CXXVII.—*The Vapour Pressure of Intensively Dried Nitrogen Tetroxide.*

By JOHN WILLIAM SMITH.

THE following experiments were commenced in 1925 with a view to extend the researches on the effect of intensive drying on physical properties. At that time, the only work on nitrogen tetroxide which had been carried out in this direction was due to H. B. Baker and Mrs. Baker (J., 1912, **101**, 2339), who had found that material which had been dried for more than a year boiled above 60°, whereas the normal b. p. is 22°, but no claim to great accuracy was made for this result on account of the small quantity of liquid available.

When the present work was nearly complete, however, a communication on the same subject was published by Smits and his collaborators (J., 1926, 2657), who found that the vapour pressure of nitrogen tetroxide, unlike that of systems previously investigated, rises on intensive drying. The results of the present work, obtained quite independently, confirm those of Smits and extend them in certain directions.

EXPERIMENTAL.

Preparation of Materials.—The nitrogen tetroxide was prepared by the method of Cundall (J., 1891, **59**, 1077) in a modified form of the apparatus used by Ray (*J. Physical Chem.*, 1925, **29**, 74). It was redistilled four times in dry oxygen and stored in sealed tubes over phosphorus pentoxide.

The phosphorus pentoxide was resublimed in pure dry oxygen in a horizontal tube of " Durosil " glass, with a side tube at the end remote from the oxygen inlet. This side tube was arranged to give a good sliding fit into the U-tube or other receiver for the sublimed material. Thus only a very narrow channel was left to allow the oxygen to escape, thereby preventing any access of moisture. The tube was well dried by passing dry oxygen through it whilst hot. It was charged by the tube-and-ramrod method described by Baker (*Phil. Trans.*, 1888, *A*, **179**, 573), with the oxygen current passing in the opposite direction. Sufficient material was introduced to eliminate the necessity of recharging during the sublimation process. The inlet tube was then inserted and the receiver slipped over the side tube. The phosphorus pentoxide was heated to 300° in a current of oxygen. Under these conditions, it sublimed steadily, condensing on the cooler part of the tube in light, feathery crystals, which were transferred to the receiver by turning a spiral rake.

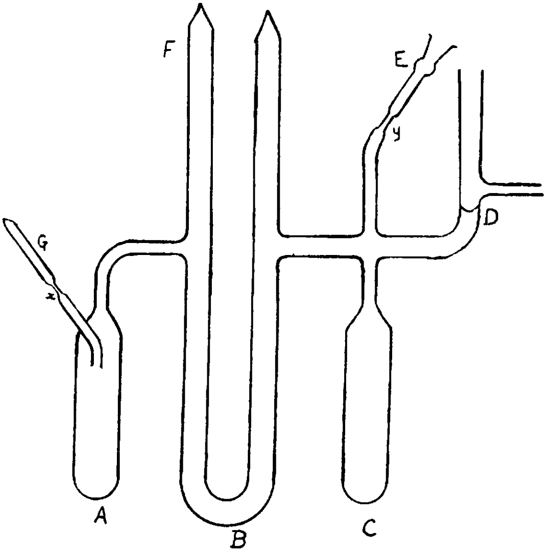
Drying Apparatus.—For a more complete investigation of the properties of intensively dried nitrogen tetroxide, it was essential to secure a more rapid method of drying than that used heretofore. For this purpose, a slightly modified form of the apparatus used by Smits and Schoenmaker in their work on sulphur trioxide (J., 1924, **125**, 2554) was adopted. This was made of selected " Durosil " glass, as free as possible from streaks and air bubbles. The drying apparatus (Fig. 1) consisted of two bulbs, *A* and *C*, connected by a U-tube, *B*. The upper part of the tube from *C* ended in a tube, *E*, which could be connected to a high-vacuum pump system through a ground glass joint, whilst a side tube led to a sealed-in glass septum, *D*.

Procedure.—After thorough cleaning, all tubes except *E* were sealed off, and *E* was connected to the vacuum-pump system. Whilst under a high vacuum, the whole apparatus was maintained at 300° for 2 days. Dry air was now admitted, and tube *E* rapidly closed.

