XLVII.—*On a Method for the Determination of Nitric and Nitrous Acids.*

BY A. VERNON HARCOURT, M.A., Student of Christ Church, Oxford.

IN the course of some experiments upon the alkaline peroxides*, I had occasion to determine the quantity of nitrogen in a mixture of nitrate and nitrite of potassium. Finding no account of a method suitable for this purpose, I was compelled to seek one experimentally. That at which I arrived, and which is briefly indicated in the paper referred to, gives very exact results, and promises to be available for the determination of any nitrate or nitrite whatsoever and however admixed.

Since that time a method has been published by Professor

* Journ. Chem. Soc., vol. 16, p. 289.

Schulze,* differing only in one important particular, the employment of platinized zinc in the place of zinc and iron, from that pursued by me. A brief account of this latter method, and its results, may, however, still be acceptable.

It has long been known, that when nitre is heated with an excess of potash, zinc, and water, ammonia gas is evolved. But the conversion effected in this way is incomplete. In a number of experiments made with the view of founding a quantitative method upon this reaction, the ammonia thus formed was collected and determined; it amounted to about $\frac{3}{4}$ ths of that quantity, which the weight of nitre used was theoretically capable of yielding. No modification in the proportions of zinc and potash solution, or in the degree of concentration of the latter, materially improved this result. Under no conditions was the relation sufficiently constant to furnish an empirical number. Nitre, heated in a combustion-tube with a mixture of powdered zinc and soda-lime, yielded only a trace of ammonia.

It was observed, I believe, by Mr. Griffin,† that, when a moderately concentrated solution of potash is poured upon a mixture of zinc and iron, hydrogen is freely disengaged, even without the application of heat. This action is electrolytic; the zinc is oxidized, and the hydrogen formed upon the surface of the iron. A similar effect is observed if platinum, copper, or tin, be substituted for iron; but the action with these metals is less energetic. The addition of a nitrate to the mixture evolving hydrogen, is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean iron filings. A small quantity (5 or 6 c.c.) of strong potash solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube: .005 grm. of nitre thus treated, gave a distinct reaction with reddened litmus paper. The employment of potassio-iodide of mercury renders this test far more delicate. The mixture should be gently boiled for five or ten minutes, and the evolved gases led into a small quantity of dilute hydrochloric acid. The acid solution is

* Chem. Central Blatt, No. 53.

† Griffin's Chemical Recreations, p. 231.

is supersaturated with potash, and tested with a drop of potassium-iodide of mercury: $\cdot 001$, $\cdot 0005$, and even $\cdot 0001$ grms. of nitre gave a distinct red coloration when thus treated.

The apparatus which I have employed for quantitative determinations is represented, on a scale of $\frac{1}{16}$ th, in the following figure.

The flask, *a*, which has a capacity of 200 C.C., is designed for the generation of ammonia by the mutual action of nitric acid, zinc, iron, potash, and water. It is connected by a bent tube, drawn out and recurved at its extremity, with the smaller flask or bulb *b*; and the two are so arranged, that they both rest at a considerable angle of inclination upon the sand-bath, *c*. The smaller flask is connected with a condenser which leads into the tubulated receiver, *d*. In the upper part of the condensing tube is a small tubulure *f*, closed during the distillation by a plug of india-rubber. The tube, *e*, which is provided with two or more bulbs and a funnel-head, has the shape indicated in the figure. It is fastened into the tubulure by means of a perforated plug of caoutchouc, which, when slightly greased, makes a tight and supple joint. A standard solution of sulphuric acid is used for the collection and determination of the ammonia. The excess of acid employed is finally determined by means of a standard solution of caustic potash.

The following is the course of the operation:—The funnel-tube, *e*, is brought into a vertical position, by being turned round in the tubulure through half a circle; a quantity of standard acid from a burette is passed through it into the receiver, more than enough to neutralize all the ammonia that can be formed. Some litmus

solution is added to render visible the progress of the action. The funnel-tube is then restored to a horizontal position, and its bulbs filled up to the proper level by a few drops more of the standard acid. The total quantity of acid that has been taken, is now read off upon the burette. The flask *a* is then removed, its tube and cork, together with the smaller flask, which should contain a little water, remaining in position upon the sand-bath. Into it is introduced about 50 grms. of finely granulated zinc, together with half that quantity of iron filings, which have been cleansed by sifting, and ignition in a covered crucible; a weighed portion of the nitrate to be determined is then introduced, with water sufficient to dissolve it; lastly, a measured quantity of a solution of caustic potash, free from nitre, is added, and the flask immediately replaced. It is essential that the quantity of the metals and of the potash employed, should greatly exceed that proportion which is theoretically necessary for the complete conversion of the nitric acid. In my experiments with nitre, I have generally taken about 0.5 grm. of that substance, 20 c.c. of water, and 20 c.c. of a solution of potash, sp. gr. 1.3. Provided the quantity of potash be sufficient, it is immaterial in what degree its solution is diluted, since, in the course of the distillation, it passes through every stage of concentration. It must not be highly concentrated at the commencement of the operation.

