

858. *The Vapour Pressures of Nitric Acid Solutions. Part II.\*  
The Behaviour of Solutes in Nitric Acid.*

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The effects of solutes upon the vapour pressure of 100% nitric acid are reported; apart from some measurements with potassium nitrate at 10° and 20°, all determinations were at 0°. The solutes potassium nitrate, ammonium nitrate, sodium nitrate, phosphoric acid, potassium dihydrogen phosphate, sulphuric acid, potassium sulphate, perchloric acid, ammonium perchlorate, and acetic acid all give solutions which yield no measurable excess of water or dinitrogen pentoxide in the vapour. There is some evidence for the dehydration of orthoboric acid by nitric acid, since the vapour contains an excess of water; acetic anhydride and acetyl nitrate yield vapours containing a marked excess of dinitrogen pentoxide. Since the data for water and the alkali-metal nitrates give straight lines (after suppression of the solvent dissociation) when the partial pressure of nitric acid  $p$  is plotted against the solute/solvent molecular ratio ( $m_2/m_1$ ), provisional values for the numbers of particles ( $\nu$ ) yielded by other solutes are derived by comparison with a graph of this kind. The same form of graph is also used to provide estimates of the extent of self-dissociation of nitric acid at 0°, 10°, and 20°, leading to results in fair agreement with those obtained by other methods. By continuing the vapour-pressure measurements to the limit of saturation, values are obtained for the solubilities of a number of substances in nitric acid.

IN view of the success of cryoscopy in the determination of the modes of ionization of solutes in sulphuric acid, attempts have been made to apply the same technique to pure nitric acid.<sup>1,2</sup> The interpretation of the results is more difficult for this solvent, however, as the far greater self-dissociation obscures that region of concentration in which an approximately linear relation between freezing-point depression and solute molality would otherwise be expected. Heats of dilution also complicate the treatment when greater solute concentrations are used. The latter difficulty is by-passed in isothermal measurements; in view of the appreciable volatility of nitric acid at ordinary temperatures, and of the fact that Chédin, Fénéant, and Vandoni<sup>3</sup> were able to represent vapour-pressure results for the solutes water and potassium nitrate in a simple way, we have tried the use of the vapour-pressure technique instead of cryoscopy to investigate the behaviour of other solutes in nitric acid. Although the interpretations of our results are not always entirely satisfactory, sufficient results have been collected to show that this technique can provide useful information.

Further measurements in the region of 100% nitric acid have led us to doubt our suggestion (Part I) that the vapour over pure nitric acid might contain 0.2% excess of water. Fortunately, however, such precision in the composition of the vapour is unnecessary in the present application, for which the vapour composition is clearly so near pure nitric acid that no complications arise in this respect. Nevertheless, data referring to water and dinitrogen pentoxide as solutes used here were obtained from the results in Part I by increasing the N<sub>2</sub>O<sub>5</sub> concentration by 0.25%. This correction also gives better agreement with the Duhem-Margules equation and with the experimental results of Vandoni and Laudy.<sup>4</sup>

\* Part I, *J.*, 1955, 2248.

<sup>1</sup> Gillespie, Hughes, and Ingold, *J.*, 1950, 2552.

<sup>2</sup> Dunning and Nutt, *Trans. Faraday Soc.*, 1951, 47, 15.

<sup>3</sup> Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, 226, 1722; 227, 1232.

<sup>4</sup> Vandoni and Laudy, *J. Chim. phys.*, 1952, 49, 99.

EXPERIMENTAL

The method for determination of vapour pressures was described in Part I. During over 2 years' use of the apparatus we have observed a slight change (<1%) in the manometer reading obtained for pure nitric acid. This has been ascribed to a slight alteration in the density of the manometer oil, which can be allowed for by occasional calibration with the vapour pressure of the pure acid. After all additions to the cell, which were always made by weight, the solution was repeatedly frozen, pumped, and thawed to remove air as described in Part I.

Materials were "AnalaR." Solids were dried at 105° and stored over concentrated sulphuric acid. Acetic acid was refluxed for 2—3 hr. with chromic anhydride, distilled off, and fractionated (b. p. 117.3—118.2°). Acetic anhydride was fractionated (b. p. 139.0—139.5°). Acetyl nitrate was prepared by adding an equivalent amount of acetic anhydride to dinitrogen pentoxide and cooling until all the crystals of the pentoxide had dissolved. Perchloric acid was used as a solution in nitric acid, prepared by adding the calculated amount of a dinitrogen pentoxide solution to an aqueous solution of perchloric acid. 100% Phosphoric acid was prepared from "AnalaR" (aqueous) phosphoric acid by adding the calculated amount of phosphoric oxide.

RESULTS

In the Tables,  $m_2/m_1$  represents the overall stoichiometric ratio of the number of moles of solute to the number of moles of solvent present in the cell, irrespective of whether or not all the solute had completely dissolved. The entries marked "(s)" (for "saturated") show that at that composition some solute remained solid. In some cases it was possible to raise the temperature to dissolve this solid and then to supercool the resultant liquid, giving a super-saturated solution [represented by "(ss)"] of the same overall composition.  $P$  represents total vapour pressure, and  $p$  the partial pressure of  $\text{HNO}_3$  or the total pressure if  $\text{HNO}_3$  is the only volatile species.