The end of tube *F* was cut off, and phosphorus pentoxide sublimed in, as already described. Careful tapping caused the pentoxide to pass round the bend into the further limb of the U-tube. In this way, *B* was filled almost completely in about 3 hours. With the oxygen current still passing, tube *F* was drawn off. Tube *G* was then reopened, and nitrogen tetroxide introduced from a storage bulb, bulb *A* being simultaneously cooled. Tube *G* was sealed off again at the constriction *x*. The tetroxide was then cooled in liquid air, *E* being connected again to the vacuum-pump system. Tube *E* was finally sealed off at the constriction *y* under a high vacuum. The tetroxide was then allowed to become warm. Distillations were carried out by immersing one bulb in ice and the other in water at room temperature, the baths being reversed every few hours.

Experiment 1.—In this case distillations were carried out for 4 months. The time necessary for a complete distillation, about 3 hours at the outset, gradually increased as drying proceeded. Meanwhile a vapour-pressure apparatus was constructed of the form shown in Fig. 2. This consisted essentially of a long tube carrying a series of small bulbs provided with constrictions, and a bulb, *J*, to contain phosphorus pentoxide. One end of this long tube was connected to the inside of an all-glass pressure gauge of one of the forms described by Jackson (J., 1911, **99**, 1066). The outer jacket of this gauge was connected to a mercury manometer and to the vacuum-pump system. The two sides of the gauge were at first connected through a tube, *L*, with a constriction suitable for vacuum sealing. A breaker, consisting of a piece of stout capillary tubing with a short piece of soft iron inside, was now placed on the septum, *D*, of the drying apparatus. The tube *M* was then sealed to the T-piece above the septum, as shown in the diagram, and the vertical tube above the septum sealed off. The apparatus was now

Fig. 1.



evacuated to a pressure of 10^{-6} mm., the whole apparatus up to the septum being heated almost to softening point for 2 days. The top of the tube from *J* was then cut off, resublimed phosphorus pentoxide rapidly introduced, and the tube drawn off again. The evacuation and heating were then repeated for some days. The capillary, *L*, was sealed off while still under a high vacuum, and the apparatus allowed to stand for a few days. Meanwhile, the gauge was calibrated by admitting air to its outer sheath. The movement of the needle of the gauge with reference to a fixed pointer, *R*, was observed through a fixed cathetometer.

The nitrogen tetroxide was finally brought into bulb *C*, where it was frozen out in solid carbon dioxide and alcohol. The breaker was then lifted by means of an electromagnet and dropped to break the septum, thus putting the nitrogen tetroxide vapour in contact with the pressure gauge. The temperature of the tetroxide was gradually allowed to rise, the pressure being roughly balanced by admitting air to the outer sheath of the gauge. The pressure was read off on the mercury gauge, fine corrections being calculated from the deflexion of the glass gauge from the normal. In this way, the vapour pressure was determined over the range 0—15°, giving the results shown in Table I.

FIG. 2.

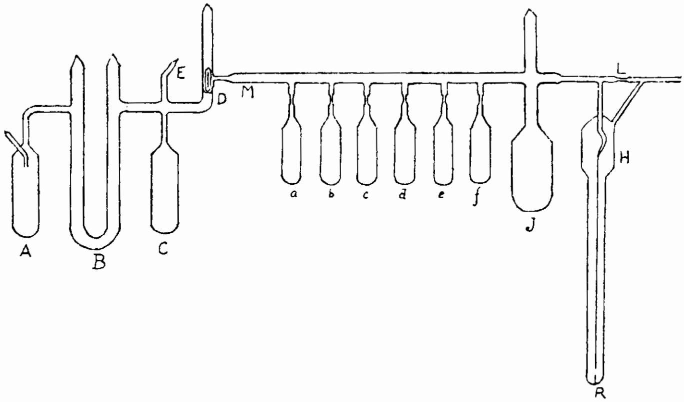


TABLE I.

	Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.
0·0°	266·3	264·0	+2·3
1·8	292·1	290·3	+1·8
8·5	411·8	408·2	+3·6
12·1°	493·7	489·5	+4·2
14·6	559·5	554·2	+5·3
15·0	571·2	565·0	+6·2

The values given under the heading "wet" were obtained by the author, using an apparatus of the type described above, with nitrogen tetroxide that had been dried for a week over phosphorus pentoxide. The results agreed very well with the values obtained by Scheffer and Treub (*Z. physikal. Chem.*, 1912, **81**, 308).

The results with the dried material all tend to show a slight rise. There are, however, a few irregularities. These were explainable after the more thoroughly dried material had been examined in Expt. 2.

Bulb *f* was then slowly cooled in a freezing mixture and finally in solid carbon dioxide and alcohol. In this way, the nitrogen tetroxide in the gauge and tubes, presumably the more volatile portion, was condensed, and slow distillation occurred from the liquid in *C*. When about 5 c.c. had condensed, *C* was also cooled in carbon dioxide and alcohol, and bulb *f* sealed off. The temperature was again allowed to rise and the vapour pressure redetermined. This operation was repeated with bulbs *e* and *d*, the vapour pressure of the residue being taken on each occasion. The results are shown in Table II.

TABLE II.

No. of fraction removed.	Temp.	Vapour pressures (mm.). Dry.	Wet.	Change.
1	0·0°	265·3	264·0	+1·3
	14·7	560·4	557·3	+3·1
2	0·0	264·6	264·0	+0·6
	14·6	558·6	554·2	+4·4
3	0·0	263·1	264·0	−0·9
	14·7	561·0	557·3	+3·7

It would appear from these results that little, if any, separation of a more volatile from a less volatile component had been effected by this means.

Expt. 2.—The apparatus and method of drying employed were exactly the same as in the previous case, but the pressure-gauge portion was somewhat simplified, and made very much more compact, the fractionating bulbs being dispensed with. Thus this portion of the apparatus could be baked out much more readily than in the previous case. The whole apparatus, up to and including the glass spring gauge, was enclosed in a large air-thermostat during the pressure determination. The technique employed was similar to that in the previous case. In this apparatus there was only about one-half as much nitrogen tetroxide as in Expt. 1, whilst there was rather more phosphorus pentoxide. It had been drying for about 6 months, and during this time had been distilled to and fro nearly 400 times.

In order to obtain a full series of results before any possible reversion to the normal form could occur, the whole temperature range 0—30° was explored in one day. All the results tended to show a distinct rise in the vapour pressure, but there were certain marked anomalies. It was found that although the apparatus was kept at constant temperature for more than an hour, the vapour pressure continued to rise, this rise being so slow that it was not at first noticed. Hence the time which had been allowed at each temperature for a constant vapour pressure to be established (about ½ hour) was clearly quite insufficient, although 10 minutes had sufficed with the undried material in a similar apparatus and under similar conditions. The value of the apparent " initial " vapour pressure, and also the rate of the change, seemed to depend on the previous history of the system. Thus, after the tetroxide had been frozen out in carbon dioxide and alcohol, the vapour pressure at 0° was some 6 hours in attaining a constant value, whilst the apparent " initial " vapour pressure was much greater when the liquid had only been cooled to about —10°. Hence the vapour pressures were determined at a few temperatures by allowing long periods for attainment of equilibrium ; the results are in Table III.

TABLE III.

	Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.
0·0°	282·6	264	+19
5·2	370·3	348	+22
15·2	595·8	571	+25
15·9	615·4	591	+24
19·6	727·8	704	+24
20·5°	757·9	736	+22
24·2	890·5	869	+21
24·7	910·3	890	+20
29·0	1100·5	1080	+20

These values were all obtained about 10 days after the septum had been broken, when the vapour pressure at 0° appeared to remain steady. Some idea of the rate of reversion to the normal form was obtained by taking the vapour pressure at 0° on different days. This value fell from 286·8 mm. on the second day after breaking the septum to 282·6 mm. on the tenth day, *i.e.*, a drop in the abnormality from 23 to 19 mm. This slight reversion was apparently caused by the slow diffusion of moisture out of the less completely dried gauge portion of the apparatus.