Heat is now applied to the part of the sand-bath immediately beneath the larger flask, and the fluid is gradually raised to the boiling point. If the bubbles of air and hydrogen pass at a moderate rate through the bulb-tube, *e*, there is no risk of a loss of ammonia. When distillation has commenced, the lamp is so placed that the water in the smaller flask *b* may also boil gently. The fluid is thus twice distilled in one operation, and the traces of potash which escape from the flask *a*, are effectually retained in the flask *b*. The end of each of the two exit-tubes is drawn out, and bent into a hook for further security. Repeated experiment has proved the sufficiency of this arrangement for keeping back in a slow distillation everything that is not volatile. The quantity of fluid in the flask *b* can be regulated by adjusting the position of the lamp. The distillation, which should occupy from one to two hours, requires only occasional attention. It may be terminated when hydrogen gas, which is evolved in larger quantity as the potash becomes concentrated, has been passing regularly, for five or ten minutes, through the bulb-tube *e*. When the fluid in *e*

has receded, as the apparatus cools, into the inner bulb, the caoutchouc plug is withdrawn from *f*, and a stream of water poured into the condensing tube, to preclude the possibility of ammonia being retained upon any portion of its surface. The tube *e* is then turned round into the vertical position, and water is passed through it two or three times, after which it is removed, and the tubulure of the receiver closed by a cork. Finally, the receiver itself is disconnected, the end of the condensing tube is rinsed externally, and the determination is completed by adding standard alkali from a burette to the fluid in the receiver till a change of colour appears. Collection in hydrochloric acid, and precipitation by choride of platinum, may be substituted, but the volumetric method gives perfectly sharp results.

The zinc and iron which remain in the generating flask need only to be washed with water, with dilute acid, and again with water, to be ready for a second determination. Metals that have once been used, generate hydrogen far less actively than zinc with a bright surface, and freshly ignited iron; but the production of ammonia proceeds as readily with one as with the other. It may be safely assumed, that the presence of any salts, which are without action upon caustic potash, or upon zinc and iron, will not interfere with the reaction upon which this method depends. The experiment was, however, made of mixing weighed quantities of nitre with various proportions of sulphate of potassium and chloride of sodium. The presence of these salts did not affect the result.

For the estimation of nitric acid in other than alkaline nitrates, the separation of the base may, in some cases, prove a necessary

preliminary. I have experimented only with nitrate of barium and nitrate of lead. The former may be determined exactly in the same way as nitrate of potassium, and with equally good results. The carbonate of barium, which separates on adding solution of caustic potash, is, as might be expected, without influence on the reaction. Nitrate of lead exhibits a slight deficiency when thus directly determined. In five experiments, instead of 8.45 per cent. of nitrogen, the following numbers were found—7.78, 7.83, 8.09, 8.28, 8.11. This deficiency is possibly due to an action of dissolved oxide of lead upon the surface of the zinc. It would certainly disappear if the lead were first separated by means of sulphate of potassium.

A few examples of determinations made by this method are given in conclusion.

A solution of pure nitre was made, and of this 10 c.c. were used in each experiment. This quantity evaporated to dryness, left a residue weighing 0.3838 grm. 1 c.c. of the standard acid employed neutralizes an amount of ammonia, containing 0.002084 grm. of nitrogen. In six consecutive experiments, the number of c.c. of this acid required was—

(1). 25.7, (2). 25.3, (3). 25.3,
(4). 25.4, (4). 25.4, (6). 25.6,

of which the mean is 25.45 c.c.: hence the total nitrogen found is 0.05304 grm.; the nitrogen per cent. 13.82; theory requires 13.86.

In eight consecutive experiments, made with the same standard acid, the quantity of nitre taken for each was 0.4986 grm.

The number of cubic centimetres required was,—

(1). 33.15, (2). 32.9, (3). 33.1, (4). 33.2,
(5). 33.05, (6). 33.1, (7). 33.15, (8). 33.2,

of which the mean is 33.1: hence the total nitrogen found is 0.069; the nitrogen per cent. 13.83.