The Vapour Pressures of Nitric Acid Solutions. Part I. New Azeotropes in the Water–Dinitrogen Pentoxide System.

By L. Lloyd and P. A. H. Wyatt.

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Vapour pressures of the water–dinitrogen pentoxide system in the range 62—90% of N_2O_5 were measured directly at −10°, 0°, +10°, and +20° by a new static technique which involves the use of chlorofluorocarbon and Silicone oils as manometric fluids. Both the total vapour pressures and the vapour-phase compositions indicate the presence of two new azeotropes, one (with a maximum pressure) near the composition of pure nitric acid and the other (with a minimum pressure) at 87—88% of N_2O_5. An inconsistency in the former pressure and vapour-composition data in this region is thus removed. The minimum vapour pressure in the nitric acid–dinitrogen pentoxide system is attributed to the extensive ionization of dinitrogen pentoxide in dilute solution.

Wyatt (*Trans. Faraday Soc.*, 1954, **50**, 352) showed that the combined vapour pressure results obtained by Wilson and Miles (*ibid.*, 1940, **36**, 356) for the water–nitric acid system and by Berl and Saenger (*Monatsh.*, 1929, **54**, 1042) for the nitric acid–dinitrogen pentoxide system were not consistent with the finding that the vapour over 100% nitric acid had the same composition as the liquid, since the total pressure was represented as increasing through the composition: 100% of HNO_3. Vandoni's more recent results (*Mém. Services chim. État*, 1950, **35**, 63) and those of Vandoni and Laudy (*J. Chim. phys.*, 1952, **49**, 99) show a greater flattening of the pressure curve in this region, but are not extensive enough to provide a satisfactory solution.

We now believe this problem to have been solved by the discovery of two new azeotropes in the H_2O–N_2O_5 system. In addition to the well-known minimum vapour pressure at about 60% by weight of dinitrogen pentoxide (*i.e.*, 70% nitric acid), there is a maximun pressure near 85·7% of dinitrogen pentoxide (100% nitric acid), followed by a further minimum near 87·5% of dinitrogen pentoxide (" 102% " nitric acid). The pressure changes in this region are small, but are definitely established by a rapid and direct technique which has been developed for the accurate measurement of nitric acid vapour pressures. The novelty of this static method lies in the use of chlorofluorocarbon and Silicone oils as manometric fluids of low density in place of the more usual Bourdon gauge and mercury manometer.

EXPERIMENTAL

The apparatus is shown in Fig. 1. There was no disadvantage in having ground-glass joints and taps in the system when these were freshly greased with chlorofluorocarbon grease (Imperial Chemical Industries Limited "Fluorube" W). A magnetic stirrer operated by a solenoid actuated twice a second ensured the attainment of equilibrium and facilitated the removal of dissolved air from the liquid in the cell before taking measurements, and gave constant and reproducible stirring conditions. The Pyrex tubing in the vacuum line was of 9-mm. bore and that of the manometer limbs of 6 mm., and the length of tubing between T_1 and T_3 was kept as short as practicable to reduce the volume of exposed vapour. For evacuation a mercury diffusion pump was backed by a Cenco Hyvac oil-pump and protected by a liquid-air trap. In order to compare the suitability of two manometric fluids simultaneously a second manometer (omitted from the diagram) identical with that shown and fitted with separate taps was connected at $M'M'$. The manometers were housed in a wooden box with a glass front to protect their fluids, which have appreciable temperature coefficients of density, from fluctuations in temperature. This was normally 21—23° and was checked so that the appropriate oil density could be used. Differences of less than 10 cm. in the manometer levels were read with a cathetometer to 0·001 cm., but for larger differences glass and wooden scales were mounted behind the manometers and checked in sections against the cathetometer.

