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Chemistry of Acetylene
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THE CHEMISTRY OF ACETYLENE

- (30) I. G. Farbenind. A.-G., Brit. P. 280,885 (1927); C. A., 22, 3499 (1928); French P. 613,387 (1927); C. A., 23, 1419 (1929).
- (31) I. G. Farbenind. A.-G., Brit. P. 377,193 (1931); Brit. Chem. Abs., 1932B, 926; French P. 724,470 (1931); C. A., 26, 4623 (1932). Schilling and Stadler (to I. G. Farbenind. A.-G.), U. S. P. 2,029,120 (1930); C. A., 30, 1610 (1936).
- (32) Hull and Imperial Chemical Industries, Ltd., Brit. P. 331,010 (1929); C. A., 25, 110 (1931).
- (33) Horaley and Rosley, to Imperial Chemical Industries, Ltd., Brit. P. 331,054 (1929); C. A., 25, 110 (1931); U. S. P. 1,854,141 (1932); C. A., 26, 3304 (1932).
- (34) Groll and Burgin, Brit. P. 400,064 (1933); C. A., 28, 2160 (1934); U. S. P. 1,945,100 (1934); C. A., 28, 5474 (1934). N. V. de Bataafsche Petroleum Maatschappij, German P. 606,343 (1934); C. A., 29, 1614 (1935); French P. 751,281 (1933); C. A., 28, 1059 (1934).
- (35) Koller, *Khim. Tverdogo Topliva*, 8, 1149-55 (1937); C. A., 32, 4018 (1938).
- (36) Isham, U. S. P. 2,063,060 (1937); C. A., 31, 710 (1937).
- (37) Taylor, U. S. P. 1,990,088 (1935); C. A., 29, 3353 (1935).
- (38) Metzger (to Air Reduction Co.), U. S. P. 1,900,665 (1933); C. A., 27, 2960 (1933); Brit. P. 401,631 (1933); C. A., 28, 2371 (1934); French P. 749,025 (1933); C. A., 28, 492 (1934).
- (39) Müller-Conradi, Eisenhut and Schilling (to I. G. Farbenind. A.-G.), U. S. P. 1,938,083 (1933); C. A., 28, 1016 (1934).
- (40) Johnson (from I. G. Farbenind. A.-G.), Brit. P. 326,817 (1928); Brit. Chem. Abs., 1930B, 440.
- (41) Minister of Navy (Hujio, inventor), Jap. P. 109,413 (1935); C. A., 29, 4218 (1935).
- (42) Bronn, *Z. angew. Chem.*, 42, 780-8 (1929).
- (43) Wulff, U. S. P. 1,938,001 (1934); C. A., 28, 1304 (1934).
- (44) Gesellschaft für Linde's Eismaschinen A.-G., Brit. P. 468,614 (1937); C. A., 32, 8 (1938); French P. 815,294 (1937); C. A., 32, 957 (1938).
- (45) Pyzel (to Shell Development Co.), U. S. P. 1,985,518 (1935); C. A., 29, 1235 (1935).
- (46) I. G. Farbenind. A.-G., French P. 667,001 (1929); C. A., 24, 1110 (1930); Brit. P. 368,752 (1930); Brit. Chem. Abs., 1932B, 401; German P. 591,181 (1934); C. A., 28, 3315 (1934).
- (47) Askaniay (to Soc. anon. pour l'industrie chim. a Bâle), German P. 550,770 (1928); C. A., 27, 312 (1933); French P. 678,830 (1929); C. A., 24, 3519 (1930); U. S. P. 1,805,422 (1932); C. A., 26, 4347 (1932).
- (48) I. G. Farbenind. A.-G., Brit. P. 325,309 (1930); Brit. Chem. Abs., 1930B, 406; French P. 668,166 (1930); C. A., 25, 752 (1931); German P. 550,770 (1932); *Frdl.*, 17, 127-9.
- (49) Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, German P. 613,210 (1937); C. A., 31, 4170 (1937).
- (50) I. G. Farbenind. A.-G., Brit. P. 278,324 (1926); C. A., 22, 2673 (1928); French P. 611,466 (1928); *Chem. Zentr.*, 1928, 11, 1036; French P. 657,927 (1928); C. A., 23, 4231 (1929).
- (51) Ferguson and Imperial Chemical Industries, Ltd., Brit. P. 342,771 (1929); C. A., 25, 5130 (1931).
- (52) Ithart and Imperial Chemical Industries, Ltd., Brit. P. 302,515 (1928); C. A., 23, 4231 (1929).

