3. *Properties of the Oxides of Nitrogen. Part IV. Formation of Two Liquid Layers in Mixtures of Nitrogen Peroxide and Water.*

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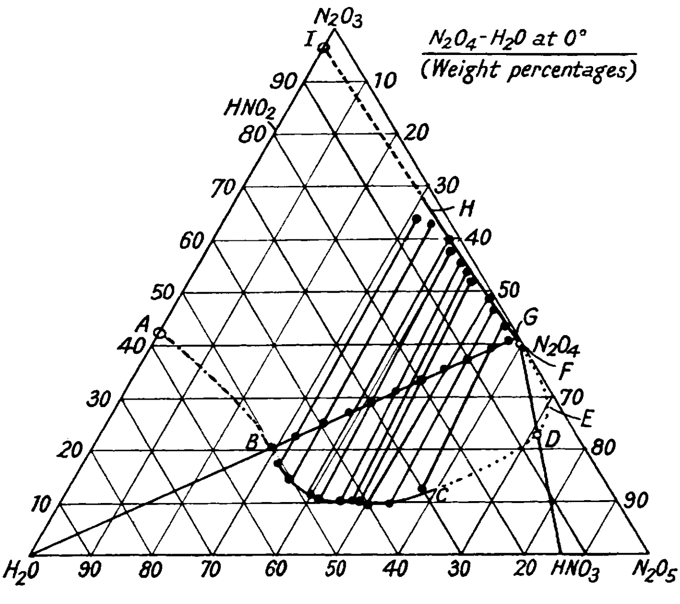
In the two preceding papers, the limits of miscibility of the aqueous and the non-aqueous layers, formed by mixtures of nitrous anhydride and of nitrogen peroxide with water, have been determined up to the temperature of complete miscibility. In the binary system N_2O_3–H_2O, the compositions of these layers appear to be substantially constant at a given temperature (compare ether and water, or phenol and water); it was therefore possible to represent the freezing points of the aqueous layer over a considerable range of total compositions by a horizontal straight line. In the pseudo-binary system N_2O_4–H_2O, this was no longer possible, since the compositions of the two layers were influenced by mutual oxidation

Fig. 1.

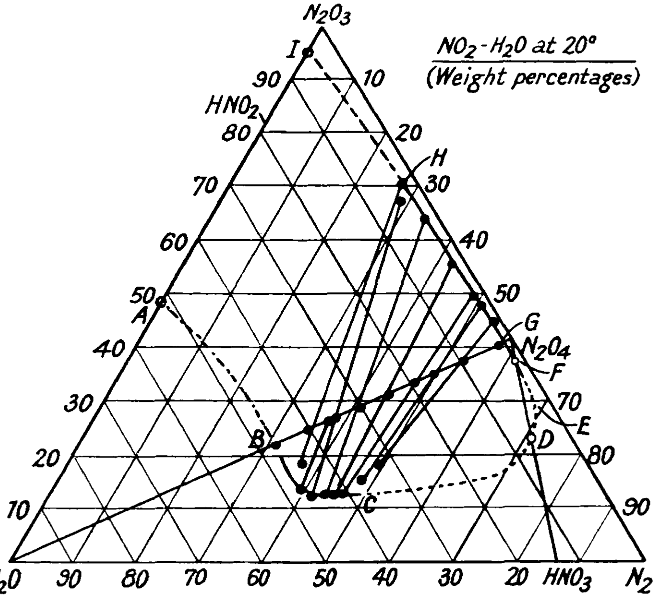


and reduction to an extent which depended on the relative masses of the components. The freezing points of the two liquid layers were therefore represented by *curves* instead of by straight lines; but no attempt was made to determine the compositions of these layers under the conditions then prevailing.

The present paper describes experiments (carried out earlier), in which analyses of the two liquid layers, formed by mixtures of nitrogen peroxide and water, were made at two temperatures only, *viz.*, 0° and 20°. The data thus obtained are recorded as % by weight in Table I, and in mols. % (for 0°) in Table II. They have also been plotted on triangular diagrams (Figs. 1 and 2), the *apices* of which are formed by the three components of the system H_2O–N_2O_3–N_2O_5, whilst the compositions of N_2O_4, HNO_2, and HNO_3 are shown on the *sides* of the diagram.

