114. *The Effect of Drying on the Vapour Pressure of Dinitrogen Tetroxide and the Vapour Density of Dinitrogen Trioxide.*

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It has long been believed that drying can materially alter the physical properties of liquids, especially boiling point, vapour pressure, vapour density, and surface tension. The vapour pressure change has been regarded as the most important of all since, according to Smits, it gives direct evidence of the change in the inner equilibrium of the liquid. The present work shows that dinitrogen tetroxide (the liquid which shows greatest vapour pressure change) reacts slowly with phosphoric anhydride even at room temperature, liberating oxygen and forming the compound $P_2O_5,2NO$; the vapour pressure increase is due entirely to this oxygen, and the dried liquid has a normal vapour pressure. It has also been shown that the increase in vapour density of vaporised dinitrogen trioxide is due to the formation of this compound, which leaves a gas richer in dinitrogen tetroxide. The vapour density increase is in agreement with this suggestion.

Smits, de Liefde, Swart, and Classen (J., 1926, 2663) found that the vapour pressure of liquid dinitrogen tetroxide increased when it was intensively dried over phosphoric anhydride and concluded that drying caused a shift of the inner equilibrium, $N_2O_4 \longrightarrow 2NO_2$, *i.e.*, towards the more volatile component. This result was recognised to be at variance with Baker's observation (J., 1912, **101**, 2341) that the boiling point of the liquid rises on drying, and the explanation offered was that, before the boiling point is reached, the liquid is partly evaporated, *i.e.*, the more volatile component is preferentially removed from the liquid and the boiling point of the remainder is consequently higher than the normal value. Smith (J., 1927, 867) obtained a similar increase in vapour pressure when the tetroxide was dried for six months by repeated distillation through phosphoric anhydride. He also found that the vapour pressure was dependent upon the immediate previous thermal history of the liquid tetroxide.

Baker (J., 1907, **91**, 1862; 1912, **101**, 2339) found that when dinitrogen trioxide was dried over phosphoric anhydride, the vapour density varied from 38·1 to 62·2 according to the degree of drying attained. It was concluded that the trioxide (V.D., 38) when dry did not dissociate into NO, N_2O_4 and NO_2 but remained unchanged or even polymerised to N_4O_6. Jones (J., 1914, **105**, 2310) confirmed these observations by determining the vapour density of the dried trioxide at a series of temperatures, pressures, and volumes.

In view of the author's discovery that phosphoric anhydride can react with dinitrogen tetroxide to form a compound $P_2O_5,2NO$ and oxygen (J., 1938, 1459), it seemed feasible that the increase of vapour pressure observed by Smits and Smith was due to the production of this oxygen. It also seemed likely that when the trioxide was dried, the composition of the vapour changed from being a mixture of NO, N_2O_4, and NO_2 to being N_2O_4 and NO_2, the nitric oxide combining with the phosphoric anhydride, thus giving rise to conditions with an abnormally high vapour density. Experiments were undertaken to check these points.

EXPERIMENTAL.

(a) *The Vapour Pressure of Dinitrogen Tetroxide.*—The liquid tetroxide, prepared by heating dry lead nitrate in a tube containing phosphoric anhydride, was dried by passing through a 2′ column of phosphoric anhydride and condensed in dry tubes. Each tube was allowed to evaporate a little before being sealed in order to sweep any residual air from the tubes.

The apparatus shown in Fig. 1 was constructed in soda-glass, all of it being made "capillary-free" except that employed for the tensimeter. The diameter of the main horizontal tube was 15 mm. and the bulbs *A*, *B*, and *C* were of about 50, 150, and 100 c.c. capacity, respectively. Phosphoric anhydride was sublimed in a current of oxygen and introduced into the bulb *C*; the apparatus was then closed and allowed to stand for one month for preliminary drying. During this time a tube of about 20 c.c. of liquid tetroxide, *D*, was inserted into the apparatus, which was then sealed off behind it. Freshly sublimed phosphoric anhydride was introduced into the bulb *A*, which was then evacuated by a mercury-vapour pump backed by a "Hyvac" pump, mercury vapour being kept out of the apparatus by using a carbon dioxide trap. The bulb *A* and the side tubes were heated with the blowpipe in order to facilitate the evacuation, and then the tube was sealed at *E*. The tube *D* was then broken by the hammer, and the liquid tetroxide distilled into the bulb *A* by cooling it in ice and salt. In this way the liquid dinitrogen tetroxide was given a good preliminary drying before being introduced into the main apparatus. When the main apparatus had dried for a month, freshly sublimed phosphoric anhydride was introduced into *F*, the bulb was sealed at *G*, and about 20 g. of the phosphoric anhydride were sublimed into *B*, in a slow current of oxygen, the bulb *F* then being removed by sealing at *H*. The main apparatus was then evacuated as completely as possible by using the mercury-vapour pump and heating the apparatus wherever possible with the blowpipe flame, and finally sealed at *J*. The internal seal *K* was then broken, and about 12 c.c. of the liquid tetroxide distilled into *B*, a freezing mixture being used; the excess liquid in the bulb *A* was removed by sealing at *L*.

