JOURNAL

OF

THE CHEMICAL SOCIETY.

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1. *Properties of the Oxides of Nitrogen. Part II. The Binary System* N_2O_3–H_2O.

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THE object of the work now described was to determine the limits of miscibility of nitrous anhydride and water, with a view to complete a triangular phase diagram for the ternary system H_2O–N_2O_3–N_2O_5. Since the quantitative preparation of mixtures of nitrous anhydride and water was difficult and troublesome, the opportunity was also taken to plot an equilibrium diagram showing the freezing points as well as the limits of miscibility of a series of mixtures in the system N_2O_3–H_2O.

The earliest indication of the formation of two liquid layers in this system is afforded by the work of Luck (*Z. anal. Chem.*, 1869, **8**, 402), who purified nitrous anhydride, greenish-blue owing to contamination by the peroxide, by adding a little ice-cold water to the strongly cooled liquid.* The latter thereupon became pure indigo-blue, and, after separation of the upper aqueous layer, was rectified at 5—10°, the receiver being cooled in ice and salt. A similar observation of the effect of adding a small proportion of water to nitrous anhydride was also made by Mallet and Gaines (*Chem. News*, 1883, **48**, 97).

H. B. and M. Baker stated in 1907 (J., **91**, 1866) that liquid " nitrogen trioxide . . . is very little, if at all, soluble in water." This statement again suggests the formation of two liquid layers; but the first clear evidence that these can exist as stable liquid phases in equilibrium with one another was provided by Briner and Durand (*Compt. rend.*, 1912, **155**, 583, 1495), who stated that, " on adding a small quantity of water to N_2O_3, which, in the liquid state, is a very dark blue, one observes the appearance of a second upper blue liquid phase; then, on continuing the additions of water, the blue coloration pales, until it is no longer appreciable." They also recorded that " During the dilution, the pressure increases, then diminishes after passing through a maximum "; but no numerical or experimental details are given in this note.

The existence of two liquid layers in mixtures of nitrous anhydride and water was confirmed by preliminary experiments made in this laboratory by Dr. W. V. Lloyd; but the high gaseous pressures blew out the stop-cocks of the apparatus, so the two layers were observed only in mixtures from which a little nitric oxide had escaped. Improved methods of working have now made it possible to avoid this loss of nitric oxide, so the total composition of the mixtures used in the present series of observations was accurately known. It was not practicable, however, to prevent a redistribution of nitric oxide between the liquid and the gaseous phase. Hence, since the latter always contains an excess of nitric oxide, the liquids must be slightly richer in oxygen and the aqueous layer may therefore contain a little nitric acid. This unavoidable change of composition was reduced to a minimum by making sure that the volume of liquid was at least equal to 40% of the total

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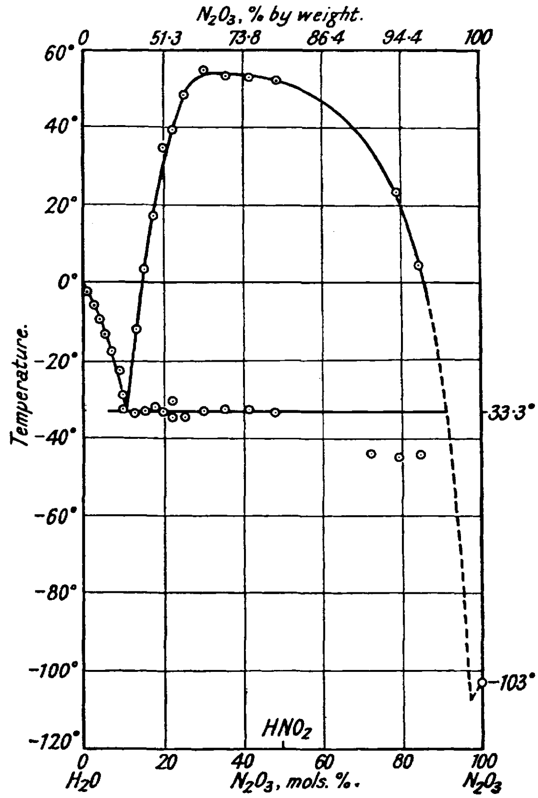
* Fritzsche (*J. pr. Chem.*, 1841, **22**, 14) had attempted to prepare nitrous anhydride by adding ice-water to chilled nitrogen peroxide, but was unable to separate the two layers on account of the violent boiling which occurred on pouring; he was therefore obliged to distil them both together, after allowing them to become warm, and collected the anhydride in the first fraction.

