XL.—Action of Heat on Peroxide of Nitrogen.

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HITHERTO the decomposition of peroxide of nitrogen by heat has been studied only for temperatures below 180°. The change which this substance undergoes when heated from 4.2-97.5° was observed by Playfair and Wanklyn (J. Chem. Soc., 1862, 15, 156), who found that the density of the gas for the higher temperature is not far removed from that calculated from the formula NO_2 , whilst that found for the lower temperature corresponds more nearly with the formula of the Deville and Troost (Compt. rend., 64, 237) have compound N₂O₄. also shown that at a temperature of 140°, N₂O₄ is completely dissociated into NO2, whilst Nauman (Ber., 1878, 2045) observed that at constant temperatures the amount of dissociation increases with diminished pressure, and for equal pressures increases with rise in Again F. and L. Natanson (Ann. Phys. Chem., 1886, temperature. 606) have found that at -12° , and at a pressure of 115.4 mm. the vapour-density of the gas is 42.54, that calculated for N_2O_4 being 46.

It has been observed by Ramsay (Trans., 1885, 678) that nitric peroxide becomes colourless at a temperature below a red heat. The author finds that when the peroxide is heated in a glass tube over a Bunsen flame, the gas becomes almost colourless at a temperature a little above 500°; on allowing the tube to cool, the gas passes through a series of colour-changes similar to those observed on heating the tube, and finally assumes its original tint at the temperature of the air. A similar experiment was made with the gas under very great pressure; it was found that the amount of dissociation was diminished by increased pressure, for in this case no diminution in the intensity of the dark-red colour of the gas was perceptible at 500°.

When one limb of a bent glass tube containing the gas was strongly heated, whilst the other limb was immersed in a freezing mixture, a dark-blue liquid condensed in the cooled limb, while the liquid which condensed before the tube was heated was of a pale-yellow colour. On warming the tube gently, the blue colour of the liquid was changed to green, and finally became red; the blue colour could be again restored by cooling the tube in a freezing mixture, even after the rest of the tube had become cold. As this blue liquid is known to be nitrogen trioxide, produced by the union of nitric oxide with nitric peroxide, its formation appears to be a conclusive proof of the presence NOL. LL. 2 E of nitric oxide as one of the dissociation products of the peroxide; it would appear also that the combination of nitric oxide with nitric peroxide takes place more readily than that of oxygen with nitric oxide, or of oxygen with the trioxide, provided there is an excess of the peroxide.

When the tube was opened immediately after heating, free oxygen was found to be present on testing the gas in the usual way. An experiment was then made to ascertain whether any further decomposition of the gas took place, and for this purpose a hard glass tube containing the peroxide was heated to between $600-700^\circ$, and then sealed. When the tube was opened under strong sulphuric acid, complete absorption of the gas took place, showing that no further decomposition of the nitric oxide had occurred.

It would appear then-

1. That nitric peroxide dissociates when heated into nitric oxide and free oxygen.

2. That nitric oxide, in presence of a large excess of peroxide, unites with the latter to form the trioxide more readily than it does with oxygen to form the peroxide; and that, under these conditions, recombination of nitric oxide with oxygen is complete only after some time, even at ordinary temperatures.

A series of quantitative experiments were then made, in order to ascertain the amount of dissociation which the peroxide undergoes at different temperatures. The peroxide was prepared by acting on arsenic trioxide with nitric acid to which an excess of strong sulphuric acid has been added, as recommended by Groves. The materials were heated gently in a retort with a drawn-out neck which dipped into a flask cooled in a freezing mixture, the condensed gas, which consisted of peroxide of nitrogen together with a considerable quantity of nitric acid, was then distilled by means of a water-bath, and the peroxide which passed over was condensed in a two-necked bulb containing phosphoric anhydride cooled in a freezing mixture.

