

THE DETERMINATION OF NITRIC AND NITROUS ACIDS IN ACETIC ACID SOLUTION. THE STABILITY OF NITRIC ACID IN ACETIC ACID SOLUTION.

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ALTHOUGH numerous papers on the determination of nitric and nitrous acids and their salts have been published, the determination of these acids in acetic acid solution has not been investigated. The inquiry arose from the need of knowing, for the purpose of experiments on the nitration of aromatic compounds, whether nitric acid was reduced by acetic acid. For these experiments very dilute solutions—not greater than 1 per cent.—of nitric acid were required. This fact was the objection to the use of the Kjeldahl-Gunning-Jodlbauer method, which would be applicable to more concentrated solutions. For example, it was used with success by Pictet and Khotinsky (*Ber.*, 1910, **40**, 1163) in the analysis of acetyl nitrate.

The method here described is based on the fact that all the nitric acid in acetic acid solution is retained as potassium nitrate if the solution is evaporated to dryness on the water-bath with a slight excess of potassium carbonate; any nitrous acid is destroyed under this treatment. The potassium nitrate, which is mixed with some acetate, is determined by the Lunge process. The nitrous acid can be best determined by Raschig's permanganate method (*Ber.*, 1905, **35**, 3911). Nitric acid is remarkably stable in acetic acid solution, and can be kept of constant concentration for many weeks. If nitrous acid (oxides of nitrogen) is present, the major part is gradually oxidised to nitric acid, the solution becoming nearly colourless. Solutions in 50 per cent. acetic acid showed similar behaviour. Reduction of the nitric acid does not occur even after prolonged exposure to diffused light, but any colour due to oxides of nitrogen originally present gradually fades, the concentration of the nitric acid somewhat increasing. This remarkable behaviour will be further investigated.

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All the well-known methods of analysis were tested. The problem resolved itself into ascertaining which of these could be used in a medium containing about 10 per cent. acetic acid, as that was practically the maximum dilution attainable in any but the permanganate method on diluting the original glacial acetic acid medium. Further, the method should be accurate in the presence of the relatively very large excess of nitric acid.

(a) The tintometric method with *m*-phenylenediamine failed completely. Compared with aqueous solutions of nitrite, solutions in dilute acetic acid (5 to 40 per cent.) showed paler tints. The discrepancy is progressively greater as the proportion of acetic acid is increased. It should be noted that the mere addition of acetic acid after diazotisation does not in itself affect the tint.

(b) The Dunstan-Dymond method. In the presence of small quantities of acetic acid (5 to 10 per cent.) this method gives high results. Moreover, in the very dilute solutions which we required, the manipulative difficulties are excessive.

(c) The method devised by Maderna and Coffetti (*Gazetta*, 1907, **37**, 595), which is based on the reduction in a Lunge nitrometer of nitrous acid to nitric oxide by potassium ferrocyanide and citric or acetic acid—an environment in which nitric acid is stable—was found to give excellent results in the analysis of fuming nitric acid, which was neutralised before introduction into the nitrometer, with slight excess of sodium hydroxide. The solubility of the nitric oxide in the more concentrated acetic acids, which were unavoidable in this method, rendered it inaccurate.

(d) In Raschig's method we found a perfectly satisfactory means of estimating minute quantities of nitrous acid in acetic acid solution. The following procedure was finally adopted :

A given volume of the acetic acid solution, 10 to 30 c.c., was added drop by drop, over a period of four minutes, to a mixture of about 20 c.c. of $\frac{N}{10}$ permanganate, 5.5 c.c. of 10 per cent. sulphuric acid and 320 c.c. of water. The permanganate should be about double that required for the oxidation of the nitrous acid; the sulphuric acid is nearly the minimum quantity required for this dilution; the nitrous acid, when added to the mixture, should not be below a dilution of 1 in 20,000. The mixture is allowed to stand for fifteen minutes, and then excess (about 8 to 9 c.c. of a 2.5 per cent. solution) of potassium iodide introduced, and the iodine titrated with $\frac{N}{20}$ of thiosulphate. The time of addition of the acetic acid solution could be considerably shortened without materially affecting the accuracy, but the fifteen minutes' standing is a minimum. The following numbers illustrate the results of determinations of nitrous acid in fuming nitric acids :

Percentage of Acetic Acid in the Permanganate Mixture.	C.c. of $\frac{N}{10}$ KMnO_4 used in oxidising Nitrous Acid.	Grms. of HNO_2 in 100 c.c. of fuming Nitric Acid.
5 ...	8.38 ...	1.97
5 ...	8.48 ...	1.99
10 ...	8.44 ...	1.98
10 ...	8.50 ...	1.99

