727. *The Vapour Pressures of Nitric Acid Solutions. Part III.*[1] *The Deuterium Oxide–Dinitrogen Pentoxide System.*

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Vapour pressures and compositions at 0° are reported for the deuterium oxide–dinitrogen pentoxide system in the range 43—90% of N_2O_5. Minima in the total vapour-pressure curve, similar to those in the corresponding water system, are observed at 53·0% and 86·2% of N_2O_5. The vapour pressure of pure DNO_3 (*i.e.*, 84·37% of N_2O_5) is 15·03 mm. Hg at 0°, over 7% higher than that of pure HNO_3, but the heats of vaporization of the two compounds are similar. The extent of self-dissociation of liquid DNO_3 is similar to that of HNO_3.

In Part I[1] vapour pressures in the dinitrogen pentoxide–water system were reported. We now present data for the corresponding deuterium oxide system for comparison. The substitution of an atom in a molecule by a heavier isotope is in some cases accompanied by an increase,[2, 3] and in others by a decrease,[3, 4] in the vapour pressure. Our data show that the deuteration of nitric acid falls into the former category since the vapour pressure of the deuterium compound is the greater by more than 7%, although the vapour-pressure minimum at higher dinitrogen pentoxide concentrations[1] still shows clearly. Of more chemical interest is the effect of the heavy isotope on the extent of dissociation of liquid nitric acid. Gillespie and his co-workers[5] have recently shown that dideuterosulphuric acid is appreciably less dissociated than sulphuric acid itself, but our measurements show that this effect is small in the case of nitric acid.

Experimental

The vapour-pressure technique was described in Part I.[1] All solutions were made up by weight and their compositions checked by acidimetry. Dinitrogen pentoxide was distilled from a nitric acid–phosphoric oxide mixture in a stream of ozone[6] and then mixed with a further quantity of phosphoric oxide before resublimation into a cooled, weighed quantity of deuterium oxide (Norsk Hydro 99·8%). After transfer of about 35 g. of this solution to the

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[1] Part I, Lloyd and Wyatt, *J.*, 1955, 2248; Part II, *idem*, *J.*, 1957, 4268.

[2] Claussen and Hildebrand, *J. Amer. Chem. Soc.*, 1934, **56**, 1820; Lewis and Schutz, *ibid.*, p. 493; Bates, Haford, and Anderson, *J. Chem. Phys.*, 1935, **3**, 415.

[3] Baertschi, W. Kuhn, and H. Kuhn, *Nature*, 1953, **171**, 1018; *Helv. Chim. Acta*, 1957, **40**, 1084 (cf. Bradley, *Nature*, 1954, **173**, 260).

[4] Lewis and Schutz, *J. Amer. Chem. Soc.*, 1934, **56**, 494, 1002; Widiger and Brown, *ibid.*, 1939, **61**, 2453; Kirshenbaum and Urey, *J. Chem. Phys.*, 1942, **10**, 706; Armstrong, Brickwedde, and Scott, *ibid.*, 1953, **21**, 1297; Giguère, Morisette, Olmos, and Knop, *Canad. J. Chem.*, 1955, **33**, 804.

[5] Flowers, Gillespie, Oubridge, and Solomons, *J.*, 1958, 667.

[6] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.

cell and measurement of its vapour pressure, additions of deuterium oxide were made and measurements carried out as described for the water–dinitrogen pentoxide system.[1] Vapour samples were collected for analysis at certain points and the liquid composition was corrected accordingly.

RESULTS

Concentration Scales.—Compositions may be referred to as $a\%$ of DNO_3, $b\%$ of N_2O_5, or $c\%$ of " free N_2O_5." The relationships for the deuterium oxide system are $b = 0{\cdot}8437a$, and $c = 6{\cdot}40(b - 84{\cdot}37)$. For simplicity all compositions in Table 1 are quoted as $b\%$ of N_2O_5.

