XXVII.—*A Gasometric Method of Determining Nitrous Acid.*

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IN the course of some experiments which I have been carrying on for some time past, it became necessary to determine the proportion of nitrous acid present in certain solutions containing both nitrates, nitrites, and ammonia, the problem being still further complicated by the presence of organic matter. The estimation of nitrous acid in such mixtures is usually effected colorimetrically by the well-known reactions of metaphenylenediamine, or of sulphanilic acid and naphthylamine hydrochloride, on an acidulated solution of the nitrite, the latter reaction being very much more delicate than the former. Both of these colorimetric methods are, however, only adapted for measuring very minute traces of nitrous acid, and were quite unsuitable for my purpose. I may, however, mention in passing that I have found the modification of the sulphanilic acid method introduced by Zambelli (Abstr., 1887, 533), very much to be preferred to either of the above well-known methods. Zambelli adds to the solution containing the nitrite a drop of a saturated solution of sulphanilic acid, then a drop of an aqueous solution of phenol, the mixture being then rendered alkaline with ammonia; the presence of nitrous acid is indicated by the appearance of a coloration, varying from faint yellow to intense reddish-yellow (like the colour of a strong solution of potassium dichromate), according to the quantity of the nitrous acid present. The author states that this method is capable of indicating the presence of 1 part of nitrous nitrogen in 40,000,000 parts of water. So that whilst its delicacy is extreme it has also the advantage, that the reagents employed are permanent in solution; the solutions of naphthylamine hydrochloride, and more especially of metaphenylenediamine becoming very rapidly discoloured on keeping. I, therefore, invariably adopt this method for qualitatively testing for nitrites, as well as for obtaining a relative estimate of the amount present in different solutions.

For the purposes of the experiments upon which I was engaged, however, it was necessary to have a method which should be capable of dealing with much larger quantities of nitrous acid than are suitable for colorimetric estimation. Owing to the presence of organic matter in the solutions in question, the ordinary method of determining nitrous acid by means of a standard solution of potassium permanganate was out of the question, and on this account a gaso-

metric method appeared to be the most suitable for the purpose, especially as only very small absolute quantities of the nitrite were available. Under these circumstances, the reaction between nitrous acid and urea naturally suggests itself as especially suitable, since the volume of nitrogen gas evolved is double that of the nitrogen in the nitrite, and the errors of experiment thus become divided by two. I have since found that this reaction had been utilised for the purpose of nitrous acid estimation by Longi (*Gazzetta*, **13**, 469—479), although his mode of operation is quite different from mine, and would not have been adapted to the determination of the small quantities of nitrous acid which I had at my disposal.

My preliminary experiments were made with a solution of sodium nitrite, standardised by means of potassium permanganate.

(1.) 20 c.c. of the standard solution of sodium nitrite are evaporated to dryness in a small beaker on the water-bath, to the residue is then added a large excess of crystallised urea (about 0.25 gram), about 2 c.c. of boiling water are then added from a wash-bottle to the mixture in the beaker, and in this the urea and nitrite rapidly dissolve; the solution is then carefully transferred to the cup of a tube similar to that used in the determination of nitric acid by the mercury-method, and as figured in the cut. This tube, which I employ, of the following dimensions (6" long by $\frac{3}{4}$ " in diam. internal, the cup

being 1" in depth) is filled with mercury, and stands in a mercury-trough. By carefully opening the tap, the liquid in the cup is

