ART. VI.—*On the Iodometric Determination of the Nitrates*;
by HIPPOLYTE GRUENER.

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

DE KONINCK and Nihoul* describe a method for the iodometric determination of nitrates, in which the decomposition of the nitrates is effected by the action of gaseous hydrochloric acid, the gases evolved being passed into potassium iodide; but the method is a cumbersome one. In a former paper† by Professor Gooch and myself a method was described according to which nitrates were decomposed successfully and easily by a solution of manganous chloride in hydrochloric acid, the products of decomposition being passed into potassium iodide, and the liberated iodine titrated with sodium thiosulphate. The ease with which hydriodic acid has been applied in this laboratory as a reducing agent in the determination of arsenic, chloric and antimonie acids‡ has suggested its application for the same end to nitric acid, and the present paper is the account of attempts in this direction.

The Action of Phosphoric Acid and Potassium Iodide upon Nitrates.—The decomposition of the last traces of nitrates in presence of potassium iodide and sulphuric acid does not occur except at very great concentrations, and, as at great concentrations sulphuric acid in presence of hydriodic acid itself liberates iodine, the use of sirupy phosphoric acid to bring about the required decomposition naturally suggested itself. Various attempts to simplify the process while still registering

* Zeitschr. f. angewandte Chemie, 1890, p. 477.

† This Journal, vol. xlv, p. 117.

‡ This Journal, vol. xl, p. 66; vol. xlii, p. 220; vol. xlii, p. 213.

the amount of reduction by arsenic acid in the residue proved futile, and a distilling apparatus was found to be necessary. For this purpose a small retort was used, the neck of which was bent downward about two inches from the body, so that the retort itself might be tipped backward, allowing the unbent portion of the retort to run upward, thus guarding against loss from spattering. Into the tubulature of the retort was ground a glass tube drawn out at both ends to serve as a perforated stopper for the entrance of carbon dioxide. The neck was passed through a rubber stopper into a side-neck Erlenmeyer flask, the exit tube of which was prolonged and dropped into a side neck test tube used as a trap. The retort was covered with a simply contrived hood which kept the upper parts warm and prevented the iodine from settling anywhere. In the retort was placed the nitrate with an excess of potassium iodide, and in the receiver a known amount of decinormal solution of arsenious oxide strongly alkaline with hydrogen sodium carbonate and diluted to a convenient bulk. The trap contained nothing but water. The phosphoric acid used was at first 10 cm³ of strong acid, specific gravity 1.7, with varying amounts of water, but when it was found that the amount of water present was an essential feature, a definite mixture was used as designated in the tables. The acid was added to the retort last of all and after carbon dioxide had been passed for a sufficient length of time heat was applied. The carbon dioxide was evolved in a Bonn generator from materials which had been carefully boiled, and cuprous chloride was added to the acid in the generator to take up the oxygen from any traces of air. Between the introduction of phosphoric acid into the retort and the application of heat a good stream of gas was passed for ten minutes, at the end of which time the bubbles escaping at the last trap were completely absorbed in potassium hydrate of the requisite strength.

The first experiments were in blank with no nitrate present. Upon warming the mixture of phosphoric acid and 2 grm. of the iodide signs of free iodine were developed, and by titration of the contents of the receiver at the end, iodine to the amount of .0014 grm. was found to have been liberated, either by residual traces of air or by dissociation. The experiment was repeated, but in this case all the water used had been boiled immediately before the experiment and here iodine to the extent of .0009 grm. only was found to have been liberated. The cause and remedy for this liberation of iodine are discussed presently. A series of experiments was performed to study the action of the reagents when nitrates were present.