10. The laboratory purification and analysis of acetylene. For laboratory use acetylene usually is either generated from calcium carbide or drawn from a commercial storage cylinder. If carbide is employed it is preferable to use a carbide to water type generator, observing precautions against localized overheating. It is also advisable to use a precipitant or an oxidative purifying agent to remove traces of phosphine and other

PHYSICAL PROPERTIES, PREPARATION, PURIFICATION 37

impurities. (See Chapter I, Section 4.) However, it is usually more convenient to use the gas from a storage cylinder. In this case most of the impurities arising from carbide have been reduced to a proportion which is negligible if the gas is to be used as a raw material for laboratory syntheses. The gas from a cylinder does contain acetone in quantities which increase with decreasing pressure in the cylinder. Sodium bisulfite solution has been employed to remove acetone. Passing the gas through strong sulfuric acid in an efficient wash bottle also removes acetone and part of the other trace impurities but may introduce sulfur dioxide and acid spray. These may be eliminated by a soda-lime tower or by a dilute sodium hydroxide wash followed by a drying agent. If it is essential to remove oxygen from the gas an alkaline solution of sodium hydrosulfite containing a little anthraquinone sulfonic acid (1) may be placed in the train. Horiuti (2) and Conn, Kistiakowsky and Smith (3) have described somewhat more elaborate purification methods. However, acetylene may contain traces of impurities such as hydrogen, nitrogen, methane, or ethane which can not be removed by chemical reagents. Accordingly if the gas must be exhaustively purified it appears essential to liquify and distil it. This procedure requires special technique and precautions which do not seem to have been adequately described in the literature.

For the qualitative detection of acetylene a variation of the cuprous acetylides precipitation is always used, since the characteristic red color of the acetylides can be seen even when present in minute quantities. (See Chapter II, Section 5.) However, the acetylides is readily oxidized with darkening by air in an alkaline medium, and a reducing agent such as hydroxylamine is necessary to preserve the pure red color. Test papers based on this reaction have been described (4). For a much more sensitive test, modifications of Mosvay's solution have been recommended (5). This consists of an ammoniacal cuprous chloride solution containing gelatin which acts as a protective colloid to keep the acetylides in a fine state of division so that its color is more readily observable at great dilution. Czaco (5) states that this reagent is sensitive to acetylene in concentrations of 2-4⁻¹⁰ per cent if proper precautions are taken.

Mosvay's solution, also has been used for the colorimetric estimation of acetylene (5,6). However, the color depends upon both the size of the colloidal particles and the absence of impurities such as traces of hydrogen sulfide or larger quantities of oxygen or carbon dioxide. Accordingly, most investigators have preferred to estimate the quantity of acetylides formed either by careful drying and weighing as the explosive carbide C_2Cu_2 (7) or better, by dissolving the acetylides in acid and determining the copper by any standard method (8). Since the red cuprous acetylides in an ammoniacal solution is readily attacked by oxygen which darkens the color and may alter the

ratio of copper to carbon, it is recommended that a reducing agent such as hydroxylamine or hydrazine be added to the ammoniacal cuprous chloride solution (5).

Chevastelon (9) and Ross and Trumbull (10) have described the estimation of acetylene, especially in the presence of ethylene, by titration of the nitric acid liberated by the gas from a neutral silver nitrate solution according to the equation, $C_2H_2 + 3AgNO_3 \rightarrow C_2Ag_3AgNO_3 + 2HNO_3$. Hoepfner and Willstätter and Marchmann (11) report that the method is not very reliable. Novotny (12) proposed that the silver in the precipitate be determined. Lebeau and Damiens and Wellers (13) used a slightly alkaline solution of mercuric iodide and potassium iodide to precipitate acetylene in the presence of olefins.