Each mixture of nitrogen peroxide and water is represented by three points on the diagram, one showing the empirical composition of the mixture, and the other two showing the actual compositions of the two layers. These three points are joined by a tie-line, and the ends of these tie-lines provide two substantial sections, *BC*, *GH*, of the boundary, *ABCDEFGHI*, of the area of the diagram within which two liquid phases are formed. Since complete separation of the two liquid layers was always difficult, the boundary line has been drawn through the outermost points on the tie-lines.

FIG. 2.



It was not practicable in the time available to plot the whole of this boundary, but the measurements in Part III provide independent data for the two points *BG* at which the boundary intersects the line H_2O–N_2O_4. Similarly, the observations recorded in Part II show that the miscibility curve cuts the H_2O–N_2O_3 side of the diagram at two widely separated points, *AI*, instead of forming a closed loop, as we supposed when we first began to plot the tie-lines. Quantitative experiments then showed that the aqueous boundary *BA* actually bends away from the non-aqueous boundary, *GHI*, in a manner that involves a reversal of curvature, when compared with the section *BC* of the boundary which had already been plotted. The data for the system N_2O_3–H_2O are, however, quite precise; and the broken lines, *AB* and *HI*, which link them with the results of the present analyses, are so nearly straight that no wide deviation from them appears to be likely to result from subsequent experimental determinations.

Two additional points, *DF*, on the other side of the H_2O–N_2O_4 line, are provided by Bousfield's measurements (J., 1919, **115**, 45) of the limits of miscibility in the system

N_2O_4–HNO_3. These two points have been joined by a broken curve, which does not diverge very far from the N_2O_4–HNO_3 line. The line *DF* between them provides an additional tie-line on the diagram; but it is much shorter than those now recorded for mixtures of nitrogen peroxide and water, since the peroxide mixes more readily with nitric acid than with water. The broken curve indicates that complete miscibility would occur in mixtures of nitric acid and the peroxide with a little nitric anhydride. This additional component appears to mix in all proportions, both with the peroxide and with the acid, up to a limit fixed by the solubility of the solid; it would therefore distribute itself somewhat evenly between the aqueous and the non-aqueous layer, and finally reduce them to identity of composition. The tie line *DF* would then vanish at the point *E*.

One of Bousfield's points, *F*, on the line N_2O_4–HNO_3 is very close to our own point, *G*, on the N_2O_4–H_2O line, and forms only a slight extension of the boundary line, *HG*. The other point, *D*, is much more isolated; but we have ventured to join it by a continuous broken line *DC* to our own curve *BC* for the aqueous layer. It must be emphasised, however, that the broken curve, *CDEF*, passes through only one experimental point, and that (apart from the complete miscibility of water and nitric acid) we have no other check upon unexpected deviations from the course suggested.

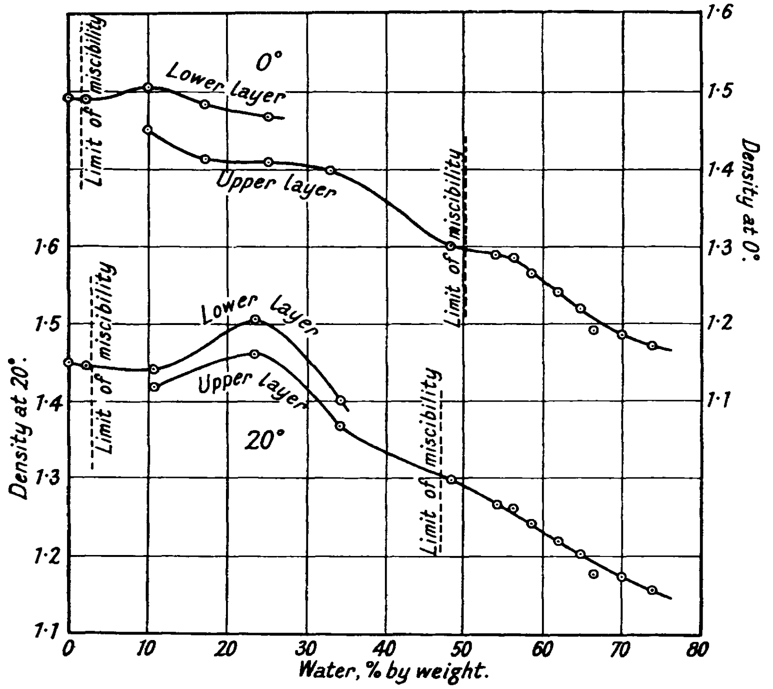
The diagram emphasises the interesting contrast between nitric anhydride, which is completely miscible, and the peroxide and sesquioxide, which are only partially miscible, with water. These two lower oxides do not differ very widely in this respect. The zone in which two liquid layers are formed therefore forms a wide strip, the boundaries of which are nearly parallel to the side of the triangular diagram which includes the three oxides. Both boundaries are, however, concave when viewed from the opposite apex, and show some tendency to be pivoted on the point, H_2O, with a minimum of solubility in water at the composition N_2O_4. When, however, the non-aqueous components have been oxidised about half-way between N_2O_4 and N_2O_5, they become almost abruptly miscible with water in all proportions, since the boundary *CD* at 20° is not far removed from a straight line passing through the " water " point on the diagram.