volume; moreover, most of the essential observations were made under conditions in which the pressure of nitric oxide was not excessive. The results of the experiments are set out in the table and plotted in Fig. 1.

Fig. 1.



Equilibrium diagram for nitrous anhydride and water.

The limits of composition within which two liquid layers are formed are approximately 48—95% N_2O_3 by weight at 20° and 42—97% at 0°. These limits are believed to be correct within about 1%, but at higher temperatures the expulsion of nitric oxide from the liquid phases into the gaseous phase becomes a serious source of error. We therefore record, with full recognition of their tentative character, the observations which showed that the liquids in the tubes became completely miscible at temperatures above 55°, and that this maximum in the miscibility curve was reached at a composition of 65% N_2O_3 by weight or 30 mols. %. The general form of the curve suggests that the critical solution temperature may be perhaps 20° higher than the figure recorded above, and that the critical composition may be much nearer to that of nitrous acid than these figures would indicate.

Below 0° the solubility of nitrous anhydride in water falls to 36% by weight at — 33·3°. At this temperature the solubility curve intersects the freezing-point curve for homogeneous solutions of the anhydride in water. Four phases are in

Freezing Points and Temperatures of Separation into Two Layers in Mixtures of Nitrous Anhydride and Water.

Composition, by wt.			H_2O content.		Vol. occupied by liquid, %.	F. p.	Turb. pt.
H_2O, g.	N_2O_4, g.	NO, g.	Wt., %.	Mols., %.			
1·9092	0·0560	0·0365	95·39	98·86	54·0	— 2·1°	
1·8064	0·1174	0·0766	90·31	97·50	49·3	— 5·6	
1·7870	0·1893	0·1235	85·10	96·00	53·3	— 8·5	
1·7660	0·2665	0·1738	80·04	94·40	53·3	— 13·0	
1·6532	0·3308	0·2157	75·16	92·73	49·5	— 17·8	
1·5658	0·4041	0·2635	70·12	90·83	42·3	— 22·6	
1·5039	0·4804	0·3133	65·45	88·88	45·0	— 29·0* — 32·7	<— 40°
1·5007	0·5796	0·3780	61·04	86·87	48·3	— 33·8	— 12·0
1·3069	0·6141	0·4005	56·30	84·47	42·9	— 33·1	+ 3·5
1·2183	0·6819	0·4446	51·96	82·07	43·8	— 32·2	+ 17·3
0·9380	0·6029	0·3931	48·50	79·90	45·1	— 33·3	+ 34·5
1·1178	0·8272	0·5394	44·99	77·53	53·1	— 30·6	+ 39·0
0·6885	0·5142	0·3354	44·76	77·38		— 34·3	
1·0034	0·8773	0·5720	40·90	74·49	44·8	— 34·8	+ 48·2
0·9117	1·0104	0·6589	35·32	69·73	52·8	— 33·4	+ 54·9
0·7800	1·1099	0·7239	29·84	64·22	52·3	— 32·6	+ 53·6
0·6511	1·1854	0·7732	24·96	58·38	50·0	— 32·8	+ 53·3
0·5435	1·3019	0·8488	20·17	51·60	53·0	— 33·7	+ 52·3
0·1558	1·0432	0·6802	8·30	27·60	42·7	— 44·2	
0·1060	1·0383	0·6769	5·82	20·69	43·3	— 45·4	+ 23·5
0·0796	1·1563	0·7540	4·00	14·95	45·0	— 44·2	+ 4·6

