Kirk-Othmer Encyclopedia of Chemical Technology
1st ed., Vol. 1, 1947

The Bureau of Explosives also requires and rigidly enforces its regulation that when an acetylene cylinder is filled, its internal pressure may not exceed 250 p.s.i.g. at 70°F.

Filling Cylinders with Acetylene. The filling of acetylene cylinders requires the compression of acetylene to pressures of about 300 p.s.i.g. The technique calls for careful design and construction of cylinder-charging plants, taking into account all hazard factors. Acetylene is compressed by standard-type compressors, which are run usually at slightly lower than normal speeds. Considerable caution is exercised to be sure that intermediate- and after-cooling are maintained adequate and constant. All piping, valves, and fittings carrying acetylene at pressures in excess of 15 p.s.i.g. are heavily constructed to withstand the maximum possible decomposition force to which the acetylene within might subject them.

The amount of acetone required to be added during charging depends upon the construction of the cylinder and its internal condition, the temperature at which it was used, and the degree to which its contents were used up. Empty cylinders are carefully weighed, and acetone is added when necessary. The precharging weight is carefully noted on each individual cylinder. This precharging empty weight is not necessarily the tare or stencil weight of the cylinder. Weighed empty cylinders are usually connected in groups to charging manifolds. A nominal pressure differential is maintained between the compressor and the cylinders so that charging of the cylinder will not be too rapid nor will any large pressure drop occur across any valve or fitting in the piping system. Since the absorption of the acetylene in the acetone gives rise to a considerable heat of solution, it is common practice to apply water sprays to the cylinders during charging in warm weather.

The contents of charged cylinders are determined by weight. Each cylinder is also checked for any possible valve or fuse-plug leaks. In addition, a constant running check is made of cylinders picked at random to make certain that the 250 p.s.i.g. pressure at 70°F. limitation of the Interstate Commerce Commission is not exceeded.

Economic Aspects of Using Acetylene from Cylinders. The shipping of acetylene adds considerably to the consumer cost of the product because it cannot be transported in liquid form or as a free gas under high pressure. On reacting completely, calcium carbide gives off acetylene equal to about 31% of its weight. Calcium carbide is thus the cheapest form in which to transport acetylene by common carriers. Acetylene, compressed and dissolved in cylinders, represents less than 10% of the total shipping weight and, when the fact that the cylinder must be returned empty is taken into account, the net efficiency of shipping is actually less than 5% of the gross weight.

Analysis

Acetylene in high concentrations may be determined by three methods:

(*1*) In apparatus of the Orsat type (see *Gas analysis*) acetylene is absorbed in fuming sulfuric acid. Olefins are also absorbed.

(*2*) The gas is passed into silver nitrate solution, precipitating silver acetylide (see "Derivatives," page 12), and the resulting nitric acid is titrated. Olefins do not give this reaction, but ammonia and hydrogen sulfide are interfering substances. The accuracy is about ±0.5% (based on the whole sample), and the method is somewhat less accurate than (*1*).

UCC
002688

(3) For extreme accuracy, fractionation in a column of the Podbielniak or McMillan type is recommended. The still must be operated at slightly above atmospheric pressure to eliminate the freezing of acetylene in the column.

Acetylene in concentrations from very slight traces up to 2% can be determined by passing the gas through an ammoniacal solution of cuprous chloride. The presence of acetylene is indicated by a pink or red precipitate of copper acetylide, which may be determined colorimetrically or gravimetrically. Higher concentrations of acetylene can also be determined with the same solution in apparatus of the Orsat type, provided carbon monoxide is absent.

Analysis of Acetylene for Impurities. Unpurified acetylene ordinarily contains about 99.6% acetylene on a dry basis. Apart from water, the chief impurity is air, which may amount to approximately 0.2% to 0.4%. The remainder is mostly phosphine, ammonia, hydrogen sulfide, and, in some instances, small amounts of carbon dioxide, hydrogen, methane, carbon monoxide, organic sulfur compounds, silicon hydrides, and arsine. Purified cylinder acetylene is substantially free from phosphine, ammonia, hydrogen sulfide, organic sulfur compounds, and arsine. The other impurities are nearly the same as in the original gas, and acetone becomes the principal impurity. On a volume basis, the acetone in the gas issuing from a full cylinder amounts to roughly 2% of the acetylene, but it must be remembered that the concentration of acetone will depend on a number of factors, such as temperature, the pressure in the cylinder, and the rate of delivery of the gas. The percentage of acetone tends to increase as the cylinder discharges, and is greatest just as the cylinder approaches atmospheric pressure. The acetone in the gas may be removed, and if necessary determined, by passing through water, activated charcoal, or a freezing unit, but in the last method the formation of liquid or solid acetylene must be carefully avoided. The quantities of moisture carried by acetylene under various pressure and temperature conditions may be determined by ordinary psychrometric methods (see *Humidity*).