The bulb *B* was placed in a thermostat, and the vapour pressure of the liquid dinitrogen tetroxide was measured at a series of temperatures from time to time. The vapour pressures at the start of the drying period were found to be :

Temp.	0°	3·1°	7·6°	9·2°	12·4°	14°	18°	20·2°
V. p., mm.	263·1	320·7	399·7	432·6	501·7	534·4	659·7	733·3

in accord with previous data (Scheffer and Treub, *Z. physikal. Chem.*, 1913, **81**, 308; Mittasch, Kuss, and Schlueter, *Z. anorg. Chem.*, 1927, **159**, 1). As the drying proceeded, the vapour pressures were as shown in the table. The original vapour pressures are graphically estimated from the data obtained at the beginning of the drying period. It is seen that the vapour pressure apparently increases gradually with time, and does not seem to approach any final value. This is understandable if the phosphoric anhydride is slowly reacting with the liquid dinitrogen tetroxide, liberating oxygen.

2 Months.				6 Months.				9 Months.			
Temp.	Pressure, mm.	Original v.p., mm.	Δ, mm.	Temp.	Pressure, mm.	Original v.p., mm.	Δ, mm.	Temp.	Pressure, mm.	Original v.p., mm.	Δ, mm.
0°	271·4	263·1	8	0°	289·7	263·1	27	0°	301·7	263·1	39
5·1	356·3	352	4	3·8	356·1	330	26	4·2	377·2	337	40
8·3	421·8	412	10	7·4	420·4	394	26	7·6	435·4	400	35
11·4	485·7	479	7	10·9	498·7	468	30	10·0	489·1	449	40
14·4	551·3	542	9	12·6	533·5	504	30	14·5	590·3	545	45
				14·5	574·0	545	29				
				14·7	581·0	549	32				

About 3 c.c. of the dried liquid were now condensed in one of the side tubes of the apparatus by means of a freezing mixture, and the tube was removed. No effect was observed on the vapour pressure of the residual liquid after the apparatus had been kept undisturbed overnight. This small quantity of dry liquid should, according to Smits's theory, possess a much higher vapour pressure than the normal value, since the more volatile component will have volatilised first. The vapour pressure of the sample was therefore measured under dry conditions. The apparatus shown in

Fig. 2 had been prepared to receive the sample of dry liquid. The bulb *A* was partly filled with freshly sublimed phosphoric anhydride, the tube of dry liquid *B* inserted, and the apparatus closed. After preliminary drying, phosphoric anhydride was introduced into *C* and sublimed into *D*, after the side tube had been sealed at *E*, the bulb *C* being finally removed by sealing at *F*. The apparatus was now evacuated by the mercury-vapour pump and sealed at *G*. The liquid sample tube was now broken, and the vapour pressure measured immediately; it was perfectly normal and showed no increase over the usual value, which agrees with the present assumption that the vapour pressure increase is due to liberated oxygen. The liquid was distilled into *D*, and the apparatus sealed at *H*. The volume of the bulb *D*, the side tubes, and tensimeter was only about 50 c.c., so if the reaction occurred as rapidly as in the first experiment a considerable increase in vapour pressure would be obtained in a comparatively short time. The results obtained were :

Fig. 1.

