ART. XXIII.—*The Generation of Chlorine for Laboratory Purposes*; by F. A. GOOCH and D. ALBERT KREIDER.

[Contributions from the Kent Chemical Laboratory of Yale College—XXXIII.]

THAT chlorine may be generated in a state of greater or less purity, variable with the conditions of evolution, by the action of hydrochloric acid upon potassium chlorate has been shown by Pebal* and Schacherl,† but the application of this fact to the practical generation of chlorine for the purposes of the

* Ann. der Chem., clxxvii, 1.

† Ibid. clxxxii, 197.

laboratory has not to our knowledge been proposed. The desirability of an automatic generator from which an abundant flow of chlorine gas may be drawn at will or shut off without danger or inconvenience has led us to a study of the conditions most favorable to the safe evolution of chlorine by the action of the chlorate.

Pebal* showed that the gas evolved at ordinary temperatures from a mixture of potassium chlorate and sodium chloride acted upon by sulphuric acid diluted with twice its volume of water consists of chlorine and chlorine dioxide in nearly equal proportions. Schacherl† found that when potassium chlorate was acted upon by hydrochloric acid diluted with twice its own volume of water the yield of chlorine was about 46 per cent or 57 per cent of the mixed gases according as the chlorate was granular or in fine powder; that hydrochloric acid of half-strength yielded a gas containing nearly 60 per cent of chlorine, and that the proportion of chlorine rose nearly to 68 per cent when the gas was passed through concentrated hydrochloric acid and then washed with water; that the chlorate when acted upon by the strongest hydrochloric acid cooled to 0° C. and then warmed only enough to start the action yielded a gas carrying 87 per cent of chlorine; and that when a solution of potassium chlorate was permitted to flow into hot strong hydrochloric acid the free chlorine constituted nearly 75 per cent of the mixture. So it appears that the highest yield of chlorine resulted when the solution of the chlorate entered gradually the hot strong acid—a condition not easily attained in an automatic generator.

The fact that chlorine dioxide is so easily decomposed by heat into chlorine and oxygen naturally suggests the possibility of increasing the proportion of chlorine evolved in the first instance by working at the highest temperatures practically attainable under the conditions. In order, however, to secure a temperature approaching the boiling point of water it is necessary to reduce somewhat the strength of the hydrochloric acid acting (in order to avoid the evolution of hydrochloric acid gas and the consequent interference with the regular automatic action of the generator), thus sacrificing the advantage naturally attending the use of acid of the highest degree of concentration. Upon experiment we find that acid of half-strength (sp. gr. 1.10) can be made to yield a very satisfactory proportion of chlorine. We have employed in our work potassium chlorate fused (best in platinum) and cast in sticks or broken into coarse lumps. A small Kipp's apparatus, holding about a half-liter of liquid in the two lower chambers, makes a convenient generator, and the requisite temperature

* Loc. cit.

† Loc. cit.

may be secured by wrapping the two lower chambers with flexible metallic tubing through which steam is driven, or, with equal convenience, by simply standing the whole apparatus in heated water. When the simple precaution is taken to heat the acid to 60° or 70° C. before allowing it to come slowly into contact with the fused chlorate no difficulty whatever is met with in the practical automatic working of the generator; but if cold acid is permitted to act upon the chlorate it becomes charged more or less with the chlorine dioxide and a subsequent rise of temperature may cause dissociation of the explosive gas with sufficient suddenness to expel the liquid from the generator with considerable violence. The gas evolved directly from the generator is never pure chlorine. To determine the relative proportions of chlorine and chlorine dioxide (the sole products of the action according to Pebal) the gas as it issued from the generator was passed through two pipettes fitted with glass stopcocks and joined to one another. After allowing a reasonable time for the complete expulsion of air from the pipettes the stopcocks were closed, and the pipettes were disconnected from one another and from the generator. The gas contained in one of the pipettes was slowly forced by means of carbon dioxide through a solution of potassium iodide; that in the second pipette was driven slowly by means of carbon dioxide through a hard glass tube filled with asbestos and heated to redness by a Bunsen burner, and then passed through a solution of potassium iodide. The iodine set free in each case was determined in the acidified solution by standard sodium thiosulphate, and the difference in the amounts of iodine found was attributed to the action of the oxygen of the chlorine dioxide. It was assumed that the gas filling the pipettes ranged in line was homogeneously distributed, and this assumption is probably nearly enough true for the purpose of this discussion. The temperature of the acid in the generator was determined by inserting a thermometer in the lowest chamber of the generator, so that the indication for the point of action is only approximate.

