volume, resulting in a high temperature. During the last half of the 19th century, torches using hydrogen and oxygen were used for cutting metals, but the highest temperatures were around 2000°C. Torches capable of using acetylene were developed in the early 20th century, and acetylene found widespread use for metal working. Another widespread use of acetylene was for illumination. Portable lamps for miners, automobiles, bicycles, and lanterns used water mixed with calcium carbide to generate acetylene that burned to produce a bright flame. Street lamps, lighthouses, and buoys also used acetylene for illumination, but by 1920 acetylene as a light source had been replaced by batteries and electric light.

One problem with the use of acetylene is its stability. Although it is stable at normal pressures and temperatures, if it is subjected to pressures as low as 15pounds per square inch gauge (psig) it can explode. To minimize the stability problem, acetylene transport is minimized. Acetylene contained in pressurized cylinders for welding and cutting is dissolved in acetone. A typical acetylene cylinder contains a porous filler made from a combination of materials such as wood chips, diatomaceous earth, charcoal, asbestos, and Portland cement. Synthetic fillers are also available. Acetone is placed in the cylinder and fills the voids in the porous material. Acetylene can then be pressurized in the cylinders up to approximately 250 pounds per square inch (psi) In a pressurized cylinder, 1 liter of filler can hold a couple of hundred liters of acetylene, which stabilizes it. Acetylene cylinders should not be stored on their sides because this could cause the acetone to distribute unequally and create acetylene pockets.

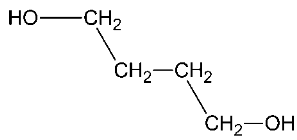
The traditional method of producing acetylene is from reacting lime, calcium oxide (CaO), with coke to produce calcium carbide (CaC_2). The calcium carbide is then combined with water to produce acetylene:

$$2CaO_{(s)} + 5C_{(s)} \rightarrow 2CaC_{2(g)} + CO_{2(g)}$$
$$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow C_2H_{2(g)} + Ca(OH)_{2(aq)}$$

Several processes for producing acetylene from natural gas and other petroleum products developed in the 1920s. Thermal cracking of methane involves heating methane to approximately 600°C in an environment deficient in oxygen to prevent combustion of all the methane. Combustion of part of the methane mix increases the temperature to approximately 1,500°C, causing the remaining methane to crack according the reaction: $2CH_{4(g)} \rightarrow C_2H_{2(g)} + 3H_{2(g)}$. In addition to methane, ethane, propane, ethylene, and other hydrocarbons can be used as feed gases to produce acetylene.

Approximately 80% of acetylene production is used in chemical synthesis. In the United States approximately 100,000 tons are used annually. Acetylene saw much wider use in the past, especially in Germany where it was widely used as in chemical synthesis. During recent decades, greater use of ethylene as a chemical feedstock and the development of more economical chemical production methods that eliminate acetylene has reduced acetylene's use in the chemical industry. Since 2000, use in the United States has decreased by approximately

50,000 tons a year. Most acetylene production is used for the production of 1,4-butanediol, which is used to produce plastics, synthetic fibers, and resins. It is also used as an organic solvent and in coatings. The traditional process to produce 1,4-butanediol involves reacting acetylene with formaldehyde using the Reppe process named for Walter Reppe (1892–1969). Reppe, who has been called the "father of acetylene chemistry," pioneered methods of using acetylene in the chemical industry.



1,4-butanediol

This Reppe process using acetylene for 1,4 butanediol is currently being replaced with processes that start with propylene oxide (C_3H_6O), butadiene (C_4H_6), or butane (C_4H_{10}).

The triple bond in acetylene makes its unsaturated carbons available for addition reactions, especially hydrogen and halogens. Reaction with hydrogen chloride produces vinyl chloride that polymerizes to polyvinyl chloride (see Vinyl Chloride). This was the chief reaction used to produce vinyl chloride before 1960. Because acetylene is highly reactive and unstable, it presented more difficulties and was more expensive than processes developed in the 1950s that used ethylene rather than acetylene. The addition of carboxylic acids to acetylene gives vinyl esters. For example, the addition of acetic acid produces vinyl acetate. Acrylic acid ($CH_2 = CHCOOH$) was once produced using Reppe chemistry in which acetylene was combined with carbon monoxide and alcohol (or water) in the presence of a nickel carbonyl catalyst. Acrylic acid is now produced more economically using propylene rather than acetylene. The addition of hydrogen to acetylene with appropriate catalysts such as nickel yield ethylene. Acetylene polymerizes to form polyacetylene.