

[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE.]

THE PREPARATION OF IODIC ACID AND ITS ANHYDRIDE.¹

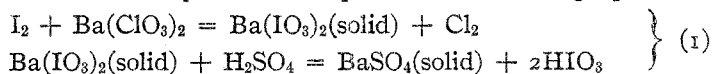
BY ARTHUR B. LAMB, WILLIAM C. BRAY AND WALTER J. GELDARD.

Received June 25, 1920.

In the work at the American University Experiment Station on the absorption of carbon monoxide,² pure, almost anhydrous iodine pentoxide was needed both in the analysis for carbon monoxide and in the preparation of one of its absorbents.³ Since an adequate supply of iodine pentoxide could not be secured, it was necessary to make in the laboratory most of our supply of this material. Moreover, since at one time the absorbent containing it appeared to be the best available one for carbon monoxide, it was necessary to have in readiness a satisfactory method for the preparation of iodine pentoxide on a large scale.

Considerable quantities of iodic acid were prepared by the usual method of oxidation of iodine with nitric acid. We soon discovered, both from our own experiments and from those carried on for us elsewhere, that while this material is perhaps suitable for the occasional preparation of small quantities in the laboratory, it is too difficult, wasteful and expensive for any larger operations. Two new methods based on well-known reactions were, therefore, worked out. Both of them start with iodine, the cheapest available source of the element, and barium chlorate, which is available in large quantities and is relatively inexpensive. In the first method the iodine is directly oxidized by an acidified solution of barium chlorate, and the resulting insoluble barium iodate is transformed into iodic acid by means of sulfuric acid. In the second method the reverse procedure is followed; a solution of pure chloric acid is prepared from barium chlorate and sulfuric acid, and the iodine is oxidized to iodic acid by means of it. The latter method proved to be particularly satisfactory, both on account of its simplicity, ease and adaptability to large scale operations, and also on account of the purity of its product. We shall first give a brief description of the barium chlorate method, and then a fuller description of the chloric acid method.

Barium Chlorate Method.—The two stages of preparation of iodic acid by the barium iodate process correspond to the following equations:



This method is evidently a simplification of the method of Millon⁴ who first oxidized iodine with an acidified solution of potassium chlorate, pre-

¹ Published by permission of the Director of Chemical Warfare Service and of the Director of the Bureau of Mines.

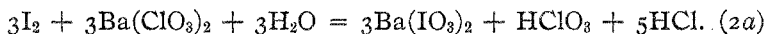
² Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920).

³ Lamb, Bray and Frazer, *loc. cit.*, p. 216.

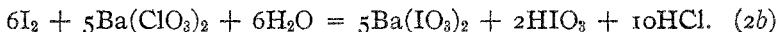
⁴ *Ann. chim. phys.*, [3] **9**, 400 (1840).

precipitated barium iodate with barium chloride, and following Gay Lussac, set free iodic acid by means of sulfuric acid.

While the first step in this process does take place substantially in accordance with the above equation, it appears certain that, as in the similar case of potassium chlorate, this equation does not represent the real mechanism of the reaction.¹ A neutral solution of barium chlorate does not react with iodine even when the mixture is heated, but the reaction can be made to take place quite rapidly at 85° if a small amount of nitric acid or hydrochloric acid is added. Moreover, after the reaction between equivalent amounts of iodine and barium chlorate (with nitric acid as inductor) the filtrate is found to contain a considerable quantity of hydrochloric acid. It is evident that in addition to Reaction 1 the following reaction takes place to some extent



In experiments in which slightly less than an equivalent amount of barium chlorate was used, the filtrate contained iodic acid in addition to hydrochloric, the corresponding reaction then being



These observations made only incidentally lead us to conclude that the real chemical reaction involved is the same as in the chloric acid process (see below); that is, namely, an *oxidation* of iodine by chloric acid or the chlorate ion in acid solution and not simply a replacement of the chlorine by the iodine. This is in agreement with the conclusions of Michael and Conn² who showed that the observations of Kaemmerer³ on which the idea of a direct replacement of one halogen by another had been based were wholly erroneous, and that all the other evidence indicated that the process was merely one of oxidation.