In two experiments made with acid of half strength and at indicated temperatures of 80° and 81° the chlorine in the gas amounted to 81.6 per cent and 84 per cent respectively of the mixture. A comparison experiment made with the strongest acid heated to 50° —the highest temperature attainable without evolution of the hydrochloric acid gas—the yield of chlorine was 77.3 per cent. It is evident that the acid of half strength acting at 80° is productive of a more favorable yield than the strongest acid at 50° .

Temperatures very much higher than those employed can hardly be secured continually under the conditions of work,

and yet it is plain that a considerable amount of the oxide still accompanied the chlorine. We made the attempt, therefore, to accomplish the destruction of the oxide by passing the mixed gases as they issued from the generator through a small wash-bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid, making use of a device previously employed in this laboratory for the decomposition of nitric acid and chloric acid.* The results of several experiments conducted in this manner are recorded in the accompanying statement. The gas after leaving the manganous chloride passed through a small wash-bottle filled with water, was dried by calcium chloride, and collected in the pipettes arranged in train, and analyzed by the method previously described.

Strength of hydrochloric acid.	Temperature of acid.	Temperature of the solution of $MnCl_2$.	Bubbles of gas passing the wash-bottle per second.	Per cent of chlorine.
Sp. gr. 1.1	83°	90°	5-6	87.5
" "	83	90	4-6	89.5
" "	70-80°	90	1-2	96.4
" "	87.5	90	3	98.6
" "	83	90	3	96.9

It is evident from these figures that the efficiency of the manganous chloride is considerable and naturally most manifest when the current of gas is slow. Indeed, during the passage of gas through the manganous salt small bubbles of chlorine are evolved from the entire surface of the liquid. The washed gas is pure enough for most laboratory purposes, but if chlorine perfectly free from chlorine oxide is desired it may be obtained by passing the washed gas through a hard glass tube filled with asbestos and heated by a Bunsen flame.

In the exceptional cases in which the ignition tube is used it is well to keep in mind the fact that in starting the generator the acid should not be thrown in too great quantity upon the chlorate at first lest an unusually large proportion of the dioxide be liberated, which may cause a slight explosion in the ignition tube. Should such be the case, however, the liquid in the wash-bottle will prevent the extension of the explosion to the gas in the generator proper, and the insertion of the wash-bottle should never be omitted when the ignition tube is to be put to use. So long as it is kept hot we have never found the apparatus other than perfectly manageable, safe, and automatic in action.

Inasmuch as a single gram of potassium chlorate produces approximately a half-liter of chlorine, and a cubic centimeter

* This Journal, xliv, 117; xlv, 231.

more than a liter, it is obvious that a very compact generator may be capable of delivering a considerable supply of the gas, and we have found the diminutive apparatus shown in the

accompanying figure an exceedingly convenient addition to the furnishings of the laboratory table when chlorine is needed frequently and in small amounts. This little generator is easily made of a side-neck test tube, funnel tube, stopper, glass stopcock, and flask. The upper chamber of the test tube, which is constricted near the middle, holds easily ten grams of the fused chlorate, and when the outer flask is filled with hot water the automatic action is satisfactory for a considerable length of time. A little wash-bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid is a desirable addition when a purer gas is needed

than that delivered directly from the generator, and the attachment of the ignition tube makes it possible to secure the chlorine entirely free from chlorine oxide, though carrying, of course, some free oxygen.