The method of procedure was as follows: The nitrate was taken for convenience from a solution of 5 grams in 500 cm³

of water. The iodide was introduced dry or in solution according to the bulk of water allowable. This mixture was boiled a moment to drive out all air, the phosphoric acid was then added, and carbon dioxide was passed as described, the receiver containing the arsenious oxide and the trap being already in position. It had been found that all but a trace of iodine was caught in the first receiver, so that the rubber stopper closing it could do no harm. When large amounts of nitrate were used the clots of solid iodine settling out in the receiver were dissolved by means of a crystal or two of potassium iodide. The solution in the retort was boiled until it was clear that all the iodine had distilled over, and usually until the boiling in the retort had ceased. It was found advisable to empty the retort so soon as it was cool enough, else the phosphoric acid became unmanageable. The retort after each experiment was washed out with ammonia and water.

The results of these first experiments are shown in Table I.

TABLE I.

Series 1.	KNO ₃ taken.	KI taken.	Water added to 10 cm ³ of phos- phoric acid, sp. gr. 1.7.	KNO ₃ found.	Error in KNO ₃ .	Error in HNO ₃ .
	gram.	gram.	cm ³ .	gram.	gram.	gram.
1	0.0005	.2	2	0.0009	0.0004 +	0.0002 +
2	0.0010	.2	2	0.0012	0.0002 +	0.0001 +
3	0.0020	.2	2	0.0021	0.0001 +	0.0001 +
4	0.0050	.2	2	0.0055	0.0005 +	0.0003 +
5	0.0100	.2	2	0.0093	0.0007 —	0.0004 —
6	0.0100	.2	2	0.0103	0.0003 +	0.0002 +
7	0.0200	.3	3	0.0216	0.0016 +	0.0010 +
8	0.0200	.3	3	0.0192	0.0008 —	0.0005 —
9	0.0200	.3	3	0.0205	0.0005 +	0.0003 +
10	0.0200	.3	3	0.0205	0.0005 +	0.0003 +
11	0.0500	.5	6	0.0496	0.0004 —	0.0002 —
12	0.0500	.5	6	0.0499	0.0001 —	0.0001 —
13	0.0300	.5	4	0.0293	0.0007 —	0.0004 —
Series 2.						
14	0.0616	1.5	1	0.0682	0.0066 +	0.0039 +
15	0.0570	2.5	1	0.0643	0.0073 +	0.0045 +
16	0.1030	1.1	1	0.1061	0.0031 +	0.0018 +
17	0.1062	1.1	1	0.1197	0.0135 +	0.0081 +

With one or two exceptions the results of Series 1 are fairly good. Those of Series 2 are very bad. The only essential difference between the two series is in the dilution of the phosphoric acid used. In the first series there is always enough water present to make the specific gravity of the phosphoric acid no higher than 1.6 for small amounts of iodide and nitrate, and lower than that number when these amounts are increased. The suggestion is obvious that dissociation of

the hydriodic acid may occur at the boiling point of the stronger acid. According to Berthelot* aqueous solutions of hydriodic acid under pressure begin to dissociate at 275° or even under. The temperature of the retort at the end of an experiment was taken and found to be far beyond the range of a thermometer reading to 360°. It is evident, then, that under the conditions there should be opportunity for dissociation. Four experiments in which potassium iodide was treated with phosphoric acid, specific gravity 1·7, undiluted, gave of liberated iodine caught in arsenious acid ·0030 grm. ·0044 grm. ·0049 grm. ·0030 grm. of iodine, corresponding to ·0008 grm. ·0012 grm., ·0013 grm., ·0008 grm. of potassium nitrate respectively. These results would account only in part for the errors noted but, they are in the same direction. Chapman† has found that concentrated hydriodic acid acting upon organic nitrates and nitrites reduces them not alone to nitric oxide but even in part to ammonia. The conditions of the experiments in Series 2 approximate to concentration of the hydriodic acid, and the reaction that Chapman found probably takes place here to a limited extent. Concentration of the hydriodic acid then must be avoided, both to eliminate dissociation and excessive reduction of the nitrate.