admitted into the tube. The beaker is now repeatedly rinsed with small quantities of boiling water, and the rinsings similarly transferred to the mercury-tube. An excess of dilute sulphuric acid (1 : 5) only amounting to a few c.c. in volume, is now poured into the cup, and admitted into the tube. A vigorous evolution of gas then commences, and continues for some five minutes. This gas consists of a mixture of nitrogen and carbonic anhydride. The decomposition in the cold with an excess of urea taking place according to Claus (*Ber.*, **4**, 140), as represented by the equation :— $2\text{CO}(\text{NH}_2)_2 + \text{N}_2\text{O}_3 = \text{CO}(\text{NH}_4\text{O}) + \text{CO}_2 + 2\text{N}_2$. After 15 minutes, when the decomposition may be taken to be complete, a strong solution (1 : 3) of pure caustic soda (free from nitrite) is added through the cup, and the mixture violently agitated until the carbonic anhydride is completely absorbed. The lower extremity of the tube is then firmly closed with the thumb, and the tube transferred to another mercury-trough, in which the gas and liquid are passed into the "laboratory-vessel" of an apparatus for the measurement of gases. The volume of nitrogen under known conditions of pressure and temperature is then ascertained, and from this the weight of nitrogen can be calculated. Thus in the experiment in question—

Volume of nitrogen = 13.79 c.c. Pressure = 255.5 mm. of mercury. Temperature = 18.9° C.

Weight of nitrogen from 10 c.c. of standard sodium nitrite solution = 0.0013615 gram.

Weight of nitrous nitrogen in ditto, determined by standard permanganate = 0.001346 gram.

(2.) 10 c.c. of the same sodium nitrite solution similarly treated, yielded—

Volume of nitrogen = 13.79 c.c. Pressure = 127.5 mm. of mercury. Temperature = 17.7° C.

Weight of nitrogen from 10 c.c. of standard sodium nitrite solution = 0.0013645 gram.

Thus the accordance of the nitrogen found with that calculated from the standardisation with permanganate is very close.

Experiments were made in order to determine whether the reaction between the urea and nitrite is really complete in 15 minutes, or whether a larger volume of nitrogen would be obtained if the time for the reaction was extended. Thus three portions, of 10 c.c. each, of a solution of sodium nitrite were evaporated in three small beakers, each of which was treated as above described; in the case of the first portion, the reaction with the urea was interrupted at the end of

15 minutes by the addition of the excess of caustic soda, whilst in the case of the second portion, the addition of the caustic soda was made after three hours, and with the third portion after 23 hours. The following results were obtained :—

	Reaction interrupted after	Volume of nitrogen.	Pressure in mm.	Temperature.	Weight of nitrogen from 10 c.c. of solution.
No. 1...	15 minutes	13·79 c.c.	252·7	13·2° C.	0·0013734 gram
„ 2...	3 hours	„	253·7	13·5 „	0·0013774 „
„ 3...	23 „	„	252·2	13·6 „	0·0013688 „

The above results show that the reaction is complete in 15 minutes, and that no more gas is evolved, even if the time is extended to 23 hours.

Comparison of Urea-method with Mercury-method of determining Nitrites.

Experiments were also made in order to compare the results of the urea-method with those obtained by the mercury-method, which does not discriminate between nitrous and nitric nitrogen. The same standard solution of sodium nitrite was employed for the purpose, with the following results :—

(1.) 20 c.c. of the solution of sodium nitrite were evaporated in a small beaker on the water-bath. The residue was then repeatedly extracted with very small quantities of hot water, and these successive extracts transferred to the mercury-tube as described above. The small beaker was then rinsed with strong sulphuric acid (free from nitrogen-compounds), and the rinsings, which amounted in volume to that of the aqueous extract, were also transferred to the mercury-tube. The mercury-tube was then closed at the bottom with the thumb of the right hand, and the tube violently shaken without, however, allowing the acid mixture in the tube to come in contact with the thumb. The evolution of nitric oxide commenced at once, and the pressure exerted by the liberation of the gas in the tube had to be relieved by withdrawing the thumb from the extremity of the tube when under mercury. The evolution of gas was complete in the course of a few minutes, and the gas was then transferred to the measuring apparatus as described before. In this case also, the volume of nitric oxide obtained is twice that of the nitrogen which it contains. Thus—

Volume of nitric oxide = 13·79 c.c. Pressure = 246·9 mm. of mercury. Temperature 16·3° C.