In each of our experiments a 250 g. portion of finely divided iodine was taken and this was usually treated with a nearly equivalent amount (320 g.) of the chlorate $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, in one liter. When a little acid was added to start the reaction, and the temperature was maintained at about 85° and the mixture shaken at intervals, the reaction proceeded steadily and all the iodine disappeared in about 90 minutes. In the second and later experiments of a series the barium chlorate was dissolved in the filtrate from the barium iodate precipitate; this procedure was adopted in order to prevent any loss of iodine by Reaction 2b, and because presence of acid in the filtrate rendered unnecessary the further addition of acid to start the reaction. In the last series of experiments the time of reaction was materially lessened by the use of a 50% excess of chlorate, 480 g. in

¹ See Bassett, *J. Chem. Soc.*, 57, 761 (1890); also Schloetter, *Z. anorg. Chem.*, 45, 270 (1905).

² *Am. Chem. J.*, 25, 89 (1901).

³ *J. prakt. Chem.*, 4, 169 (1870).

one liter, in the first experiment. As this excess remained in the filtrate, the usual amount, 320 g., was dissolved in the filtrate in the second and subsequent experiments of the series. An important advantage of the use of excess chlorate is that no iodine distilled into the neck of the flask during the run, as had been the case in the earlier experiments. A practically quantitative yield of barium iodate was secured in this way.

The second step in the process is not so satisfactory. The reaction between solid barium iodate and dil. sulfuric acid is slow and could not be made to take place in a reasonable time even when the solid was digested with an excess of the dil. sulfuric acid. This difficulty is perhaps in part due to the solubility of barium sulfate in iodic acid solution.¹ If an excess, or indeed if only an equivalent amount of sulfuric acid is used it is very difficult to remove the sulfuric acid with which the filtrate will be contaminated,² and the presence of even a small amount of sulfuric acid in the iodic acid promotes decomposition during dehydration.

The best method which we have found for purifying the iodic acid from this impurity is recrystallization from diluted nitric acid. A convenient quantity of iodic acid, *e. g.*, 300 g., is dissolved in an equal weight of hot water; an equal volume of conc. nitric acid, sp. gr. 1.42, is added, and the mixture is evaporated in a large evaporating dish without boiling for about 30 minutes, until crystallization is fairly complete, and then allowed to cool. The supernatant liquid is drained off and either evaporated further or added to a second solution of the iodic acid in water. The crystals of iodic acid are washed 3 times with ice-cold nitric acid, sp. gr. 1.42, then dissolved in a small volume of hot water and the solution evaporated to dryness. This yields a product practically free from sulfate and containing but a trace of nitric acid which can be removed if necessary by repeated solution and evaporation.

As a result of the incompleteness of this second step in the process and the losses incident to recrystallization, no more than 85 or 90% of the theoretical yield of iodic acid is usually obtained from a definite weight of iodine.

The Chloric Acid Method.—While it is known that iodine can be transformed into iodic acid by means of chloric acid,³ quantitative data seem to be lacking, and it was necessary for us to determine experimentally whether a simple, rapid and economical manufacturing process could be developed.

¹ Guichard, *Compt. rend.*, 147, 1306 (1909).

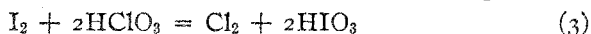
² This agrees with the observation of Stas, who concludes that pure iodic acid cannot be secured in this way, and with the statements of Baxter (*THIS JOURNAL*, 32, 1591 (1910)), who found that 11 crystallizations were necessary for the complete elimination of sulfate.

³ *E. g.*, Friend, "Text-book of Inorganic Chemistry," 8, 238 (1915).

