PERCHLORIC ACID—A NEGLECTED CHAPTER IN GENERAL CHEMISTRY

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An examination of a dozen or more college textbooks on general chemistry showed that only one of them gave perchloric acid more than passing notice. The omission of this substance from the list of important inorganic compounds cannot be due to any lack of industrial importance. A recent estimate is that 300,000 to 500,000 pounds of perchlorates are produced each month. This puts perchloric acid approximately in the class with phosphoric acid.

The fact that perchloric acid has come into importance only recently may have something to do with its omission. Authors are hesitant about giving space to new compounds as long as there is any question as to their eligibility to a chemical "Who's Who" or "What's What." The compass of textbooks is limited, and "a new topic cannot be squeezed in without squeezing something else out." To displace another topic, a substance must have definite industrial value or scientific significance. For example, if it is an analytical reagent, it must be able to compete with other reagents of recognized standing. This consideration has counted against perchloric acid, for so many analysts are so comfortable in precipitating potassium with chloroplatinic acid that they are unwilling to give a newcomer a trial.

Perchloric acid has a reputation for being a treacherous explosive. A while ago a graduate student argued against including perchloric acid in courses in general chemistry on the ground that its excessive explosiveness would tempt young students to make illicit experiments that might turn out disastrously. This idea of spontaneous explosiveness is not limited to students. It is held by many mature chemists who ought to know better. The fact is, concentrated perchloric acid is quite stable, and cannot be exploded by shock or otherwise. Like nitric acid, it may be used in making explosives. If perchloric acid is to be banned for this reason, consistency would call for a similar exclusion of glycerine and toluene, or even sulfur and saltpeter.

In my opinion, the strongest objection to including perchloric acid in the subject matter of elementary courses is a pedagogical one. Many of the perchlorate reactions that have been studied appear so involved and anomalous, that the student is dismayed and comes to doubt if there are any fundamental principles controlling the course of chemical reactions. An illustration is the awe-inspiring equation proposed for the preparation of perchloric acid from ammonium perchlorate:

$$34NH_4ClO_4 + 36HNO_3 + 8HCl \rightarrow 34HClO_4 + 4Cl_2 + 35N_2O + 73H_2O$$

Other discouraging equations from the literature are:

$$14Fe + 48HClO_4 \rightarrow 14Fe(ClO_4)_3 + 3Cl_2 + 24H_2O$$

$$Cr_2O_3 + 2HClO_4 + H_2O \rightarrow 2H_2CrO_4 + Cl2 + 2O_2$$

Properties of Perchloric Acid

Perchloric acid comes on the market as a clear mobile solution, with a density of 1.69, and containing about 72 per cent $HClO_4$. This solution boils at 203° with slight decomposition. Judged by its electrical conductivity, concentrated perchloric acid is a very weak acid. According to Linde, the 72 per cent acid is only 5 per cent ionized. This accounts for its very slow reaction with active metals.

Concentrated perchloric acid is a dehydrating agent and chars wood and other cellulosic materials by the extraction of water. Very naturally, the intensity of this effect varies with temperature.

At ordinary temperatures concentrated perchloric acid is a weak oxidizing agent —not as active as nitric acid. Upon heating to 150° or above, it shows marked oxidizing power, converting Cr^{+++} ions

TABLE 1.—THE REACTIONS OF METALS WITH 72% PERCHLORIC ACID

Metal	Products	Metal	Products
Magnesium	Mg^{++}, H_2	Lead	Pb^{++}, H_2, Cl_2, HCl
Aluminum	Al^{+++}, H_2, Cl^- (trace)	Copper	Cu_2^{++}, Cu^{++}, HCl
Zinc	Zn^{++}, H_2, Cl^- (trace)	Mercury	Hg^{++}, HCl
Cadmium	Cd^{++}, H_2, Cl^- (trace)	Arsenic	H_3AsO_4, HCl
Chromium	(1) Cr^{+++}, Cr^{++}(?), (2) CrO_4^{--}, HCl	Antimony	Sb_2O_4, HCl
Iron	Fe^{+++}, Fe^{++}, H_2, HCl, Cl_2	Bismuth	Bi^{+++}, Cl^-
Cobalt	Co^{++}, H_2, HCl	Silver	AgCl, Ag^+
Nickel	Ni^{++}, H_2, HCl	Platinum	No reaction
Tin	SnO_2, Cl_2, Cl^-	Gold	$AuCl_4^-$ (trace)

into the CrO_4^{--} form. This notable increase in oxidizing strength with temperature can be explained only by some change in the molecular composition of the solution. Although liquid perchloric acid is stable and very hard to reduce, gaseous perchloric acid is very unstable and therefore a powerful oxidizing agent. It is likely that this oxidizing action is inherent in the anhydrous $HClO_4$ molecules.

Reactions with metals.—The reactions of perchloric acid with metals have been summarized in Table 1. From these results it appears that only active metals react at low temperatures, and that they liberate hydrogen with no reduction of the perchlorate group. At high temperatures, the active metals continue the displacement of hydrogen, but with some reduction of the ClO_4^- group; the nobler metals also react, but in their case no hydrogen is evolved, and the perchlorate group is reduced, forming chloride in most cases. Marked passivity is noted in certain cases; e.g., iron, chromium, nickel, etc.

The various reactions of perchloric acid may be simply explained in terms of its ionic and molecular composition, which may be represented by the following equilibrium:

$$H^+ + ClO_4^- \overset{\text{dilution}}{\leftrightarrows} HClO_4.\text{hydrate} \overset{\text{heat}}{\rightleftarrows} HClO_4 + H_2O$$

The liberation of the hydrogen by active metals is characteristic of the H^+ ion. It is interesting to note that this reaction becomes very vigorous when water is added to a hot mixture of acid and aluminum or magnesium.

