

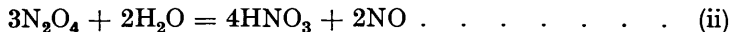
## 2. Properties of the Oxides of Nitrogen. Part III. The Pseudo-binary System $N_2O_4-H_2O$ .

By T. M. LOWRY and J. T. LEMON.

UNLIKE the binary system  $N_2O_3-H_2O$  (Part II, preceding paper), where internal oxidation and reduction are only of secondary importance, the components of the pseudo-binary system  $N_2O_4-H_2O$  do not merely dissolve in one another, or unite to form a hydrate, but interact reversibly to give products of a higher and a lower degree of oxidation, as shown by the equation



When the initial proportion of  $N_2O_4$  exceeds about 50%, two liquid layers are formed, *viz.*, (i) a liquefied gas layer consisting almost entirely of  $N_2O_3$  and  $N_2O_4$ , and (ii) an aqueous acid layer, containing nitric acid, a smaller proportion of nitrous acid, and a considerable amount of dissolved  $N_2O_3$  and  $N_2O_4$ . A second form of interaction, represented by the equation



(Schönbein, *J. pr. Chem.*, 1860, **81**, 268), may result in the escape of nitric oxide into the gaseous phase, and thus produce a change in the composition of the liquid; but the pressures of nitric oxide developed in this way are smaller than in the system  $N_2O_3-H_2O$ ; the interaction represented by equation (i) is therefore here much more important than that by equation (ii). These equilibria are of considerable industrial interest in connexion with the manufacture of nitric acid, and have therefore been studied extensively from this point of view; \* but the phase-rule study here described appears to be entirely novel.

\* Saposchnikoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 506; Förster and Koch, *Z. angew. Chem.*, 1908, **21**, 2161, 2209; Lewis and Edgar, *J. Amer. Chem. Soc.*, 1911, **33**, 292; Partington and Parker, *J. Soc. Chem. Ind.*, 1919, **38**, 75; Forster, Burchardt, and Fricke, *Z. angew. Chem.*, 1920, **33**, 113, 122, 129; Rideal, *J. Ind. Eng. Chem.*, 1920, **12**, 536; Sanfourche, *Ann. Chim. Phys.*, 1924, **1**, 5; Klemenc *et al.*, *Z. anorg. Chem.*, 1924, **141**, 231, *et seq.*; Abel *et al.*, *Z. physikal. Chem.*, 1928, **132**, 55, *et seq.*; Abel, Schmid, and Stein, *Z. Elektrochem.*, 1930, **36**, 692; see also Webb, "The Absorption of Nitrous Gases" (Arnold).

The earliest observations on the interaction of nitrogen peroxide and water were made by Priestley ("Experiments and Observations on Different Kinds of Air," Vol. 3, p. 198), who passed the gas through three wash-bottles in series containing water, and observed that the water, after becoming warm, began to "sparkle" and evolve gas; it then became successively blue, green, and finally yellowish-green. The gas which escaped from the last wash-bottle was found to be nitric oxide. He also placed some of the green solution in an open dish and blew upon it, whereupon copious red vapours were evolved, leaving a yellow residue of nitric acid (*op. cit.*, p. 204).

Dulong (*Ann. Chim. Phys.*, 1816, 2, 317) found that a very small quantity of water was sufficient to turn liquid nitrogen peroxide green; when poured drop by drop into water, the liquid fell to the bottom and became a very deep green. He also observed that, on adding successive amounts of liquid nitrogen peroxide to water, the evolution of nitric oxide diminished and finally ceased, although the liquid still continued to take up the peroxide. During the addition, the water exhibited the same changes of colour as were observed on passing nitric oxide through aqueous nitric acid of various concentrations.

Fritzsche and Mitscherlich in 1832 observed that, when liquid nitrogen peroxide was allowed to take up water slowly from the air, two green liquids were formed, which separated again after shaking, like those given by nitrogen peroxide and nitric acid. Fritzsche (*J. pr. Chem.*, 1841, 22, 14) separated and distilled the two liquid layers produced by the gradual addition of water to liquid nitrogen peroxide cooled in ice and salt. The lower, dark green layer began to boil at 17°, giving an almost pure blue distillate; the temperature then rose gradually to 28°, whilst the liquid lost its green colour and finally showed the yellow-brown colour of nitrogen peroxide. The upper, grass-green layer began to boil at 20°, and a few drops of blue liquid collected in the cooled receiver; the boiling point then rose rapidly to 120°, at which the pale yellow residue of aqueous nitric acid distilled unchanged. When a larger quantity of water was added to liquid nitrogen peroxide, the lower blue-green layer was so dark as to be transparent only in thin layers. On distilling this mixture, without separating the two layers, the lower layer began to boil below 0°, liberating nitric oxide, and giving a pure indigo-blue distillate of nitrous anhydride; when redistilled, this began to boil again below 0°, with evolution of nitric oxide, giving an indigo-blue distillate in the cooled receiver; but the boiling point gradually rose to 28°, the residue consisting of nitrogen peroxide. From his experiments, Fritzsche concluded that nitrous anhydride decomposes into nitric oxide and nitrogen peroxide on distillation, and that the green colour of the liquid products was due to the admixture of deep blue nitrous anhydride with yellow-brown nitrogen peroxide.

