PERCHLORATES

Their

Properties, Manufacture and Uses

Edited by

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1. HISTORY

The discovery of potassium perchlorate was reported in Germany in 1816 by Count Friederich von Stadion[61] of Vienna. He fused a small quantity of potassium chlorate in a retort and then carefully added a small amount of sulfuric acid. Chlorine dioxide was given off and the residue was identified as a mixture of potassium sulfate and a difficultly soluble salt which he identified as potassium perchlorate.

In the course of identifying the composition and structure of this new salt, von Stadion[60] prepared perchloric acid by electrolyzing a saturated aquous solution of chlorine dioxide and also by distilling the new acid from a heated mixture of sulfuric acid and potassium chlorate. He also prepared potassium perchlorate by (1) neutralizing perchloric acid with potassium hydroxide and (2) electrolyzing a saturated solution of potassium chlorate between platinum electrodes.

In addition to his important discoveries relating to the preparation and identification of perchloric acid and potassium perchlorate, von Stadion recognized the importance of electrochemistry as an effective means of synthesis.

In 1830, Serullas[51] reported his discovery of a new method of preparing perchloric acid. He observed that during the distillation of chloric acid, one part splits into chlorine and oxygen and that another part, almost one-third of the chloric acid employed, is converted to perchloric acid. He also observed that perchloric acid is very stable and may be distilled at an elevated temperature without decomposition.

In 1831, Serullas[54] reported his discovery of a new method of transforming potassium chlorate into potassium perchlorate. When he had first noted an almost insoluble salt-like residue remaining upon the incomplete decomposition of potassium chlorate by heat, he attributed it to cohesion. It seemed improbable to him that earlier investigators had neglected to ascertain what actually took place. Later he identified the residue as potassium perchlorate.

Serullas observed that the formation of potassium perchlorate by the action of sulfuric acid on the chlorate, and the formation of perchloric acid by the simple boiling of concentrated chloric acid are comparable reactions. This observation led him to believe that the simple action of elevated temperature, maintained between certain limits, causes potassium chlorate to pass to the state of perchlorate when part of the oxygen is transferred to the undecomposed chlorate.

Having thus found a simple method of preparing potassium perchlorate,

he proceeded to develop a new method of preparing perchloric acid, from potassium perchlorate and fluosilicic acid. He mixed potassium perchlorate and hydrofluosilicic acid and then evaporated the resulting solution; this was followed by cooling to precipitate potassium fluosilicate.

Continuing his research with perchloric acid, Serullas[53] prepared ammonium perchlorate and a number of metal perchlorates. During the course of this work his attention was attracted toward the remarkable difference that exists between the solubility of potassium perchlorate and that of sodium perchlorate. This difference suggested to him a valuable method of distinguishing between these two alkali metal ions and a means of separating them.

Serullas[51] can also be credited with popularizing the use of the term "perchlorate" as distinguished from the term "oxychlorate" used by von Stadion and others during the period between 1816 and 1831. Serullas used the terms interchangeably in his papers, and thereafter the word "perchlorate" was used almost exclusively, if not entirely.

Following the important discoveries of von Stadion, and later those of Serullas, a continuing and almost constant effort was made by a large number of investigators to characterize and find new methods of preparing and using perchloric acid and its salts. This effort was motivated to a large extent by scientific curiosity, but also by a desire to utilize these substances in a variety of ways in analytical chemistry, and as an ingredient in explosives, pyrotechnics and rocket propellants.

With regard to the characterization of perchlorates, von Stadion's determination of the composition of potassium perchlorate was confirmed by Mitscherlich,[37] Serullas,[53] and Marignac.[34] Roscoe[45] later prepared and identified perchloric acid in three forms: namely, the anhydride, the monohydrate—a solid crystalline substance which had been discovered by Serullas but not identified by him—and the dihydrate, a constant boiling liquid. Roscoe also pointed out that the anhydride, Cl_2O_7, had not been isolated, and almost 40 years elapsed before Michael and Conn[35] succeeded in preparing and isolating it. In 1902, van Wyk[70] studied the relationship of freezing point versus composition and was thus able to identify five hydrates of perchloric acid.

