XXXVI.—*Velocity of Decomposition and the Dissociation Constant of Nitrous Acid.*

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SOME of the previous workers in this field have prepared nitrous acid by the interaction of silver nitrite and hydrochloric acid (Schümann, *Ber.*, 1900, **33**, 533; Veley, *Proc. Roy. Soc.*, 1893, **52**, 28). The disadvantage of this method is obvious, as, on account of the very sparing solubility of silver nitrite in water, only an extremely dilute solution of nitrous acid could be obtained; thus, at 18°, the solubility of silver nitrite in water is only 0.02067 gram-molecule per litre (Naumann and Rücker, *Ber.*, 1905, **38**, 2293). Veley obtained an acid of comparatively higher strength by suspending an excess of silver nitrite in water and treating it with aqueous hydrochloric acid.

In the present series of experiments, barium nitrite was substituted for silver nitrite, as there were several advantages in its favour. In the first place, on account of its high degree of solubility, solutions of nitrous acid of the strength required for the experiments could readily be obtained by treating it with its equivalent of dilute sulphuric acid; not only could double decomposition be brought about at once, but as the heavy barium sulphate settles down within an hour or so, a clear solution of

nitrous acid of known strength could be secured, whereas by suspending silver nitrite in water, as in Veley's method, an acid of uncertain strength is obtained, since the reaction in this case is never complete, the insoluble coating of silver chloride, once formed, protecting the enclosed nitrite from further action. Veley had thus to determine the strength of the nitrous acid by titration with potassium permanganate. By using barium nitrite, however, the strength of the corresponding nitrous acid set free could be at once ascertained, and titration with permanganate was resorted to only as an additional check.

The preparation of barium nitrite has already been described by one of us (Rây, T., 1905, **87**, 177). The salt was further purified by fractional crystallisation.

The estimation of nitrous acid was made both by the carbamide and the permanganate method. Preference was given to the latter, as it has been found to be more trustworthy. The velocity constant of decomposition at temperatures varying from 0° to 40° has been studied, and the dissociation constant of the acid at 0° determined.

Estimation of Nitrous Acid by the Carbamide Method.

The decomposition of free nitrous acid by carbamide presented some anomalies without any apparent reason. The experiments were performed in a Crum-Frankland nitrometer. It was found that when the nitrous acid solution was at a temperature lower than that of the room (21°), the evolution of nitrogen was extremely slow, no matter how much carbamide was added. Addition of sulphuric acid and constant shaking were found to be necessary to hasten the reaction even when the temperature had risen to 21° . The decomposition, however, was not complete until twenty minutes to half an hour had elapsed. The estimation of nitrous acid in nitrites did not present any such difficulty.

Five c.c. of $N/32$ -nitrous acid (prepared by double decomposition of equal volumes of $N/16$ -barium nitrite and $N/16$ -sulphuric acid at 0°) gave 1.9 c.c. N_2 (moist) at 24° and 760 mm. pressure. $N=11.84$; $Ba(NO_2)_2$ requires $N=11.34$ per cent.

Rate of Decomposition of Nitrous Acid.

Veley's method (*loc. cit.*) was found to yield accurate results. A known volume of nitrous acid solution at 0° was run into a known volume of permanganate solution acidified with sulphuric acid. The vessel was kept covered for half an hour, so as to ensure complete oxidation of the nitrous acid. Potassium iodide

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was now added in excess, and the amount of iodine liberated was titrated with *N*/10-thiosulphate solution.

Ten c.c. of *N*/32-nitrous acid required for complete oxidation 6.26 c.c. *N*/10-potassium permanganate. $\text{HNO}_2 = 0.01460$ gram; Calc., $\text{HNO}_2 = 0.01468$ gram.

Rate of Decomposition of Nitrous Acid.

The rate of decomposition was determined at 0°, 21°, and 40°. Equal volumes of *N*/16-barium nitrite and *N*/16-sulphuric acid were separately allowed to attain the temperature of the experiment before they were mixed together, the temperature being kept constant throughout. Barium sulphate gradually settled, and the clear, free nitrous acid was estimated at intervals by Veley's method. From the rate of decomposition, the velocity constants for the three temperatures were calculated according to the equation $k = 1/t \log c_0/c_1$, which holds good for unimolecular reactions.

TABLE I.

At 0°.		
Time in minutes.	Grams of HNO_2 in 10 c.c.	<i>k</i> .
0	0.01468	—
90	0.01363	0.00014
150	0.01317	0.00013
210	0.01224	0.00015
		Mean 0.00014

TABLE II.

At 21°.		
Time in minutes	Grams of HNO_2 in 10 c.c.	<i>k</i> .
0	0.01468	—
90	0.01292	0.00024
135	0.01247	0.00021
195	0.01175	0.00021
		Mean 0.00022

TABLE III.

