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## THE ACTION OF NITROGEN ON WATER VAPOR AT HIGH TEMPERATURES.

BY O. F. TOWER.

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THAT nitrogen unites with oxygen at high temperatures has been known for a long time. Recently, the equilibrium between these gases has been studied by Nernst, who has shown that the reaction follows the law of mass action. He passed air through an iridium tube heated to about  $1800^{\circ}$ , and determined the quantity of nitric oxide formed.<sup>1</sup> The percentage of gas converted into nitric oxide at certain absolute temperatures and at atmospheric pressure is given in Table I.

TABLE I.

T.	NO formed. Per cent.
1500	0.10
2000	0.61
2500	1.79
3000	3.60

Nernst and von Wartenberg<sup>2</sup> have also recently shown that the dissociation of water vapor at high temperatures into hydrogen and oxygen takes place quantitatively, according to the following thermodynamical equation:

<sup>1</sup> *Nachrichten Kgl. Ges. Wiss.*, Göttingen, 1904, Heft 4.

<sup>2</sup> *Ibid.*, 1905, Heft 1.

$$\log \frac{2x_1^3}{\left(2 + \frac{x_1}{100}\right) \left(1 - \frac{x_1}{100}\right)^2} =$$

$$11.51 - \frac{25030}{T} + 2.65 \log \frac{T}{1000} - 0.00055 (T - 1000).$$

T indicates the absolute temperature and  $x_1$  the percentage of dissociation. The degrees of dissociation at a few temperatures and atmospheric pressure as calculated from the above equation are given in Table II.

TABLE II.

T.	Water dissociated. Per cent.
1000	0.000031
1500	0.022
2000	0.561
2500	3.43
3000	12.9

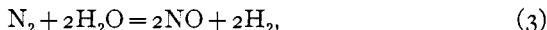
The equations for these two reactions are:



and



The sum of these two equations gives



which shows that nitrogen must react on water vapor at high temperatures to a certain extent.<sup>1</sup> The constants of the first two reactions at equilibrium can be calculated from the values of Tables I and II for 2000° C. (2273° abs.) and are as follows:

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = K_1 = 8.5 \cdot 10^{-4};^2$$

$$\frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} = K_2 = \frac{P}{RT} \times 2.9 \times 10^{-6}.$$

The product of these two equations gives the condition of equilibrium of the third reaction at the same temperature, *viz.*:

$$\frac{[\text{NO}]^2[\text{H}_2]^2}{[\text{N}_2][\text{H}_2\text{O}]^2} = K_1K_2 = K = \frac{P}{RT} \times 2.5 \times 10^{-9}. \quad (4)$$

To calculate the completeness of the reaction, assume a gaseous mixture three-fourths of which is nitrogen and one-fourth water vapor, and let the total concentration before the reaction be repre-

<sup>1</sup> A suggestion of this is to be found in the Dissertation of Löwenstein, Göttingen, 1905.

<sup>2</sup> This nomenclature is used to indicate the concentrations of the bracketed substances.

sented by 1. Also let  $x$  represent the amount of nitric oxide formed. Then the total concentration after the reaction will be  $1 + \frac{x}{2}$ , and the concentrations of the different gases will be the following:

$$[\text{NO}] = [\text{H}_2] = \frac{P}{RT} \frac{x}{1 + \frac{x}{2}} = \frac{P}{RT} \frac{2x}{2+x}$$

$$[\text{N}_2] = \frac{P}{RT} \frac{0.75 - \frac{x}{2}}{1 + \frac{x}{2}} = \frac{P}{RT} \frac{1.5 - x}{2+x}$$

$$[\text{H}_2\text{O}] = \frac{P}{RT} \frac{0.25 - x}{1 + \frac{x}{2}} = \frac{P}{RT} \frac{0.5 - 2x}{2+x}$$

Substituting these values in equation (4), we have

$$\frac{P}{RT} \frac{16x^4}{(2+x)(1.5-x)(0.5-2x)^2} = \frac{P}{RT} \times 2.5 \times 10^{-9}. \quad (5)$$

In the denominator  $x$  is so small compared with the other numbers that it can be neglected without sensible error. We, therefore, obtain

$$x = 0.0033,$$

which means that theoretically 0.33 per cent. of the gaseous mixture can be converted into nitric oxide. Similar calculation for 3000° C. gives 1.5 per cent. for the amount of nitric oxide formed.