We first assured ourselves that the preparation of pure chloric acid solution would present no difficulties. When to a hot barium chlorate solution (2 molal or less) an equivalent amount of hot sulfuric acid solution is added slowly, the barium sulfate settles quickly and is easily filtered, and a solution of chloric acid of any desired concentration up to 33% can be obtained. In practice a very slight excess of barium chlorate was used in order to ensure the absence of sulfate in the chloric acid solution, since as has already been mentioned, a sulfuric acid impurity in the resulting iodic acid is harmful. Small quantities of more concentrated solution were obtained by evaporation at low temperature (40°) and reduced pressure, and one sample of 40% chloric acid was prepared. The concentrations were determined by the Bunsen distillation method with conc. hydrochloric acid, the chlorine being passed into potassium iodide solution and the iodine formed titrated with thiosulfate.

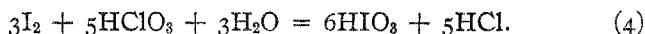
Small scale experiments were performed with chloric acid solutions of various concentrations to determine the most satisfactory conditions for the oxidation of iodine. 10% chloric acid does not react at room temperature, and after the reaction is started by heating it proceeds rather slowly, even when the mixture is heated nearly to boiling; with equivalent amounts of iodine and chloric acid considerable iodine vaporizes from the heated mixture. When very concentrated chloric acid (33 to 40%) is used the reaction starts practically immediately at room temperature, and proceeds with almost explosive violence; it is necessary to cool the container with ice-cold water during the reaction. 24 to 26% acid finally was chosen as the most suitable (though a somewhat more dilute acid, 20%, was also satisfactory). The reaction usually did not begin at once, but when once started (after standing 10 or 15 minutes, or by gentle heating) the iodine disappeared in 15 or 20 minutes; the reaction was very rapid but cooling was unnecessary. Iodine fumes were not given off during the reaction, nor when the resulting solution was boiled.

This behavior indicates an autocatalytic reaction. The beginning of the reaction appears to depend on the formation of a little chlorine, one of the products of the reaction. Suddenly the evolution of chlorine becomes rapid, the solution turns yellow and any iodine vapor in the flask is replaced by the heavy yellow fumes of iodine trichloride and chlorine. These indications that the mechanism of the reaction is not a simple replacement of the chlorine in the chloric acid by iodine according to the equation

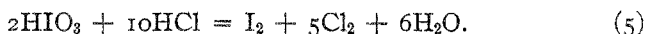


were corroborated by analyses of the final solution after it had been heated to boiling: large amounts of hydrochloric acid and some chloric acid were found, which were smaller as the concentration of the chloric acid used was increased. Since when the mixture was boiled some hydro-

chloric acid must have reacted with chloric or iodic acid, it is certain that much larger amounts of hydrochloric acid would have been found if the solution had been analyzed after the iodine had disappeared but before the mixture had been boiled. Evidently much of the chloric acid is reduced to chloride during the reaction (*cf.* Reaction 2b).



The presence of hydrochloric acid in the iodic acid solution seemed likely to prevent the development of a quantitative method, since it was known that iodic acid is reduced by hydrochloric when a solution containing the two substances is evaporated.¹



In fact the existing method for recovering iodic acid from such solutions involves the removal of the chloride by precipitation as silver chloride.² However, Reaction 5 is reversible and rapid; the reverse reaction is known to take place rapidly when sufficient water is present, and the direct reaction between iodic acid and hot conc. hydrochloric acid, although at first rapid, is by no means complete. This last point was demonstrated by experiments with the Bunsen distilling flask: about $\frac{1}{3}$ of the iodic acid remained unreduced after half of the conc. hydrochloric acid had been distilled out of the flask. We concluded that an equilibrium is established fairly rapidly between the substances listed in Equation 5 (and iodine trichloride), and that in the solution to be evaporated the iodic and hydrochloric acids are so dilute that the concentration of iodine is negligibly small. Furthermore, it seemed possible that the presence of chloric acid in the solution would maintain the iodine as iodic acid even while the solution was evaporated, and also remove the chloride as chlorine. This idea proved to be correct, and a 3% excess of chloric acid (based on Reaction 3) was found to be sufficient to prevent any loss of iodine. In fact, during evaporation the net reaction is simply



though it is possible that this reaction is catalyzed by the iodic acid present. In contrast to Reaction 5 which is rapid and reversible, Reaction 6 is slow and under the present conditions irreversible.