Therefore the plan was adopted of diluting the solution, so that the temperature and concentration should be effective in decomposing the nitrate, but should not bring about the complications just mentioned. A blank experiment made thus, 18 cm³ of a solution of phosphoric acid of specific gravity 1·39, being used, gave of liberated iodine only ·0004 grm. corresponding to ·0001 grm. of potassium nitrate. So that under these conditions we may be assured that dissociation occurs if at all to only a slight extent. In the following experiments, therefore, the nitrate is decomposed in presence of dilute phosphoric acid, the dilution and the quantity taken being included in Table II.

The iodine of 41 was collected in potassium iodide and titrated with thiosulphate. Series 3 requires little special comment. The experiments ran along smoothly, the manipulation was easy, the care required in watching very little and the results are fairly satisfactory. The causes leading to the high results of Series 2 seem entirely eliminated by the dilution. Series 4 is a direct continuation of Series 3, differing in the single point that larger amounts of nitrate are handled. These results with some exceptions are decidedly low. It appears that with a fair percentage of water present, as the amounts of nitrate grew larger, the error became a negative one. The explanation for this seemed to be that the last portions of nitric acid must have

* *Ann. de Chim. et Phys.*, (IV), xx, p. 392.

† *Journ. of the Chem. Soc.*, vol. xx, 1867, p. 166.

distilled before decomposition, whenever the original amount was large. Nitric acid was accordingly tested for in the distillate, and to this end all the conditions of the experiment were repeated, except that the receiver contained only water. Of the nitrate 0.4 gram. and of the iodide 4 gram., twice the amount theoretically necessary were put into the retort, and at the end of the experiment the solution in the receiver was boiled with hydrogen peroxide to decompose the hydriodic acid and drive out the iodine, care being taken to keep enough water to hold any nitric acid present. When all the iodine was gone sodium carbonate was added, the solution evaporated and the residue ignited and tested with a saturated solution of manganous chloride in hydrochloric acid, as described in the previous paper above mentioned. By this means 0.0002 gram. potassium nitrate are very easily detected in 10 cm³ of solution. Nitric acid was found in the distillate of this experiment as well as in two others conducted with 0.2 gram. and 0.1 gram. of the nitrate respectively. The residues in the retorts of these three tests showed no trace of nitric acid.

TABLE II.

	KNO ₃ taken.	KI taken.	Found.	Sp. Gr. of solution of phosphoric acid.	Amount of sol. used.	Error KNO ₃	Error HNO ₃
Series 3.	gram.	gram.	gram.			gram.	gram.
18	0.0500	1.	0.0500	1.43	17cm ³	0.0000	0.0000
19	0.0200	0.5	0.0201	1.43	17	0.0001 +	0.0001 +
20	0.0200	1.	0.0198	1.43	17	0.0002 -	0.0001 -
21	0.0250	1.	0.0250	1.43	17	0.0000	0.0000
22	0.0300	1.	0.0307	1.43	17	0.0007 +	0.0004 +
23	0.0300	1.	0.0312	1.43	17	0.0012 +	0.0007 +
24	0.0350	1.	0.0353	1.43	17	0.0003 +	0.0002 +
25	0.0400	1.	0.0409	1.35	20	0.0009 +	0.0006 +
26	0.0450	1.	0.0444	1.35	20	0.0006 -	0.0004 -
27	0.0500	1.	0.0499	1.37	20	0.0001 -	0.0001 -
Series 4.							
28	0.0600	1.	0.0568	1.37	20	0.0032 -	
29	0.0600	1.	0.0575	1.37	20	0.0025 -	
30	0.0600	1.	0.0576	1.37	20	0.0024 -	
31	0.0600	2.	0.0588	1.37	20	0.0012 -	
32	0.0600	2.	0.0605	1.37	18	0.0005 +	
33	0.0700	2.	0.0708	1.37	18	0.0008 +	
34	0.0800	2.	0.0811	1.37	18	0.0011 +	
35	0.0900	2.	0.0842	1.37	18	0.0058 -	
36	0.1000	2.	0.0996	1.37	18	0.0004 -	
37	0.1000	2.	0.1012	1.37	18	0.0012 +	
38	0.1000	1.5	0.0909	1.37	18	0.0091 -	
39	0.1000	2.5	0.0979	1.37	18	0.0021 -	
40	0.1021	3.	0.1005	1.43	17	0.0016 -	
41	0.1032	2.	0.0949	1.43	17	0.0085 -	