Studies on the structure of perchloric acid were carried out by Volmer,[67] Smith and Goehler[59] and later, by Fonteyne.[19] Volmer used x-ray techniques. Smith and Goehler used a melting point-density relationship technique. Fonteyne employed Raman spectra.

Earlier in 1881, Berthelot[6] had studied the thermochemistry of chlorates and perchlorates and showed that the transformation of potassium chlorate to potassium perchlorate is exothermic. This led him to observe that the perchlorates are considerably more stable chemical compounds than the corresponding chlorates.

The curious fact of the occurrence of perchlorate in the natural deposits of nitrates in Chile was first reported by Beckurts[4] in 1886. Following this discovery, damage to grain crops in Belgium was laid to the perchlorate present in the Chilean nitrate used as plant food.[33, 56-58, 66] To this day the question as to the origin of this naturally occurring perchlorate remains unanswered. However, in this connection, small amounts of perchlorate have been reported quite recently[3] in sea water, as well as in a number of natural brines and saline deposits in Australia and elsewhere. It has been suggested that such natural occurrences may be caused by the action of microorganisms, but one can also speculate on a purely chemical mechanism. In either case a possible new method of producing perchlorates is suggested.

A series of compounds in which nitrogen oxides and perchlorate are combined have been prepared, beginning with the discovery of nitrosyl perchlorate, $(NO)^+(ClO_4)^-$, by Hofmann and Zedtwitz[25] in 1909. Hantzsch and his co-workers,[21] in 1928, found that when dry nitric and perchloric acids were mixed in various proportions, two different compounds were formed. They were named nitracidium perchlorate, $[O{:}N\cdot(OH)_2]^+ClO_4^-$, and hydronitracidium perchlorate, $[N(OH)_3]^{++}(ClO_4)_2^-$. In 1940 Gordon and Spinks[20] discovered nitroxyl perchlorate, $NClO_6$, or $(NO_2)^+ClO_4^-$.

In 1947, Rohrback and Cady[44] identified fluorine perchlorate, $FClO_4$, which they prepared from fluorine and perchloric acid. Another compound, perchloryl fluoride, $FClO_3$, was prepared by Bode and Klesper[8] in 1951, by fluorinating potassium chlorate.

Hofmann and his co-workers[23] in 1906 began studies of compounds formed when aqueous perchloric acid (72 per cent) is added to various organic compounds including alcohols, amines, ketones. Most or all of these compounds were thermally unstable and would detonate on heating. Hofmann[24] found that perchloric acid offers advantages over picric acid for separation of carbinols, ketones and amines from the resinous materials formed during their preparation. He concluded that perchloric acid apparently does not add to double bonds. He also found that perchloric acid has very slight oxidizing power under the conditions employed because pyrogallol or hydroquinone may be recrystallized from a mixture of perchloric and acetic acids. He prepared esters of epichlorhydrin and perchloric acid, compounds he found to be more explosive than nitroglycerine.[26]

Other than Kolbe's verification[32] of von Stadion's early work on electrolysis of chlorate to perchlorate, at which time he also confirmed Berzelius'[7] preparation of aqueous acid by the electrolysis of chloric acid solution, little work was done on the electrolytic methods of production and use until about 1890. In that year, Oscar Carlson, founder and president of Stockholms Superfosfat Fabriks AB (Fosfatbolaget), applied for a

patent for diaphragmless electrolytic cells for the production of sodium chlorate.[13] The formation of perchlorate was observed. Research to find conditions favorable to perchlorate formation was intensified in the laboratory and in the pilot plant which Fosfatbolaget built in 1892. A commercial plant was constructed in 1893 at Mansbo, Sweden, and in 1898, small quantities of ammonium perchlorate were produced, but with variable results. Sometimes a bath of sodium chlorate solution could be oxidized to perchlorate in 5 or 6 days; other times the process lasted many weeks. By 1904, production was running smoothly; potassium perchlorate was first manufactured at Mansbo in 1905.[62]

Meanwhile, Carlson had been experimenting on the production of explosives containing ammonium perchlorate; in 1897 he received a patent in this field[12]; the well-known explosive "Carlsonsit" was later developed and covered by many patents.