In gas volumetric analysis methods, reagents, containing copper, silver or mercury which are capable of absorbing acetylene are nearly always capable of taking up lesser quantities of olefins, diolefins, carbon monoxide or higher acetylenic hydrocarbons, so that methods depending upon loss of gas volume in such reagents are of questionable accuracy.

A microchemical method for the estimation of acetylene by reaction with a bead of cuprous chloride made alkaline with ammonium hydroxide has been proposed (14).

The analysis of carbide acetylene for common impurities has been described in several treatises on calcium carbide and acetylene (see Ref. 1, Introduction) and a few reviews (15). A number of methods which describe special adaptation of these procedures to particular gas mixtures cannot be discussed in this work.

References

- (1) Feiser, *J. Am. Chem. Soc.*, 46, 2630-47 (1924).
- (2) Horiuti, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 17, 130 (1931); *C. A.*, 26, 2101 (1932).
- (3) Conn, Kistiakowsky and Smith, *J. Am. Chem. Soc.*, 61, 1868-76 (1939).
- (4) Llorens, *Anal. Fis. Quim.*, 10, 139 (1912); 11, 320 (1913). Denigou, *Bull. soc. pharm. Bordeaux*, 1921, No. 2; *Repart. pharm.*, 53, 232 (1931); *C. A.*, 18, 305 (1922).
- (5) Rosvay, *Ber.*, 32, 2697-9 (1899); *Z. anal. Chem.*, 40, 123-4 (1901). Czako, *Z. angew. Chem.*, 44, 388 (1931). Riess, *ibid.*, 44, 701-3 (1931). Schulze, *ibid.*, 44, 703 (1931). Pistach and Kotkowi, *ibid.*, 44, 369-12, 388, 703 (1931). Novotny, *Coll. Czechoslov. Chem. Communications*, 9, 514-27 (1934); *C. A.*, 28, 2478 (1935).
- (6) Weaver, *J. Am. Chem. Soc.*, 36, 852 (1916). Schulze, *Z. angew. Chem.*, 29, 341 (1916).
- (7) Scheiber, *Z. anal. Chem.*, 48, 637 (1909).
- (8) Scheiber, *Ber.*, 41, 3816 (1908); Muller, *Bull. soc. chim.*, 27, 69 (1920); Arnold, Molluay and Zimmermann, *Ber.*, 63, 1034 (1920); Willstätter and Maschmann, *ibid.*, 53, 939 (1920).
- (9) Chevastelon, *Compt. rend.*, 128, 245 (1897); Tucker and Moody, *J. Am. Chem. Soc.*, 23, 671-4 (1901).
- (10) Ross and Trumbull, *J. Am. Chem. Soc.*, 41, 1180 (1919).

PHYSICAL PROPERTIES, PREPARATION, PURIFICATION 39

- (11) Hoepfner, *Z. Nahr. Genussm.*, 34, 463 (1917); Willstätter and Maschmann, *Ber.*, 53, 939 (1920).
- (12) Novotny, *Collection Czechoslov. Chem. Communications*, 7, 84-9 (1935).
- (13) Lebeau and Damiens, *Compt. rend.*, 156, 567 (1913); Wellers, *Stahl u. Eisen*, 42, 1440 (1922).
- (14) Ilacot, MacDonald and Leighton, *Ind. Eng. Chem. Anal. Ed.*, 5, 272-4 (1933).
- (15) Horites, *Chem. Listy*, 24, 493-6 (1930); *C. A.*, 25, 2664 (1931). Korschak, *Acetylen Wiss. Ind.*, 35, 118-22 (1932); *C. A.*, 28, 3029 (1934). Aasman, *ibid.*, 35, 184-6 (1932); *C. A.*, 28, 3029 (1934). Strizhevskii and Checkhovitch, *Zavodskaya Lab.*, 8, 220-2 (1939); *C. A.*, 33, 9108 (1939).