The experimental evidence was obtained by carefully investigating Reactions 3 and 4. Preliminary experiments with equivalent amounts of iodine and chloric acid (based on Reaction 3) had indicated a loss of from 2 to 10% iodine in the preparation of the iodic acid solution, but in these experiments the yield of iodic acid was determined by the possibly inaccurate method of precipitating and weighing barium iodate. Accordingly methods were developed for analyzing the iodic acid solution for

¹ Sodini, *Ber.*, **9**, 1126 (1876).

² Friend, *loc. cit.*, **8**, 237 (1915).

acid, iodate, chlorate and chloride; for determining the amount of iodine in the small precipitate of barium iodate formed (the chloric acid solution contained a trace of barium chlorate); and for determining iodine and chlorine in the gas evolved during the reaction. In the last case the gas was absorbed in excess alkaline sulfite solution, and the iodine and chlorine could be present only as iodide and chloride, respectively.

Analytical Methods.—The iodic acid solution and the alkaline sulfite solution were diluted to known volumes and portions of each taken for the various determinations. If any barium iodate precipitate formed during the run, or on cooling the resulting solution, it was collected on a filter before the solution was diluted.

Acid was determined with 0.1 *N* potassium hydroxide solution and phenolphthalein.

Iodate was determined iodimetrically. That the presence of chloric acid did not interfere when the concentrations of sulfuric acid and iodide were low was proved by test analyses with iodic acid alone and in the presence of an amount of chloric acid comparable to that in the solutions to be analyzed. The amount of barium iodate was determined by the same method; all of the precipitate was washed into an iodide solution acidified with hydrochloric acid, and an aliquot part of the resulting solution was titrated with thiosulfate.

Chlorate, in the absence of iodate, was determined by the Bunsen distillation method already referred to. The iodate in the portion of the solution to be analyzed for chlorate, was precipitated as barium iodate; the precipitation was found to be practically complete only when the solution was neutral and nearly ice-cold. Barium chloride was used as the precipitating agent, since nitrate would interfere with the chlorate analysis.

Chloride, in the absence of iodate, was determined by the Volhard method. The method of removing iodate was the same as that described in the preceding paragraph, except that barium nitrate was used instead of barium chloride. Chloride in the alkaline sulfite solution was also determined by the Volhard method after the removal of sulfite and iodide (see below) by means of potassium permanganate; any excess of permanganate added was removed by the addition of a small amount of a dilute solution of sulfurous acid.

Iodide in the sulfite solution was tested for by the permanganate-carbon tetrachloride method recommended by Bray and MacKay.¹ Test analyses showed that the method was applicable in the presence of sulfite.

Experiments with 24-Gram Portions of Iodine.—Several experiments were performed with 24 g. of iodine and 28.5 to 34% chloric acid in small excess, which was 5 to 10% excess referred to Reaction 3. After the iodine had disappeared the solution was heated to boiling for several

¹ Bray and MacKay, *THIS JOURNAL*, 32, 1193 (1910).

minutes and a slow current of air passed through it to carry the chlorine over into the alkaline sulfite solution contained in 2 wash bottles arranged in series. Complete absorption of the chlorine was demonstrated by the fact that a potassium iodide solution beyond the sulfite solution remained colorless. The results in the various experiments were concordant, and details will be given for only one run.