Experiments were carried out as follows. Approximately 100% nitric acid was prepared

(Wilson and Miles, *loc. cit.*; Hughes, Ingold, and Reed, *J.*, 1950, 2438; Dunning and Nutt, ***Trans. Faraday Soc.*, 1951, 47**, 15) by distillation from a 1·3 : 1 (by volume) mixture of 98%-sulphuric and 70% nitric acids and stored in liquid air or deep freeze till required. For compositions below 100% of HNO_3, this acid was cooled and mixed with water. For compositions above 100% of HNO_3, dinitrogen pentoxide was prepared and mixed with the nitric acid (Dunning and Nutt, *loc. cit.*; see also Berl and Saenger, *loc. cit.*, and Gillespie, Hughes, and Ingold, *J.*, 1950, 2552). About 50 c.c. of the mixture were transferred to the weighed cell *C*, a sample was withdrawn for analysis, and the cell (having glass caps at the joints *X* and *Y*) was reweighed and then joined to the vacuum apparatus at *Y*, with the side-arm connected at *X* and carrying a bulb *S* as shown in Fig. 1. The cell *C* was then immersed in solid carbon dioxide–acetone until the contents were solid, T_1 was opened to the vacuum and the apparatus pumped out for several min. through T_1, T_2, T_3, and T_4. After *C* was isolated by closing T_1, the liquid was allowed to warm to about 5° and stirred to expel air. It was then frozen and pumped out as before. This procedure was repeated until no further bubbles appeared on warming, after which T_2 was closed and *C* was connected with the manometer *M via* T_1 and T_3, T_4 still being open to the vacuum line.

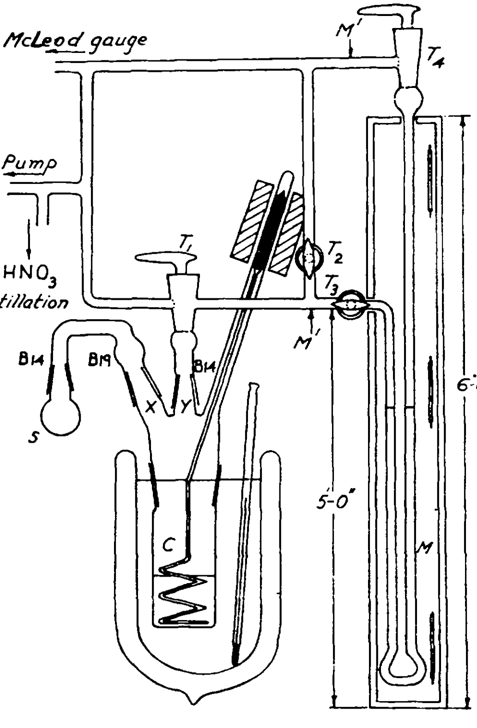

FIG. 1. *Apparatus for the determination of vapour pressures (manometer not to scale).*

The most reproducible manometer readings were obtained by warming the cell to about a degree above the temperature required and then bringing the bath (a Dewar flask fitted with a stirrer and thermometer) rapidly to the required temperature. The difference between the manometer limbs became constant and remained so after 10—15 min. from the time when the cell was first warmed, and T_1 was normally kept closed and T_2 open during this period to minimize errors due to the slight solubility of the acid vapours in the manometer fluids. A period of exposure of about 5 min., which usually sufficed for the measurements, was found to be well within the safety limit for absorption, and the manometer limbs were always pumped out thoroughly immediately after exposure. For measurements at 20° on the dinitrogen pentoxide side of the last azeotrope the pressures always steadily increased after the preliminary drop when the temperature was lowered from 21°. Decomposition of dinitrogen pentoxide in the vapour was obviously becoming important here and the (less accurate) vapour pressures quoted in Table 2 were in this case estimated by extrapolation.