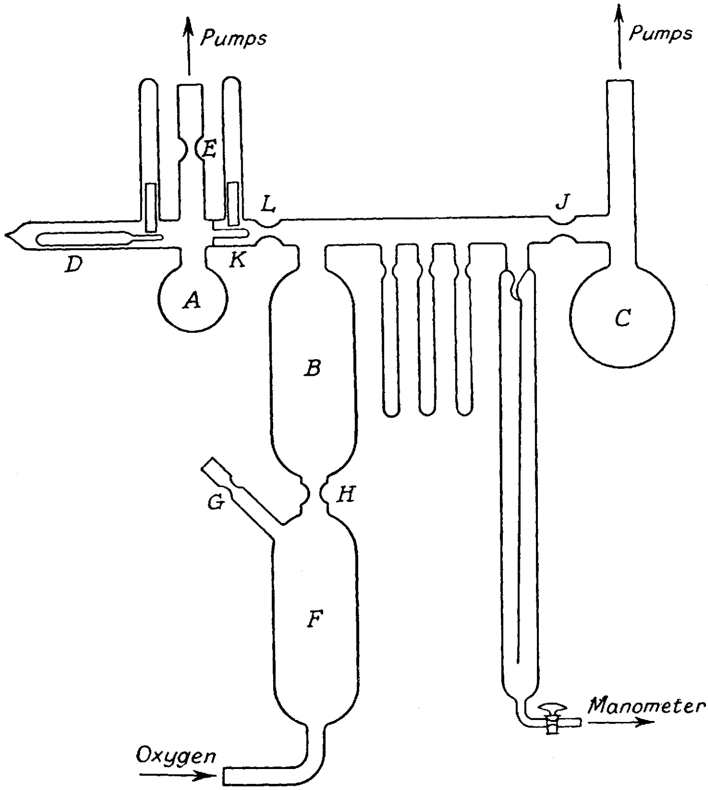
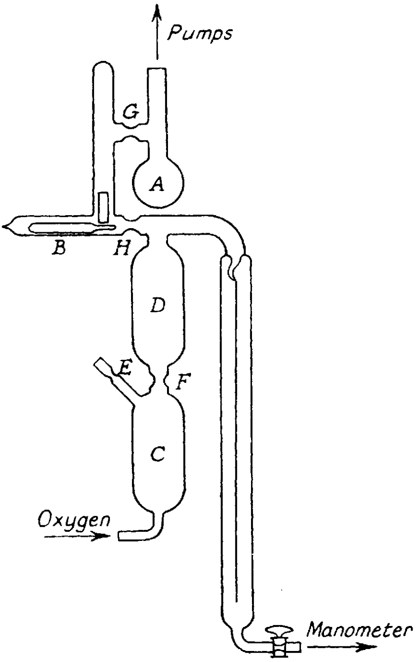


Fig. 2.



Time, weeks	0	1	2	4	8	12
V. p. at 15°, mm.	563·0	569·1	575·0	584·6	596·1	610·8

If the observed pressure increase is due to oxygen, then cooling the liquid to -80° should condense the whole of the dinitrogen tetroxide and leave a residual pressure due to this oxygen. The experiment showed that the residual pressure was 32 mm. and was due to a colourless gas. The apparatus was now dismantled and the solid in *B* was placed in a tube filled with dry mercury; admission of a little water liberated a colourless gas which proved to be nitric oxide. It was therefore concluded that the reaction described in the author's earlier paper can occur slowly at room temperature, bringing about an apparent increase in vapour pressure. Two other samples of dry liquid were removed from the original apparatus but both behaved in a perfectly normal manner when the vapour pressures were measured. The solid finally left in bulb *B* of Fig. 1 also liberated nitric oxide when treated with water.

(b) *The Vapour Density of Dinitrogen Trioxide.*—The trioxide was prepared from arsenious oxide and nitric acid. The vapours, after being dried over phosphoric anhydride, were condensed in tubes cooled in solid carbon dioxide. The apparatus shown in Fig. 3 was constructed as usual in soda-glass, rendered capillary-free as far as possible. A cluster of four bulbs, each of about 200 c.c. capacity, was incorporated for the density determinations. The sample of liquid *A* was inserted into the apparatus, and bulb *B* filled with sublimed phosphoric anhydride and sealed at *C*. After the preliminary 6 weeks' drying, freshly sublimed phosphoric anhydride was introduced into *D*, sublimed as usual into *E*, and the bulb *D* removed by sealing at *F*. The apparatus was now evacuated as completely as possible by means of the mercury–vapour pump, the bulbs and side tubes being heated to hasten the production of a hard vacuum. After sealing at *G*, the tube of liquid was broken open, the liquid allowed to vaporise completely, and the apparatus finally sealed at *H*. The vapour-density bulbs and the drying bulb *E* were immersed in a thermostat, and four vapour-density determinations carried out as drying proceeded by noting the temperature and pressure of the vapour, sealing off one of the bulbs, and treating it as a Dumas bulb. The observations for the first apparatus were :