The qualitative features of the vapour-pressure curve are similar to those for ordinary nitric acid (see Part I,[1] Fig. 2). There is a minimum on each side of the composition DNO_3, that on the D_2O side being displaced slightly in the direction to be expected from the greater volatility of DNO_3 and the smaller volatility of D_2O than of the corresponding hydrogen compounds. In the D_2O–DNO_3 region application of the Duhem–Margules equation gave p_{D_2O} values at 93·05, 86·48, 83·61, 80·18, 77·00, 74·79, 71·55, 69·52, 66·10, and 59·45% DNO_3 of 0·01, 0·05, 0·08, 0·15, 0·25, 0·34, 0·49 (fixed), 0·57, 0·75, and 0·96 mm. Hg respectively, whilst the observed values (from the vapour analyses) were 0·04, 0·04, 0·08, 0·12, 0·26, 0·36, 0·49, 0·57, 0·73, and 0·96 mm. Hg. This test was less successful in the N_2O_5–DNO_3 system, where at compositions of 85·10, 85·79, 86·53, 86·92, 87·24, 87·52, 87·75, and 88·02% of N_2O_5 the calculated values of p_{DNO_3} were 14·9, 14·1, 12·7 (fixed), 11·9, 11·3, 10·5, 9·8, and 9·1 mm. Hg and the observed 14·7, 13·8, 12·7, 12·2, 12·4 (?), 12·1, 11·4, and 9·3 mm. Hg. The obvious drift is probably due to the difficulty of preventing water

TABLE 1. *Vapour pressures of* N_2O_5 *solutions at* 0°.

(*a*) N_2O_5 concentrations greater than 84·37% (100% DNO_3).

N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)	N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)	N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)
89·68(s)	57·49	—	87·70	22·21	—	86·03	14·18	—
89·38(s)	57·58	—	87·55	20·40	—	85·77	14·31	—
89·13(s)	57·61	—	(87·52)	(19·95)	92·5	(85·79)	(14·27)	85·2
(88·75)	(57·6)	98·7 *	87·49	19·49	—	85·81	14·23	—
88·57	45·26	—	87·31	17·91	—	85·67	14·37	—
(88·52)	(43·13)	97·4(?)	(87·24)	(17·20)	90·5	85·58	14·41	—
88·47	41·01	—	87·17	16·49	—	85·46	14·51	—
88·32	35·93	—	86·94	15·63	—	85·32	14·62	—
88·06	29·39	—	(86·92)	(15·32)	89·0	85·09	14·80	—
(88·02)	(28·39)	96·5	86·89	15·01	—	(85·10)	(14·80)	84·6
87·98	27·39	—	86·54	14·37	—	84·85	14·97	—
87·81	24·34	—	(86·52)	(14·37)	87·1	84·43	15·02	—
(87·75)	(23·28)	94·3	86·28	14·14	—	(84·37)	(15·03)	—

(*b*) N_2O_5 concentrations less than 84·37% (100% DNO_3).

N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)	N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)	N_2O_5 in liquid (%)	p (mm. Hg)	N_2O_5 in vapour (%)
(84·37)	(15·03)	—	77·92	10·94	—	63·49	2·12	—
84·05	14·98	—	77·35	10·49	—	(63·08)	(2·03)	79·0
83·61	14·87	—	76·66	9·98	—	61·45	1·75	—
83·48	14·84	—	76·10	9·49	—	60·38	1·56	73·9
83·17	14·68	—	75·49	9·02	—	58·66	1·45	70·1
82·86	14·59	—	73·30	7·17	—	56·91	1·34	—
82·62	14·44	—	(72·95)	(6·91)	84·2	55·77	1·32	61·5
81·61	13·74	—	70·69	5·19	—	54·64	1·30	58·6
81·36	13·61	—	(70·57)	(5·11)	83·4	52·96	1·26	—
80·32	12·87	—	67·83	3·58	—	50·13	1·32	46·0
80·02	12·58	—	67·62	3·50	83·4	47·44	1·38	35·1
79·20	11·99	—	65·35	2·60	—	43·18	1·60	22·0
(78·50)	(11·40)	84·3	(64·98)	(2·50)	80·9			

Figures in parentheses are interpolated.