Following Sweden's pioneering work, France, Germany, Switzerland and the United States also began to produce perchlorates. In 1901, potassium, sodium and ammonium perchlorates were produced electrolytically at Chedde, France. Gesellschaft für elektrochemische Industrie Turgi (now Elektrochemie Turgi) began manufacturing potassium perchlorate in Switzerland, in 1907.[15] Oldbury Electro-Chemical Company (now Hooker Electrochemical Company) began experimental work on the electrolysis of sodium chlorate using platinum anodes, producing sodium perchlorate in 1908; by 1910 potassium perchlorate was produced at the rate of 150 tons per year at their plant at Niagara Falls, New York.[27]

Until the first World War broke out, however, the total volume of perchlorate production in the world was not more than 2,000 to 3,000 tons per year. The lack of nitric acid during the war forced Germany to promote the development of perchlorates, and the factory of Chemical Works Griesheim Elektron at Bitterfeld produced about 20,000 tons during the war years.[14] Elektrochemie Turgi also manufactured ammonium perchlorate, in addition to sodium and potassium perchlorates, at their Spreitenbach factory.[15] Fosfatbolaget, in 1915, erected a second plant with a capacity of 750 tons of ammonium perchlorate and 475 tons of potassium perchlorate a year. This plant, in Trollhatten, is today the main producer of sodium chlorates and perchlorates in Sweden.[62]

After the first World War, commercial production decreased to a minimum. There was no very significant new demand for the perchlorates, other than for use in fireworks, railway signals, etc., until the late 1930's and during World War II, when the present major interest began.

Canada produced perchlorates during the years 1942 to 1946. At that time Electric Reduction Company of Canada built facilities at Buckingham, Quebec, to produce ammonium, barium and potassium perchlorate for military use.[10]

Potassium perchlorate was placed on the list of strategic chemical in the United States in 1940 and production was stepped up, increasin 20-fold, reaching about 20,000 tons per year during the years 1941–194 The number of domestic manufacturers increased from one to four; th three new producers built four new plants.

Beginning in 1941, the Cardox Corporation, to take care of its ow needs for potassium perchlorate in the mining field, produced potassiu perchlorate at its Claremore, Oklahoma plant. In 1943, they constructe and operated for the Government another potassium perchlorate plant a the same location.[11] Vick Chemical Company built a plant in 1943 fo the production of ammonium perchlorate in Greensboro, North Carolin

In 1942, Western Electrochemical Company, now American Potash Chemical Corporation, built the first West Coast electrolytic potassiu perchlorate plant at Los Angeles, California. Support was received for th program from the Guggenheim Aeronautics Laboratory at the Californi Institute of Technology. Various perchlorates were prepared for exper mental production of rocket propellants. Soon thereafter Aerojet Enginee ing Corporation, now Aerojet General Corporation, started commerci production of rocket motors. Thus a new and increasing demand for pe chlorates was established.

In 1945, Western Electrochemical Company took over some of the i stallations of Basic Magnesium Inc., Henderson, Nevada, and converte them into a perchlorate manufacturing plant to satisfy the needs of t military rocket program. Immediately following World War II the deman for perchlorates began to shift from potassium to the ammonium salt. Al at this time Thiokol Chemical Company, and others, started to manufa ture solid rocket propellants.