The process seems reliable enough, then, for estimating nitrates in small quantities not exceeding an equivalent of 0.04 gm. or 0.05 gm. of potassium nitrate. Every experiment performed with quantities not larger than 0.05 gm. has been given here, except four in which an imperfection in the apparatus showed an obvious mechanical loss. The errors in these experiments lie between the extremes of 0.0016 gm. + and 0.0008 gm. — on the nitrate, with an average error of 0.00016 gm. If series 3 alone is taken, in which the dilution of the phosphoric acid was regulated, we have as extreme errors 0.0012 gm. + and 0.0006 gm. — with a mean error of 0.0002 gm. +. With quantities of nitrate above 0.05 gm. the process does not seem a safe one, inasmuch as with a moderate amount of water present some nitric acid distills over undecomposed, and with little water present other complications as seen above arise.

The method so far as it is applicable may be summed up as follows. The nitrate not to exceed in amount 0.05 gm. of potassium nitrate, is introduced into a retort, together with ten times its weight of potassium iodide, and 17 to 20 cm³ of phosphoric acid, of specific gravity 1.43. All water used should be recently boiled. Carbon dioxide is passed from a receiver carefully set up. The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, alkaline with a good excess of hydrogen sodium carbonate and diluted to a convenient bulk. To this flask is attached for additional safety a simple trap containing water. The solution in the retort is boiled until it is clear that no more iodine remains, when the receiver, after proper washing and addition of the liquid in the trap, is titrated with iodine to find the amount of arsenious oxide still left. This gives the measure of the iodine evolved and consequently of the nitrate present, according to the equation

The Decomposition of Nitrates by Antimonious Chloride.

—The failure mentioned above, in attempting to use arsenious oxide to register the action of nitric acid, led to the trial of antimonious chloride as a substitute, inasmuch as this substance is easily oxidizable and less volatile than arsenious chloride in presence of hydrochloric acid. This latter fact is of great importance in the decomposition of a nitrate. The point to be tested was whether the complete decomposition of nitrates by the action of antimonious chloride in hydrochloric acid solution, and the absorption of the nascent oxygen to form antimonious chloride would be secured, so that the antimonious chloride left at the end as compared with the amount taken should give the measure of the nitrate used, according to the equation:

Antimony chloride was dissolved in strong hydrochloric acid, and the solution standardized by diluting convenient portions, adding tartaric acid, nearly neutralizing with 25 per cent solution of sodium hydrate, treating with excess of hydrogen sodium carbonate and titrating with decinormal solution of iodine in presence of starch, the blue color being taken as the end reaction.

Known portions of this solution boiled with potassium nitrate for a considerable length of time, then diluted, neutralized and titrated (all a simple quick process), showed oxidation to the extent of about 90 per cent of the nitrate present. The evidence pointed to the conclusion that the nitrate was broken up, but that the residue failed to register the amount of decomposition. The products of decomposition when passed in a current of carbon dioxide into potassium iodide set free iodine, but had no oxidizing effect upon an alkaline solution of arsenious oxide. The conclusion was drawn that nitrosyl chloride was probably given off, which breaking up on contact with water into hydrochloric and nitrous acids exerts no effect upon arsenious oxide in alkaline solution. To see if the nitrosyl chloride was set free in exact measure of the nitric acid lost the following experiments were made.

