154. *Properties of the Oxides of Nitrogen. Part I. The Binary System* N_2O_4–N_2O_5.

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Preparation and Purification of Nitric Anhydride.

NITRIC anhydride, first prepared by the action of dry chlorine on silver nitrate (Deville, *Ann. Chim. Phys.*, 1850, **28**, 241), was afterwards generally made by the action of phosphoric anhydride on nitric acid (Weber, *J. pr. Chem.*, 1872, **6**, 342; *Pogg. Ann.*, 1872, **147**, 113; Berthelot, *Bull. Soc. chim.*, 1874, **21**, 53; *Ann. Chim. Phys.*, 1875, **6**, 203). The distillate obtained by heating the mixture separates into two layers, of which the upper one crystallises when cooled, after which a partial purification of the crystals may be effected by pouring off the mother-liquor and repeating the crystallisation; but the material thus produced is not usually pure enough for physicochemical measurements. For instance, in our experiments, two samples, prepared by dehydration under reduced pressure, were apparently free from nitric acid, but the third sample, in a mixture containing 74% N_2O_4, became turbid when cooled to − 8° and was obviously hydrated. Since the yields of the anhydride were always poor (10—20%), and it was found difficult to remove the last traces of nitric acid, even by sublimation through a tube of phosphoric oxide in a stream of ozonised oxygen (Russ and Pokorny, *Sitzungsber. Akad. Wiss. Wien*, 1913, **122**, 439; *Monatsh.*, 1913, **34**, 1027), the dehydration method was abandoned in favour of direct ozonisation of nitrogen peroxide (Helbig, *Atti R. Accad. Lincei*, 1902, **11**, ii, 311; 1903, **12**, i, 211). Quantities of 2—3 g. can thus be prepared very conveniently, with a yield of about 30—40% of the ozone supplied. The materials used in this preparation are all anhydrous; but great care was needed to exclude all traces of moisture from the apparatus, since it was almost impossible to get rid of nitric acid when it had once appeared in the system.

Helbig's method appears to depend on two consecutive reactions : $NO_2 + O_3 = NO_3 + O_2$ and $NO_2 + NO_3 = N_2O_5$ (Schumacher and Sprenger, *Z. physikal. Chem.*, 1929, *A*, **140**, 281; cf. Sprenger, *ibid.*, 1928, **136**, 49). It has the advantage that the lower oxides produced by the decomposition of nitric anhydride, $N_2O_5 = N_2O_3 + O_2$ and $N_2O_3 + N_2O_5 = 4NO_2$, but not $N_2O_5 = NO_2 + NO_3$, are immediately reoxidised instead of having to be removed by fractional distillation. On the other hand, since the hyperoxide (NO_3?) is only formed in presence of ozone, and probably interacts with nitrogen peroxide to form nitric anhydride, it is not likely to persist as an impurity in the solid product.

Melting Point of Nitric Anhydride.—The m. p. of nitric anhydride was given as 30° ± 1° by four of the earlier authors (Deville; Weber; Berthelot; Helbig; *locc. cit.*). On the other hand, Russ and Pokorny (*loc. cit.*) attribute this m. p. to the presence of nitric acid or to the formation of nitrogen peroxide, and conclude that the pure material passes directly from the solid into the vapour state. Their experiments were made with nitric anhydride, which had been sublimed, from a mixture of nitric acid and phosphoric oxide, through a tube of phosphoric oxide, in a current of ozonised oxygen, and condensed in a glass receiver cooled to − 80°. Specimens of 1—2 g., condensed in glass tubes, sealed, and stored at a low temperature, became liquid in 9 mins. at 34°, and in 15 mins. at 30·5°, but never gave a well-defined m. p., although in each case the necessary heat-transfer was complete in 3—4 mins. Analysis of a sample which had thus been melted at 30—30·5° showed the presence of 6% N_2O_4. A sample of 1 g., prepeared by Helbig's method, in a **U**-tube protected from the air by phosphoric oxide, sublimed rapidly at 35° but was not observed to melt.

Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1131) also observed that 5 g. of nitric anhydride, resublimed in a current of ozone, and condensed in a glass apparatus, which was then evacuated and sealed, showed signs of melting after 45 mins. at 30°; but they concluded that " It is not a true melting, but a phenomenon complicated by the dissolving of nitrogen tetroxide in the surface of the crystals." At 35° " the contamination with nitrogen tetroxide and the appearance of melting occurs in the first few minutes " (*loc. cit.*, p. 1138).

