PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXI.—*On a Method of Estimating Nitric, Chloric, and Iodic Acids.*

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1. OF the many processes which have been proposed for the estimation of nitric acid, those which depend upon its conversion into ammonia by nascent hydrogen, are on the whole the least liable to objection in point of principle. The means which we already possess of determining ammonia, whether in large or in small quantities, are expeditious and accurate. Starting from this principle, Schulze appears to have been the first to devise a method of estimating nitric acid capable of affording accurate results. The subsequent processes of Harcourt, of Siewert, and of Chapman, based upon the influence exerted by nascent hydrogen generated by the action of a strong solution of potash upon mixtures of iron and zinc or upon aluminium alone, are well known and are often used.

2. The principle of the method which forms the subject of the present communication, is identical with these in so far as it depends upon the conversion of the nitric acid into ammonia, but the manner of generating the hydrogen is entirely dissimilar. The new method is based upon a remarkable reaction recently described by Messrs. Gladstone and Tribe in the Proceedings of the Royal Society (vol. xx, p. 218). Some zinc-foil was allowed to remain in a solution of copper sulphate until its surface was covered with spongy copper. The metals were washed with distilled water and placed in a bottle of pure water. Small quantities of hydrogen were quickly evolved, the amount of which rapidly increased on gently heating the liquid. It was distinctly noticed that the hydrogen was evolved from the copper, and that zinc hydrate was simultaneously formed.

I have found that if a small quantity of nitre be added to the pure water surrounding the two metals, and the liquid be gently heated, not a trace of hydrogen will be evolved, but a distinct smell of ammonia will be perceived. A slip of turmeric paper placed in the flask over the heated liquid is turned brown, and if on boiling, the steam be led into water containing a few drops of reddened litmus solution, the colour will be changed to blue, and the water in the flask will acquire a permanent alkaline reaction from the formation of potassium hydroxide. The following experimental results show that the conversion of the nitric acid into ammonia is complete :

I. 40 grms. of thin sheet zinc were placed in a flask and coated with a bulky precipitate of copper by the action of a tolerably concentrated solution of copper sulphate for 10 or 15 minutes. The metals were repeatedly washed by decantation with distilled water, care being taken to remove as little of the adherent copper as possible. The weighed quantity of potassium nitrate was then added, together with about 40 c.c. of water, and the flask was fitted with a caoutchouc stopper and bent tube connected with a three bulbed U-tube containing a small quantity of dilute hydrochloric acid. The liquid in the flask was gently boiled for 1 hour, and the contents of the U-tube were rinsed out into an evaporating basin, mixed with platinum tetrachloride and evaporated to dryness.

0.5090 grm. KNO_3 gave 1.0498 gram $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ and
0.0301 gram metallic platinum.

Equivalent to 0.50908 grm. KNO_3 .

II. The liquid in the flask was poured away, a small quantity of dilute hydrochloric acid was added, and the well washed residue was again covered with a solution of copper sulphate. After removing the sulphates by washing, a second quantity of nitre was weighed out into the flask and the above process was repeated.

0.4183 grm. KNO_3 gave 0.9208 gram $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ and
0.0013 gram metallic platinum.

Equivalent to 0.4188 gram KNO_3 .

III. A dilute solution of nitre was prepared by dissolving 0.9478 gram of pure nitre in water and diluting to 500 c.c. 25 c.c. of this solution, containing 0.04739 gram KNO_3 , were used in all the following experiments. From 5 to 13 grams of sheet zinc were employed: the solution was occasionally gently heated for some time and then rapidly boiled for 15 or 20 minutes; sometimes, however, the liquid was heated directly to the boiling point and maintained in brisk ebullition for about an hour. The volume of the liquid in the flask was in general about 50 c.c., *i.e.* 25 c.c. of water were added to an equal bulk of the nitre solution. The ammonia was estimated as platinum-ammonium chloride. The following are some of the numbers obtained:—

KNO_3 used.	KNO_3 found.
0.0474 gram.	(1.) 0.0476 gram.
—	(2.) 0.0473 "
—	(3.) 0.0487 "
—	(4.) 0.0469 "

3. As the following experiments show, the presence of alkaline chlorides and sulphates is without influence upon the result.