Into a diminutive retort—made from a pipette shaped like a Liebig's drier and connected by a sliding joint covered by rubber into a Kjeldahl tube used as a receiver, and so placed that carbon dioxide passing through the apparatus should enter from below—lifting the air before it—was introduced the nitrate, dry, washed down with a few drops of recently boiled water, or, if more liquid was required, with hydrochloric acid lest the liquid become too dilute. From a burette a definite amount of antimonious chloride solution, somewhat in excess of the nitrate taken, was introduced. The receiver was charged with 0.25 grm. potassium iodide diluted with recently boiled water and was joined to a trap filled with water. After carbon dioxide was passed through the apparatus for about ten minutes, the solution was warmed on a high boiling bath (103°–107°) to ensure the safety of the retort, to keep the antimony pentachloride from breaking up, to retain the bulk of the acid in the retort and to prevent mechanical loss. This method of procedure was found entirely satisfactory. After fifteen minutes digestion the receiver and trap were washed out and at once titrated with sodium thiosulphate. The residue in the retort was treated exactly as was the antimonious chloride when it was standardized. The solution here must be kept dilute, lest at the great heat caused by neutralizing strong

solutions there be action upon the pentachloride on the part of the small amount of tartaric acid now present. The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidized by the nitrate, and by difference we have the measure of the nitrate present. The results are given in series I and II. In experiments (1) to (8) the receivers were washed with ordinary distilled water; after that with water recently boiled.

SERIES I.

	KNO ₃ taken. gram.	KNO ₃ correspond- ing to I found in receiver. gram.	Entire KNO ₃ found. gram.	Error in KNO ₃ . gram.	Error in HNO ₃ . gram.
1	0·0222	0·0020	0·0233	0·0011 +	0·0007 +
2	0·0336	00·026	0·0333	0·0003 —	0·0002 —
3	0·0470	0·0045	0·0471	0·0001 +	0·0001 +
4	0·0553	0·0057	0·0554	0·0001 +	0·0001 +
5	0·0664	0·0076	0·0679	0·0015 +	0·0009 +
6	0·0759	0·0082	0·0752	0·0007 —	0·0004 —
7	0·0837	0·0103	0·0841	0·0004 +	0·0002 +
8	0·0934	0·0113	0·0955	0·0021 +	0·0013 +
9	0·1034	0·0134	0·1036	0·0002 +	0·0001 +
10	0·0262	0·0024	0·0259	0·0003 —	0·0002 —
11	0·0127	0·0007	0·0130	0·0003 +	0·0002 +
12	0·0065	0·0003	0·0067	0·0002 +	0·0001 +
13	0·0026	0·0001	0·0023	0·0003 —	0·0002 —
14	0·1232	0·0098	0·1227	0·0005 —	0·0003 —
15	0·1540	0·0146	0·1540	0·0000	0·0000
16	0·1878	0·0210	0·1865	0·0013 —	0·0008 —

Three more experiments were performed to see if the titration of the iodine set free in the receiver could be accomplished as well in alkaline solution by means of arsenious oxide. For this purpose the solutions from the receivers were poured into a strong solution of sodium bicarbonate, care being taken to prevent loss during effervescence.

SERIES II.

17	0·0530	0·0052	0·0533	0·0003 +	0·0002 +
18	0·0547	0·0065	0·0549	0·0002 +	0·0001 +
19	0·0541	0·0063	0·0537	0·0004 —	0·0002 —

The results run from extremes of ·0021 gram. + to ·0013 gram. — with a mean error of ·00016 gram. +, which tends to emphasize the well known fact that it is impossible to remove every trace of air from reagents and generator. The operation is quick, taking in all three-quarters of an hour and requiring very little watching. The experiments given are all that were performed with the apparatus as described, it not having been found necessary to reject a single determination for mechanical mischances.

Neither of the processes described presents in general advantages equal to those of the manganous chloride method to which reference has been made, but under special conditions they may be found useful.

In concluding I would express my thanks to Professor Gooch for valuable advice and assistance given during the course of the investigation.