References

- (1) Hare, *L'Institut*, 1840, 312; *Am. J. Sci.* (1), 37, 269 (1839).
- (2) Deville and Debraye, *Ann. mines* (5), 18, 1 (1859); *Jahresber. über die Fortschritte der Chemie*, 1859, 254-6.
- (3) Wöhler, *Ann.*, 124, 220 (1862).
- (4) Willson, U. S. P. 492,377 (1893); *Progress Age*, 1896, 51; *Am. Manufactures*, 1896, Dec., 16; *Brit. P.* 16,342 (1894), 16,705 (1894); *J. Soc. Chem. Ind.*, 15, 103 (1896); *Brit. P.* 15,300 (1895); *ibid.*, 16, 582 (1896). Willson and Suckert, *J. Franklin Inst.*, 139, 221 (1895).
- (5) Boehm, U. S. P. 552,020 (1895); *Mineral Industry*, 9, 64 (1901); *Technologist*, 6, 9, 265 (1901).
- (6) Moissan, *Compt. rend.*, 116, 1031-2 (1892); *ibid.*, 118, 501-6 (1894); *Bull. soc. chim.* (3), 11, 1002-7 (1894).
- (7) Bullier, German P. 77,108 (1894); *Chem. Zentr.*, 1895, I, 191.
- (8) Eimer, *Trans. Am. Electrochem. Soc.*, 51, 73-8 (1927).
- (9) Hilbert and Frank, German P. 92,838 (1895); *Chem. Zentr.*, 1897, II, 878. Morehead, U. S. P. 862,092 (1907); *C. A.*, 1, 3008 (1907). Yasuda, *Jap. P.* 35,500 (1919); *C. A.*, 14, 3623 (1920). Soc. d'études chimiques pour l'industrie, French P. 675,411 (1920); *C. A.*, 24, 2842. Swiss P. 134,612 (1928); *C. A.*, 24, 1700 (1928). Seyfried, U. S. P. 1,777,582 (1930); *Brit. Chem. Abs.*, 1931B, 537.
- (10) Jacobsen, German 89,959 (1895); *Chem. Zentr.*, 1897, I, 528. Limb, German P. 117,920 (1899); *Chem. Zentr.*, 1901, I, 427. Voiret, French P. 712,603 (1931); *C. A.*, 26, 2021 (1931).
- (11) Harrison, *Brit. P.* 477,100 (1937); *C. A.*, 32, 4290 (1938).
- (12) Krylov, *Metallurg*, 12, No. 7, 15-24 (1927); *C. A.*, 32, 6157 (1938).
- (13) Aall, *Compt. rend.*, 204, 1340-1 (1937).
- (14) Allmand and Williams, *J. Soc. Chem. Ind.*, 36, 303-4R (1919). Anon., *Engineering*, 87, 405, 443, 477, 522, 540, 729 (1900). Anon., *J. four electr.*, 36, 105-7 (1927). Bergeron, *Bull. soc. Franc. elec.*, 8, 75-80 (1925); *Rev. gen. elec.*, 22, 797-802 (1927). Mantell, "Industrial Electrochemistry," pp. 405-24 (1931). Meneghini, *Atti ist. Veneto sci.*, 94, 587-90 (1935).
- (15) Flusin, *Eng. Mining J.*, 107, 479 (1918). Brunot, *Rev. gen. elec.*, 5, 913-23 (1920). Furusaki, *J. Chem. Ind. Japan*, 25, 24-36 (1922). Baumann, *Chem. Ztg.*, 50, 629-31 (1926). Schlumberger, *ibid.*, 50, 879 (1926); *Z. angew. Chem.*, 40, 141-6 (1927). Gal, *Chem. Ztg.*, 51, 251-2 (1927). Danuol, *Z. Elektrochem.*, 36, 474-82 (1930).
- (16) Aktiengesellschaft für Stickstoffdünger, French P. 809,308 (1937); *C. A.*, 31, 6506 (1937).
- (17) Ruff and Forster, *Z. anorg. allgem. Chem.*, 131, 321-47 (1923). Ruff, *Z. Elektrochem.*, 30, 350-64 (1924). Ruff and Josephy, *Z. anorg. allgem. Chem.*, 163, 17-32 (1926). Schlumberger, *Chem. Ztg.*, 50, 970 (1926); *Z. angew. Chem.*, 39, 213-20 (1926); *ibid.*, 40, 141-6 (1927). Danuol, *Z. Elektrochem.*, 36, 474-82 (1930). Dutoit and Rossier, *J. chim. phys.*, 29, 238-41 (1932).
- (18) Morehead, U. S. P. 825,234 (1907); *C. A.*, 1, 115 (1907). Schickler, *Z. Elektrochem.*, 26, 400-14 (1919). Soc. anon. l'exploitation brevets Jullien, French P. 699,459 (1929); *Fr. P.* 608,570 (1929); *C. A.*, 24, 1686 (1930); *C. A.*, 25, 3256 (1931). Hilger, German P. 522,573 (1925); *C. A.*, 25, 3578 (1931); *Ger. P.* 541,305 (1929); *C. A.*, 26, 1806 (1932); *Ger. P.* 580,262 (1933); *C. A.*, 27, 4714; *Ger. P.* 596,176 (1934); *C. A.*, 28, 4321 (1934). Ilibi, *Jap. P.* 90,215 (1931); *C. A.*, 25, 2928 (1931). Cartoux, *Chaleur et ind.*, 19, 419-21 (1938); *C. A.*, 32, 6951 (1938).
- (19) Domenico, *Boll. cent. Volpi elettrotecnica*, No. 2, 11-12 (1938).
- (20) Gardener, *Brit. P.* 490,294 (1938); 496,295 (1938); *C. A.*, 33, 3541-2 (1939).
- (21) Pincas, *Chem. Age*, 37, 109-70; *C. A.*, 31, 8839 (1937).