Densities of Liquid Phases.—The densities of a series of homogeneous mixtures of nitrogen peroxide and water were determined by the method of flotation; but this became difficult to apply in mixtures containing more than 44% N_2O_4, and had to be abandoned altogether above 50% N_2O_4, where two liquid layers were formed; the intense colours of such solutions prevented proper observation of the floats, even under strong illumination, and the use of narrower observation tubes proved impracticable, because the floats tended to adhere to the wall of the vessel. In such solutions, and especially in systems containing two liquid layers, it was also found that the floats themselves adhered together very obstinately. In these circumstances the densities of the two liquid layers were determined by means of a capillary pyknometer. For this purpose mixtures were prepared in a separator of the type illustrated in Fig. 4, but with narrow pyknometer tubes in place of the bulbs D_1 and D_2. The ready formation of comparatively stable emulsions, however, made it impracticable to obtain data for mixtures containing 34—47% of water.

The numerical results are summarised in Table IV, and are plotted in Fig. 3.

In these mixtures the non-aqueous layer was always the denser and the more strongly coloured. This does not remain true, however, throughout the ternary system, since density measurements have substantiated the fact that, in mixtures of nitrogen peroxide with nitric acid, the *lower* layer consists of nitric acid with dissolved nitrogen peroxide, whilst the *upper* layer consists mainly of liquid nitrogen peroxide (Pascal and Garnier, *Bull. Soc. chim.*, 1919, **25**, 309; Bousfield, *loc. cit.*). Hence, in the ternary system, the densities of the two layers must become identical and change over at a contour line on the triangular equilibrium diagram lying between the lines representing the two binary systems HNO_3–N_2O_4 and H_2O–N_2O_4. This reversal of densities was actually observed in mixtures of nitrogen peroxide and water by Heberlein (Thesis, Geneva, 1926, p. 20), who states that, at 4% H_2O the aqueous layer " is always heavier than the layer of liquefied gas," that " at 6% H_2O, the two layers have nearly the same density," whilst " at 8% H_2O and above, the aqueous layer rises to the surface." Observations by Lowry and Lemon, however, showed that in a mixture containing 3% H_2O, the density of the aqueous layer

FIG. 3.



Densities at 0° *and* 20° *of mixtures of nitrogen peroxide and water.*

TABLE I.

Miscibility of Nitrogen Peroxide and Water.

(Percentages by weight.)

At 20°.

Total	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5. %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
2·8	Separation into two layers begins.					
9·55	44·8	54·1	1·0	18·7	49·0	32·3
15·41	47·8	51·0	1·2	15·0	48·1	36·9
19·02	49·7	48·1	2·2	12·6	46·0	41·0
24·45	55·4	42·3	2·3	12·8	44·8	43·4
30·00	63·7	33·8	2·5	12·8	43·3	43·8
34·81	67·10	28·5	4·4	12·4	41·6	45·9
36·40	—	—	—	13·7	39·4	46·9
40·52	70·3	27·1	2·6	18·5	37·2	44·3
47·0	Separation into two layers ends.					