Reacting substances:	Iodine 24.24 g. 99%	= 0.1891 gram atoms
	Chloric acid 61.7 cc. (28.5%)	
	By analysis	= 0.2080 mol chlorate
		and 0.2011 equivalent acid
		Gram atoms

Total Iodine recovered:	As HIO_3 in solution	0.1830
	In barium iodate \downarrow	0.0064
	In sulfite solution	0.0000
		<hr/>
		0.1894
		= 100.2%

Total Chlorine recovered:	As HClO_3 in solution	0.0225
	As HCl in solution	0.0437 (?)
	In sulfite solution	0.1491
		<hr/>
		0.2153
		= 102.2%

Total acid in Iodic acid solution:	0.2371 equivalent
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Increase in acid during the run = 0.2371 — 0.2011 = 0.0360 equivalent.

Since, by Equation 4, 5 mols HCl are formed when the increase in acid is 6 equivalents, the calculated amount of HCl is 0.0300 equivalent.

The striking result of this and other runs is that all the iodine used was converted into iodic acid in solution, and none was carried over with the chlorine into the alkaline sulfite solution.

In the above experiment there was evidently an error in the determination of the amount of hydrochloric acid in the iodic acid solution, since in another run the amount of hydrochloric acid calculated by means of Equation 4 agreed fairly well with that found by direct analysis.¹ This point was not more carefully investigated because the real purpose of the experiments had been attained, *viz.*, the demonstration of the quantitative yield of iodic acid in solution.

The next question investigated was the recovery of iodic acid by evaporation in the presence of the small excess of chloric acid. In each of the following experiments 0.2 of the iodic acid solution obtained in the above run was evaporated to dryness; in the first case the residue was heated for a short time at 100°, in the second case for one hour in a flask in a Crisco bath at 210°. In each case no iodine fumes were evolved, and the residue was pure white in color.

¹ This was also shown by the fact that the sum of the separately determined acids exceeded the observed value by 0.0121 equivalent.

	HIO ₃ .	HClO ₃ .	HCl.	
Original solution (one-fifth) contained.....	0.0366	0.0045	0.0060 (?)	mols
Residue from the 1st evaporation expt. contained.....	0.0371	0.0008	0.0026	mols
Residue from the 2nd evaporation expt. contained.....	0.0368	0.00014	0.0000	mols

These results and others which are not quoted demonstrated conclusively that there is no loss of iodic acid on evaporation, that much of the hydrochloric and chloric acids are removed by evaporation and heating at 100°, and that all the former is destroyed by heating at 210°. Subsequent experiments showed that the removal of the chloric acid is complete during the dehydration process at 240°, which will be described below.

Experiments with 500-Gram Portions of Iodine.—Having thus demonstrated that the process was most satisfactory, we proceeded to manufacture iodic acid in the laboratory. 500 g. portions were found to be convenient and several runs were made simultaneously. In connection with the first runs the minimum excess of chloric acid necessary was found to be about 3% (based on Equation 3). It was not necessary, although more convenient, to add this excess at the beginning of the experiment, since the danger of loss of iodine was greater during the evaporation than during the oxidation of the iodine. When less than the 3% excess chloric acid was added the dark color of free iodine appeared during the evaporation or heating; but loss of iodine could then be prevented by adding at once a small amount of chloric acid. The concentration of chloric acid finally chosen was 24 to 26%.

39 runs of this sort were made, and the total yield of powdered iodic anhydride obtained, based on its weight and the weight of iodine used, was 99.6%.

The procedures used are outlined below.

Preparation of Chloric Acid.—The preparation was carried out in large earthenware crocks, and the quantities of materials used depended on the size of the crocks. The proportions were as follows. 625 g. of barium chlorate (90% Ba(ClO₃)₂) was dissolved in one liter of nearly boiling water and poured into the crock; the barium sulfate was precipitated by slowly adding, with stirring, the required quantity of hot sulfuric acid solution. The latter solution was prepared by adding 200 g. of H₂SO₄, sp. gr. 1.84, to 109 g. water, these quantities corresponding to equal parts by volume. It is necessary to have a very small excess of barium chlorate rather than of sulfuric acid, and the chloric acid solution should be tested for sulfate and for barium until the procedure is standardized. The mixture was allowed to stand until the barium sulfate settled out, which required at least one hour. About 2/3 of the chloric acid solution could then be removed by decantation or by a siphon, but filtration of this

solution was sometimes necessary. Nearly all of the remaining acid was separated from the precipitate by filtration through a Büchner funnel with suction. The barium sulfate can be washed and saved if desired.