When taking samples for estimating vapour-phase compositions, the (weighed) bulb *S* was cooled in solid carbon dioxide–acetone to collect about 1 c.c. of distillate (usually about 20 min.). Taps T_2 and T_4 were then closed, the contents of *C* frozen, T_1 was connected to the vacuum line, and air was allowed to leak into *C via* the liquid-air trap. *S* was then disconnected, its joint rapidly wiped free from grease and immediately closed with a B14 cap. When it had reached the laboratory temperature, the bulb was dried and weighed. The contents were then re-frozen, the stopper removed, and bulb and stopper dropped into a 500 c.c. wide-mouthed, stoppered bottle containing 100 c.c. of distilled water. The acid sample thus diluted was titrated directly (phenolphthalein) with 0·5N- and 0·05N-NaOH which was standardized against sulphuric acid made up from the cryoscopically determined 100% acid (Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 3472) and checked with potassium hydrogen phthalate and succinic and adipic acids. Precautions were taken to exclude carbon dioxide. The weights of nitric acid samples were generally such that 50 ml. of the 0·5N-alkali (by pipette) left a small excess of acid to be titrated by the 0·05N-alkali.

Several experiments were usually carried out on each solution in the cell *C*. In some runs the same solution was retained in *C* and the pressure was measured at different temperatures, small corrections being made to the liquid composition if vapour samples were withdrawn. In others, weighed additions of water were made through *X* (after freezing the acid) and a series of compositions was studied at a fixed temperature. Whenever air was allowed into the cell, repeated freezing, pumping, and thawing was always carried out subsequently.

The densities of the manometric oils (in g. cm.$^{-3}$) were found with a pyknometer to be

	0°	10°	20°
Chlorofluorocarbon oil (thin grade)	1·9723	1·9606	1·9479
Silicone fluid (M.S. 200)	0·9859	0·9775	0·9685

Thus the former gives readings about 7 times and the latter about 14 times as great as those of mercury. The chlorofluorocarbon oil proved to be excellent for the purpose, but the Silicone seemed to absorb vapours too readily and often became cloudy after only a short exposure. All the data quoted were obtained with the chlorofluorocarbon manometer.

RESULTS

Concentration Scales.—It is sometimes convenient to refer to a given solution as a% HNO_3, and sometimes as b% N_2O_5 or c% "free N_2O_5." The relationships are: $b = 0{\cdot}8570a$, $c = 7b - 600$.

To check the method, measurements were carried out on acids of composition 72—100% of nitric acid at four temperatures (see Table 1). The total pressures at 20° are about 2 mm. higher than those found by Wilson and Miles (*loc. cit.*) except at 99·8% where our value is 1 mm. lower. Vapour-phase analyses in this region are being further investigated and have not been quoted; it seems that the vapour over pure nitric acid contains about 0·2% excess of water. (If this is not the case, all composition data in this paper will be subject to a correction of not more than +0·2%.)

TABLE 1. *Vapour pressures of nitric acid solutions.*

Concn.	Total vapour pressures (mm. Hg)				Concn.	Total vapour pressures (mm. Hg)			
(% HNO_3)	−10°	0°	10°	20°	(% HNO_3)	−10°	0°	10°	20°
72·4	1·10	2·02	3·69	6·46	91·8	4·83	9·82	18·06	32·09
77·7	1·31	2·77	5·52	10·45	96·3	6·30	12·64	23·35	41·47
83·3	2·26	4·67	8·89	16·41	99·8	6·97	14·02	26·42	46·96
87·1	3·40	6·56	12·54	22·09					

Table 2 contains the results for compositions above 100%: relative liquid compositions are known to two places of decimals. At the highest concentrations the withdrawal of vapour samples affected the liquid composition appreciably and the figures in parentheses represent interpolated mean values of liquid concentration and vapour pressure calculated from the values before and after sampling the vapour. At all temperatures unmistakable signs of azeotropic behaviour are shown both in the total pressures and in the vapour-phase compositions (see Fig. 2). Corroborative evidence is also provided by the behaviour of the vapour at 20°: when progressive amounts of water were added to a concentrated solution of dinitrogen pentoxide at that temperature the manometer readings increased with time until the minimum pressure was reached, after which point the normal constant readings were obtained. This change occurred quite sharply, as would be expected from a rapid change in the partial pressure of dinitrogen pentoxide in this region. In order to define more accurately the shape of the curve in the neighbourhood of 100% HNO_3 the following results obtained by adding small amounts of water to 99·6% nitric acid at 0° have also been plotted in Fig. 2.