Similar conclusions regarding the origin of the green colours in mixtures of nitrogen peroxide and water were reached by Briner and Durand (*Compt. rend.*, 1912, 155, 583, 1495), who found that these mixtures behaved in much the same way as mixtures of nitrous anhydride and water (see Part II). Finally, Heberlein (Thesis, Geneva, 1926), by measurements of conductivities, confirmed the totally different character of the two liquid layers, since the lower layer of liquefied gas had a specific resistance of the order of 10<sup>6</sup> ohms, whereas that of the upper aqueous acid layer was of the order of 2—12 ohms.

#### EXPERIMENTAL.

The methods used in the present investigation were as described in Part II, but the preparation of the mixtures was simplified by the omission of nitric oxide from the components. The results are set out in the table and plotted in the figure. Three of the mixtures had been prepared by Dr. W. V. Lloyd; the observations now made with these specimens are shown by crossed circles in the figure. The limits of miscibility at 0° and 20°, which he deduced from his analyses, are indicated by crosses, as follows:

At 0°: 49.9 and 98.2% by wt. (or 16.3 and 91.4 mols. %) N<sub>2</sub>O<sub>4</sub>

At 20°: 53.0 and 97.2% by wt. (or 18.1 and 87.2 mols. %) N<sub>2</sub>O<sub>4</sub>

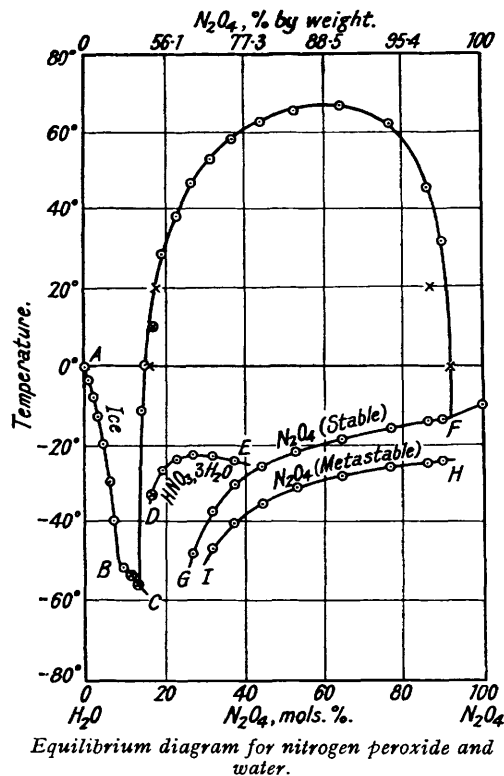
With the exception of the higher limit at 20°, which appears to be in error, these numbers conform closely with the measurements now recorded.

*Description of the Equilibrium Diagram.*—(a) The curve *AB* represents the temperature of

crystallisation of ice from the homogeneous aqueous solutions. Beautiful fern-like growths were frequently obtained when freezing was initiated by cooling the tip of the tube with solid carbon dioxide; but at the lower temperatures the increasing viscosity of the aqueous solutions caused the crystals to grow more slowly, and compact clumps of ice were produced. The temperatures were recorded at which the first signs of melting were observed.

(b) At about  $-50.3^\circ$  and 32.7%  $N_2O_4$ , the ice-line is intersected by a short curve *BC*, corresponding to the crystallisation of some new compound. This compound (which was not observed in the system  $N_2O_3-H_2O$ ) crystallised in cubic aggregates, which were obviously different from ice: it is perhaps a hydrate of nitric or nitrous acid, but its composition was not determined.