In 1948, Western Electrochemical Company built an ammonium pe chlorate pilot plant at Henderson, Nevada. In 1951, acting as prime co tractor for the Navy and Army, Western Electrochemical Company init ated a program leading to the design and construction of an ammoniu perchlorate plant with a capacity many times greater than any other plan The plant started production in 1953 and has been in operation, althou at less than full capacity, since start-up. In 1958, increased interest in sol propellants created new demands for perchlorates and a new round expansion was started. H.E.F. Inc., (owned by Hooker Electrochemic and Foote Mineral), and also Pennsalt Chemicals Corporation, have a nounced plans for construction of new perchlorate facilities. Americ Potash & Chemical Corporation, the largest producer of perchlorates, h also announced plans for increasing production.

Many improvements and modifications in the electrolysis of chlorat to perchlorates, in efforts to increase yields, have been demonstrated. Wh the electrolytic process was adapted for use in the commercial producti

of perchlorates, speculation arose as to what reactions actually took place at the anode in chlorate electrolysis. Foerster,[18] in 1897, and Winteler,[69] in 1898, reported their investigations to determine conditions under which perchlorate is obtained with maximum current yield. Winteler stated that either platinum or superoxide electrodes could be used, although he did not specify the nature of the superoxide. Both Foerster and Winteler observed the evolution of ozone during the electrolytic formation of perchlorate, especially from concentrated solutions.

In 1903, Oechsli[39] proposed that the reaction is not a direct addition of oxygen to ClO_3, with the formation of ClO_4. It is rather a secondary reaction involving the discharge of the chlorate ion followed by reaction of the free radical with water in the vicinity of the anode, forming chlorous and perchloric acids and liberating oxygen; the unstable chlorous acid then spontaneously oxidizes to chloric acid.

Bennett and Mack[5] took exception to Oechsli's theory in 1916, when they attempted to show that chlorates may be oxidized to perchlorates by persulfuric acid, ozone or hydrogen peroxide. They cited Schoch's experiments to show that perchlorates are formed at the anode at a potential far below that necessary for the continuous discharge of any ions present in the solution.

Later, in 1920, Knibbs and Palfreeman,[31] considering that neither of these theories were adequate, presented their own theory, a modification of Oechsli's, maintaining that perchlorate formation is due to chlorate ion discharge, but that the reactions taking place subsequently are analogous to those in the formation of persulfate.

In 1953, Sugino and Aoyagi[64] actually measured polarographically the current-potential curves for the electrolytic oxidation of chlorate. This mechanism assumed the discharge of the chlorate ion and subsequent hydrolysis.

At the University of Texas, in 1955, Philipp and Morgan[43] observed the similarities between conditions favorable to the electrolytic and to the chemical oxidation of aqueous chlorates, the same factors in each process favoring high yields. They postulated that the mechanism for the electrolytic formation of perchlorates involves an unusually high valence oxide which forms on the anode surface. In the highly acidic conditions existing there, the oxide is unstable and reacts similarly to higher oxides in chemical oxidation experiments.

There has been no general agreement on the mechanism of the electrolytic formation of perchlorate. This suggests additional studies of the mechanism, using lead dioxide anodes and also the chemical oxidation in aqueous acid and neutral solutions, using oxidizing agents such as the platinum superoxide of Philipp and Morgan, or lead dioxide of the type suitable for electrolytic work.

Until recently, platinum has been the most favored anode material in spite of its high initial cost and losses during operation. However the search for a substitute for platinum has been under way almost from the time that electrolytic production of perchorates was begun commercially.

Ferchland[17] patented a process for preparing a lead dioxide anode in 1905. Schoch and Randolph[49] made a study of the behavior of iron and nickel cathodes in 1910. Huth[29] patented a process for producing an anode of crystalline manganese dioxide embedded with pieces of lead dioxide in 1919, Sato[47] produced an anode of iron oxide, clay and sodium nitrate.