TABLE 2. *Vapour pressures of* N_2O_5 *solutions at* −10°, 0°, 10°, *and* 20°.

N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)
Temp. −10°		
89·08	11·71	—
88·75	9·17	—
(88·71)	(8·80)	93·7
88·05	6·76	89·6
87·63	6·30	87·5
87·63	6·29	87·2
86·97	6·44	86·0
86·50	6·71	85·5
85·81	6·90	—
Temp. 0°		
89·68	37·83	—
(89·63)	(36·66)	97·6
89·59	35·65	—
89·58	35·49	—
(89·52)	(33·44)	97·1
89·47	31·39	—
(89·26)	(26·4)	95·9
89·26	26·26	—
(89·24)	(25·9)	96·0
Temp. 0°		
89·17	25·61	—
(89·12)	(24·43)	96·3
89·08	23·25	—
(88·99)	(21·3)	95·0
88·91	19·47	—
(88·89)	(19·30)	94·2
88·66	16·71	—
(88·58)	(16·2)	92·0
88·64	17·1	—
(88·58)	(16·2)	91·6
88·14	14·64	90·6
88·10	14·05	89·8
87·85	13·16	87·6
87·83	13·16	—
87·75	13·13	87·6
87·61	12·98	87·4
87·38	13·18	85·5
87·31	13·16	85·8
87·10	13·36	—
Temp. 0°		
86·57	13·58	—
86·00	13·87	85·5
85·72	13·99	85·5
Temp. 10°		
88·02	30·13	91·2
87·84	25·84	88·0
87·39	25·87	87·6
86·86	25·40	86·9
86·51	25·65	—
86·50	25·66	86·3
85·70	26·26	85·4
Temp. 20°		
87·76	52·5	92·4
87·40	48·1	88·2
87·15	46·6	87·3
86·91	46·8	86·6
86·63	47·0	86·2

HNO_3 (%)	99·60	99·33	98·97	98·63	98·29	97·63	94·91	92·93	90·53	87·11	84·99
p (mm. Hg)	13·96	13·92	13·80	13·74	13·57	13·26	12·01	10·51	8·78	6·56	5·40

Increase of temperature appears to shift the minimum vapour pressure towards the composition of pure nitric acid : from graphs it is estimated that this azeotrope occurs at about 88% of dinitrogen pentoxide at −10°, 87·8% at 0°, and about 87% at 10° and 20°. The minimum pressure is always of the order of 1 mm. below the value for pure nitric acid and the azeotropic behaviour is therefore most marked at −10°, where the depression amounts to 10% of the vapour pressure of pure nitric acid. The partial pressures of dinitrogen pentoxide and nitric acid do not satisfy the simple Duhem–Margules equation well, but this is probably due to the great precision in analysis required for such a sensitive test in this region.

The total-pressure data of Berl and Saenger (*loc. cit.*) are considerably higher than the present values, presumably owing to vapour phase decomposition, and give no indication of azeotropes. Those of Vandoni (at 0°, *loc. cit.*) are, however, in good agreement apart from a slight shift in the composition axis, but show only one point in the azeotropic region (at 86·4% of dinitrogen pentoxide), for which, however, the static pressure is clearly too high (Fig. 2). Vandoni appears to have overlooked the evidence from his dynamic results at this point, which give not only a lower total pressure than at 100% of nitric acid but a reduced concentration of dinitrogen pentoxide in the vapour (3% of free dinitrogen pentoxide) as compared with the liquid (5% of free dinitrogen pentoxide).