#### QUALITATIVE EXPERIMENTS.

The first experiments were made simply to see whether nitric oxide could be obtained in measurable quantity, and if so, whether it was accompanied by an equivalent quantity of hydrogen.

The nitrogen for all the experiments was prepared by heating a solution of ammonium sulphate and potassium nitrite. The gas was collected in a gasometer and was purified just before use by passing it through sulphuric acid and over glowing copper.

The method employed for detecting nitric oxide was that of Lunge, and consisted in admitting oxygen to the mixed gases, thus converting nitric oxide into nitrogen peroxide, which latter was absorbed by sulphuric acid. The sulphuric acid was afterwards shaken with mercury in a Lunge eudiometer. This lib-

erated nitric oxide, the volume of which could thus be easily determined. Sulphuric acid of 85 per cent. strength was used for this purpose, as nitric oxide is not appreciably soluble in acid of this concentration.

A mixture of nitrogen and water vapor was first passed over a Nernst light, but no appreciable quantity of nitric oxide was obtained. The temperature in this case was about 2000°. The failure to obtain nitric oxide was therefore probably due to the fact that only a small fraction of the gas came into contact with the hot body.

The method, which was finally found to yield measurable quantities of nitric oxide, consisted in passing nitrogen and water vapor over a spark gap. The nitrogen was saturated with water vapor by bubbling through water at a given temperature. The mixed gases then passed directly into the spark bulb. This was 3 cm. in diameter and was provided with platinum electrodes, the terminals of which were 0.7 cm.<sup>1</sup> apart. To avoid the condensation of moisture, the bulb and the tubes leading to and from it, were kept warm. Immediately after the bulb came a small Winkler drying-tube containing sulphuric acid. This tube will hereafter be designated as tube i. Next came the oxygen inlet and then a larger Winkler tube with sulphuric acid, tube ii. After this, in some of the experiments, was another sulphuric acid tube, tube iii. The object of tube i was to remove most of the water vapor and also to prevent oxygen from diffusing backwards into the spark bulb, which would otherwise happen, especially when the velocity of the gases was small. Tube ii served to absorb nitrogen peroxide, and tube iii was a check to show whether this absorption was complete.

In these experiments with the spark bulb, hydrogen was also determined in the following manner. The gases from tube iii were passed over hot copper oxide and then through another sulphuric acid drying-tube, tube iv. The copper oxide acted simply as a catalytic agent, for oxygen was already present in sufficient excess to oxidize the hydrogen. From the increase in weight of tube iv the amount of hydrogen could be easily calculated.

The results with this apparatus are given in Table III. The water through which the nitrogen bubbled was kept at 83° during

<sup>1</sup> Sparks across shorter gaps, *e. g.*, 0.4 cm. yielded only traces of nitric oxide.

these experiments. At this temperature water has a vapor-pressure of half an atmosphere. Therefore, the gas entering the spark bulb consisted of equal volumes of nitrogen and water vapor.

TABLE III.

Nitrogen passed through. Liter.	Length of experiment. Hours.	Water found. Mg.	Nitric oxide found. Cc.	Nitric oxide calculated from water. Cc.
1.0	2	2.3	2.4	3.0
1.25	2	1.6	2.1	2.1
0.85	2	3.6	4.1	4.8
1.5	2	3.1	3.8	4.1

Tube iii was used in the first two of these experiments, but as no nitric oxide was found in it, it was not used in Expts. 3 and 4. No nitric oxide was found in tube i in any of the experiments, which shows that the gases entering the spark bulb were free from oxygen. The amounts of nitric oxide found and the amounts calculated from the water agree sufficiently to show that nitric oxide and hydrogen are produced in equivalent quantities, and that the reaction, therefore, follows the equation given above. Since the temperature was unknown in these experiments, we are unable to make any quantitative use of the results. The reaction, however, probably had not reached an equilibrium, for the amounts of nitric oxide do not depend on the quantity of gas passed through, but rather on the steadiness of the sparks. The sparks were steadier in the last two experiments.