Howard[28] was unsuccessful in his attempts to oxidize sodium chlorate to perchlorate using a magnetite anode. In 1934, Angel[1] investigated the use of tungsten and molybdenum anodes, but later that same year, Ange and Mellquist[2] deposited lead dioxide on iron-, steel-, copper- and silver-plated sheets. It was Kato and Koizumi[30] who applied their lead dioxide anode, made more compactly by the addition of a colloidal matter, to the successful production of perchlorates. In 1939, Sugino, Koizumi and Kitahara[65] patented a process for preparing perchlorates using a lead dioxide anode and a cathode of gold, silver, platinum or rhodium. Shibasaki in 1948 pressed and molded an anode of powdered lead dioxide and vinyl chloride.[55]

Mizuguchi[38] studied the surface processes which take place on lead dioxide anodes during electrolytic oxidation and suggested the addition of hydrofluoric acid to decrease this activity.

In 1950 Sugino[63] outlined new methods for the production of lead dioxide anodes by the electrolytic deposition of lead dioxide from a neutral lead nitrate solution upon (1) the inner surface of an iron or nickel cylinder or (2) the outer surface of a soft and nonmetallic conductor, such as a rod with a surface of a paraffin-graphite mixture.

In 1951, Pennsalt received a research contract from the Office of Naval Research to explore alternate anodes to replace platinum; they evolved a lead dioxide anode made by the electrodeposition of lead dioxide from a lead nitrate bath onto tantalum, which was demonstrated to the Office of Naval Research in January, 1954.[40]

American Potash & Chemical Corporation, also under contract to the Navy, designed, constructed and operated successfully a pilot plant cell in which lead dioxide anodes were used.

Although all the present commercial producers of perchlorates now employ the electrolytic process, it is conceivable that a commercial non electrolytic process may be developed in the future to meet the growing demands for perchlorates.

CHRONOLOGY

1816 von Stadion reported his discovery of potassium "oxychlorate" (perchlorate) and "oxygenated chloric acid" (perchloric acid).[60]

1830 Serullas prepared perchloric acid by thermal decomposition of chloric acid.[51]

1831 Serullas prepared:

1. Aqueous perchloric acid by chemical reaction of potassium perchlorate and fluosilicic acid.[54]
2. A solid form of perchloric acid, later identified as the monohydrate.[52]
3. Potassium perchlorate by thermal decomposition of potassium chlorate.[54]

Serullas devised the perchlorate method for the separation of potassium and sodium.[53]

1835 Berzelius prepared aqueous perchloric acid by electrolysis of chloric acid solution.[7]

1840 Penny prepared aqueous perchloric acid by chemical reaction of chlorate with nitric acid.[41]

1841 Hare and Boye prepared the ethyl ester of perchloric acid.[22]

1843 Millon observed that aqueous solutions of chlorine dioxide, ClO_2, in light, decomposed into chlorine and perchloric acid.[36]

1847 Kolbe prepared perchloric acid by electrolysis of hydrochloric acid solution.[32]

1862 Roscoe prepared anhydrous perchloric acid and identified the solid acid obtained by Serullas as the monohydrate.[45]

1871 Schloesing prepared sodium perchlorate by thermal decomposition of sodium chlorate and transformed sodium perchlorate to ammonium perchlorate by the addition of ammonium chloride.[48]

1874 Fairley prepared perchloric acid or a perchlorate by passing ozonized air through a solution of hypochlorous acid or sodium hypochlorite.[16]

1881 Berthelot showed how thermochemistry accounts for the characteristic properties of the perchlorates, pointing out that the change of potassium chlorate to perchlorate by heat is exothermic.[6]

1886 Beckurts discovered perchlorate in nature in Chilean saltpeter.[4]

1890 Carlson patented an electrolytic process using cells without diaphragms for the manufacture of chlorate and perchlorate.[13]

1893 First commercial perchlorate plant constructed at Mansbo, Sweden.[61]

1895 Carlson started experiments on the production of explosives containing ammonium perchlorate.[12]

1897 Foerster studied the electrolytic formation of perchlorate to determine most favorable conditions.[18]

1898 Winteler observed the formation of ozone during electrolysis of concentrated aqueous perchlorate solutions.[69]

1900 Michael and Conn isolated the anhydride of perchloric acid, Cl_2O_7.[35]

1902 Van Wyk identified five hydrates of perchloric acid.[70]

1903 Oechsli presented a theory for the mechanism for electrolytic formation of perchlorate postulating discharge of the chlorate ion.[39]