(c) The curve *DE* represents the temperature of separation, from the aqueous acid layer, of a compound which crystallised in long prisms with triangular facets at the ends. This was almost certainly the trihydrate of nitric acid, which was described by Pickering (J., 1893, 63, 436) as forming "rather transparent large crystals." This identification is justified by the fact that the maximum of the curve at  $-22.5^\circ$  lies only  $4^\circ$  below that of the trihydrate in the system  $HNO_3-H_2O$ , where it has a considerable range of existence (Küster and Kremann, Z. anorg. Chem., 1904, 41, 22); moreover, in each case the freezing-point curve has a flat maximum, indicating that it is largely dissociated on fusion. On the other hand, the monohydrate, even in pure aqueous solutions, has a maximum freezing point at  $-38^\circ$ , which could not be raised to  $-22^\circ$  by the presence of other components in our mixtures.



liquefied gas. This layer consists almost entirely of nitrogen peroxide and nitrous anhydride and its f. p. falls continuously, from right to left of the diagram, as the concentration of the nitrous anhydride increases (by the elimination of the higher oxide as nitric acid) when the proportion of water is increased. The f. p. of the layer was recorded as the temperature at which the first signs of melting could be observed in a small quantity of solid in contact with the solution.

The upper curve *FG* corresponds to separation of the ordinary stable form of nitrogen peroxide, in small bright granular crystals, or occasionally in aggregates of hexagonal crystals. The lower curve *HI* represents the crystallisation of a new, metastable form of the peroxide. This was obtained as the initial product by chilling the tube in a bath of alcohol cooled by carbon dioxide, and then holding the tip of the tube in contact with solid carbon dioxide to initiate crystallisation; but it reverted to the stable form when the contact was continued, or the tube was sharply tapped. The new form usually crystallised in long, broad needles, like sword blades, which soon acquired irregular and serrated edges as growth continued; but pointed and diamond-shaped crystals were occasionally observed, the latter sometimes fused together to form sheets with serrated edges. In addition, the solid often separated as an ice-like crust on the walls of the tube; but all these varieties appeared to have the same m. p.

(d) At higher concentrations of nitrogen peroxide, the upper aqueous layer deposited yellow crystals when cooled with acetone and solid carbon dioxide, but the temperatures of separation were not determined. When the tubes were then placed in a bath at  $-30^\circ$ , the yellow crystals soon developed a green and then a blue colour and decomposed with much bubbling, leaving a residue which appeared to consist of solid nitrogen peroxide. These crystals were probably the compound,  $N_2O_4 \cdot 2HNO_3$ , which Pascal and Garnier (Bull. Soc. chim., 1919, 25, 309) described as decomposing at  $-48.5^\circ$ .

(e) The two roughly parallel curves *FG* and *HI* represent the temperatures of crystallisation of nitrogen peroxide from the lower layer of

## Freezing Points and Temperatures of Separation into Two Layers in Mixtures of Nitrogen Peroxide and Water.

Composition by wt.		H <sub>2</sub> O content.		Vol. occupied by liquid, %.	Freezing points.			Turb. pt.	Solid phase separating from aq. layer.
N <sub>2</sub> O <sub>4</sub> , g.	H <sub>2</sub> O, g.	Wt. %.	Mols. %.		Aqueous layer.	N <sub>2</sub> O <sub>4</sub> , ordinary form.	Liquefied gas, N <sub>2</sub> O <sub>4</sub> , new form.		
0.1241	2.6333	95.50	99.10	76.8	— 3.3°	—	—	Ice	
0.2743	2.5607	90.30	97.94	77.8	— 7.5	—	—	"	
0.4117	2.3810	85.27	96.73	68.3	— 12.5	—	—	"	
0.5494	2.2601	80.43	95.46	73.2	— 19.5	—	—	"	
0.7233	2.1705	75.00	93.88	70.4	— 29.3	—	—	"	
0.8593	2.0432	70.38	92.40	66.1	— 39.9	—	—	"	
1.0307	1.9379	65.29	90.58	69.4	— 51.2	—	—	New solid	
	L <sub>1</sub>	61.20	88.96	71.8	— 53.0	—	—	"	
	L <sub>2</sub>	56.62	86.95	48.5	— 55.4	—	—	"	
0.7540	0.9207	54.97	86.18	67.0	*	—	— 10.9° †	"	
0.7837	0.8865	53.08	85.25	62.6	*	—	— 0.1 †	"	
	L <sub>3</sub>	49.40	83.30	52.4	— 32.7	—	+ 10.5 †	HNO <sub>3</sub> , 3H <sub>2</sub> O	
1.7936	1.4419	44.56	80.38	68.2	— 26.4	—	28.9 †	"	
2.1169	1.3766	39.40	76.85	72.5	— 23.7	—	38.7 †	"	
2.3449	1.2295	34.40	72.82	73.2	— 22.5	— 47.4°	47.1 †	"	
2.5976	1.0756	29.28	67.90	69.2	— 22.8	— 37.0	53.3 †	"	
2.7846	0.9042	24.52	62.39	73.3	— 23.9	— 30.2	58.5 †	"	
1.6363	0.3997	19.63	55.49	73.3	—	— 25.4	62.4 †	"	
1.8309	0.3198	14.86	47.14	77.1	—	— 22.1	65.5 †	"	
1.8705	0.2007	9.70	35.43	74.7	—	— 18.8	66.8 †	"	
2.0629	0.1201	5.50	22.92	81.8	—	— 16.0	61.9 †	"	
2.0128	0.0617	2.98	13.55	74.4	—	— 14.2	45.7 †	"	
2.0154	0.0437	2.12	9.96	75.2	—	— 13.6	31.8 †	"	