From their vapour-pressure curves (*Sitzungsber. Akad. Wiss. Wien*, **1913**, **122**, 415), Russ and Pokorny deduced, by extrapolation from 17·5°, a sublimation temperature of 34° (*loc. cit.*, p. 447), and concluded that : " Pure N_2O_5 does not exist at atmospheric pressure in a liquid phase." In the same way, Daniels and Bright report that : " The vapour pressure reaches an atmosphere at 32·5°, as shown by a short extrapolation of the curve. The melting-point lies above the sublimation-point, as stated by Russ and Pokorny " (*loc. cit.*, p. 1139).

In our opinion, these results are not conclusive, since experiments in sealed tubes do not allow any adequate opportunity for getting rid of nitrogen peroxide by vaporisation, and, in order to secure a correct m. p., a much more rapid procedure is needed, exactly as in the case of compounds such as benzoylcamphor (Lowry, MacConkey, and Burgess, J., 1928, 1337) which undergo reversible isomeric change when melted. Since a knowledge of the m. p. was required in order to complete the equilibrium diagram, a series of observations was made in which these considerations were kept in view.

In a first series of experiments, the receivers in which the anhydride was condensed were not sealed off, but were filled with dry air and allowed to warm to room temperature. One of the taps being open to the atmosphere, the receiver was then transferred to a bath of water at a temperature a few degrees below the m. p., and heated at a rate of about 1° per min. The initial temperature and rate of heating were noted, in addition to the temperature at which incipient melting (as distinguished from mere sintering) could be seen. As the m. p. was approached, evaporation became rapid and the yellow colour of nitrogen peroxide began to appear, to an extent which depended on the duration of heating. By progressively raising the initial temperature, and thus reducing the time during which decomposition could take place, the m. p. was finally raised above 40°.

Sample.	M. p.	Initial temp. of bath.	Time interval, mins.	Rate of heating.
1	37·3°	28°	9—10	1°/min.
2	38·8	30—31	8—9	,,
3	40·7	36·8	4	,,

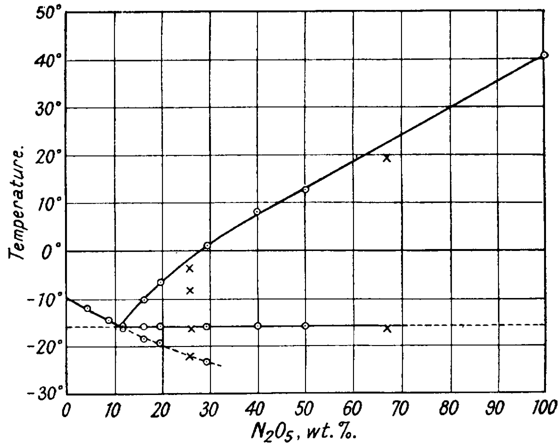
Subsequent experiments were based on the assumption that the most trustworthy results would be obtained by determining the m. p. *in presence of ozonised oxygen.* For this purpose, nitric anhydride was condensed in a narrow U-tube, about 3 mm. in internal diameter, which had been drawn out from a wider tube in order to reduce the thickness of the walls. Since it was essential to avoid cooling by the current of ozonised oxygen, the gas was made to pass through a glass coil, immersed in the same water-bath, before entering the U-tube. Under these conditions it was found that, even if an initial melting took place at a temperature as low as 35°, when the water-bath was filled abruptly with tepid water, the wet solid always dried up quickly as soon as a slow current of ozonised oxygen was turned on. The residue appeared to be a highly purified nitric anhydride, from which all traces of decomposition product had been vaporised.

At this stage, a new difficulty presented itself, since it was very difficult indeed to melt this residue in a stream of ozonised oxygen. This difficulty we attributed mainly to cooling by evaporation of the extremely volatile solid. For instance, on one occasion a central core of loose crystals, left at the bottom of one arm of the U-tube, was heated for about 5 mins. at 45°, with continual evaporation, until the ozonised oxygen was turned off, whereupon the material soon sintered and melted at the bottom of the tube. On two occasions, however, a small plug of crystals, which appeared to be exceptionally free from decomposition products, was left at the point of entry of the gas, where the tube was slightly constricted, and where supplies of ozone were most abundant. In a critical experiment, this plug was watched carefully, and was seen to drop through the constriction at a temperature of 41°. This temperature, which agrees with those of the first series, has been used to complete the freezing-point diagram ; but we are not prepared to assert categorically that melting, as contrasted with sublimation, can occur in the complete absence of decomposition products. On the other hand, any m. p. below 40°, can, we think, be rejected as incompatible with adequate purity of the material.