1905 Ferchland patented a process for preparing lead dioxide anodes.[17]

1906 Hofmann and his co-workers prepared perchlorates of many organic compounds.[23]

1908 Borelli prepared the complex mercury cyanide perchlorate, $(HgCN)ClO_4$.[9]

1909 Hofmann and Zedtwitz prepared nitrosyl perchlorate.[25]

1911 Salvadori prepared various complexes of cobalt and perchloric acid.[46]

1916 Bennett and Mack presented a theory of the electrolytic formation of perchlorate postulating the direct addition of oxygen to the chlorate.[5]

1920 Knibbs presented his theory of electrolytic formation of perchlorate postulating chlorate ion discharge followed by chemical reactions in a mechanism similar to that of persulfate formation.[31]

1921 Weinland isolated anion complex perchlorate salts.[68]

1928 Hantzsch and Berger prepared nitronium perchlorate, $(H_2O_2N)ClO_4$, from absolute perchloric acid and absolute nitric acid.[21]

1934 Angel and Mellquist substituted lead dioxide anodes for platinum in electrolysis of chlorates.[2]

1936 Fonteyne began studies of the structure of perchloric acid employing Raman spectra.[19]

1939 Sugino, Koizumi, and Kitahara patented process for preparing perchlorates by electrolysis using a lead dioxide anode.[65]

1940 Gordon and Spinks reported the discovery of nitroxyl perchlorate, $NClO_4$.[20]

1942–1945 New military uses for perchlorates caused manifold expansion of the industry in the United States and Canada.

1946 Pernert patented a perchloric acid process based on the chemical reaction of sodium perchlorate and hydrochloric acid.[42]

1947 Rohrback and Cady reported discovery of fluorine perchlorate, $FClO_4$.[44]

1951 Bode and Klesper reported the discovery of perchloryl fluoride, $FClO_3$.[8]

1953 Sugino and Aoyagi measured the anodic potential of perchlorate formation and presented a theory of the mechanism of reaction.[64]

1955 Philipp and Morgan proposed a theory of the mechanism of electrolytic formation of perchlorate postulating a high valency platinum oxide intermediate.[4]

1956 Schumacher patented ammonium perchlorate process based on continous reaction of liquid anhydrous ammonia, a mineral acid and sodium perchlorate.[5]

1958 New expansion of perchlorate industry began.

REFERENCES

1. Angel, G., *Z. Elektrochem.*, **40**, 641 (1934).
2. Angel, G., and Mellquist, H., *Z. Elektrochem.*, **40**, 702 (1934).
3. Baas-Becking, L. G. M., Haldane, A. D. and Izard, D., *Nature*, **182**, (4636), 645 (1958).
4. Beckurts, H., *Arch. Pharm.*, **224**, 333 (1886).
5. Bennett, C. W., and Mack, E. L., *Trans. Am. Electrochem. Soc.*, **29**, 323 (1916).
6. Berthelot, M., *Compt. rend.*, **93**, 240 (1881).
7. Berzelius, J. J., "Lehrbuch der Chemie," Section 2, p. 77, Germany, 1835.
8. Bode, H. and Klesper, E., *Z. anorg. u. allgem. Chem.*, **266**, 275 (1951).
9. Borelli, V., *Gazz. chim. ital.*, **38** [I], 361 (1908).
10. Canadian Consulate General, private communication, Nov. 12, 1957.
11. Cardox Corporation, private communication, Dec. 10, 1957.
12. Carlson, O. F., Sweden Patent 8487 (Nov. 27, 1897).
13. Carlson, O. F., Sweden Patent 3614 (June 11, 1892).
14. E. Merck Aktiengesellschaft, private communication, Nov. 21, 1957.
15. Electrochemical Works Turgi, private communication, Jan. 28, 1958.
16. Fairley, T., *Brit. Assoc. Advancement Sci., Rep.*, **44**, 57 (1874).
17. Ferchland, P., German Patent 206,329 (Feb. 4, 1909).
18. Foerster, F., *Z. Elektrochem.*, **4** (16), 386 (1897).
19. Fonteyne, R. *Nature*, **138**(3499), 886 (1936).
20. Gordon, W. E., and Spinks, J. W. T., *Can. J. Research*, **18B**, 358 (1940).
21. Hantzsch, A., and Berger, K., *Ber.*, **61B**, 1328 (1928).
22. Hare, C., and Boye, H., *Phil. Mag.*, **19**(3), 370 (1841).
23. Hofmann, K. A., and Arnoldi, H., *Ber.*, **39**, 3146 (1906).