1.0345 gram of nitre was dissolved in water, and the solution was diluted to 500 c.c. 25 c.c. of this solution would contain 0.05172 gram KNO_3 . This amount of the liquid was used in all the following experiments:—

2.122 gram of common salt and 2.322 gram of potassium sulphate were dissolved in water, and the solution was diluted to 100 c.c. 5 c.c. of the solution of the mixed salts would contain 0.1061 gram NaCl and 0.1162 gram K_2SO_4 . This quantity of the solution was mixed with the nitre in all the following determinations. The conditions of experiment were in other respects similar to those in the foregoing series. The same sheet zinc was used repeatedly after washing with dilute hydrochloric acid and water. The copper solution was always allowed to remain in contact with the zinc until a thick spongy coating of the reduced metal was obtained. The following are some of the results:—

Nitre taken.	Nitre found.
0.05172 gram.	0.0516 gram.
—	0.0520 „
—	0.0518 „
—	0.0516 „
—	0.0517 „
—	0.0512 „

In the final determination only 2 grams of sheet zinc were used, covered, however, with a thick coating of spongy copper.

4. *Calcium nitrate* in solution decomposes with equal readiness on boiling with zinc and copper. 0.6322 gram of marble was dissolved in nitric acid, the liquid was evaporated twice to dryness to expel the last traces of free acid, and the solution was diluted to 250 c.c. 25 c.c. (the quantity employed in each of the following trials) would contain 0.1026 gram CaN_2O_6 :—

CaN_2O_6 taken.	CaN_2O_6 found.
0.1026 gram.	0.1028 gram.

The presence of alkaline sulphates and chlorides has no retarding effect upon the decomposition of the nitrate.

25 c.c. of the calcium nitrate solution mixed with 5 c.c. of the solution of sodium chloride and potassium sulphate, and diluted with 25 c.c. distilled water, was boiled for thirty minutes with about 9 grams of zinc covered with spongy copper. Two experiments were made:—

Ca_2NO_3 taken.	Found.
0.1026 gram.	(1.) 0.1019 gram.
—	(2.) 0.1026 „

5. *Lead nitrate*, and therefore in all probability, the nitrates of

silver, mercury, copper, thallium, and in fact of all metals precipitated by zinc, are similarly decomposed, the zinc nitrate which is formed being afterwards reduced. One determination only, however, and with lead nitrate was made. The weighed quantity of the salt was boiled for about two hours with 20 grams of zinc and spongy copper. The experiment gave 0.5419 gram of $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ and 0.0019 gram of Pt:—

Pb_2NO_3 taken.	Found.
0.4053 gram.	0.4051 gram.

6. Of all the nitrates experimented upon, the most difficult of reduction appears to be *ammonium nitrate*. From the irregularity of the results at first obtained, I was inclined to believe that the decomposition was incomplete, or that hydroxylamine might be formed, or possibly Divers' hyponitrous acid. Direct experiments, however, have failed to point out the formation of these substances. The discordances appear to depend upon differences in the strength of the solution and the amounts of zinc and copper taken. If the solution is too strong, nitrogen dioxide is evolved, and if the amount of zinc and copper be insufficient the reduction is incomplete.

0.2140 gram NH_4NO_3 gave 1.1805 gram $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ and 0.0034 gram Pt, on boiling with 40 grams of zinc and copper for three hours:—

Percentage amount of total nitrogen.	
Found.	Calculated.
34.81	35.00

7. The mixture of zinc and copper appears to have but a very slight action upon *urea*.

0.1094 gram of this substance (prepared from ammonium cyanate) was dissolved in about 70 c.c. of water in contact with 20 grams of thin sheet zinc covered with spongy copper. The mixture was allowed to stand for about 18 hours in the cold, and was then boiled for two hours.

The distillate gave 0.0110 gram $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ and 0.0005 gram Pt:—

Calculated amount of nitrogen.	Found.
46.66 per cent.	0.69 per cent.

0.2137 gram of urea was dissolved in 10 c.c. of water in contact with about 20 grams of zinc and copper, and the solution was boiled down to dryness. A small quantity of water was then added to the flask, and the liquid was again evaporated to dryness, this process being repeated three or four times. The distillate gave 0.0255 gram $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$:—

Calculated N.	Found.
46.66 per cent.	0.74 per cent.

If the urea had been completely decomposed, the above quantity should have given 1.588 gram of the platinum salt. The minute quantity of ammonia found might be due to a trace of ammonium salt in the urea, arising from the mode of its preparation, or, which is more probable, since the substance was recrystallised five times from alcohol, it may have been produced by the gradual decomposition which urea is known to experience by long-continued boiling with water.