4. The generation and purification of acetylene from carbides.* The acetylenic carbides described in the preceding sections were found by the earliest investigators to react rapidly with water, giving acetylene and the corresponding metallic hydroxides. The heat of hydrolysis (1) may produce localized temperatures high enough to polymerize a part of the acetylene, unless overheating is prevented by the use of excess water or by some other means. The hydrolysis of calcium carbide has of course been studied most thoroughly, and the heat of this reaction has been reported by Lewes (2) to be about 475 cal. per gram of pure carbide, and by Mason, Anderson, and Jane (5) as 106 Btu per cubic foot of acetylene generated. Lewes (2) claimed that when a minimum of water reacts with a mass of carbide a part of the acetylene may react with steam to give carbon monoxide and hydrogen; and in a few cases localized decomposition of acetylene to hydrogen and carbon has been reported.

Besides moisture, air, finely divided solids, and condensation products resulting from overheating, the crude acetylene also may be contaminated with a small percentage of other gases arising from impurities in commercial carbide* (5). Nitrogen, sulfur, phosphorus, silicon and arsenic may be present in carbide in combination with calcium or other metals. On treatment with water the hydrides, ammonia, phosphine, silicomethane and arsine, may be evolved to some extent, while most of the hydrogen sulfide is held in the alkaline solution. Modern methods of carbide manufacture minimize these impurities by careful control of the composition of the charging materials. Analysis of acetylene generated from a typical modern carbide is said to show the presence of .015-.025 per cent of phosphine, less than .015 per cent of ammonia, less than .01 per cent of hydrogen sulfide, and less than .0003 per cent of arsine. At the high temperatures occurring when little water is present during the hydrolysis of calcium carbide, the simple hydrides above noted if present may be condensed with acetylene to give volatile organic derivatives which are difficult to remove.

Kennedy and Holm (10) have identified divinyl sulfide as an important impurity, and state that more is present if the temperature of hydrolysis of the carbide is high. They have suggested removal of this impurity by scrubbing with Chloramine T or sulfuric acid. Hydrogen is sometimes present in very small quantities. Methods for the estimation of impurities in crude acetylene have been reviewed by Brown (4) and others.†

A high reaction temperature during the hydrolysis of carbides results in a decomposition and condensation of the acetylene which both con-

* The generation of acetylene from carbide, and the impurities and purification of the gas have been extensively discussed in special treatises; see Introduction (1, 2).