* — 29·0° refers to a point on the ice line, and — 32·7° to one on the eutectic line.

equilibrium at this quaternary point, *viz.*, (i) a vapour phase, consisting mainly of nitric oxide, (ii) an aqueous phase, consisting mainly of aqueous nitrous acid with free nitrous anhydride, $2HNO_2 \rightleftharpoons H_2O + N_2O_3$, (iii) a heavy blue liquefied gas phase, containing more than 94% N_2O_3, and (iv) a colourless solid phase of pure ice.

The temperature of separation of ice should remain constant at − 33·3° so long as two liquid layers are present; but in practice, lower freezing points were recorded in mixtures containing more than 50 mols. % N_2O_3. This may perhaps be attributed to the escape into the gaseous phase of an appreciable amount of nitric oxide from mixtures richer in N_2O_3 than nitrous acid itself.

It would be expected that, when the aqueous layer had dissolved completely in an excess of nitrous anhydride, the freezing point would fall to another quaternary point below the freezing point of nitrous anhydride at − 103° (Wittorff, *Z. anorg. Chem.*, 1904, **41**, 85), but no attempt was made to extend the observations to this range of concentrations.

Colour of the Mixtures.—When the tubes containing the mixtures were removed from the bath of liquid nitrogen used in preparing them, the contents remained almost colourless * for about 3 minutes, after which the strong blue colour of nitrous anhydride appeared suddenly. It is probable that this compound begins to be formed at − 112°, the eutectic temperature of nitrogen peroxide and nitrous anhydride (*idem, ibid.*), at which a liquid phase first becomes possible in the system. The vapour pressure of nitric oxide at this temperature is about 28 atm., according to Olszewski (*Compt. rend.*, 1885, **100**, 940); but Adwentowski (*Bull. Acad. Cracow*, 1909, 742) gives the pressure as 21·6 atm. at − 112·6°.

Dilute solutions of nitrous anhydride in water are colourless, but the blue colour of the anhydride begins to be apparent, in columns of 10 cm., at a concentration of about 5% N_2O_3, or at about 10% N_2O_3 when viewed in the narrow sealed tubes. The colour is still weak at 15 and 20% N_2O_3, but becomes fairly strong at 25 and 30%. At higher concentrations, the solutions in the sealed tubes begin to look like a blue ink; but the aqueous phase is still transparent to transmitted light even at concentrations at which two liquid layers are formed.

The aqueous layers are pure blue at room temperatures. Those mixtures which were heated to 35—40° during the observations of turbidity developed a marked greenish tint, and those which were heated above 45° became deep green; but the original pure blue colour was invariably restored on cooling to room temperature.

The lower layer, which separates from mixtures containing more than about 48% by weight of nitrous anhydride, consists mainly of this oxide. It is mobile, like liquid nitrogen peroxide, and is considerably denser than the aqueous layer. At room temperatures it is such a deep blue as to be transparent only in thin layers. It has a slight greenish tinge which becomes more marked when the temperature is raised.

EXPERIMENTAL.

Materials.—(i) *Nitric oxide.* This was prepared by dropping aqueous sodium nitrite into a concentrated solution of ferrous sulphate containing about one-tenth of its volume of sulphuric acid (Thiele, *Annalen*, 1889, **253**, 246), and was collected in an aspirator over water. The apparatus used for purifying it, and for preparing mixtures of nitrous anhydride and water, is shown in Fig. 2; it was originally constructed by Dr. W. V. Lloyd and used by him for preparing mixtures of the former with nitrogen peroxide.