8. The readiness with which aqueous solutions of nitrates and nitrites yield ammonia by the action of zinc and spongy copper, would appear to indicate that this reaction might be usefully applied to the determination of these substances when present in drinking waters. It is an objection to the aluminium or zinc and iron methods, as applied to water analysis, that, unless great care is taken, a far larger quantity of nitrates may be introduced in the potash or soda which is needed in such large proportion, than is actually present in the water. Moreover, the strong alkaline solution is extremely liable to froth over on distilling, and if the disengagement of the hydrogen is active, it is almost impossible to boil it without portions of the turbid liquid finding their way into the distillate; and a turbid distillate is of course fatal to the determination of ammonia by Nessler's test.

As the zinc and copper process presents none of these disadvantages, I have sought to make the process applicable to water analysis.

The following is a convenient and expeditious method of operating. The weighed residue in the platinum dish obtained in the determination of the total soluble matter in the water is treated with 10 or 12 c.c. of water, to which a small piece of previously ignited lime about the size of a hemp-seed is added, and the liquid is gently boiled until about 4 or 5 c.c. only remain. The primary object in adding the lime is to facilitate the evolution of the ammonia. A very dilute solution of nitre was boiled with zinc and copper, until ammonia could no longer be detected in the distillate by Nessler's solution; the volume of the liquid required to be distilled was about 120 c.c. When the same quantity of nitre solution was boiled with the previous addition of a minute fragment of lime, but otherwise under the same conditions as before, all the ammonia came over in the first 25 c.c. of the distillate. Three or four grams of thin sheet zinc (that used in all the experiments described was about 0.084 mm. in thickness; 1 gram would therefore expose a surface of 17.89 mm.) previously cleaned by a little dilute acid, and cut into small pieces, are placed into the flask A, which has a capacity of 100 c.c. The zinc is covered with a moderately concentrated solution of copper sulphate, which is allowed to act until a thick dark brown spongy covering of copper is precipitated. The metals are washed four or five times by decantation with cold water, care being taken to detach the copper particles as slightly as possible from the zinc. At the last

washing the water is drained away as far as practicable. The nitrate solution is transferred from the platinum dish, and the last portions are rinsed out by a few c.c. of cold water, until the liquid in the flask amounts to 25 or 30 c.c. A caoutchouc stopper is then inserted; this is pierced with two holes, through one of which passes a funnel-tube, provided with a well-fitting glass stopcock C, through the other

passes the tube D, bent twice at right angles and ending in the wide test-tube B, which is also fitted with a caoutchouc stopper. The tube B has a capacity of about 60 c.c.; it is 18 cm. long, and is graduated to hold 50 c.c. The tube E is partially filled with well-washed fragments of glass. Before inserting the stopper, one drop of pure dilute hydrochloric acid is placed in B, together with 2 or 3 c.c. of water; the glass in the bent tube E is also moistened with two drops of the dilute hydrochloric acid. The liquid in the flask is now caused to boil, to decompose the nitrate; the escaping steam and ammonia condense in B, which is cooled

by immersion in cold water. Any ammonia that may escape condensation in B is retained in the bent-tube E. The liquid in the flask is evaporated nearly to dryness, the lamp is drawn aside, and the funnel is filled with boiling distilled water, the stopcock is opened, and the water is permitted to run into the flask. This process is repeated until B contains about 40 c.c. of water. The lamp is now drawn aside, and the tube E is filled with water; as the steam condenses in the flask the water is of course driven into B; by refilling the tube once or twice, the fragments of glass will be thoroughly washed. B is detached from the cork, and a second tube containing 1 or 2 c.c. of water acidulated with one drop of hydrochloric acid is placed in its stead; a drop of hydrochloric acid is permitted to run on to the fragments of glass, and the distillation is continued until a second portion of 40 c.c. has passed over. The glass fragments are rinsed, and a third tube is substituted. Unless the nitrates are present in exceptionally large quantity, the first 40 c.c. will contain the whole of the ammonia. The amounts of ammonia contained in the several portions of the distillate are then estimated by Nessler's solution. The contents of the