† See Introduction (1, 2).

taminates the product and reduces the yield. Accordingly, it has been the commonest practice to prepare acetylene by the total immersion of calcium carbide in a comparatively large volume of water which acts as a cooling medium. Methods and devices for the hydrolysis of calcium carbide by this method have been studied extensively, but most of the technical literature* covers small automatic generators for local or domestic acetylene supply.

Recently Mason, Anderson and Jane (5) have described a large-scale method of hydrolyzing calcium carbide using little more than an equivalent quantity of water, which is based to some extent on earlier methods (6). This procedure consists in spraying the crushed carbide either in a ball mill or in a rotating screen drum with a minimum of water, and continuously separating the powdered calcium hydrate. By this method localized overheating is prevented and no temperature above 240°F was observed. A few other recent patents and articles (7) describe the hydrolysis of calcium carbide with a minimum of water. The Prestolite Company controls United States patents (7a) on a process and apparatus by which water is brought into reaction with calcium carbide near the bottom of a cylindrical reaction chamber, provided with an agitator rotated about a vertical axis. The acetylene and powdered calcium hydroxide rise to the top of the cylinder, and in one modification the powdered hydroxide, which overflows the top of the cylinder fills an annular seal similar to a liquid seal. If the recovered dry hydrate could be converted to a briquet or lump form (8), it could be used profitably for calcium carbide manufacture. Since in some localities the accessible supply of limestone suitable for carbide manufacture is somewhat limited, recovery of the calcium hydroxide is of interest.

Even when prepared in the best type of generator from a good grade of carbide, commercial acetylene usually contains traces of impurities. These are said not to be deleterious in the gas used for welding or cutting (11, 12) but may act as poisons for the catalysts employed in the chemical utilization of acetylene. For some purposes it has been common practice to oxidize these impurities, particularly phosphine, by reagents which scarcely attack acetylene and to remove the acidic oxidized products by contact with alkalis or by precipitation. Solutions or porous masses containing calcium hypochlorite or potassium permanganate were at one time used or proposed, and masses containing chromic acid appear to have been extensively used in Europe. A purifying material, which was originally patented by Granjon (15) and which is at present used in the U. S., consists of a mixture of ferric chloride, ferric oxide, manganese dioxide, mercuric chloride, and cupric sulfate. The mercuric chloride appears to bind the

* See Introduction (1, 2).

phosphine in a complex which is then oxidized by the ferric salts, and the cupric sulfate catalyzes the reoxidation of the ferrous salts by air and thus regenerates the purifying material. This method is said to remove 95 per cent of the phosphine. At the present time nitre cake is said to be used also in the commercial purification of acetylene. Oxidation of phosphine by sulfuric acid of about 85 per cent concentration at about 70° is reported to be an industrial method of purification. Methods of evaluating commercial preparations for the purification of acetylene and some comparative tests on such materials have been published (9, 13, 14). An older proposed method of purification consisted in the complete precipitation of these impurities by cuprous chloride or mercuric chloride with other chloride salts. However, these solutions are not perfectly inert toward acetylene, and a small percentage of volatile addition products usually was formed. The drying of acetylene by refrigeration, or by the use of aluminum oxide with proper precautions, or by countercurrent washing with saturated calcium chloride solution are said to be accepted industrial practices.

There is reason to believe that a trace of oxygen is a very important impurity in acetylene to be used in certain syntheses, but this possibility has received little attention. A small quantity of oxygen is known to be very deleterious in the preparation of vinylacetylene, and probably has effects in the polymerization, halogenation and hydration of acetylene. The acetylene mixtures prepared by pyrolytic processes are probably more nearly free from oxygen than acetylene derived from carbide. Both commercially and in the laboratory, oxygen can best be removed from acetylene by washing with an aqueous alkaline solution of sodium hydro-sulfate containing a small percentage of anthraquinone β -sulfonic acid (10).