Purification was effected substantially as described by Purcell and Cheesman (J., 1932, 826). For this purpose the whole apparatus was first evacuated to a pressure of less than 0·01 mm. by means of a mercury-diffusion pump backed by an oil pump, and all the taps were closed. Nitric oxide was then admitted slowly from the aspirator *A*, through the sulphuric acid bubbler, *B*, and a column *C* packed with pieces of caustic soda. It was condensed and frozen to a solid in the trap *D* by means of liquid nitrogen. A little nitrogen, present as an impurity in the nitric oxide, remained uncondensed; it was pumped away, and washed out by allowing a little of the nitric oxide to evaporate. The nitric oxide was then sublimed into a second trap *E*, and the purific-

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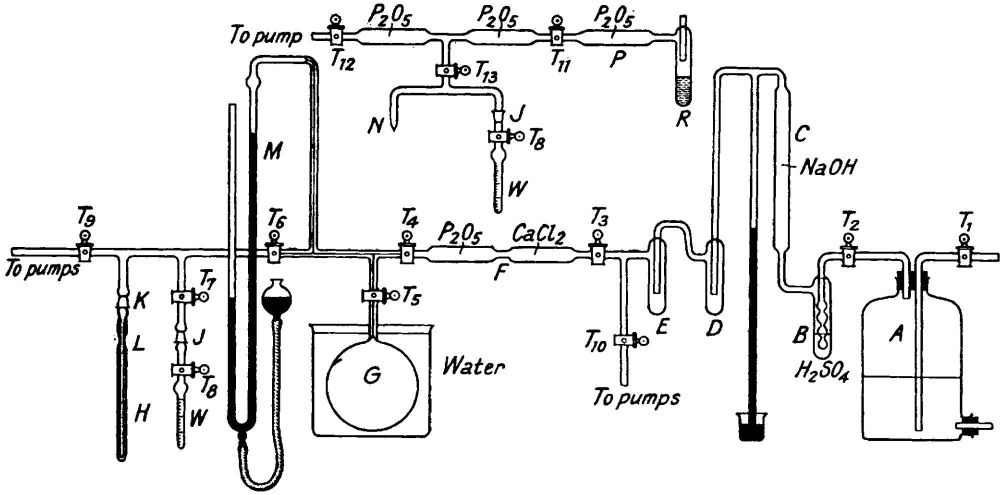
* The solid or liquid nitric oxide showed a weak blue colour. A light reddish (burnt Sienna) colour was sometimes seen in patches where gaseous nitric oxide was in contact with solid N_2O_4; but in presence of blue N_2O_3 this appeared as a light purple tint.

ation repeated. The tap T_6 was then closed and T_5 opened. The nitric oxide in E was allowed to liquefy and evaporate, and was passed through the drying tubes, F, into the bulb G; the last fraction was retained in E and was finally excluded by closing the tap T_4.

The bulb G and manometer M constituted a gas-measuring apparatus from which known quantities of nitric oxide could be drawn (cf. Baume and Robert, *Compt. rend.*, 1909, **148**, 1322; 1919, **169**, 968; Maass and Russell, *J. Amer. Chem. Soc.*, 1918, **40**, 1847). For this purpose the bulb was immersed in a thermostat, and the level of the mercury in the manometer M was always brought to the 90-cm. mark on the scale before reading the pressure. The volume of the bulb G (907·2 c.c.) and of the connecting tubes T_4, T_5, T_6, M to the 90-cm. mark (20·3 c.c.) had been determined previously by alternately exhausting them and then filling them (three times) with dry air from a gas burette. Since the capacity of the capillary connecting tubes was only a little more than 2% of that of the bulb, and their temperature did not often differ from that of the bath by more than 3°, the error introduced by deviations of the room temperature from that of the bath could be neglected.

FIG. 2.