At 0°.

Total	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
1·8	Separation into two layers begins.					
5·01	43·12	55·87	1·07	12·31	57·52	30·17
10·35	46·24	52·36	1·40	9·94	53·68	36·38
14·97	48·53	50·94	0·53	9·63	50·19	40·18
19·59	51·81	46·01	2·18	10·21	48·77	41·02
19·91	53·32	44·67	2·01	10·03	47·51	42·46
24·84	55·28	42·89	1·83	10·13	45·46	44·41
29·58	57·51	40·02	2·48	10·70	41·93	47·39
34·39	59·80	38·81	1·39	11·23	40·08	48·69
39·51	62·98	34·10	2·92	14·27	35·10	50·63
45·31	63·84	31·22	4·94	17·16	31·94	50·90
50·1	Separation into two liquid layers ends.					

TABLE II.

Miscibility of Nitrogen Peroxide and Water at 0°.

(Molecular percentages.)

Total,	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
8·56	Separation into two layers begins.					
21·22	49·76	45·37	4·92	6·87	22·50	70·63
37·10	51·93	41·40	6·67	4·94	18·76	76·30
47·34	56·00	41·37	2·63	4·49	16·48	79·03
55·42	55·46	34·67	9·87	4·69	15·78	79·53
55·96	57·18	33·72	9·10	4·51	15·03	80·47
62·73	59·30	32·39	8·31	4·46	14·09	81·45
68·20	59·81	29·30	10·89	4·46	12·30	83·24
72·80	64·33	29·38	6·29	4·59	11·53	83·88
76·95	63·41	24·17	12·42	5·65	9·78	84·57
80·90	59·87	20·61	19·42	6·75	8·85	84·40
84·87	Separation into two liquid layers ends.					

TABLE III.

Densities of Homogeneous Liquids.

H_2O, %.	Temp.	*d.*	$d^{0°}$.	$d^{20°}$.
73·9	− 3·6°	1·17335	1·1705	1·1560
	+ 19·45	1·15690		
70·0	− 11·60	1·19380	1·1845	1·1705
	+ 17·94	1·17335		
66·4	− 26·10	1·21018	1·1910	1·1765
	− 1·65	1·19380		
	+ 25·65	1·17335		
64·7	+ 10·21	1·21018	1·2179	1·2010
	+ 20·12	1·20184		
	+ 31·0	1·19380		
61·9	− 2·49	1·24081	1·2381	1·2190
	+ 16·29	1·22255		
	+ 29·78	1·21018		
58·5	+ 5·0°	1·25732	1·2621	1·2415
	+ 14·7	1·24680		
	+ 20·01	1·24081		
56·2	− 20·40	1·30590	1·2822	1·2600
	− 9·30	1·29286		
	+ 15·45	1·26608		
54·1	− 17·7	1·30590	1·2885	1·2647
	− 6·2	1·29286		
	+ 18·8	1·26608		
50·5	+ 20·19	1·29286		

TABLE IV.

Densities of Two Liquid Phases.

(*a*) At 0°.			(*b*) At 20°.		
H_2O, %.	Upper layer.	Lower layer.	H_2O, %.	Upper layer.	Lower layer.
0	—	1·49250	0	—	1·44750
2·15	—	1·49029	2·15	—	1·44450
10·12	1·44988	1·50508	10·67	1·41784	1·43914
17·23	1·41171	1·48256	23·48	1·46011	1·50308
25·32	1·40831	1·46690	34·17	1·36581	1·39881
32·98	1·39734	—	48·31	1·29622	—
48·31	1·29893	—			

at room temperature (about 14°) was slightly less than that of the non-aqueous layer, but that when the mixture was warmed in the hand and shaken, the densities of the layers were reversed, and the acid layer sank to the bottom. The point of inversion is therefore at a lower concentration of water than that recorded for very narrow tubes by Heberlein.