Weight of nitrogen from 10 c.c. of standard solution of sodium nitrite = 0·001328 gram.

(2.) 20 c.c. of the solution of sodium nitrite treated in a perfectly similar manner yielded—

Volume of nitric oxide = 13·79 c.c. Pressure = 256·2 mm. of mercury. Temperature = 16·6° C.

Weight of nitrogen from 10 c.c. of solution = 0·001376 gram.

(3.) 20 c.c. of the solution of sodium nitrite were evaporated to dryness in a small beaker, and the nitrous nitrogen determined by the urea-method. Thus—

Volume of nitrogen = 13·79 c.c. Pressure = 256·0 mm. of mercury. Temperature = 16·7° C.

Weight of nitrogen from 10 c.c. of solution = 0·001375 gram.

(4.) 20 c.c. of the solution of sodium nitrite similarly treated yielded—

Volume of nitrogen = 13·79 c.c. Pressure = 256·2 mm. of mercury. Temperature = 16·9° C.

Weight of nitrogen from 10 c.c. of solution = 0·001375 gram.

Weight of nitrous nitrogen in 10 c.c. of solution of sodium nitrite (as determined by standard permanganate) = 0·001346 gram.

The results obtained by both gasometric methods thus not only agree very closely together, but also with the permanganate estimation.

Determination of Nitrous Acid in Presence of Peptones and Ammonia Salts.

On applying the urea-method to the actual solutions in which I wished to determine the nitrous acid, I found that the results obtained were invariably very decidedly low. The solutions in question contained calcium nitrate, invert-sugar, peptone, and carbonate of lime in suspension, besides very minute quantities of calcium chloride, magnesium sulphate, and potassium phosphate. Thus—

Potassium phosphate	0·1	gram	} per 1000 c.c.
Magnesium sulphate	0·02	„	
Calcium chloride	0·01	„	
Nitrogen (combined in the form of calcium nitrate)	0·168	„	
Invert-sugar	0·3	„	
Peptone	0·25	„	

This solution was in fact prepared for the cultivation of certain micro-organisms, in order to ascertain their action on the nitric acid

present. Although this solution was in the first instance quite free from ammonia, yet during the growth of some of the micro-organisms under examination ammonia was produced, and it became necessary to have a method for determining the nitrous acid in the presence of the latter.

Experiments were first made by adding known quantities of a standard solution of nitrite to the above solution free from ammonia, which may for convenience be designated as Solution A.

(1.) In the first place, the nitric nitrogen in Solution A was determined by evaporating 10 c.c., and treating the residue by the mercury-method; this gave—

Weight of nitric nitrogen in 10 c.c. Solution A = 0.00337 gram.

(2.) 20 c.c. of a solution of sodium nitrite was similarly treated, the nitrous nitrogen being determined by the mercury-method; this gave—

Weight of nitrogen in 10 c.c. solution of sodium nitrite = 0.001445 gram.

(3.) 20 c.c. of sodium nitrite solution were evaporated, and the nitrous nitrogen determined by the urea-method; this gave—

Weight of nitrogen in 10 c.c. of solution of sodium nitrite = 0.001405 gram.

A mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite solution was evaporated, and the nitrous and nitric nitrogen in the residue determined by the mercury-method; this gave—

Total weight of nitrogen = 0.00277 gram,

if from this the nitric nitrogen in the 5 c.c. of Solution A is subtracted, only 0.001085 gram N is left for the 10 c.c. of sodium nitrite.

(5.) A similar mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite solution was evaporated, and the nitrous nitrogen determined by the urea-method; this gave—

Nitrous nitrogen = 0.00104 gram.

this coincides, therefore, very closely with the amount found by difference in the previous experiment.

(6.) A similar mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite, treated similarly to (5), gave—

Nitrous nitrogen = 0.00103 gram.