(ii) *Nitrogen peroxide.* Purified liquid nitrogen peroxide was supplied in sealed Carius tubes by the Research Department of Messrs. Nobel's Explosives Company, Ardeer, and was handled by methods already developed by Dr. Ellis Lloyd. For this purpose, the Carius tube was first cooled in ice and cracked open. The open end was connected by a glass tube, firmly sealed on with paraffin wax, to a receiver R (Fig. 2, inset) of about 100 c.c. capacity, provided with a phosphoric oxide tube P. The nitrogen peroxide was then distilled over from the Carius tube by immersing the receiver in liquid air and reducing the pressure with a water-pump. When the receiver was full, the connexion leading to the Carius tube was sealed off at a constriction. The receiver with its drying tube was then exhausted to less than 1 mm. with an oil-pump and sealed off in a vacuum.

When required, the receiver was attached to the filling apparatus (Fig. 2, inset), but the nitrogen peroxide was kept frozen as long as possible, and transferred from one vessel to another by sublimation under low pressure, in view of the fact that the Apiezon L grease, which was used as a lubricant for taps and ground joints in these investigations, was noticeably attacked if exposed to this gas at ordinary pressures for more than short periods (about 10—15 minutes).

The nitrogen peroxide was weighed in a graduated tube W (Fig. 2), provided with a tap T_8 and ground-glass joint J. For this purpose the tube W was evacuated and weighed, and was then attached to the filling apparatus by means of the ground joint J. The nitrogen peroxide in the receiver R was frozen in liquid air, and the apparatus was exhausted to less than 1 mm. The tap T_{12} was then closed, and a suitable quantity of nitrogen peroxide sublimed into W by cooling it in liquid air, whilst the receiver R was allowed to warm up somewhat. Taps T_8 and T_{13} were then closed. The weighing tube W was removed, the ground joint J cleaned with light petroleum, and the tube rapidly weighed to give the exact weight of nitrogen peroxide taken. The peroxide was immediately frozen in liquid air, and the tube attached to the nitric oxide apparatus shown in Fig. 2.

Preparation of Mixtures.—The mixtures were prepared in tubes of soda glass, of 4·5—5 mm. bore and with walls 1·5—2 mm. thick; these had a final over-all length of 23 cm. and a capacity of about 4 c.c. The tube *H* was constricted at *L* with special care in view of the pressures which it had to withstand. A suitable quantity of water was first introduced and frozen by immersing the tube in liquid nitrogen. The tube was then attached to the measuring and filling apparatus by means of the ground-glass joint *K*, and the nitrogen peroxide, which had been weighed in the graduated tube *W*, was distilled over into it. Finally, gaseous nitric oxide from the measuring bulb *G* was condensed in quantities corresponding with the equation $NO + NO_2 = N_2O_3$. The tubes in which the three layers had been frozen were sealed off as robustly as possible, and allowed to warm to room temperature in a box covered with a sheet of plate glass. This precaution was fully justified by the bursting of 4 out of 27 tubes during the dangerous stage between the vaporisation of the nitric oxide and its absorption by the other components of the mixture.

Measurement of Temperature.—Temperatures below 0° were obtained by immersing the tubes in alcohol (about 1500 c.c.) in a transparent Dewar flask, and cooling the alcohol by blowing liquid nitrogen on the surface (Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851; Terrey and Spong, J., 1932, 219), or by the addition of solid carbon dioxide. The alcohol was stirred mechanically, and a copper–constantan thermocouple was used to measure its temperature. This couple had been calibrated at the m. p.'s of ice, purified carbon tetrachloride (− 22·9°), and mercury (−38·87°). Before observations were made, the tubes were cooled and shaken, in order to absorb as much nitric oxide as possible. They were illuminated from behind, and viewed under magnification by a lens system.

Temperatures above 0° were obtained by using a clear glass vessel containing water, with the same arrangements for stirring and observation. The temperature of the water was controlled by adding hot or cold water or ice as required. Observations above room temperature were made through a cage of wire gauze as a protection in case the tube should burst when warmed.