EXPERIMENTAL

Preparation and Separation of the Mixtures.—(i) *At* 20°. The mixtures were made up by weight in the separator shown in Fig. 4. This consisted of a cylindrical vessel *S*,* 20 cm. long and 1—2 cm. wide, into which three tubes were sealed, *viz.*, a central filling tube A_0 at the top, and two lateral " drawing-off " tubes B_1 and B_2, the former reaching nearly to the bottom of the central tube and the latter to within about 1 cm. of the bottom. These tubes were connected to two bulbs, D_1 and D_2, for collecting the two liquid phases. The connecting tubes and taps are shown in the figure. Since substantial pressures, ranging from 1 to 3 atm., were developed in the separator, the taps C_1 and C_2 were held firmly in position with elastic bands. They were lubricated with a little Apiezon L grease, but in later experiments this was replaced by the phosphoric acid lubricant used by Daniels and Verhoek (*J. Amer. Chem. Soc.*, 1931, **53**, 1250).

The requisite amount of water was weighed out in a pyknometer, the delivery tube of which was drawn out into a long fine capillary for insertion down A_0. By blowing gently down the short arm of the pyknometer, the water could be caused to syphon over. The pyknometer was then withdrawn and again weighed, thus giving the weight of water taken.

The water in the separator was frozen in liquid air, and the separator sealed on to the nitrogen peroxide filling apparatus at *N* (Part II, Fig. 2 inset), through a constriction, and exhausted. A weighed quantity of nitrogen peroxide was then distilled over from the weighing tube *W* of the filling apparatus into the separator *S*, and the latter was finally sealed off under vacuum at the constriction.

With the taps C_1 and C_2 fully open, the contents of the separator were allowed to warm to room temperature very slowly, since any sudden change of pressure in the apparatus caused the liquid to be forced up the inner tubes into the two bulbs D_1 and D_2. Before commencing the separation, it was frequently necessary to clear the two inner tubes B_1 and B_2 from mixtures of the two liquid phases. This was effected by closing the taps C_1 and C_2, and warming the bulbs D_1 and D_2 by hand to force the liquid out of the tubes.

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* The first separator was of uniform width throughout; a second was wider in the upper half.

The separator was then immersed as far as possible in a thermostat at 20°, and kept for at least an hour before the separation was started. The lower layer was first drawn off into the bulb D_1 by arranging the separator so that D_1 came outside the thermostat, and closing the tap C_1; D_1 was then cautiously cooled by bringing a Dewar flask of liquid air near it, and the difference of pressure caused the lower layer to be forced up B_1 and over into D_1. As soon as the upper layer was seen to be rising in B_1, the tap C_1 was opened to equalise the pressure and stop the transference of liquid. The upper layer was then similarly drawn off into D_2, the process being stopped by opening the tap C_2, whilst the excess of liquid remained in the central tube. Some practice and great care were necessary in order to obtain homogeneous samples of the two layers.

Finally, D_1, D_2, and the central reservoir of the separator were immersed simultaneously (in order to avoid distillation) in three small Dewar flasks of liquid air and, when the contents were completely frozen, the two bulbs D_1 and D_2 were sealed off at the constrictions provided.

FIG. 4.

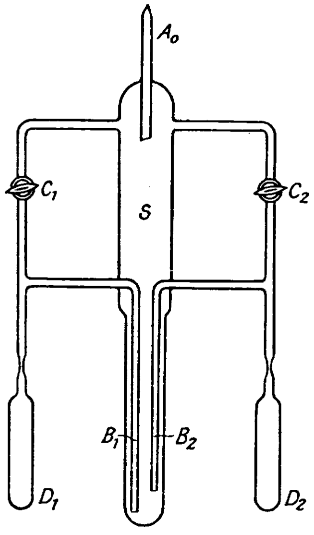
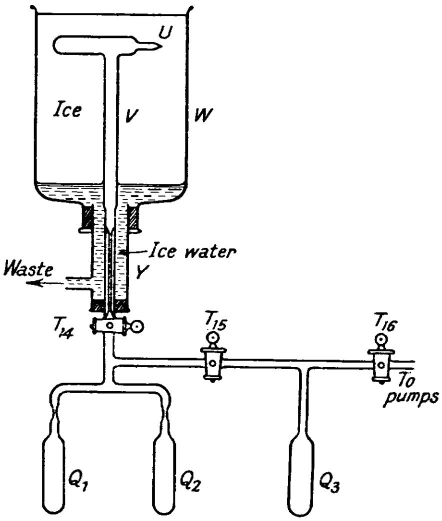


FIG. 5.