L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub> = mixtures prepared by W. V. Lloyd.

\* In these two mixtures the aqueous phase remained very turbid after cooling, and its freezing point could not therefore be determined.

† Globules fall.

‡ Globules rise.

Since the eutectic of the N<sub>2</sub>O<sub>3</sub>-N<sub>2</sub>O<sub>4</sub> system is situated at about - 112° (cf. Baume and Robert, *Compt. rend.*, 1919, 169, 968; Wittorff, *Z. anorg. Chem.*, 1904, 41, 90), it might be expected that the temperatures of separation of the peroxide from these more complex mixtures would fall to a still lower temperature. The extension of the curves *FG*, *HI* to lower temperatures could not be observed, however, for the lower layer became so intensely blue that it was extremely difficult to observe melting, even when the tube was inverted so that the lower layer filled the pointed end; moreover, this difficulty was accentuated by the fact that the lower layer tended to remain a little turbid. An approximate idea of the composition of the lower layer at its f. p. can be derived from the f. p.'s of the system N<sub>2</sub>O<sub>4</sub>-N<sub>2</sub>O<sub>3</sub>, as plotted by the above authors, since the ready and complete volatility of this layer shows that it contains only minimal amounts of water or nitric acid in addition to the two main components.

(f) The miscibility curve, *CF*, is similar in general shape to the corresponding curve for the system N<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O, but is rather flatter and more symmetrical when plotted on a scale of mols. %. The limits of miscibility deduced from this curve are

At 0°: 46.9 and 98.4% by wt. (14.7 and 91.5 mols. %) N<sub>2</sub>O<sub>4</sub>

At 20°: 52.3 and 98.1% by wt. (17.7 and 90.8 mols. %) N<sub>2</sub>O<sub>4</sub>

The highest observed temperature of separation was at 67° in a mixture containing 89% N<sub>2</sub>O<sub>4</sub> (62 mols. %), but the real critical solution temperature must be a little higher, and at a rather lower concentration of N<sub>2</sub>O<sub>4</sub>, on account of the escape of nitric oxide from the liquid phases into the gaseous phase. The displacement is, however, obviously much smaller than in the system N<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O, because the pressures developed were much less, so that none of the tubes burst either on warming or on subsequent heating, although some of them were heated above 70°. Moreover, the volume of the gaseous phase was reduced from about 60% of the total volume in the system N<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O to about 25% in the system N<sub>2</sub>O<sub>4</sub>-H<sub>2</sub>O, so the errors introduced from this cause would be relatively small.

## SUMMARY.

1. Two liquid phases are formed over a wide range of compositions in mixtures of nitrogen peroxide and water.

2. The limits of miscibility (by weight) are 47—98%  $N_2O_4$  at  $0^\circ$  and 52—98%  $N_2O_4$  at  $20^\circ$ . A maximum temperature of separation was observed at  $67^\circ$  in a mixture containing 89%  $N_2O_4$  (62 mols. %); but these figures may be slightly lowered by the escape of nitric oxide from the liquid phases into the gaseous phase.

3. The homogeneous aqueous solutions deposit ice at temperatures down to  $-50^\circ$  and compositions up to 33%  $N_2O_4$ . They then deposit a compound of unknown composition over a narrow range down to  $-56^\circ$  and up to 44%  $N_2O_4$ . Non-homogeneous mixtures, containing more than 44%  $N_2O_4$ , deposit the trihydrate of nitric acid from the upper aqueous-acid layer, at temperatures which reach a maximum of  $-22.5^\circ$  at a gross composition of about 67%  $N_2O_4$  for the whole mixture. The lower layer of liquefied gas deposits nitrogen peroxide, either in the ordinary stable form or in a metastable form which melts about  $11^\circ$  lower.

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