Gaseous hydrocarbons, carbon monoxide and hydrogen are much more difficult to remove from acetylene; the total elimination of these impurities is not attempted commercially, since they are not particularly detrimental in the use of acetylene either as a fuel or for chemical synthesis.

References

- (1) Fal'kovich, *Khimstroj*, 6, 442-5 (1934).
- (2) Lowes, *J. Soc. Chem. Ind.*, 17, 532-42 (1898).
- (3) Willgerodt, *Ber.*, 28, 2107-8 (1895). Lunge and Cedercerantz, *Z. angew. Chem.*, 10, 661-5 (1897). Moissan, *Compt. rend.*, 127, 457-63 (1898); *Ann. chim. phys.* (7), 18, 343-51 (1899). Wolff, *Z. angew. Chem.*, 11, 931-41 (1898). Caro, *J. Gasbeleuchtung*, 42, 616-7 (1899); *Chem. Zentr.*, (1899) II, 642. Keppeler, *J. Gasbeleuchtung*, 45, 777-82, 802-5, 820-25 (1902); *Chem. Zentr.*, 1902, II, 1481-5. Bullior and Maquonne, *Rev. gen. de chimie pure et appl.*, 6, 348-50 (1903); *Chem. Zentr.*, 1903, II, 643.
- (4) Brown, Carnegie-Illinois Steel Company, Pamphlet (1927); *C. A.*, 21, 3327 (1927).
- (5) Mason, Anderson and Jane, *Can. Chem. Met.*, 19, 183-6, 102 (1935).

- (6) Dolan, U. S. P. 638,443 (1899). Dickinson, U. S. P. 604,139 (1898); U. S. P. 671,693 (1901). Davies, U. S. P. 701,852 (1902). Gibbs, "Lighting by Acetylene," p. 89, (1899).
- (7) Weibezahn and Walter, U. S. P. 1,947,120 (1934); C. A., 28, 2371 (1934). U. S. P. reissue 20, 527 (1937); C. A., 31, 8549 (1937). Mues (to I. G. Farbenind. A.-G.), U. S. P. 2,122,889 (1938); C. A., 32, 6842 (1938). I. G. Farbenind. A. G., Ger. P. 648,087 (1937); C. A., 31, 8549 (1939). Mues, Z. Kompr. Gas. Guss, 33, 57-60 (1937); C. A., 33, 6093 (1939). Bayerische Stickstoff-Werke A. G. (Wilm, Volkmann and Kaeas, inventors) Ger. P. 67,303 (1939); C. A., 33, 6349 (1939). Autogenwerk Sirius G.m.b.H. (Becker, inventor) Ger. P. 673,779 (1939); C. A., 33, 6099 (1939).
- (7a) Kojolo and O'Brian, Brit. P. 483,601 (1938); C. A., 32, 7249 (1938); U. S. P. 2,201,181 (1940); C. A., 34, 6048 (1940). O'Brian, U. S. P. 2,189,762 (1940); C. A., 34, 3956 (1940). Ness and Kojolo (to Prestolite Co.) U. S. P. 2,233,108 (1941); 2,233,100 (1941); C. A., 35, 4942 (1941).
- (8) Winter and Hartmann, U. S. P. 2,017,558 (1935); C. A., 29, 7834 (1935).
- (9) Sumiya and Yamada, J. Chem. Soc. Japan, 33, 537-9 (1930); C. A., 25, 1300 (1931).
- (10) Fieser, J. Am. Chem. Soc., 46, 2630-47 (1924).
- (11) Rimarski, Kantor and Stroh, Forsch. Gebiete Ingenieurw., No. 317 (1929).
- (12) Holzhauser, Autogens Metallbearb., 23, 286-96 (1931); 34, 192 (1931); C. A., 25, 3302 (1931).
- (13) News Bulletin of the Compressed Gas Manuf. Assoc., July 21 (1931), New York.
- (14) Sherun, Chem. Fabrik (1938), 207-10.
- (15) Granjon, Fr. P. 434,137; U. S. P. 1,074,501 (1913); J. P. Acetylene, (1934), 457-61.
- (16) Kennedy and Holm, Can. Chem. Process Inds., 23, 490-5 (1930).