The acid solution was stored in glass-stoppered bottles. It was practically colorless and did not change appreciably in concentration in several weeks, even when exposed to the diffused light of the laboratory. Acid kept in an unstoppered bottle in the hot laboratory increased in concentration due to the loss of water by evaporation. Each sample of acid was analyzed for chlorate.

Oxidation of the Iodine.—500 g. of commercial "resublimed" iodine was weighed into a 3-liter glass flask, and to this was added an amount of chloric acid 3% in excess of the theoretical amount (one mol of chlorate per gram atom of iodine). The flask was connected with an absorption train of 3 wash bottles partly filled with a cold 20% solution of sodium hydroxide (or with milk of lime if bleaching powder was desired instead of sodium hypochlorite solution; the latter was used in another process in our laboratory). A slow current of air was passed through the apparatus after the reaction started. If the mixture was heated to start the reaction and again when only a small amount of iodine remained, a run could be completed in 20 minutes. When the initial heating was omitted the reaction started within 10 or 15 minutes.

The solution was then cooled, filtered to remove barium iodate or any foreign matter, transferred to a large evaporating dish, and evaporated just to dryness with frequent stirring. If during the evaporation a yellow-brown color appeared, a small amount of chloric acid was at once added. The material was heated in a hot-air oven at a temperature of 150–160° for 3 hours, and then removed from the evaporating dish for more complete dehydration.

Dehydration of Iodic Acid.—In the dehydration process finally adopted the coarsely powdered dry material was loosely packed in glass tubes 30 mm. in diameter and closed at one end. The column of iodic acid was held in position by glass wool at each end. A thermometer was imbedded in the iodic acid to show the actual temperature of the material. Near the bottom of each tube a small tube was inserted, through which a slow current of dry air could be drawn; the air was thus preheated by passing through the length of the oven before reaching the iodic acid. The air was dried by passing through a train which consisted of a sulfuric acid bead-tower and a U-tube containing phosphorus pentoxide and soda lime. The rate of flow was regulated by observation of the bubbling through the acid tower.

One or more tubes were placed in a horizontal position in a well insulated horizontal oven which was uniformly heated by a number of gas flames. A constant temperature of 235–240° was maintained for at least 3 hours,

during which time the slow current of dry air was drawn through the material.

When material prepared by the chloric-acid process was dehydrated in this way the product was of a uniform white or faintly pink color, and contained not more than 0.2 or 0.3% water (see below). The intensity of the color as it varies from pink to violet is an indication of the amount of decomposition during dehydration, due to local overheating or to the presence of impurities. It was found that pure iodic anhydride may be heated to 250° without the slightest liberation of iodine.

The dehydrated material was ground in a ball mill to pass an 80-mesh screen. During this process it absorbed a small amount of water vapor from the air, and the final product contained 0.5 to 0.6% of water vapor. As this material is hygroscopic it was stored in sealed containers.

Iodic acid prepared by the nitric acid method was not easily dehydrated without decomposition. A temperature of 200° could not be exceeded, at least in the first hour or two, and the dehydration was correspondingly less complete in a 3-hour treatment. Iodic acid contaminated with sulfuric acid decomposed even more readily during dehydration. The chloric acid process thus has a marked advantage over the other processes in this respect.