24. Hofmann, K. A., Metzler, A., and Hobold, K., *Ber.*, **43**, 1080 (1910).
25. Hofmann, K. A., and Zedtwitz, A., *Ber.*, **42**, 2031 (1909).
26. Hofmann, K. A., Zedtwitz, G. A., and Wagner, H., *Ber.*, **42**, 4390 (1910).
27. Hooker Electrochemical Company, private communication, Oct. 28, 1957.
28. Howard, H. C., *Trans. Am. Electrochem. Soc.*, **43**, 51 (1923).
29. Huth, M. (to Siemens and Halske A. G., Germany), U. S. Patent 1,043,937 (Nov. 12, 1912).
30. Kato, Y., and Koizumi, K., *J. Electrochem. Assoc. Japan*, **2**, 309 (1934).
31. Knibbs, N. V. S., and Palfreeman, H., *Trans. Faraday Soc.*, **16**, 402 (1920).
32. Kolbe, H., *Ann.*, **64**(1), 237 (1847).
33. Maercker, *Landw. Vers.-Sta.*, **52**, 34 (1899).
34. Marignac, C., *Ann.*, **44**, 11 (1842).
35. Michael, A., and Conn, W. T., *Am. Chem. J.*, **23**, 444 (1900).
36. Millon, N. A. E., *Ann. chim. et phys.*, **7**(3), 298 (1843).
37. Mitscherlich, E., *Pogg. Ann.*, **25**, 300 (1832).
38. Mizuguchi, J., *J. Electrochem. Assoc. Japan*, **17**, 258 (1949).
39. Oechsli, W., *Z. Elektrochem.*, **9**, 807 (1903).
40. Pennsalt Chemicals Corporation, private communication, Oct. 31, 1957.
41. Penny, F. *Ann.*, **37**, 203 (1841).
42. Pernert, J. C. (to Oldbury Electrochemical Co.), U. S. Patent 2,392,861 (Jan. 15, 1946).
43. Philipp, W. H., and Morgan, L. O., Technical Report No. 4 to Office of Naval Research, Contract Nonr 375(04), Univ. of Texas, Dept. of Chem. (Oct., 1955).
44. Rohrback, G., and Cady, G. H., *J. Am. Chem. Soc.*, **69**, 677 (1947).
45. Roscoe, H. E., *Proc. Roy. Soc.*, **XI**, 493 (1862).
46. Salvadori, R., *Gazz. chim. ital.*, **40(II)**, 9 (1911).
47. Sato, E. (to Kabafuto-Kwako and Co.), Japan Patent 34,913 (Sept. 11, 1919).
48. Schloesing, T., *Compt. rend.*, **73**, 1269 (1871).
49. Schoch, E. P., and Randolph, C. P., *J. Phys. Chem.*, **14**, 719 (1910).
50. Schumacher, J. C., (to Western Electrochemical Co.) U. S. Patent 2,739,873 (March 27, 1956).
51. Serullas, G. S., *Ann. chim. et phys.*, **45**, (2), 270 (1830).
52. *Ibid.*, **46**, (2), 294 (1831).
53. *Ibid.*, p. 297.
54. *Ibid.*, p. 323.
55. Shibasaki, Y., Japan Patent 175,562 (Jan. 29, 1948).
56. Sjollema, B., *Chem.-Ztg.*, **20**, 1002 (1896).
57. Sjollema, B., *Chem. Weekblad*, **1**, 125 (1904).
58. *Ibid.*, p. 201.
59. Smith, G. F., and Goehler, O. E., *Ind. Eng. Chem., Anal. Ed.*, **3**, 58 (1931).
60. Stadion, F. von, *Ann. chim. et phys.*, **8**(2), 406 (1818).
61. Stadion, F. von, *Gilbert's Ann. Phys.*, **52**, 197 (1816).
62. Stockholms Superfosfat Fabriks Aktiebolag, private communication, Nov. 25, 1957.
63. Sugino, K., *Bull. Chem. Soc. Japan*, **23**, 115 (1950).
64. Sugino, K., and Aoyagi, S., *Bull. Chem. Soc. Japan*, **26**, 185 (1953).
65. Sugino, K., Koizumi, K., and Kitahara, S., Japan Patent 129, 657 (April 7, 1939).
66. Verweij, A., *Chem. Weekblad*, **1**, 155 (1904).
67. Volmer, M., *Ann.*, **440**, 200 (1924).
68. Weinland, R., *Z. Angew. Chem.*, **34**, Aufsatzteil, 354 (1921).
69. Winteler, F., *Chem.-Ztg.*, **22**, 89 (1898).
70. Wyk, H. J. van, *Z. anorg. Chem.*, **32**, 115 (1902).