Freezing Points of Mixtures of N_2O_4 *and* N_2O_5.—A receiver containing a known weight of the pentoxide was cooled with solid carbon dioxide and acetone, and attached to an apparatus from which a known weight of nitrogen peroxide could be sublimed into it. The receiver was then sealed, and transferred to a large transparent Dewar vessel containing 1—1½ l. of alcohol, which was stirred mechanically and cooled as required by the addition of solid carbon dioxide, or by blowing liquid nitrogen on to the surface (cf. Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851). For temperatures above 0°, a water-bath cooled with ice, or controlled by a flow of warm or cold water, was used instead of alcohol. The mixtures were stirred electromagnetically, by a piece of iron sealed into a glass tube and operated by a solenoid (cf. Terrey and Spong, J., 1932, 219).

Nitrogen peroxide crystallised readily from the stirred mixtures in the sealed tubes, with not more than 2—3° of supercooling. It separated in small, bright, heavy, granular crystals, which grew and multiplied rapidly. Slow growth in an undisturbed liquid gave rise to relatively large hexagonal crystals on the walls of the tube; but, when detached, the crystals fell to the bottom, and were not readily carried up by the stirrer, since they were markedly denser than the liquid. The f. p. was recorded as the temperature at which a small quantity of solid peroxide remained in equilibrium with the liquid, without either growing or dissolving.

FIG. 1.



Nitric anhydride exhibited such remarkable supercooling that it was possible to determine the f. p. of nitrogen peroxide far beyond the eutectic temperature. In this way the (metastable) freezing-point curve was extended from 11% to 30% N_2O_5, the supercooling then being 24°. Similar supercooling was noticed by Berl and Saenger (*Sitzungsber. Akad. Wiss. Wien*, 1929, **138**, 1036; *Monatsh.*, 1929, **53—54**, 1036) in mixtures of nitric anhydride with anhydrous nitric acid.

On account of this supercooling, it was necessary to initiate crystallisation of nitric anhydride by chilling the liquid either in ice or in carbon dioxide snow and acetone, and then shaking the tube or agitating the liquid with the internal stirrer. The crystals thus formed adhered tenaciously to the sides of the tube, but, when detached, were readily carried up into suspension by the stirrer, and could thus be distinguished easily from crystals of nitrogen peroxide. Slow growth from concentrated solutions gave white needles, similar to those produced by slow condensation from the vapour. The temperature at which a small deposit of nitric anhydride just disappeared, when the tube was allowed to warm in the observation bath at the rate of 0·2—0·3°/min., was taken as the f. p. of the system.

The f. p.'s thus determined are shown in Table I and plotted in Fig. 1. The eutectic temperatures are those at which the first signs of melting could be seen in the completely frozen mixtures. Each temperature is, as a rule, the result of at least three concordant observations.

TABLE I.

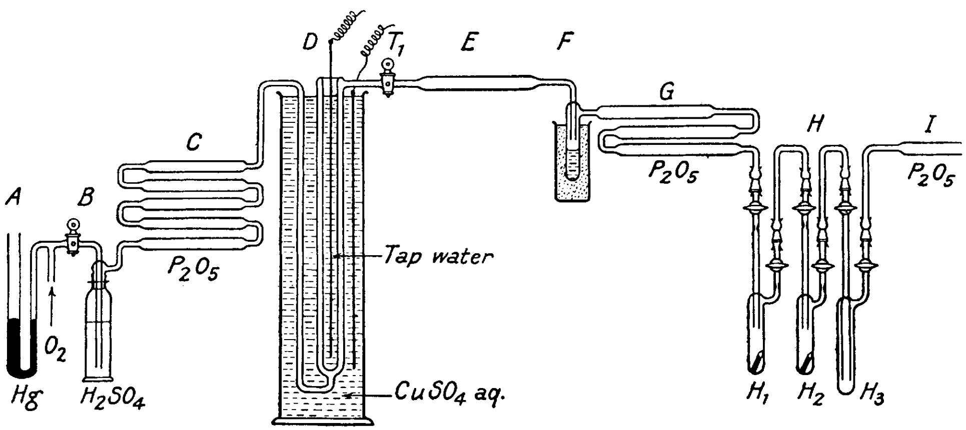
Freezing Points of Mixtures of N_2O_5 *and* N_2O_4.

Composition by wt.		Composition, wt. %.		Eutectic line temp.				
N_2O_5, g.	N_2O_4, g.	N_2O_5.	N_2O_4.		F. p.	Solid phase.	F. p.	Solid phase.
0·1287	2·8669	4·29	95·71	—	−11·8°	N_2O_4	—	—
0·2835	2·9529	8·76	91·24	—	−14·3	,,	—	—
0·2556	1·9077	11·86	88·14	−15·8°	−16·3	,,	—	—
0·4959	2·5813	16·12	83·88	−15·8	−18·2	,,	−10·1°	N_2O_5
0·5871	2·4301	19·46	80·54	−15·6	−19·1	,,	− 6·4	,,
0·9704	2·3404	29·31	70·69	−15·7	−23·2	,,	+ 1·1	,,
1·0624	1·6031	39·86	60·14	−15·8	—	—	+ 8·0	,,
1·6157	1·6122	50·05	49·95	−15·7	—	—	+12·9	,,

The eutectic point is at 10·8% N_2O_5 and − 15·8°, and there is no evidence of the formation of any compound of the two components.