In agreement with the greater stability of iodic acid and iodic anhydride prepared in this way is our observation that it does not decompose when in the course of the analysis for carbon monoxide it is heated with pure air. Iodic anhydride, as usually prepared, when heated hot enough to react satisfactorily with carbon monoxide, invariably gives a positive blank, for which a correction must be applied even with the purest air. This difficulty, which is the limiting factor in the precise analysis of small concentrations of carbon monoxide, can be eliminated by using iodic anhydride prepared in the above way.

Analysis of Iodine Pentoxide, Water Content.—The water content of the iodine pentoxide samples was determined by a method devised by Baxter¹ depending on its decomposition by heat into iodine, oxygen and water vapor, the removal of the iodine by means of metallic silver and the absorption and weighing of the water.

The silver used was prepared by placing copper wire spirals in silver nitrate solution. The precipitated silver was washed thoroughly and finally heated to constant weight at a temperature of 350–400°. As this heating had a tendency to clump the silver, it was broken up and made to pass through a 16-mesh screen before use.

One half of an 80 cm. hard, glass combustion tube, 2 cm. in diameter, was packed with alternate layers of the silver and glass wool. This method of packing was adopted to prevent the formation of lumps of silver iodide

¹ THIS JOURNAL, 31, 210 (1909).

during the analysis. By means of a suction pump, air, dried in a train consisting of sulfuric acid, soda lime and phosphorus pentoxide, was drawn through the apparatus and then through an absorption tube which could be conveniently weighed. Between this tube and the pump a phosphorus pentoxide tube was inserted to prevent access of water vapor through the pump. A convenient form of absorption tube was a U-tube half filled with pumice or glass beads moistened with sulfuric acid, and containing enough acid just to seal the bend.

The combustion tube containing the silver was strongly heated and the current of dry air was passed until the absorption tube was constant in weight. A weighed amount of the iodine pentoxide to be analyzed, in a porcelain boat, was introduced into the combustion tube in front of the silver packing, and this portion of the tube was carefully heated until the pentoxide was completely decomposed. The current of air brought the iodine into contact with the heated silver and swept the water vapor into the absorption tube.

The accuracy of the method is demonstrated by the duplicate analyses of the samples in the following list, marked (a) and (b).

1. Nitric acid process, one 3-hour dehydration at 200°.
(a) 1.10% H₂O, corresponding to 21.6% hydration.¹
(b) 1.13% H₂O, corresponding to 22.1% hydration.
2. General Chemical Company, as received.
(a) 1.84% H₂O, corresponding to 35.9% hydration.
(b) 1.83% H₂O, corresponding to 36.0% hydration.
3. Chloric acid process, one dehydration at 240°.
0.31% H₂O, corresponding to 6.0% hydration.
4. Ditto, after grinding.
0.53% H₂O, corresponding to 10.7% hydration.

Many other samples were analyzed, but the above results are representative. It is to be noted that iodine pentoxide as ordinarily prepared is far from being completely dehydrated.

Other Analyses and Tests were made in examining the various samples of iodine pentoxide. The iodine pentoxide content was determined iodimetrically: one mol of iodine pentoxide liberates 12 gram atoms of iodine. The free iodine content could have been determined by adding a weighed amount of the sample to water, extracting the iodine with carbon tetrachloride, and adding the latter to a potassium iodide solution for titration with thiosulfate; but this analysis was not necessary since the amount of iodine obtainable from a pink sample was negligible. The non-volatile matter was determined after ignition; it did not exceed 0.1%, which proved the absence of appreciable amounts of barium iodate. The test for sulfate was made after precipitation of silver iodate by the addition of silver nitrate solution in excess. Nitrate was tested for by

¹ The water is assumed to be present as HIO₃.

the method recommended by A. A. Noyes,¹ which depends on the removal of the iodate by means of silver sulfate, and distillation of the filtrate with sulfuric acid and ferrous sulfate.

Summary.