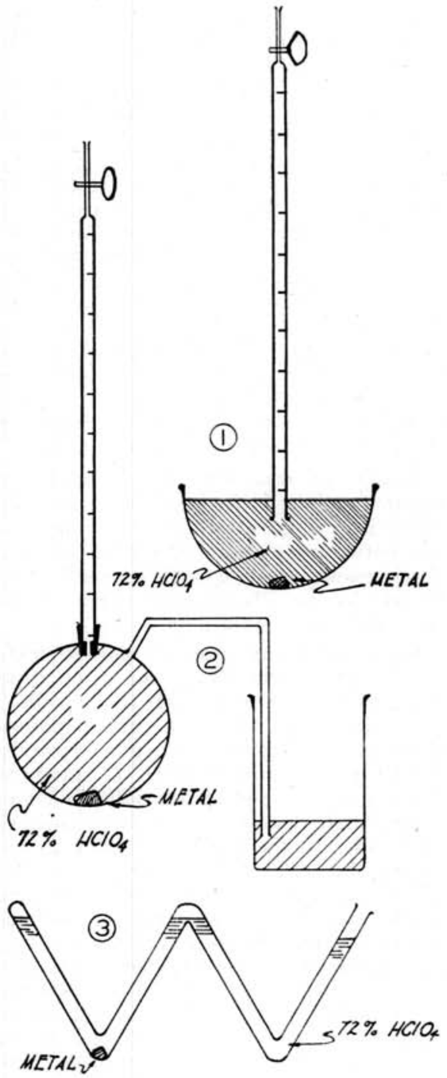
The dehydration effects are inherent in the anhydrous perchloric acid, and therefore proceed more rapidly with rise in temperature.

Oxidation is a property of the perchloric acid molecule, particularly the anhydrous $HClO_4$. The ClO_4^- ion is not an oxidizing agent; its neutral solutions will not react with the most vigorous reducing agents. In these reactions perchloric acid shows a definite similarity to nitric acid, e.g., in the passivity effects noted above.

As hydrogen chloride is formed by the reduction of perchloric acid, the solution contains a mixture of hydrochloric and perchloric acid which is analogous in composition to aqua regia. This combination does not have any solvent action on platinum, but its reaction with gold is appreciable. Evidently perchloric acid is not as effective as nitric acid in the oxidation of hydrogen chloride.

Determination of Reaction Products.—The determination of the products formed in perchlorate reactions is a matter of some difficulty. Weighed samples of the metals were completely reacted with an excess of 72 per cent perchloric acid, and the products were analyzed qualitatively and quantitatively. As far as possible, volumetric methods were used for gaseous products, and wet methods for dissolved products. Lack of space prevents extended description. The general procedure may be outlined as follows:

For low-temperature reactions, in which hydrogen is the general product, the apparatus shown in figure 1 was used. For high-temperature work, a closed system is necessary to avoid fuming and possible loss of volatile products. The apparatus in figure 2 was designed for that purpose. In both cases, the apparatus was filled with the acid by suction at the stopcock of the burette. Another type of apparatus was found very useful, especially for high-temperature reactions. It consisted of a tube closed at one end and bent in the shape of a W (fig. 3). The tube was filled with 72 per cent perchloric acid, and the metallic sample was introduced and maneuvered into the bend next to the closed end. Heat was applied at this point. In this way the gases evolved were retained in the end and the second bend. These gaseous products were then transferred under water to other tubes for analysis.



Apparatus for the analysis of the reaction products of perchloric acid.

The displacement-of-hydrogen proceeded simply in the cases of the more reactive metals—i.e., those occurring above hydrogen in the E. M. F. series. In these cases, an equivalent weight of the metal forms a one-half molar volume of hydrogen. In oxidation reactions, the predominant reduction product was gaseous hydrogen chloride, insoluble in concentrated perchloric acid. The ratio of equivalents of metal consumed to Cl^- ion formed found in all cases to be close to 8:1, showing the "oxidation number" of perchloric acid to be +8. This indicates that the fundamental decomposition of perchloric acid may be represented: $HClO_4 \rightarrow HCl + 4O$. Illustrative equations are:

$$4Ni + HClO_4 + 8H^+ \rightarrow 4Ni^{++} + HCl + 4H_2O$$

$$8Bi + 3HClO_4 + 24H^+ \rightarrow 8Bi^{+++} + 3HCl + 12H_2O$$

In cases of prolonged heating, this ratio was frequently exceeded. The source of this excess chloride was found to be due to a slight decomposition of perchloric acid into hydrogen chloride and oxygen.

The equations obtained by analytical methods are overall equations, and give no information about the concurrent or consequent reactions that may be involved. When concurrent reactions are involved, their relative speeds may vary with conditions, and the overall equations are not definite and are without significance.

Summary.—The very complex equations found in the literature of perchloric acid are a deterrent to the inclusion of this subject in inorganic textbooks.

These discouraging expressions may be eliminated by considering the reactions of perchloric acid to be a summation of the behaviors of the ionic and molecular constituents of the solution. Two or more reactions may take place simultaneously, and their effects are therefore superposed.

In general, perchloric acid shows two modes of reaction: (1) Displacement of hydrogen, without any decomposition of the ClO_4^- group; (2) oxidation, with the reduction of the ClO_4^- group to Cl^- mainly.