Formation of Two Liquid Layers.—Liquid mixtures of N_2O_4 and N_2O_5 are homogeneous, but readily separate into two layers when contaminated with a small proportion of moisture; *e.g.*, when the anhydride is prepared by dehydrating nitric acid, the distillate gives an upper darker-coloured layer of the two oxides, and a lower layer of nitric acid containing the two oxides in solution. Two mixtures containing a trace of moisture are indicated by crosses in Fig. 1, where the f. p.'s are a little below those of the dry series of mixtures. One of these wet mixtures, containing 25·7% N_2O_5, froze at − 3·5°; but, when supercooling of this oxide occurred, the liquid became turbid at − 8·2°, and deposited the tetroxide at − 22°. In both cases it was noticed that the completely frozen mixtures at temperatures a few degrees below the eutectic temperature exhibited a more pronounced light yellow colour than the completely anhydrous mixtures, which were only very pale yellow at these temperatures.

FIG. 2.



The exact concentrations at which two liquid layers are formed are not yet known; but, since Bousfield (J., 1919, **115**, 45) found that the limit of solubility of nitric acid in nitrogen peroxide at 18° is 8·05% by weight of HNO_3 (or 1·15% H_2O, 6·9% N_2O_5), it is clear that the addition of little more than 1 part of water would suffice to bring about a separation of nitric acid in a mixture of 7 parts of nitric anhydride with 92 parts of nitrogen peroxide. The small proportion of water that is required to produce two liquid layers, especially at low temperatures, is shown by the fact that a sample, which was wet enough to be turbid at − 8·2°, gave a f. p., which was only about 2° below the curve for the dry mixtures.

EXPERIMENTAL.

The apparatus is shown in Fig. 2. All taps and ground joints were lubricated with a little Apiezon L grease, which is comparatively resistant to attack by the substances used. Oxygen from a cylinder was passed through a sulphuric acid bubbler B, and dried in a series of phosphoric oxide tubes C, before passing through the ozoniser D, 50 cm. in length and cooled by circulating tap-water through the inner tube, in which about 8% ozone was produced by a silent discharge of 500 cycles at 8000—10,000 volts. The ozonised oxygen passed through a tap T_1, and drying tube E, into a receiver F, which had been filled in a vacuum with liquid nitrogen peroxide and sealed on to the ozoniser whilst the nitrogen peroxide was frozen hard. Dry oxygen was passed through the apparatus for 15—20 mins. before the nitrogen peroxide was allowed to melt. The receiver F was then surrounded by a water-bath, the temperature of which was adjusted to control the rate of evaporation of the liquid and to eliminate the heat of reaction of nitrogen peroxide and ozone; injection of the vapour of nitrogen peroxide into a stream of ozone was abandoned, on account of difficulty of control. The vapour was decolorised by the ozone, and, after passing through the drying-tubes G, was condensed in three receivers H_1, H_2, H_3, cooled with solid carbon dioxide and acetone. These were fitted with taps and interchangeable ground joints, so that they could be connected together or transferred to an apparatus from which known weights of nitrogen peroxide could be condensed in them. The first two, about 1 cm. in diameter, were weighed and used to condense quantities up to 2 g. of nitric anhydride, from which two mixtures with the tetroxide could then be made. The third receiver, which was larger and had a longer and wider inner tube, served to condense the residual pentoxide, which was afterwards transferred to one of the smaller receivers. Blocking of these receivers with solid pentoxide was provided for by a " blow-off " A at the other end of the apparatus. The residual gas, after passing through a drying tube I, was heated to decompose the excess of ozone, and bubbled through aqueous caustic soda to remove nitrogen peroxide.

The rate of evaporation of nitrogen peroxide was regulated so that it was completely decolorised; if the condensed pentoxide still contained by chance a trace of peroxide, this was removed by allowing the receiver to warm to room temperature, with the tap leading to the pump line closed, and momentarily opening the tap as many times as was necessary to remove the whole of the brown peroxide from the vapour. The exhausted receivers were allowed to warm to room temperature for weighing, and then cooled again as quickly as possible. The product was a white crystalline powder, which became yellow and wet when allowed to decompose.

SUMMARY.

Nitrogen peroxide and nitric anhydride give a simple freezing-point diagram, with a eutectic at 10·8% N_2O_5 and − 15·8°.

We are indebted to Imperial Chemical Industries, Limited, for grants.

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