When vapour ceased to distil over, the receiver was sealed, and shaken to bring the liquid in contact with the phosphoric anhydride, and allowed to stand for 12 hours; in order to remove all traces of impurities, it was distilled three times from fresh phosphoric anhydride, the gas being led through a **U**-tube containing the same substance. The liquid so obtained was sealed up in a bulb, and at ordinary temperatures was of a clear red colour, changing to a pale-yellow tint on being cooled. All connections of cork or india-rubber were avoided, the different parts of the distilling apparatus being sealed together. The vapour-density of the peroxide was determined by "Dumas' method," and when temperatures not higher than 358° were required the bulb was heated in the vapours of the following substances, which were known to be pure:---

Chlorobenzene, b. p. at 760 mm	132·1° C.
Aniline, b. p. at 760 mm	184.5
Methyl salicylate, b. p. at 760 mm	223.0
Bromonaphthalene """	280.5
Triphenylmethane ", ",	358.0

For higher temperatures, Ramsay and Young's method was adopted, that is to say, the required temperature was obtained by causing the substance to boil under known pressures higher or lower than that of the atmosphere; in this case, sulphur was used, the boiling points of which, under pressure between 500 and 2000 mm., has been accurately determined by Regnault.

The apparatus in which the bulb was heated consisted of an iron pot, A (see Fig. 1), having a grooved flange on the open end. This vessel was of such a size that the experimental bulb, B, could be suspended in it without coming in contact with the sides; the lid, C, was provided with a projection, which fitted into the grooves on the flange to which it was screwed by means of clamps; a wide glass tube, D, passed through the centre of the lid; this tube was drawn out at E into a narrow neck which was fitted with a stout piece of indiarubber tubing, through which passed the stem, H, of the experimental bulb, the two joints being carefully wired; a side tube was sealed on to D at F, which was connected with the air-pump I, and pressure gauge J. As far as possible the lid and glass tube were made airtight by means of white lead, but in order to avoid errors through leakage, a large receiver was connected with the apparatus; by this means the alteration in pressure produced by leakage was reduced to a minimum. To use the apparatus, the bulb was suspended in its place in the pot, which was previously charged with fragments of sulphur, the lid was then screwed down, and a sufficient amount of the cooled peroxide was poured into the bulb; next the required pressure was obtained by means of the air-pump, and the apparatus was heated till the sulphur boiled. As soon as the vapour appeared in the glass tube, the stem of the bulb was sealed off in the blowpipe, and the apparatus allowed to cool, the lid was then unscrewed, and the bulb removed, cleaned, and weighed.

As it was often a considerable time before the sulphur vapour rose in the tube, the chance of diffusion of the peroxide from the neck of the bulb was avoided, by fitting a second bulb, G, over the stem, which was drawn out to a long capillary at one end, this bulb remained full of the peroxide during the experiment.

The highest temperature that could be conveniently obtained by

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Vapour-densities of Nitric Peroxide at Temperatures between 619.5° and 130°.