(i) The separation of ice was always accompanied by supercooling; this was overcome by dipping the tip of the tube into acetone cooled with solid carbon dioxide, and then replacing the tube in the bath. The bath was allowed to warm spontaneously at a rate of 5—10° per hour, and the temperature was recorded (at least three times) at which the last residue of ice began to melt.

(ii) Points on the eutectic line represent the temperature at which melting began in the frozen aqueous layer, as indicated by the movement of globules of the blue " liquefied gas " phase entangled in the crystals of ice.

(iii) The formation of two liquid layers was observed by cooling mixtures which had been rendered homogeneous by warming and shaking. Turbidity appeared suddenly in the aqueous solution, and the temperatures of separation could be reproduced within 0·3°. At the lower temperatures the progressive absorption of nitric oxide from the gas phase on repeated cooling and shaking caused a rise in the temperature at which turbidity appeared : this was as much as 2° at + 3° and 8° at − 10°. The temperatures of separation recorded in the table must therefore be regarded only as minimum values; but they vary so rapidly with changes of concentration that no substantial error is likely to be introduced in our estimate of the critical composition for complete miscibility at atmospheric temperatures, or below.

(iv) Further evidence of the rapid change of the temperature of separation with variations of composition in the lower part of the curve was provided by the behaviour of a super-cooled mixture (No. 7) containing 34·45% N_2O_3. This should have deposited ice at a temperature a little above the quaternary point at − 33·3°, at which a mixture containing 36% N_2O_3 deposits ice and becomes turbid simultaneously. Actually, it was super-cooled to − 40° without becoming turbid; and even when ice was beginning to appear at temperatures below − 40°, no turbidity was developed during the crystallisation.

(v) At concentrations greater than 52% N_2O_3, the temperatures of separation rise more slowly, since the curve is already bending over towards a maximum. Moreover, the increased proportion of nitrous anhydride in the aqueous layer makes the solutions so dark that the separation into two layers is difficult to observe. The highest temperature of separation was 55°, at which complete miscibility occurred in a composition of 65% N_2O_3 or 30 mols. %.

(vi) The mixtures richest in nitrous anhydride developed the highest pressures whilst being allowed to warm to room temperature. The proportion of free space in the tube was therefore increased to rather more than one-half, and the solid nitrogen peroxide was distributed over the walls of the tube in order to increase the area of contact during the absorption of the nitric oxide. The limits of composition within which two liquid layers are formed on this side of the solubility curve are very narrow, but two mixtures containing 94·2 and 96·0% N_2O_3 gave observed temperatures of separation of 23·5° and 4·6°.

(vii) The limits of miscibility read off from the curve are 48·6 and 94·5% by weight N_2O_3 at 20°, 42·4 and 96·3% at 0°. Since these limits are brought closer together by the passage of nitric oxide into the gaseous phase, a small correction was introduced automatically by selecting integral percentages *below* and *above* the observed decimal readings on the *left* and the *right* arm of the curve respectively. We therefore estimate the limits of partial miscibility in integral percentages as 48—95% N_2O_3 at 20°, 42—97% N_2O_3 at 0°, and regard it as unlikely that these are in error by more than one unit.

SUMMARY.

1. Two liquid phases are formed over a wide range of composition in mixtures of nitrous anhydride and water.

2. The limits of miscibility (by weight) are 42—97% N_2O_3 at 0° and 48—95% at 20°. A maximum temperature of separation was observed at 55° in a mixture containing 65% N_2O_3 or 30 mols. %; but these figures are all lowered by the escape of nitric oxide from the liquid phases into the gaseous phase, and in particular, the critical solution temperature may be as much as 20° higher than the limit thus recorded.

3. A quaternary point, at which one gaseous and two liquid phases are in equilibrium with pure ice, was observed at — 33·3° and 36% N_2O_3. A second quaternary point, with nitrous anhydride as the solid phase, may be expected to occur below — 103° at a concentration greater than 98% N_2O_3.

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