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The procedure we adopted is as follows : To an aliquot part of the acetic acid solution, which is placed in a glass dish, covered by a clock-glass, a slight excess (5 to 25 per cent.) of $\frac{N}{10}$ potassium carbonate solution is cautiously added. The liquid is then evaporated on the water-bath until no odour of acetic acid remains, the clock-glass being left on the dish. The slightly moist solid is then transferred by a spatula to the cup of a Lunge nitrometer. The spatula is then washed with 0.3 c.c. of water into the cup, and the liquid drawn into the tube. Five c.c. of pure concentrated sulphuric acid (96.6 per cent.) are poured into the glass dish, when the all but negligible residue is dissolved, and then introduced into the nitrometer. It was found by trial that 4.5 c.c. of the 5 c.c. of the sulphuric acid used reached the nitrometer tube. This proportion of water and acid gave a concentration of 93.2 per cent. in the nitrometer. In shaking, etc., we followed the directions which Marquayrol and Florentin (*ANALYST*, 1911, **36**, 243) recommend in their recent critical study of the Lunge method. It was found that, after two of the shakings described by these authors,

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occupying one minute each, the maximum volume of gas was obtained. In calculating the results, the nitric oxide absorbed by the sulphuric acid, as given by Lunge, was allowed for, namely, 0.15 c.c. for 5 c.c. of sulphuric acid.

This method was tested by blank experiments (a) with potassium nitrate, (b) with mixtures of potassium nitrate and nitrite.

(a) On evaporating pure potassium nitrate with acetic acid on the water-bath, no nitric acid was lost, since no acetic acid was recognisable in the residue by any of the usual qualitative tests. The following numbers illustrate the results :

C.c. of Acetic Acid.	KNO ₃ used.	C.c. of NO.	KNO ₃ found.	Percentage Error.
5	0.1188	25.81	0.1180	0.7
5	0.1192	25.94	0.1181	0.95
5	0.1185	25.84	0.1175	0.80

(b) Mixtures of potassium nitrate and nitrite were evaporated with glacial acetic acid. The residue gave no trace of the reactions of nitrous acid. Quantitative determinations of the nitrate showed that no nitrite had been oxidised to nitrate.

C.c. of Acetic Acid.	Potassium Nitrite as a Percentage of Nitrate.	KNO ₃ used.	KNO ₃ found.	Percentage Error.
5	2.5	0.1160	0.1147	1.1
5	2.5	0.1160	0.1156	0.36
5	9.48	0.1160	0.1147	1.1

A comparison of determinations of the concentrations of a fuming nitric acid by direct titration, and by this method, shows that, with these quantities, there is a constant error, probably manipulative, of about 0.7 per cent.; the addition of this loss would not be unjustifiable.

THE STABILITY OF NITRIC AND NITROUS ACIDS IN ACETIC ACID SOLUTION.

For testing the stability of nitric and nitrous acids in acetic acid solution, we used the purest glacial acetic acid, which is not attacked by chlorine in the dark (Orton, Edwards and King, *J. Chem. Soc.*, 1911, **99**, 1178).

At first the solutions were carefully preserved in the dark, but, as we found later, exposure to diffused light has no perceptible influence. When nitrous acid is present, the original colour of the solution fades quickly to a scarcely perceptible tint. Concentrations of nitric acid, varying from 1 to 7 per cent., were used. As the nitrous acid disappears, the nitric acid increases somewhat in quantity. No reduction of the nitric acid was observed in any of the solutions which were prepared. The following numbers will illustrate the evidence we obtained :

1. *Glacial Acetic Acid Solutions*.—(a) The solution was made up to contain 7.03 grms. HNO₃ and 0.102 gram. HNO₂ per 100 c.c. :

Time after making up.	Grms. of HNO ₂ per 100 c.c.	Grms. of HNO ₃ per 100 c.c.	
2 hours	0.084	—	—
6 "	0.069	—	—
25 "	0.048	—	—
4 days	0.021	—	—
5 " 7 hours	—	(i.) 7.198	(ii.) 7.172
7 " 1 hour	0.0123	(i.) 7.170	(ii.) 7.172
29 "	0.0026	(i.) 7.247	(ii.) 7.247

(b) The solution was made up to contain 1.0164 grms. HNO_3 per 100 c.c. :

Time after making up.	Grms. of HNO_2 per 100 c.c.	Grms. of HNO_3 per 100 c.c.	
7 days	—	(i.) 1.037	(ii.) 1.042

2. *Fifty per Cent. Aqueous Acetic Acid.*—The solution was made up to contain 3.51 grms. HNO_3 and 0.0557 gm. HNO_2 per 100 c.c. :

Time after making up.	Grms. of HNO_2 per 100 c.c.	Grms. of HNO_3 per 100 c.c.	
2 hours	0.044	—	—
45 "	0.015	—	—
96 "	—	(i.) 3.562	(ii.) 3.565

3. *Glacial Acetic Acid Solutions exposed to Light.*—The solution was made up to contain 2.13 grms. HNO_3 and 0.03 gm. HNO_2 per 100 c.c. :

Time of exposure to light.	Grms. of HNO_2 per 100 c.c.	Grms. of HNO_3 per 100 c.c.	
10 hours	0.009	(i.) 2.136	(ii.) 2.128
20 "	0.009	—	—
64 "	—	(i.) 2.167	(ii.) 2.172

The solution was made up to contain 7.02 grms. HNO_3 and 0.100 gm. HNO_2 per 100 c.c. :

Time of exposure to light.	Grms. of HNO_2 per 100 c.c.	Grms of HNO_3 per 100 c.c.	
32 hours	0.052	(i.) 7.11	(ii.) 7.15

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