tubes are diluted until they measure 50 c.c., water being poured into the tube, until its level is coincident with the mark on the glass, and the liquid in each is mixed by agitation with a thin and narrow glass tube, on which a bulb has been blown of sufficient diameter to pass readily into the tube. By drawing the tube up and down once or twice in the liquid, it will be thoroughly mixed. 10 c.c. of the liquid in the first tube are then transferred by means of a pipette to a similar tube, also graduated to hold 50 c.c., and further diluted to the mark with pure water. 1 c.c. of Nessler's solution is added, and in a few minutes the colour is noted. If it is measurable it is then compared in the usual manner with that produced by a standard ammonium chloride solution. If the colour is too dark for accurate comparison, 5 c.c. only of the original liquid are withdrawn; if very light, the remaining 40 c.c. may be used. The intensity of colour given by the first 10 c.c. will indicate the proper quantity to be withdrawn to give the tint which the operator finds by experience to be the best suited for comparison. The standard ammonium chloride solution which I find most convenient to use contains 0.07867 gram NH_4Cl per litre. 1 c.c. is equivalent to .025 mgrm. of ammonia. 5 c.c. (or 110 drops from my burette, which is of Mohr's pattern, with glass stopcock) of this solution may be added to the liquid, before the addition of the 1 c.c. of Nessler's solution gives the least turbidity. To test this method of determining nitrates in water, a solution of nitre was diluted, until 1 c.c. of the liquid contained 0.167 mgrm. KNO_3 ; the quantity of nitre contained in 10, 15, and 20 c.c. was then determined in the manner described.

Taken.	Found.
(1.) 10 c.c. = 1.67 mgrm. KNO_3 .	1.68 mgrm.
(2.) 10 c.c. = 1.67 „ „	1.72 „
(3.) 15 c.c. = 2.50 „ „	2.42 „
(4.) 15 c.c. = 2.50 „ „	2.49 „
(5.) 25 c.c. = 4.16 „ „	4.01 „

In each case all the ammonia was contained in the first 40 c.c. of the distillate.

9. This reaction with zinc and copper in presence of water will doubtless admit of many other useful applications. For example, I find that the two metals completely reduce *alkaline chlorates* to the state of chlorides, as the following experiments show :—

I. 0.4990 gram potassium chlorate was dissolved in water, and gently boiled with 15 grams of sheet zinc coated with copper. The liquid was filtered, and the amount of chlorine in solution as chloride estimated by decinormal silver solution and potassium chromate. The liquid required 40.1 c.c. silver solution.

II. 0.2995 gram potassium chlorate treated with 10 grams of zinc and copper, required 20.2 c.c. of silver solution.

Cl found.		
I.	II.	Calculated.
28.52	28.77	28.96

10. *Iodic acid* is in like manner reduced by this treatment.

0.1040 gram ammonium iodate treated with zinc and copper, gave 0.0968 gram silver iodide, and 0.0135 gram metallic silver.

Iodine calculated.	Found.
65.81	65.42

11. The two metals would, in all probability reduce hypochlorous acid with equal readiness: this reaction might constitute a simple method of determining the total chlorine contained in bleaching powder. Zinc and spongy copper when heated with potassium ferricyanide reduce that salt to potassium ferrocyanide. Messrs. Gladstone and Tribe have already remarked that the metals act on chloroform and ethyl iodide. The metals, however, have no action on hyposulphites, phosphates, and arseniates. A solution of codeine boiled with zinc and copper evolves no ammonia.

12. If the amount of substance to be reduced is at all considerable, it is by no means a matter of indifference how much copper is deposited upon the zinc. The quantity of hydrogen eliminated from water by the action of the metals depends to a certain extent upon the quantity of copper present, as the following experiments show:—

I. 9 grams of sheet zinc were coated with a *thin* film of coherent copper: on boiling with water for one hour, 148.2 c.c. of hydrogen, measured at 0°, and 760 mm. were evolved.

II. 9 grams of zinc covered with a bulky deposit of copper gave 484.3 c.c. of hydrogen at 0°, and 760 mm. after boiling for one hour with water.

Moreover the *condition* of the copper is of importance; brass, however finely divided, is without reducing action upon nitrates. Indeed, the spongy copper *alone* is able to reduce small quantities of nitrates. A thick sheet of zinc was immersed in copper sulphate solution, and the precipitated metal was rinsed into the distilling flask A (Fig. 1) by the aid of the wash-bottle. 20 c.c. of the standard nitre solution (par. 8) was then boiled with the copper, and the amount of ammonia evolved was determined by Nessler's solution.

KNO ₃ taken.	Found.
3.34 mgrm.	3.22 mgrm.

4.73 grams of spongy copper boiled with 0.098 gram of nitre gave

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0·1667 gram of double chloride of platinum and ammonium and ·0040 gram metallic platinum. This would be equal to 0·0797 gram of nitre; or 81 per cent. of the salt was decomposed.

My thanks are due to Mr. James B. Hannay for his assistance in many of the experiments described in this communication.