The Effect of Dinitrogen Tetroxide on the Azeotropes.—All solutions of concentration greater than 85·7% of dinitrogen pentoxide were more or less pale yellow in colour and it was therefore necessary to investigate the effect of dinitrogen tetroxide on the appearance of the azeotropes. Liquid dinitrogen tetroxide was prepared from lead nitrate (Addison and Thompson, *J.*, 1949,

TABLE 3. *Effect of adding* N_2O_4 to 85·5% N_2O_5 *at* 0°.

g. N_2O_4/100 g. acid	0·000	0·573	1·266	2·468	7·125
p, mm. Hg	14·02	14·76	15·21	15·86	18·46

TABLE 4. *Effect of adding* N_2O_4 *to* 88·1% N_2O_5 *at* 0°.

g. N_2O_4/100 g. acid	0·000	0·711	2·182	4·147	7·387
p, mm. Hg	14·66	15·93	17·93	20·47	24·75

S218) and dissolved in pure nitric acid to make a concentrated solution, which could then be manipulated in a weight pipette. Successive additions were made to acids of 85·5% and 88·1% of dinitrogen pentoxide and the total pressures at 0° were noted (Tables 3 and 4). The dinitrogen tetroxide clearly increased the total pressure to a greater extent in the dinitrogen pentoxide-rich solution (*i.e.*, 88·1%, near the composition of minimum vapour pressure) than in the purer nitric acid, whence it was concluded that the effect of the dinitrogen tetroxide impurity would be to mask rather than enhance the appearance of azeotropes. The colour of a 0·5% solution of dinitrogen tetroxide was also considerably deeper than those encountered during the work, so that it could be estimated that the tetroxide impurity when present was only of the order 0·1%.

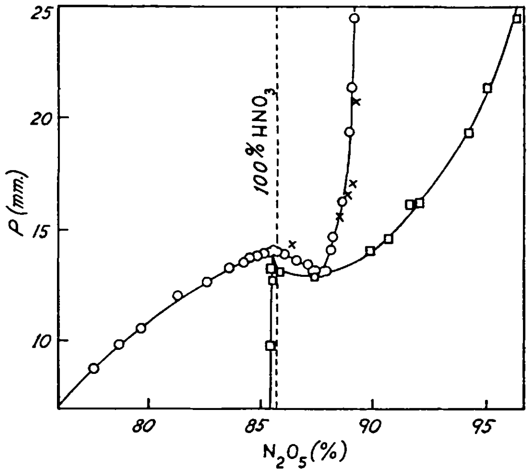

FIG. 2. *Vapour pressures in the neighbourhood of* 100% HNO_3 *at* 0°.

○ *Liquid composition.*
□ *Vapour composition.*
× *Vandoni's static data.*

DISCUSSION

Vapour pressures in the nitric acid–dinitrogen pentoxide system now emerge with a similar pattern to those in the water–nitric acid system. It therefore seems likely that the same explanation will hold for both systems, *i.e.*, the minimum in the vapour pressure curve is mainly due to the extensive ionization of one constituent in dilute solution (dinitrogen pentoxide in nitric acid and nitric acid in water), which produces a relative lowering of the partial pressure of that constituent as compared with its contribution to the pressure of more concentrated solutions. An increase in the self-dissociation of nitric acid in the liquid phase would reduce the initial depression of p_{HNO_3} caused by added N_2O_5 and would therefore tend to mask the effect just described. Thus the reduction in the importance of the dinitrogen pentoxide–nitric acid azeotrope with increasing temperature could be due to an accompanying increase in the self-dissociation of nitric acid.

Complications due to the simple dissociation $2HNO_3 \rightleftharpoons H_2O + N_2O_5$ in the vapour seem most unlikely in view of the following argument. The vapour-phase reaction $4HNO_3 \rightleftharpoons 2H_2O + 4NO_2 + O_2$ has a measurable equilibrium at the pressures involved in these experiments; whence for $4HNO_3 \rightleftharpoons 2H_2O + 2N_2O_5$ to be measurable the equilibrium $2N_2O_5 \longrightarrow 4NO_2 + O_2$ would also have to be measurable. But this would be in conflict with kinetic work, in which the decomposition of dinitrogen pentoxide is described as going to completion (Daniels and Johnstone, *J. Amer. Chem. Soc.*, 1921, **43**, 53). Thus the equilibrium vapour concentration of dinitrogen pentoxide in the presence of free water must be very small. It also follows that if either water or dinitrogen pentoxide is volatile as such over pure nitric acid (dissociated in the liquid) the other must be effectively involatile.

SHEFFIELD UNIVERSITY.

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