5. The equilibrium of acetylene with carbon and hydrogen and its bearing on the direct synthesis, decomposition and storage of acetylene. Berthelot (1) prepared small quantities of acetylene by means of an arc between carbon electrodes in an atmosphere of hydrogen. Dowar (2) concluded that this reaction resulted solely from the high temperature attained. The equilibrium of carbon and hydrogen with acetylene has been investigated by a number of workers (3-7, 9-11). In the equilibrium mixtures produced, either from acetylene or from the elements, little acetylene appears to exist between 1000° and 1700°, and above 1700° the concentration increases with rising temperature up to a point at which the equilibrium changes because of the formation of atomic hydrogen. Frost (12) states that considerable yields can be obtained only in the region of 3100° to 3200°. The continuous formation of acetylene in this high temperature range may be due in part to a tendency of complex carbon structures to break down under these conditions into C₂ groups rather than into any other simple units. The proportion of acetylene recoverable from the carbon arc in hydrogen has been reported as about seven to eight per cent. Since a higher concentration of acetylene can be made by the pyrolysis of hydrocarbons, the synthesis of acetylene from the elements has not usually been considered suitable for commercial application, although Brading (13) has patented an arc apparatus for this purpose. A somewhat related method consists in cracking hydrocarbons in the electric arc in the presence of finely divided carbon (22).

Of greater practical significance is the fact that acetylene, being an endothermic compound, can decompose to its elements with the evolution of heat. The decomposition at pressures not much above one atmosphere will first be considered. Berthelot (14) noted that at atmospheric pressure and a dull red heat in vessels of inert material, polymerization was the principal reaction of acetylene (see Chapter V, Section 2), while at somewhat higher temperatures the polymerization was associated with decomposition to carbon and hydrogen. He considered that this decomposition took place through a mechanism involving the formation and total dehydrogenation of polymers. Haber (15) observed that heat was evolved during these reactions. It was later found that the decomposition of acetylene was practically complete in the range 1150°-1325° (7, 16), and that noticeable decomposition began in porcelain tubes at about 480° and became the chief reaction at 800° (9).

Several metals have been found to increase the rates of polymerization or decomposition and to influence somewhat the nature of the products. Some of these metals, when finely divided, have also been reported to initiate the reactions at comparatively low temperatures. Thus Moissan and Moureau (17) found that pyrophoric iron, nickel and cobalt, and finely divided platinum became incandescent when placed in a rapid stream of acetylene at room temperature, and noted the formation of hydrogen, carbon and oily products. Since these reactions are promoted by increased heat and pressure, it appears probable that the catalytic effect of metals is at least partly due to the localized heat of adsorption of the acetylene and also to the high concentration of acetylene in the adsorbed layer. Berthelot (8) first discovered the catalytic decomposition of acetylene by iron. A similar effect of iron, nickel and cobalt has been observed by several workers at temperatures between 200° and 400° (18-23). Extensive decomposition of acetylene in contact with iron has been noted at higher temperatures (24-28), and a few iron compounds have been found to produce a similar effect (29, 30). Finely divided platinum (18, 31) and palladium (32) have been reported to induce the decomposition of acetylene at moderate temperatures. Copper and to a lesser extent a few other metals cause the condensation of acetylene to cuprene at about 250° (see Chapter V, Section 3), but the catalytic decomposition of acetylene over copper at somewhat higher temperatures has been observed also (21, 25, 27, 33, 34). Manganese (21) was found to promote acetylene decomposition above 480°. Most of these reactions were accompanied by hydrogenation and the appearance of traces of oily condensation products of acetylene. In many cases particles of the metals became distributed throughout the carbon deposits, so that coating of the metal with carbon did not completely stop the catalytic effect. Metals other than those mentioned above appear to have little effect on the rate of decomposition of acetylene (8). The effect