#### QUANTITATIVE EXPERIMENTS.

In order to determine whether the reaction attains the theoretical equilibrium, use was made of an electrically heated iridium tube, which was kindly placed at my disposal for this purpose by Professor Nernst. This tube had been used by Professor Nernst for similar experiments and reference is made to his papers for further details.<sup>1</sup>

The iridium tube occupied the position of the spark bulb of the preceding experiments. Its temperature, which was maintained at about 2000°, was determined by observation of the interior by means of a Wanner pyrometer immediately before and after each experiment. The mean of these two readings was considered to be the temperature of the experiment. In

<sup>1</sup> *Z. Elektrochem.*, 1903, 623; also *Nachrichten Kgl. Wiss.*, Göttingen, 1904, Heft 4; and also a paper of Jellinck soon to appear in *Z. anorg. Chem.*

these experiments the water through which the nitrogen bubbled was kept at 66° so that the gases entering the iridium tube were in the ratio of 3 volumes of nitrogen to 1 volume of water vapor. The results of the experiments are shown in Table IV.

TABLE IV.

Expt. No.	Temp. °C.	Length of experiment. Hours	Nitrogen passed through. Liter.	Total gas volume $N_2 + H_2O$ . Liter.	Liter per hour.	Nitric oxide found.			
						I. Cc.	II. Cc.	I+II. Cc.	Per hour. Cc.
1	2009	1.07	2.00	2.67	2.50	0.00	0.50	0.50	0.47
2	2000	1.02	0.7	0.93	0.91	0.22	0.48	0.70	0.69
3	1978	1.50	0.45	0.60	0.40	1.60	1.32	2.92	1.95
4	1987	1.50	0.40	0.53	0.35	0.72	0.69	1.41	0.94
5	1974	0.97	1.55	2.07	2.13	0.14	1.18	1.32	1.36

Under "Nitric oxide found," I indicates the nitric oxide found in tube i, II that found in tube ii, and I+II the sum of these. It will be observed that these experiments differ strikingly from those with the spark bulb, in that nitric oxide was found in tube i in all except the first experiment. This finds its explanation for the most part in the fact that some hydrogen diffused through the hot iridium tube leaving oxygen in excess, which oxidized part of the nitric oxide to nitrogen peroxide. In addition, in Expts. 2 and 3 a small leak was found in the tube, which may have admitted some air. These experiments are, therefore, less trustworthy, but the quantity of air admitted could not have been great, else all the nitric oxide would have been converted into nitrogen peroxide and absorbed in tube i.

That hydrogen actually does diffuse through hot iridium was shown by passing water vapor through the iridium tube first at 1000° and then at 2000°. The issuing gases were tested for excess of oxygen by exploding with hydrogen in a eudiometer. No diffusion could be detected at 1000°, but at 2000° considerable amounts were obtained, as is shown in Table V.

TABLE V.

Water passed through. Gram.	Length of experiment. Minutes.	Oxygen in excess. Cc.	Water passed through. Gram.	Length of experiment. Minutes.	Oxygen in excess. Cc.
1.00	1.25	0.75	1.10	5.0	1.7
1.00	1.25	0.70	1.35	5.0	2.9
0.95	1.25	0.85	0.80	5.0	1.5
Mean, 0.98	1.25	0.77	1.08	5.0	2.1