* Calculated by using the v. p. of solid N_2O_5 at 0°, viz. 50·0 mm. Hg. (ref. 12).

contamination of the vapour samples at the higher N_2O_5 concentrations rather than to any chemical complications in the vapour.[7]

The Self-dissociation of Deuteronitric Acid.—From a graph[8] of $\Delta \log_{10} p_{DNO_3}/\Delta m_2$ against $\bar{m}_2$ (where m_2 represents the molality of D_2O in the solvent DNO_3), it was estimated that $\partial^2 \log_{10} p_{DNO_3}/\partial m^2_2$ is $-(75 \pm 3) \times 10^{-3}$ at $\bar{m}_2 = 0$. Hence,[8] $\alpha_0 = 0{\cdot}024abs/(a + b)$, where α_0 represents the degree of dissociation of pure DNO_3, a and b the numbers of particles formed in solution per molecule of D_2O and N_2O_5 respectively, and s the number of DNO_3 molecules involved in the dissociation equation. For the general dissociation scheme

$$s\mathrm{DNO_3} \rightleftharpoons \mathrm{D_2O,DNO_3} + \mathrm{NO_2}^+(\mathrm{DNO_3})_x + \mathrm{NO_3}^-(\mathrm{DNO_3})_y$$

in which a D_2O molecule yields one particle and an N_2O_5 molecule 2 particles, *i.e.*, $a = 1$, $b = 2$, we conclude that $\alpha_0/s = 0{\cdot}016$; the value of α_0 depends upon the degree of solvation assumed for the dissociation products. The total molality of dissociation products in the pure acid is not arbitrary in this respect, however, for it is given by $3m_1\alpha_0/s$, *i.e.*, $0{\cdot}048m_1$, or 0·75m. When the data are sufficiently precise, calculation of the extent of dissociation in this way is preferred to the method adopted in Part II,[1] since it does not depend upon measurements for solutions of much greater concentration than the dissociation products in the pure acid.

Since, however, the results[1] for ordinary nitric acid were more scattered than those presented here, the extents of dissociation of the two acids were compared by the method of Part II, *viz.*, plotting the solvent partial pressure against m_2/m_1 and extrapolating the straight line obtained at higher concentrations back to the abscissa at the vapour pressure of the pure solvent. [Applied in this simple form, the latter method tends to give an underestimate since the residual solvent dissociation at higher concentrations is ignored (cf. Gillespie[9]). It is however quite adequate for demonstrating any significant *difference* in the extents of dissociation of two solvents.] By this method both acids yielded the same (low) results for the molality of dissociation products of $0{\cdot}037m_1$, showing that their extents of dissociation must be very similar. The KNO_3 data lead to the same conclusion, but are not given great weight in view of the slight excess of D_2O (~0·3%) in the initial acid. The vapour pressures of this acid at 0° and 20° (Table 2) yield a heat of vaporization of 9·55 kcal. mole^{-1}, which is close to that for nitric acid itself (*viz.*, 9·44,[10] 9·65,[11] or 9·56[12] kcal. mole^{-1}).

TABLE 2. *Vapour pressures of deuteronitric acid–potassium nitrate mixtures at* 0° *and* 20°. (*The deutero-nitric acid contained a slight excess of deuterium oxide.*)

Mole of KNO_3/mole of DNO_3	0·000	0·0211	0·0419	0·0631	0·0905	0·1217
p (mm. Hg) at 0°	14·98	14·60	14·04	13·42	12·51	11·44
p (mm. Hg) at 20°	49·77	48·51	46·57	44·63	42·04	38·99
Mole of KNO_3/mole of DNO_3	0·1579	0·1884	0·2231	0·2889	0·4103	
p (mm. Hg) at 0°	10·29	9·09	7·92	7·72 (s)	7·73 (s)	
p (mm. Hg) at 20°	35·61	31·68	27·94	21·06	15·22 (s)	

(s) indicates that some solid remained undissolved.

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[7] Wyatt, *Trans. Faraday Soc.*, 1954, **50**, 352.
[8] Wyatt, *ibid.*, 1956, **52**, 806.
[9] Gillespie, *J.*, 1950, 2493; see p. 2499.
[10] Wilson and Miles, *Trans. Faraday Soc.*, 1940, **36**, 356.
[11] Berl and Saenger, *Monatsh.*, 1929, **54**, 1036.
[12] Lloyd, Ph.D. thesis, Sheffield, 1956.