Determination of Oxygen in Acetylene. A sample of the acetylene is treated with a suspension of manganous hydroxide in the presence of potassium hydroxide-potassium iodide solution, and the acetylene is then removed with a vacuum pump. Any oxygen present oxidizes the manganous hydroxide to higher valence states, and on the addition of sulfuric acid the equivalent amount of iodine is liberated. Thus, indirectly:

$$O_2 + 4\,HI \longrightarrow 2\,H_2O + 2\,I_2$$

The iodine is titrated with sodium thiosulfate. Hydrogen sulfide, if present, will react with the liberated iodine as follows:

$$H_2S + I_2 \longrightarrow 2\,HI + S$$

Hence one volume of hydrogen sulfide reduces the apparent oxygen content by one-half volume and, if appreciable hydrogen sulfide is present, it should first be removed by passing the sample through lead acetate solution.

Alternatively, oxygen may be determined volumetrically in the usual manner by absorption in alkaline pyrogallol after treatment with fuming sulfuric acid.

Determination of Phosphorus and Sulfur in Acetylene. A measured volume of acetylene is passed slowly through a 3% sodium hypochlorite solution; any phosphine present is absorbed and oxidized to phosphate, which can be estimated as

UCC
002689

ammonium phosphomolybdate. Acetylene can also be passed through fuming nitric acid to absorb both phosphorus and sulfur, which can be determined as ammonium phosphomolybdate and as barium sulfate. If hydrogen sulfide is removed first, the organic sulfur can be determined in this way. Total sulfur can also be determined by a modification of the London Gas Referee's method for coal gas, using larger equipment. A measured sample is burned in air containing ammonia, and the resulting ammonium sulfate and sulfite are removed in a water scrubber. After oxidation of any sulfite to sulfate, the total sulfur is determined as barium sulfate.

Determination of Ammonia in Acetylene. The ammonia is absorbed in dilute hydrochloric acid and estimated by the Nessler method after the dissolved acetylene has been driven off.

Industrial Uses

Acetylene production in the U.S. has been of the order of 400,000,000 lb. per year. Of this, about 30% has been used for such applications as welding and lighting (the latter being of minor importance), and 70% for chemical syntheses. It is possible to use acetylene for an almost infinite number of organic chemical syntheses, but its use in this country has been less intensive than in Europe owing to the ready availability of petroleum, from which competitive syntheses are often possible, in many cases through ethylene (*q.v.*).

CHEMICAL USES

The syntheses from acetylene of greatest importance in America are listed briefly below:

Acetaldehyde: see *Acetaldehyde*; *Acetic acid.*

$$CH{:}CH + H_2O \xrightarrow[\text{dil. } H_2SO_4]{H_2SO_4 \text{ in}} CH_3CHO$$

Tetrachloroethane: see *Chlorine compounds, organic*; *Solvents.*

$$CH{:}CH + 2\,Cl_2 \longrightarrow CHCl_2CHCl_2$$

Chloroprene: see *Rubber, synthetic.*

$$2\,CH{:}CH \xrightarrow[\text{copper salt}]{\text{aqueous soln. of}} \underset{\text{vinylacetylene}}{CH{:}C.CH{:}CH_2}$$

$$CH{:}C.CH{:}CH_2 + HCl\ (\text{gas}) \longrightarrow \underset{\text{chloroprene}}{CH_2{:}CCl.CH{:}CH_2}$$

Vinyl Chloride and Vinyl Acetate: see *Vinyl compounds.*

$$CH{:}CH + HCl \longrightarrow CH_2{:}CHCl$$

$$CH{:}CH + CH_3COOH \longrightarrow CH_3COOCH{:}CH_2$$

Of secondary importance are the manufacture of vinyl ethers, and of acetylene black (see *Carbon*), numerous miscellaneous vinylations, and syntheses of biochemical materials such vitamin A.

In Germany during the years 1925–1945, under the direction of Dr. Walter

UCC
002690