(ii) *At* 0°. The separator described above proved unsuitable for use at 0°, and was replaced by another (see Fig. 5). The vessel, V, in which the mixtures were prepared consisted of a cylindrical bulb of about 30 c.c. capacity attached to a tube 12 cm. long and terminating in a wide capillary 10 cm. long, closed at the far end by a tap T_{14}. The mixtures were prepared, as described above, with the cylindrical bulb in a vertical position. A known amount of water was first introduced through the tube U and frozen; U was sealed to the nitrogen peroxide filling apparatus at N (Part II, Fig. 2 inset), through a constriction, a known weight of nitrogen peroxide was introduced, and the vessel was sealed off. The contents of the bulb were then allowed to become warm and mix thoroughly.

The separator was mounted in an ice-bath, but the tap T_{14} was left outside the bath, as shown in Fig. 5. The bulbs Q_1, Q_2, Q_3 were then sealed on below the tap. The vessel V was surrounded by washed and crushed ice, while the glass tube Y, through which the capillary was observed, was maintained at 0° by keeping it filled with ice-water from the bath above. This precaution was found to be essential, since any inequality of temperature produced violent disturbance of the liquids in the capillary and rendered separation impossible.

The mixture was maintained at 0° for at least ½ hour before the separation was started. The part of the apparatus below T_{14} was then exhausted, and tap T_{16} closed. The mixed liquids in the capillary were first removed by cooling the bulb Q_3 in liquid air and cautiously distilling the contents of the capillary into it by opening tap T_{14}. When the capillary was occupied exclusively by the homogeneous lower layer, tap T_{15} was closed, and a sample of the lower layer was distilled into Q_1 by cooling it in liquid air. Tap T_{14} was then closed, and the bulb Q_1 sealed off at the constriction. In a similar manner, a sample of the homogeneous upper layer was sealed off in Q_2.

The method of separation employed at 0° had the advantage that the liquids were adequately protected from temperature disturbances and could be controlled satisfactorily; moreover, the line of demarcation between the two layers could be very readily observed in the capillary; finally, the interposition of a tap between the main bulk of liquid and the sample to be frozen obviated any risk of distillation during the freezing of the samples.

Chemical Analysis of the Mixtures.—The analytical results are expressed in terms of the components H_2O, N_2O_3, and N_2O_5. The total nitrogen and the total tervalent nitrogen were determined directly by chemical analysis, their difference giving the quinquevalent nitrogen. The weight of water was obtained by subtracting the combined weights of N_2O_3 and N_2O_5 from the total weight of the sample analysed.

The method of analysis first tried consisted in dissolving the sample in excess of standard alkali and determining the total nitrogen by back titration with standard acid, the tervalent nitrogen being estimated by titration with *N*/10-permanganate (Lunge and Berle, *Z. angew. Chem.*, 1906, **19**, 807; Raschig, *ibid.*, 1905, **18**, 1281); but, when the method was tested on pure nitrogen peroxide, it was found, in agreement with Lunge and Berle, that the nitrite value was about 5% too low. These investigators attributed this discrepancy to oxidation of the nascent nitrite by atmospheric oxygen, since they obtained the theoretical result only when the absorption was carried out in an atmosphere of nitrogen. A more probable explanation is that of Sanfourche (*Compt. rend.*, 1922, **175**, 469), *viz.*, that nitric oxide is produced in the reaction with water and is then oxidised by the atmospheric oxygen. Satisfactory results with pure nitrogen peroxide were, however, obtained by using a second method, described by Lunge and Berle (*loc. cit.*) and by Marchlewski (*Ber.*, 1891, **24**, 3271).

In this method the samples are absorbed in concentrated sulphuric acid, and (i) the total nitrogen is estimated as nitric oxide by the Lunge nitrometer, while (ii) the tervalent nitrogen is again determined by titration with permanganate. A typical test analysis with 0·001524 g.-mol. of pure nitrogen peroxide gave by (i) 0·001526 g.-mol. and by (ii) 0·001533 g.-mol.