The water vapor was passed through at two different speeds. It is seen that the amount of hydrogen which diffuses increases

as the speed of the water vapor diminishes. Since water vapor is about 2 per cent. dissociated at  $2000^{\circ}$ , 1 gram of water would yield 12 cc. oxygen (room temperature), while the average amount found at the smaller speed was 2.1 cc., about 16 per cent. of the possible quantity. Since the rate at which the gases pass through the iridium tube in the nitrogen water vapor experiments was on an average only about one-twentieth of the slower rate of Table V, the diffusion would be somewhat greater, perhaps 50 or 60 per cent. of the possible quantity. But since only one-fourth of the gas was water vapor, we may estimate the oxygen left in excess under the conditions of the experiment at about 15 per cent. of the possible free amount. This is a sufficient quantity to account for the finding of nitric oxide in tube 1, and yet not enough to cause any great displacement of the equilibrium of the reaction. That no nitric oxide was found in this tube in Expt. 1 may be because the speed of the gases was greater in this case.

To find whether the results of Table IV throw any light on the equilibrium of the reaction, Expts. 1, 4 and 5, those during which there was no leak in the apparatus, have been recalculated on the basis of 1 liter of gas. The results are given in Table VI.

Number of experiment.	One liter gas passed through in $x$ minutes.	NO per liter. Cc.
1	24	0.19
5	28	0.64
4	170	2.66

The reaction, it is seen, proceeds very slowly, owing probably to the inertness of nitrogen and to the small concentration of the oxygen. According to the results of the table, the reaction had not reached equilibrium even in Expt. 4. Extrapolating for infinitely slow passage of the gas, we obtain 4.0 cc., approximately, as the amount of nitric oxide per liter. The theoretical value calculated is 3.3 cc. per liter (see above). The agreement is good, but the value extrapolated is somewhat uncertain both on account of the extrapolation and on account of the diffusion of hydrogen through hot iridium.

The reaction here investigated is interesting, chemically, because it shows that water is reduced by nitrogen at high temperatures. The reduction can be increased at will by increasing the quantity of nitrogen.

This research was undertaken at the suggestion of Professor Nernst, and it is a pleasure to express my gratefulness for his help and constant interest in the work. I am also indebted to Dr. von Wartenberg for the results on the diffusion of hydrogen through iridium.

PHYSICAL-CHEMICAL INSTITUTE OF THE UNIVERSITY OF BERLIN,  
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### COLUMBATES.<sup>1</sup>

BY M. HUME BEDFORD.

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AN EXAMINATION of the literature relating to the columbates of the alkali metals shows decided variations in the ratios existing between the base and the acid. For example, the following sodium columbates have been recorded:

- (1)  $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$  or  $9\text{H}_2\text{O}$  (Rose);
- (2)  $3\text{Na}_2\text{O} \cdot 2\text{Cb}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$  (Rose);
- (3)  $3\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5$  (Rose);
- (4)  $4\text{Na}_2\text{O} \cdot 5\text{Cb}_2\text{O}_5$  (Rose);
- (5)  $3\text{Na}_2\text{O} \cdot 4\text{Cb}_2\text{O}_5 \cdot 21\text{H}_2\text{O}$  (Hermann).

The first salt was obtained by fusing columbic oxide with sodium hydroxide in a silver crucible. Rose pronounced it the best crystallized and most stable of the columbates. The second salt was obtained simultaneously.

When columbic oxide was fused for some time with sodium carbonate the third salt was formed. The fourth salt was described as the only acid salt of exact ratio, while Hermann obtained the fifth salt upon the addition of an excess of sodium hydroxide to a solution of potassium columbium oxyfluoride.

It was resolved, having an abundance of the latter compound, to repeat Hermann's experiment. Accordingly, 50 grams of potassium columbium oxyfluoride were dissolved in a liter of hot water and to this solution a concentrated solution of 150 grams of sodium hydroxide was added. A white, finely divided precipitate separated. It was filtered out and washed with cold water until the filtrate became milky. It was then dried as far as possible by suction and was recrystallized three times from dis-

<sup>1</sup> From the author's thesis for the Ph.D. degree.