That these rises in the vapour pressure were not due to any leakage in the apparatus during the 6 months' drying was shown by freezing out the nitrogen tetroxide in liquid air, whereupon no residual gas pressure was observed.

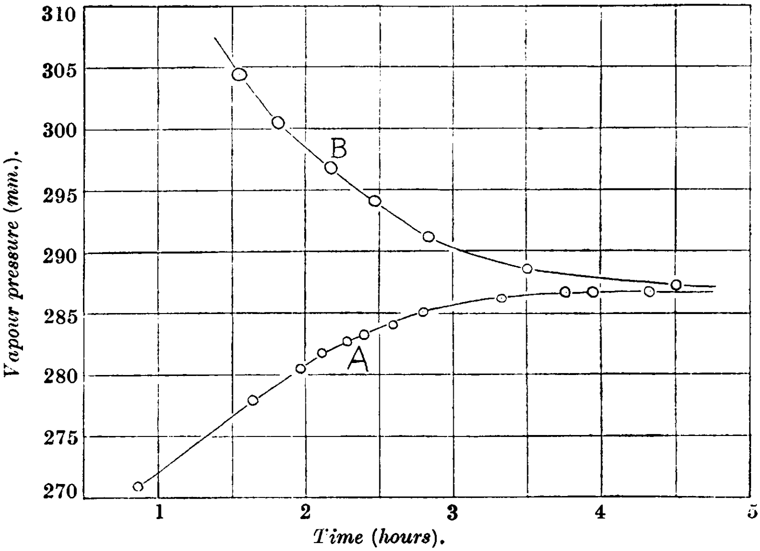
The slow establishment of a steady vapour pressure was further investigated. The liquid was cooled to about —10° for some 3 hours, and then immersed in pure ice and water, which was stirred continuously. Readings were taken at frequent intervals during 4 hours. The corresponding readings were also taken after the system had been cooled from 12° to 0°. The vapour pressure–

time curves are shown in Fig. 3. These values were obtained on the second day after breaking the septum.

The high vapour pressures obtained and this slow change in the vapour pressure on standing at constant temperature seem to indicate that the equilibrium is shifted by the intensive drying, but at the stage when it was examined it was not completely fixed. Hence, when the temperature was raised, a corresponding, but slow, change occurred in the inner equilibrium, a less volatile component passing into a more volatile one. It would be natural to suppose that intensive drying would affect the known inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, but it is not possible to say, from the experiments recorded in this paper, to what extent changes in this equilibrium might account orthe observed phenomena.

FIG. 3.

Vapour pressure–time curves at 0°.



A. *After cooling to* —10°.
B. *After heating to* 19·6°.

Some indication of the form of a constant composition–vapour pressure curve was obtained by reaching equilibrium at one temperature, and then warming quickly to another temperature. These values can only be taken as approximate, however, as it is difficult to separate the two factors—ordinary thermal equilibrium and inner equilibrium. Two examples of the type of result obtained are given in Table IV. These values were obtained by reaching equilibrium at the temperature given in the first column, immersing the liquid in a bath at the temperature shown in the second column, and taking the vapour pressure after 15 minutes.

TABLE IV.

		Vapour pressure (mm.).		
Temp. at which equilibrium was attained.	Temp. of measurement.	After thermal equilibrium was established.	Normal.	Change.
0·0°	0·0°	282·6	264	+19
	9·4	437·2	428	+ 8
	12·6	505·2	503	+ 2
5·4	5·4	373·1	351	+22
	14·9	562·6	562	+ 0·6

Summary.

(*a*) It has been shown that after intensive drying at room temperature the vapour pressure of nitrogen tetroxide is increased throughout the range 0—30°.

(*b*) In accordance with the view developed by Smits, this would suggest a shift in the inner equilibrium towards the side of a more volatile component.

(*c*) The vapour pressure took a considerable time to reach a constant value. This is attributed to slow internal changes in the system, consequent upon temperature change.

In conclusion, I desire to express my indebtedness to the Tuffnell Trustees for a Scholarship, to the Department of Scientific and Industrial Research for a grant, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was carried out, for his kindly advice and criticism throughout the progress of the research.

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[*Received, February* 11*th,* 1927.]