At 40°.		
Time in minutes	Grams of HNO_2 in 10 c.c.	<i>k</i> .
0	0.01468	0.00058
67	0.01196	—
120	0.01020	0.00057
180	0.00853	0.00057
		Mean 0.00057

Veley has noticed that there is always an equilibrium between nitric acid and nitrous acid in a mixture, the ratio being generally

15.5:1. The unimolecular reaction holds good, since the equilibrium ratio nitrous acid:nitrous acid is very small.

An attempt was made to determine the maximum possible concentration of nitrous acid at 0° . $N/5$ -Solutions of barium nitrite and sulphuric acid were separately cooled to 0° , and then mixed together in equal volumes. The vessel was now placed in a bath of ice and salt, and ice was allowed to freeze out of the solution. As the solution gained in concentration, bubbles began to be evolved after some time. The strength of nitrous acid in solution was determined by Veley's method. The maximum concentration obtained was $0.185N$.

The Dissociation Constant of Nitrous Acid.

The dissociation constant of nitrous acid was first determined by Schumann (*loc. cit.*), who measured the conductivity of mixtures of sodium nitrite and hydrochloric acid in equivalent proportions at a dilution of 512 and upwards. The molecular conductivity of nitrous acid was obtained by deducting from the observed value the known molecular conductivity of sodium chloride. This method is, however, open to objection. Sodium chloride is a strong electrolyte, whilst nitrous acid is a weak one, and the data obtained by the method of difference are therefore subject to large experimental errors. Blanchard (*Zeitsch. physikal. Chem.*, 1902, **41**, 681) has also determined the dissociation constant of nitrous acid by another method, based on the influence of acids on the decomposition of ammonium nitrite. He found that $0.222N$ -acetic acid has the same influence as $0.05N$ -nitrous acid. He obtained 4×10^{-4} as the dissociation constant of nitrous acid, which he believed to be 10—20 per cent. too low, that of Schumann being 4.5×10^{-4} . In view of these results, it was thought desirable to determine afresh the dissociation constant for nitrous acid. It has been observed before that a solution of nitrous acid, although not absolutely stable at 0° , yet has only a small rate of decomposition at that temperature. The conductivity measurements were therefore carried out at 0° . Twenty-five c.c. of $N/16$ -barium nitrite were poured into a closed conductivity vessel immersed in a bath of ice. When the barium nitrite solution had attained the temperature of the ice-bath it was mixed with 25 c.c. of $N/16$ -sulphuric acid, also cooled to 0° , and the conductivity determined immediately after. The whole series of measurements from dilution 32 to 1024 did not take more than forty-five minutes. That the change in conductivity due to decomposition of nitrous acid is very small within this short interval of time will be

apparent from the data in table V. The maximum error possible due to the formation of nitric acid was within +3 per cent.

The water used in these measurements was prepared by Jones and Mackay's method (*Zeitsch. physikal. Chem.*, 1894, **14**, 317) and had a conductivity of 2×10^{-6} .

Vogel's value (*Zeitsch. anorg. Chem.*, 1903, **35**, 403) for the ionic mobility of nitrosion (61.7 at 25°) was used to calculate μ_a for nitrous acid at 25°. By applying Kohlrausch's equation:

$$U_{t^{\circ}} = U_{18^{\circ}} \{1 + \alpha(t^{\circ} - 18^{\circ}) + \beta(t^{\circ} - 18^{\circ})^2\}.$$

μ_a for nitrous acid at 0° was found to be 256. Several series of conductivity determinations were carried out which yielded concordant results.

TABLE IV.

Molecular Conductivity of Nitrous Acid at 0°.

<i>v.</i>	μ .	<i>k.</i>
32	33.5	6.15×10^{-4}
64	45.8	6.10×10^{-4}
128	62.0	6.04×10^{-4}
256	82.5	5.98×10^{-4}
512	107.0	5.94×10^{-4}
1,024	138.0	6.10×10^{-4}
		Mean $k = 6.00 \times 10^{-4}$

TABLE V.

Influence of Time on the Molecular Conductivity of Nitrous Acid at 0°.

V = 32.

Time in minutes	0	60	120	180
μ	33.5	34.1	35	36.2

The observed values for μ lies within ± 2 per cent. of the real value, and therefore the probability of maximum error is $(+3 \pm 2)$ per cent. It will be noticed that the value for K_{HNO} given above is about 33 per cent. greater than that of Schumann and Blanchard.

Summary and Conclusion.

From the foregoing investigation it would appear that:

1. The velocity constant of decomposition follows the unimolecular reaction, the constant being 0.00014 at 0°, 0.00022 at 21°, and 0.00057 at 40°.
2. The maximum concentration of nitrous acid available at 0° is 0.185*N*.
3. The dissociation constant of nitrous acid at 0° is 6×10^{-4} .

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