(7.) Another experiment was made to see whether the amount of

nitrous nitrogen lost was diminished by increasing the proportion of nitrite to Solution A. For this purpose, a mixture of 5 c.c. Solution A and 20 c.c. of sodium nitrite was evaporated, and the nitric and nitrous nitrogen determined together by the mercury-method. The result was—

$$\text{Total nitrogen} = 0\cdot00412 \text{ gram.}$$

Subtracting the nitric nitrogen of the 5 c.c. Solution A, the nitrous nitrogen left amounts to 0·002435 gram for the 20 c.c. sodium nitrite employed, or 0·001218 gram for 10 c.c.

Thus, by increasing the proportion of nitrite to a given quantity of Solution A, the proportional loss of nitrous nitrogen is diminished.

From rough experiments, in which the nitrogen evolved by the urea-method was measured in the common nitrometer, I have every reason to believe that the ingredient of Solution A which causes the loss of nitrous nitrogen on evaporation, is the peptone and not the invert-sugar. In fact, possibly the peptone and nitrite enter into a reaction of a similar kind to that which takes place when a solution of an alkaline nitrite is heated with a solution of an ammonium salt, thus—

It occurred to me that such an action of the peptone might possibly be counteracted by the presence of an excess of caustic alkali during the evaporation of the solution on the water-bath. To ascertain whether this was the case or not, the following experiments were made:—

(1.) 20 c.c. of standard sodium nitrite were mixed with 10 c.c. of Solution A, and 2 drops of a strong solution of caustic potash (1 : 2) were added to the mixture which was then evaporated to dryness, and the nitrous nitrogen determined by the urea-method. The result was—

Volume of nitrogen = 13·79 c.c. Pressure = 258·2 mm. of mercury. Temperature = 16·4° C.

Nitrous nitrogen per 10 c.c. = 0·001388 gram.

(2.) A perfectly similar mixture to which no potash had been added, gave—

Volume of nitrogen = 13·79 c.c. Pressure = 216·7 mm. of mercury. Temperature = 16·8° C.

Nitrous nitrogen per 10 c.c. = 0·0011631 gram.

(3.) 10 c.c. of the sodium nitrite solution alone, gave—

Volume of nitrogen = 13·79 c.c. Pressure = 127·5 mm. of mercury. Temperature = 17·7° C.

Nitrous nitrogen per 10 c.c. = 0·0013645 gram.

From these experiments, it is evident that the addition of the caustic potash had entirely prevented the loss of nitrous nitrogen during the evaporation of the nitrite with the peptone.

The influence of ammonia salts on the determination of nitrous acid had next to be ascertained. For this purpose, the following experiments were made:—

(1.) 25 c.c. of the standard solution of sodium nitrite (0.001346 gram N per 10 c.c.) were added to 5 c.c. of a standard solution of ammonium chloride (1.5735 grams NH_4Cl per litre), four drops of the strong solution of caustic potash being added to the mixture; this was then evaporated to dryness, and the nitrous nitrogen determined by the urea-method. The result was—

Volume of nitrogen = 13.79 c.c. Pressure = 317.0 mm. of mercury. Temperature = 13.8° C.

Nitrous nitrogen per 10 c.c. = 0.0013754 gram.

(2.) 25 c.c. of sodium nitrite, with 10 c.c. of ammonium chloride and four drops of caustic potash, were treated in a precisely similar manner:—

Volume of nitrogen = 13.79 c.c. Pressure = 311.2 mm. of mercury. Temperature = 14.4° C.

Nitrous nitrogen per 10 c.c. = 0.0013474 gram.

(3.) 25 c.c. of the sodium nitrite solution were evaporated with 10 c.c. of the ammonium chloride without any addition of caustic potash. On treating the residue according to the urea-method, not a trace of gas was evolved, showing that the whole of the nitrous nitrogen had been dissipated by evaporation with ammonium chloride.