	ON	PER	:03	XII	ΟE	01	F .	NI	TRO	GEN	I.					40
Per cent. of NO ₂ molecules decomposed.	100.00	58·71 55·84	55 <b>·</b> 00	57.84	50.40	43 28	34.48	35 05	17 -09	13.57	13.10	5 .26	4.17	5.80	4.33	]
Vapour-density.	15 • 300	17 ·780 17 ·980	18.040	17.840	18.370	18 .980	19.630	19.570	$21 \cdot 190$	21.530	21.590	22.400	22.520	22 ·350	22.450	23 • 260
Volume of gas in c.c.	19-57	58 · 65 58 · 47	86.92	87.72	61 63 01 222	91 95 89-95	92.99	97.34	78.34	115.82	116.56	84-46	130.97	106 15	143 .47	155 • 48
Weight of gas in grams.	0 •02682	0.09320 0.09361	0.14015	0.13988	61101.0	0.11526	0.16304	0.17025	0.14833	0.22290	0:22557	0.19580	0.26411	0.21210	0.28743	0.32320
Barometer.	mm. 760 · 00	$742 \cdot 00$ $743 \cdot 00$	00.194	763 -50	755 -50	744.15	739.68	740.00	769.50	$733 \cdot 00$	741.50	755 .60	747.50	757 ·10	$752 \cdot 00$	718 • 50
Temperature.	619°50	494.40 494.40	490.00	$485 \cdot 40$	466 30	447 -00	$423 \cdot 20$	390 ·00	358.00	$278 \cdot 40$	279 .20	222 -50	$222 \cdot 10$	184.10	184.00	130 .00
	Bulb heated in Air-bath Sulvhur boiling under	1500.00 mm. pressure	1422.80 ", ",	1325.00 ,, ,,	1000.00 ,, ,,	744-15	500.00	272:30 ,, ,,	Triphenylmethane boiling under 769'50 mm. pressure	Bromonaphthalene boiling under 733-00 mm messure	741.50 ,, ,,	Methyl salicylate boiling under 755:00 mm. pressure	747.50 ,, ,,	Aniline boiling under 758-10 mm. pressure	752-00 ,, Č ,,	Chlorobenzene boiling under 718·50 ,,

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this method was 494.4°, that is, sulphur boiling under a pressure of 1500 mm. For higher temperatures, a cylindrical air-bath was used, and the temperature was indicated by means of an air-thermometer, which consisted of a hard glass tube drawn out into a narrow neck; the volume of this tube having been previously determined, it was suspended from the lid of the bath for 15 minutes, it was then sealed at the neck, and removed, and another tube at once substituted which contained a little of the liquid peroxide, this tube was allowed to take the temperature of the bath, and then sealed, and weighed when cold; finally the temperature was again taken by another air-tube similar to The temperature was calculated by opening the air-tubes the first. under water, from which all air had been expelled by prolonged boiling; the volume of residual air in the tubes was then found by weighing, the required data being obtained, the temperature could be calculated. Temperatures taken in this way agreed with each other within 10°, and by taking the mean of the temperatures given by several tubes, a pretty close approximation to the true temperature could be obtained. Tubes containing the peroxide, when removed from the bath heated to 620°, were perfectly colourless, the colour returning as the tubes cooled. The complete dissociation of the peroxide into nitric oxide and oxygen is represented by the equation  $2NO_2 = 2NO$ + O₂, the vapour-density of the peroxide being 23, that of the product 15.33.

From the experimental results given in the table (p. 401), it will be seen that at a temperature of 140° the vapour-density of the gas is expressed by the formula NO₂, whilst as the temperature rises, the number representing the vapour-density of the substance becomes smaller, and finally at a temperature of 619.5°, it corresponds with that of complete dissociation. It appears, then, that the peroxide undergoes dissociation in two distinct stages, giving a double dissociation curve, and that the dissociation of N₂O₄ into NO₂, which is complete at 140°, is immediately succeeded by a further dissociation of NO₂ into NO and O, which is complete below 620°. The form of the curve (Plates I and II) representing the second part of the change, is that usually exhibited by dissociating substances, the change of density being most rapid at the temperature at which half the total number of molecules of the original substance is decomposed.

In conclusion, I may add that on passing a series of electric sparks through the peroxide at the ordinary temperatures in a sealed glass tube, a white solid is deposited on the sides of the tube. This substance is also formed when the gas is heated to about 400°, also when a tube containing the liquid is exposed to sunlight for some months. No deposit was observed in tubes which had not been placed under one of these conditions.

# CURVE SHOWING VAPOUR DENSITY OF NITRIC PEROXIDE

BETWEEN 25° AND 620°



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This substance was soluble in water, from which it could be again deposited on evaporation; at a temperature between 500° and 600°, it volatilised, but as it is only very sparingly formed enough of the substance has not yet been obtained for analysis.