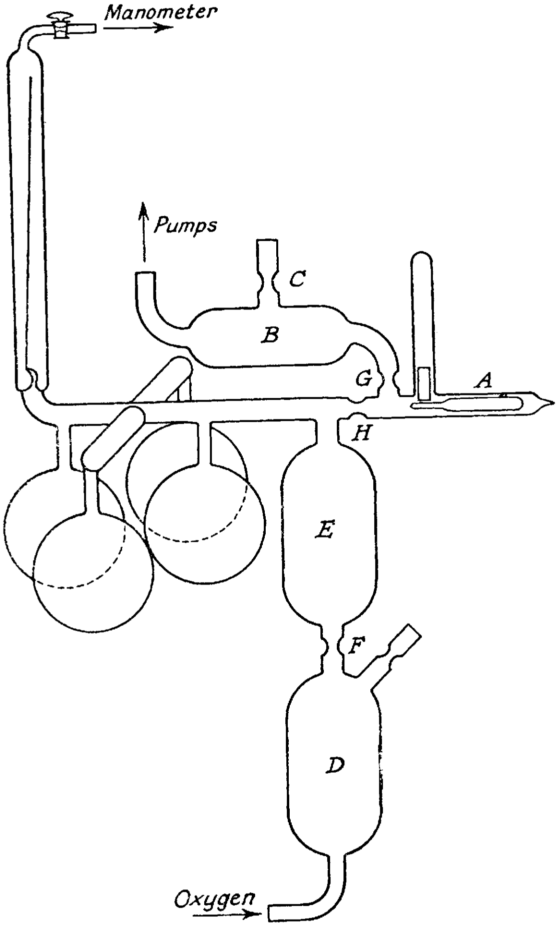
Time of drying, weeks	0	2	4	8	12
Pressure of gas, mm.	533·4	514·0	500·2	473·1	441·7
Vapour density	—	28·1	28·4	29·4	30·9

and for the second :

Time of drying, months	0	2	6	10	15
Pressure of gas, mm.	647·2	567·8	468·3	403·1	338·5
Vapour density	—	28·6	32·1	34·2	36·3

The phosphoric anhydride at the end of each experiment was removed from the apparatus and allowed to react with water; nitric oxide was evolved, showing that the phosphoric anhydride had reacted to form the compound with nitric oxide.

Fig. 3.



Phosphoric anhydride and a small amount of liquid dinitrogen trioxide were sealed in a tube and slowly heated to 130°. The resultant gas was colourless, and when the tube was examined by the method previously described (*loc. cit.*), the gas proved to be oxygen.

Conclusion.—Baker and Smits claimed to have proved that the physical properties of liquids were modified by drying. Some of the most definite data were the changes in vapour pressure, and the explanation offered was that the internal state of a liquid could be changed on drying. Smits (*Z. physikal. Chem.*, 1927, **129**, 33) had considered the possibility of a reaction between the liquid and the phosphoric anhydride but dismissed it after carrying out drying experiments in apparatus which enabled only slow diffusion of gases to occur, *i.e.*, slow removal of moisture. (He overlooked the fact that this would also decrease the rate of reaction.) Of all the liquids investigated, dinitrogen tetroxide showed by far the greatest change in vapour pressure on drying. The present work shows that the effect is due entirely to a chemical change, and consequently but little evidence remains for change in vapour pressure on drying.

The phosphoric anhydride–dinitrogen trioxide system also undergoes chemical change, so the product becomes richer in $N_2O_4 \rightleftharpoons 2NO_2$. Drying brings about an increase in vapour density and it appears that this vapour density approaches the value expected for the $N_2O_4 \rightleftharpoons 2NO_2$ system as drying proceeds. In the second experiment, the highest vapour density was 36·3 and the pressure had fallen to 338·5 mm. At this pressure, the vapour density for $N_2O_4 \rightleftharpoons 2NO_2$ is approximately 37·8. The phosphoric anhydride remaining at the end of the experiment contained the compound $P_2O_5,2NO$, confirming the view that the increase of vapour density was due to the vapour becoming richer in tetroxide and poorer in nitric oxide.

The conclusion from this work is that drying produces no abnormal results in the vapour pressure of liquid dinitrogen tetroxide or the density of the vapour from the trioxide that cannot be satisfactorily explained by the observation that a reaction occurs in each case with the phosphoric anhydride. These observations, together with those of Lenher (*J. Amer. Chem. Soc.*, 1929, **51**, 2948; *J. Physical Chem.*, 1929, **33**, 1579) on boiling points, of Briscoe, Peel, and Robinson (J., 1929, 368) on surface tension and liquid density, and of Riley (J., 1929, 1026) on dielectric constant, lead to the general conclusion that drying does not influence physical properties.

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