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Editorial

Discovery by Accident: Calcium Carbide

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Abstract

Thomas L.Willson (1860-1915) did not succeed in 1892 to produce aluminum by reduction of Al_2O_3 with coal in the electric furnace instead he discovered by accident calcium carbide which produced acetylene on contact with water. Although acetylene had no use at the time but later on it proved to be a very important gas.

Keywords

Electric furnace; Acetylene; Aluminum; Cyanamid; Ammonia; Welding; Cutting

Calcium Carbide

The electrical engineer Thomas L. Willson (1860-1915) attempted in 1892 to produce aluminum by reduction of Al_2O_3 with coal in the electric furnace to compete with the Hall-Héroult electrolytic process. His approach was to use a high-temperature electric furnace discovered about the same time by the French chemist Henri Moissan. He was just one among many seeking an economical way to make aluminum. He did not succeed in his venture. He then tried to produce calcium from lime by reduction with carbon to use it to make aluminum. He obtained crystalline fragile black mass that generated a gas when a sample taken for analysis was cooled in water. It was thought that hydrogen was formed as a result of the reaction of calcium with water since the gas was flammable. However, the gas was mysterious because it burnet with a luminous flame (Figure 1) [1].

Chemists at the University of North Carolina, identified the gas as acetylene:

 $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

In 1836, Edmund Davy (1785-1857) professor of Chemistry at the Royal Cork Institution in Ireland (a cousin of Humphry Davy), discovered a gas which he recognized as "a new carburet of hydrogen." It was an accidental discovery while attempting to isolate potassium metal. By heating potassium carbonate with carbon at very high temperatures, he produced a residue of what is now known as potassium carbide, (K_2C_2), which reacted with water to release the new gas. In the paper he read to the British Association at Bristol, Davy anticipated the value of acetylene as an illuminating gas. This was forgotten until Marcellin

Berthelot (1827-1907) in France rediscovered this hydrocarbon compound in 1860, for which he named acetylene from acetyl radical + ene in accordance with ethylene C_2H_4 [C_2H_3]

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radical + H]. Berthelot prepared acetylene by passing an electric charge between two carbon electrodes in an atmosphere of hydrogen. Berthelot's empirical formula was C_4H_2 , as well as the alternative name "quadricarbure d'hydrogène" were incorrect because chemists at that time used the wrong atomic mass for carbon (6 instead of 12). The correct formula is C,H, or H-C=C-H.

Friedrich Wöhler (1800-1882) in Germany in 1862 had also prepared calcium carbide by heating a zinc-calcium alloy with coal and noted its reaction with water to form acetylene, but this was only a laboratory curiosity. Thus a cheap method was found by Willson to prepare calcium carbide on large scale. But, there were no uses for either calcium carbide or acetylene at the time (Figure 2).

Cyanamid and Ammonia

Not long afterwards (in 1895) it was discovered by Nikodem Caro (1871-1935) and Adolf Frank (1834 –1916) that calcium carbide



Figure 1: Thomas L. Willson



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Figure 4: Pipe cutting by oxy-acetylene flame

when heated in atmosphere of nitrogen would form cyanamid, itself a fertilizer and from which ammonia and a number of other products could be made [2]:

 $CaC_2 + N_2 \rightarrow CaCN_2 + C$

The cyanamide-carbon mixture was then mixed with a flux (NaCl) and heated in electric furnace to form molten crude calcium cyanide:

 $CaCN_{2} + C \rightarrow Ca(CN)_{2}$

Ammonia can be produced from calcium cyanamide by hydrolysis:

 $CaCN_2 + 3H_2O \rightarrow 2NH_3 + CaCO_3$

Oxygen-Acetylene Welding and Cutting

French engineers Edmond Fouché and Charles Picard became the first to develop oxygen-acetylene flame cutting and welding in 1903. A high temperature is obtained by burning acetylene in oxygen that is suitable for this purpose. While oxy acetylene welding is obsolete today, there was a time when it was the most common process utilized throughout the world (Figure 3).

Organic Chemicals and Macromolecules

Following Willson's synthesis of chloroform and aldehydes from acetylene in 1894, acetylene soon became the starting material in the synthesis of a host of organic substances, particularly for the solvent, plastics, and synthetic rubber and fiber industries. By 1896, work in Germany led to chlorinated solvents by partial or complete chlorination of acetylene In Germany after World War I, butadiene made from acetylene was the basis of a rubber substitute. Also in Germany, beginning in 1925, J. Walter Reppe in Badische Anilin- und Soda Fabrik pioneered the study of acetylene chemistry at pressures as high as 200 atmospheres (Figure 4) [3].

Acetylene from Petroleum

In the past years, acetylene has increasingly been derived from petroleum by raising the temperature of various hydrocarbons to the point where their atomic bonds break in what is known as a thermal cracking process. The chemical reaction for converting methane into acetylene:

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

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