From experiments (1) and (2), however, it is evident that the quantity of caustic potash there added had been quite sufficient to prevent any destruction of nitrous nitrogen during evaporation.

Finally, a series of experiments was made in order to ascertain whether in a mixture containing nitrates, nitrites and ammonia, the nitrate could be determined by the mercury-method after evaporating the solution to dryness with an excess of ammonium chloride, and the nitrite by the urea-method after evaporating with an excess of caustic potash. Thus—

(1.) 10 c.c. of a solution of calcium nitrate were evaporated and the nitric nitrogen determined by the mercury-method; this gave—

Volume of nitric oxide = 22.63 c.c. Pressure = 306.6 mm. of mercury. Temperature = 17.2° C.

Weight of nitric nitrogen per 10 c.c. = 0.0053937 gram.

372 A GASOMETRIC METHOD OF DETERMINING NITROUS ACID.

(2.) Ditto in every respect.

Volume of nitric oxide = 22·63 c.c. Pressure = 310·4 mm. of mercury. Temperature = 17·7° C.

Nitric nitrogen per 10 c.c. = 0·005451 gram.

The strength of the solution of calcium nitrate may thus be taken as 10 c.c. = 0·00542 gram nitrogen.

(3.) 20 c.c. of a solution of sodium nitrite were evaporated, and the nitrous nitrogen determined by the urea-method; thus—

Volume of nitrogen = 13·79 c.c. Pressure = 249·7 mm. of mercury. Temperature = 15·5° C.

Nitrous nitrogen per 10 c.c. = 0·001346 gram.

(4.) 10 c.c. of the solution of calcium nitrate with 20 c.c. of the solution of sodium nitrite, and 20 c.c. of solution of ammonium chloride (1·5735 gram NH_4Cl per litre), were evaporated to dryness on the water-bath, and the nitric nitrogen determined by the mercury-method. Thus—

Volume of nitric oxide = 13·79 c.c. Pressure = 512·4 mm. of mercury. Temperature = 15·1° C.

Nitric nitrogen per 10 c.c. = 0·0055335 gram.

(5.) Ditto in every respect.

Volume of nitric oxide = 13·79 c.c. Pressure = 511·2 mm. of mercury. Temperature = 16·9° C.

Nitric nitrogen per 10 c.c. = 0·005485 gram.

(6.) 10 c.c. of the solution of calcium nitrate with 20 c.c. of the solution of sodium nitrite, and 10 c.c. of ammonium chloride were evaporated with five drops of strong caustic potash, the nitrous nitrogen being then determined by the urea-method. Thus—

Volume of nitrogen = 13·79 c.c. Pressure = 268·4 mm. of mercury. Temperature = 14·5° C.

Nitrous nitrogen per 10 c.c. = 0·001452 gram.

(7.) Ditto in every respect.

Volume of nitrogen = 13·79 c.c. Pressure = 259·2 mm. of mercury. Temperature = 15·0° C.

Nitrous nitrogen per 10 c.c. = 0·001400 gram.

These results show that the difficult task of quantitatively determining nitric and nitrous acids in the presence of ammonia can be

ACTION OF SPECIFIC MICRO-ORGANISMS ON NITRIC ACID. 373

satisfactorily accomplished by means of the mercury- and urea-methods respectively, the destruction of the nitrous acid on the one hand being effected by means of an excess of ammonium chloride, whilst on the other hand all loss of nitrous acid can be avoided by evaporation with excess of caustic alkali.

This mode of procedure has a great advantage over all differential methods of determining nitrous and nitric acids, as each acid is determined individually and quite independently of the other.

The urea-method of determining nitrous acid as described above, is both convenient, rapid, and trustworthy, and is suitable for all cases in which only small quantities of nitrous acid are available.

The method may also be adapted for use with the common nitrometer when larger quantities of nitrite are present.