1. A simple and rapid method has been developed for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24-26% chloric acid solution, the evaporation of the solution, and the dehydration of the iodic acid. The product is pure white, analyzes practically 100% oxidizing value, and contains no detectable impurities except traces of water and barium iodate. It is decidedly more stable towards heat than is iodic anhydride as ordinarily prepared, and, therefore, possesses decided advantages for use in the analysis for small quantities of carbon monoxide in air. The yield of pentoxide from iodine is almost theoretical.

2. In the preparation a small excess (3%) of chloric acid is intentionally used; this ensures the complete removal of the hydrochloric acid formed during the oxidation process, which otherwise would reduce the iodic acid during the evaporation.

3. When this small excess of chloric acid is used the net result of the oxidation reaction is expressed by the equation



The mechanism of this reaction undoubtedly does not correspond to a direct replacement of the chlorine by the iodine. The second product of the reaction, chlorine gas, can be conveniently recovered as sodium hypochlorite solution or bleaching powder.

4. The chloric acid solution is made by the direct action of sulfuric acid on barium chlorate solution. There is no decomposition of the chloric acid, and the only loss is the small amount of solution absorbed by the barium sulfate. The by-product, barium sulfate, can be recovered if desired.

5. The various analytical methods needed in this investigation were carefully tested. Several of them, though not absolutely new, have previously received little attention.

6. The chloric acid method, when tried on a semi-manufacturing scale presented no difficulties.

7. Two other methods for the preparation of iodine pentoxide were used in the laboratory but gave less satisfactory results. One of these was the conventional nitric acid method, and the other involved the preparation of barium iodate and the treatment of this difficultly soluble substance with sulfuric acid.

In conclusion we wish to acknowledge our indebtedness to the following

¹ A. A. Noyes, "Qualitative Analysis," 1914, p. 113.

members of the Chemical Warfare Service for their assistance in the experimental work: A. W. Kenney, C. L. Dougherty, W. M. Craig and D. O. E. Peterson.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

CONDUCTIVITY AND FREQUENCY.

By E. D. EASTMAN.

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There is reason to suppose that the general form of the conductivity-frequency curve for solutions of electrolytes may correspond in type to that shown in Fig. 1. The features of this general curve are the rise, from *A* to *B*, to a maximum of conductivity as the frequency is increased from zero, and the subsequent decrease, from *B* to *C*, and asymptotic approach to zero conductivity at infinite frequency. The necessity of the approach to zero as the frequency is indefinitely increased is obvious, and the por-

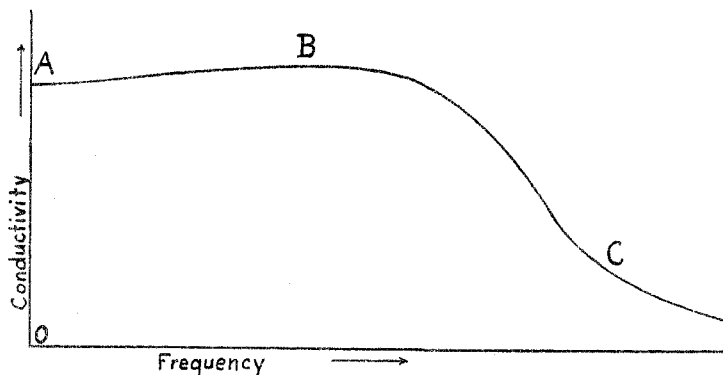


Fig. 1.—Theoretical form of conductivity-frequency curve.

tion of the curve from *B* to *C* requires little comment other than to point out the possibility that certain resonance effects may make the curve less simple in this region than the one here shown, and that the decrease in conductivity undoubtedly begins only at frequencies far higher than those ordinarily used in conductivity measurements. It is in the portion *AB* of the curve that the interest of the present paper centers, and the basis of the assumption of increase in conductivity in this portion of the curve may be briefly discussed.

If current theories are correct there are present in solutions of electrolytes numerous electric dipoles, or multipoles, consisting of molecules or ions of solute in various stages of dissociation and solvation. Under the influence of an alternating electric field these polar molecules should all be more or less free to take part in oscillatory rotation about their centers,