To carry out the analysis, a fine scratch was made on the neck of the bulb containing the sample, and the whole weighed. The sample was then allowed to come to equilibrium at 20° or 0°, and suddenly frozen in liquid air. The neck of the bulb was then cracked open at the scratch, care being taken to retain every piece of glass for future weighing, and the bulb was dropped into a small (200 c.c.) flask containing about 100 c.c. of concentrated sulphuric acid. The flask was immediately stoppered with a tightly fitting cork thinly coated with paraffin wax. On melting, the frozen sample dissolved immediately in the sulphuric acid, and after a few minutes a colourless solution was obtained. This was transferred to a graduated flask and made up to the mark with more concentrated sulphuric acid, all washing of the absorption flask and small bulb being effected with this agent. The small bulb was washed free from acid, dried, and weighed, together with the end which had been cracked off, thus giving the weight of the sample taken for analysis. The total nitrogen was determined by shaking a known portion of the sulphuric acid solution with mercury in a Lunge nitrometer and measuring the nitric oxide produced. It was found that theoretical results could only be obtained if the sulphuric acid solution was diluted with water to about 80% acid before use in the analysis. The tervalent nitrogen was determined by running the acid solution into *N*/10-permanganate at 40° from a burette with its tip just below the surface of the permanganate, in order to prevent volatilisation of the nitrous acid (Lunge, *Ber.*, 1877, **10**, 1075).

Measurements of Density.—(a) *Flotation.** The floats (about 15 mm. long and 2 mm. in diameter) were made from thin-walled tubing of Pyrex glass, closed at one end and melted down to a solid tail at the other; they were kept for some months before being calibrated, in order to diminish the strain in the glass (Turner and Cousen, J., 1928, 2654). Twenty-six floats were adjusted to give increments of density varying from 0·006 to 0·039 between 1·15 and 1·6, and were calibrated in mixtures of toluene and bromoform.

For determining the densities of the mixtures of nitrogen peroxide and water, three floats were placed in a tube about 12 mm. in diameter and 12 cm. long. Known amounts of water and of nitrogen peroxide were introduced as described above, and the vessel was then sealed off and allowed to become warm. The density became steady after a few hours, but the mixtures were usually allowed to stand over-night before observations were begun. Flotation temperatures above 0° were observed in a water-bath, but for temperatures below 0° the bath consisted

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* Compare Richards and Shipley, *J. Amer. Chem. Soc.*, 1914, **36**, 1; Richards and Harris, *ibid.*, 1916, **38**, 1000; Robinson and Briscoe, J., 1926, 70; Robinson and Smith, *ibid.*, p. 1262; Lowry and Jessop, J., 1929, 1421.

of an unsilvered Dewar flask containing ether, which was cooled to the required temperature by cautious addition of carbon dioxide snow to the well-stirred liquid.

Some 40 readings were taken of each flotation temperature, and the densities of each mixture at 0° and 20° were then deduced by graphical interpolation.

(b) *Capillary pyknometer.* In order to determine the densities in systems containing two liquid phases, a sample of each layer was sealed off in a capillary pyknometer tube by the method described above. After being kept over-night, the tube containing the sample was immersed in a thermostat at 20° with the tapered end downwards. After an hour, a fine mark was made on the glass at the level of the meniscus, and the process was repeated at 0° by immersing the tube in a bath of washed crushed ice. The tube was then dried and weighed, its contents transferred to the rounded end, and frozen in liquid air. The tube was broken open at a fine scratch made with a sharp glass knife, a perfectly clean fracture being obtained in all cases; the two portions of the tube were then washed, dried, and weighed, thus giving the weight of the sample. The portion with the rounded end was than discarded, and the weight of water filling the other portion to each of the fine marks was determined. From these data, the density of the sample at 0° and 20° could be calculated. On account of the smallness of the volumes of liquid handled, it was necessary to exercise great care in adjusting liquid levels and in weighing, and observations were repeated a few times wherever possible.

SUMMARY.

1. The compositions of the two liquid layers formed in mixtures of nitrogen peroxide and water have been determined by analysis.

2. The limits within which two liquid layers are formed in the system H_2O–N_2O_3–N_2O_5 at 0° and 20° have been plotted on triangular diagrams.

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