2. PERCHLORIC ACID

ANHYDROUS PERCHLORIC ACID

Preparation

Anhydrous perchloric acid can best be prepared by vacuum distillation from a mixture of fuming sulfuric acid and commercially available 72 per cent perchloric acid. Smith[48] reports that 75 per cent yields of anhydrous perchloric acid may be obtained in this way by distillation at pressures of 1 mm or less from a mixture of four volumes of oleum to one of 72 per cent perchloric acid.

The anhydrous acid is a clear, colorless, mobile liquid with a viscosity of 0.76 centipoises at 20°C and 0.563 centipoises at 50° as determined by Van Wyk.[70] The liquid is unstable at ordinary temperatures, slowly developing a yellowish to brown color and becoming explosive. The electrical conductivity of aqueous solutions has been studied by Usanovich and Sumarokova[62] and found to decrease rapidly from 0.7828 at 10 mole per cent perchloric acid to 0.0106 at 100 per cent acid.

The Raman spectrum has been studied by Redlich and co-workers,[32] by Fonteyne[10, 11] and by Simon and co-workers.[42, 44, 45] Simon concludes from spectroscopic and viscosimetric measurements that the anhydrous acid exists only in the pseudoform state. Goehler and Smith[14] found that during the low pressure distillation of concentrated (73 per cent) perchloric acid, a dissociation takes place as follows:

$$4HClO_4 \cdot 2H_2O \rightarrow 2HClO_4 \cdot 3H_2O + 2OH_3 \cdot ClO_4$$

$$2OH_3 \cdot ClO_4 \rightarrow HClO_4 \cdot 2H_2O + HClO_4$$

They have prepared anhydrous perchloric acid in yields of approximately 10 per cent by this method.

Reactions

Anhydrous perchloric acid is an extremely powerful oxidizing agent. It will cause explosions upon contact with most organic substances. Vorländer and Kaascht[67] studied several of the reactions of the anhydrous acid. They found that chlorine dioxide will turn the acid yellow to dark brown and form a mushy crystalline precipitate. The crystalline mass and supernatant brown liquid deflagrate on contact with ice water. The crystals form a yellow solution in chloroform. In dry atmosphere the crystals melt at 0°C to form a red-brown solution which loses chlorine dioxide. A dark brown solution results also from the addition of potassium chlorate to the