*Determination of Solubilities.*—When the solute is a solid, vapour-pressure measurements can be continued to the limit of solubility. Further additions should have a reduced effect upon the vapour-pressure, and no effect at all if the solid phase in equilibrium with the liquid

TABLE 1. *Vapour pressures of nitric acid over potassium nitrate-nitric acid mixtures at 0°, 10°, and 20°.*

$m_2/m_1$	$p$ (mm. Hg)			$m_2/m_1$	$p$ (mm. Hg)			$m_2/m_1$	$p$ (mm. Hg)		
	0°	10°	20°		0°	10°	20°		0°	10°	20°
0.000	14.02	26.40	47.00	0.099	11.47	21.48	38.56	0.299	7.30 (s)	10.87 (s)	19.05
0.021	13.70	25.46	45.80	0.134	10.25	19.36	34.90	—	5.36 (ss)	10.22 (ss)	—
0.042	13.15	24.68	44.04	0.202	7.84	14.98	27.87	0.347	—	11.10 (s)	15.23 (s)
0.071	12.35	23.14	41.35	0.262	7.23 (s)	12.20	22.25				

TABLE 2. *Vapour pressures at 0° of some nitric acid solutions having no measurable excess of water or dinitrogen pentoxide in the vapour.*

Solute	$m_2/m_1$	$p$ (mm. Hg)	$m_2/m_1$	$p$ (mm. Hg)	$m_2/m_1$	$p$ (mm. Hg)	$m_2/m_1$	$p$ (mm. Hg)	$m_2/m_1$	$p$ (mm. Hg)
$\text{NH}_4\text{NO}_3$	0.026	0.056	0.107	0.175	0.244	0.275				
		13.54	12.87	11.30	9.05	8.78 (s)	8.54 (s)			
$\text{NaNO}_3$	0.047	0.093	0.114							
		13.30	12.71 (s)	12.73 (s)						
$\text{H}_3\text{PO}_4$	0.024	0.059	0.093	0.130	0.160	0.193	0.227	0.289		
		13.64	13.22	12.99	12.85	12.44	12.24	12.20	11.87	
		0.367	0.442	0.853	1.665					
$\text{KH}_2\text{PO}_4$	0.114	10.95	8.73	6.83 (s)	6.12 (ss)					
		11.44	10.95	8.73	6.83 (s)	6.12 (ss)				
$\text{H}_2\text{SO}_4$	0.011	0.036	0.064	0.091	0.121	0.151	0.184	0.208		
		13.79	12.91	11.85	11.00	9.74	8.77	7.30	6.22	
$\text{K}_2\text{SO}_4$	0.030	0.133	0.189	0.249						
		13.15	11.03	10.13	9.65					
$\text{HClO}_4$	0.016	0.040	0.070	0.098	0.135	0.155	0.183			
		13.66	12.09	10.13	8.23	5.92 (s)	5.44 (s)	4.76 (s)		
$\text{NH}_4\text{ClO}_4$	0.075	0.099	0.145	0.220	0.308					
		12.00	11.33	10.44	9.75 (s)	9.34 (s)				
$\text{NH}_4\text{ClO}_4$	0.009	0.031								
		13.83	13.54 (s)							

TABLE 3. Total vapour pressures of boric acid-nitric acid mixtures at 0°.

[At higher concentrations, excess of water was detectable in the vapour: the vapour composition at  $m_2/m_1 = 0.512$  was 99.4% (by wt.) of nitric acid.]

$m_2/m_1$	0.018	0.050	0.097	0.148	0.208	0.265	0.322
$P$ (mm. Hg)	13.85	13.30	12.57	11.39	10.22	9.12	7.98
$m_2/m_1$	0.388	0.452	0.512				
$P$ (mm. Hg)	6.86	6.54 (s)	6.60 (s)	$(p = 6.48 \text{ mm. Hg})$			

TABLE 4. Total vapour pressures of nitric acid-acetic acid mixtures at 0°.

[The vapour was found to contain only nitric acid up to a concentration of at least  $m_2/m_1 = 0.337$ .]

$m_2/m_1$	0.025	0.060	0.101	0.149	0.215	0.273	0.337		
$m_1/(m_1 + m_2)$	0.975	0.943	0.909	0.871	0.823	0.785	0.748		
$P$ (mm. Hg)	13.70	13.15	12.47	11.75	10.47	9.49	8.35		
$m_1/(m_1 + m_2)$	0.630	0.570	0.489	0.402	0.273	0.296	0.215	0.122	0.000 *
$P$ (mm. Hg)	4.82	3.39	2.12	1.41	1.56	1.53	1.75	2.70	3.63 †

\* Pure acetic acid was also found to have a vapour pressure of 12.72 mm. Hg at 20°, and 6.91 mm. Hg when supercooled to 10°.

† Supercooled.

TABLE 5. Total vapour pressures of nitric acid-acetic anhydride mixtures at 0°.

[The vapour contained excess of dinitrogen pentoxide: at  $m_2/m_1 = 0.076$  the vapour contained 88.48% of  $N_2O_5$ , indicating a nitric acid partial pressure of 10.29 mm. Hg, and at  $m_2/m_1 = 0.122$  the vapour contained 94.5% of  $N_2O_5$ , giving  $p = 9.53$  mm. Hg.]

$m_2/m_1$ .....	0.015	0.045	0.064	0.076	0.101	0.122	0.209	0.285
$P$ (mm. Hg)	13.55	11.91	11.69	12.95	18.13	24.53	33.98	28.26

TABLE 6. Total vapour pressures of nitric acid-acetyl nitrate mixtures at 0°.

[The vapour contained excess of dinitrogen pentoxide.]

$m_2/m_1$	0.035	0.055	0.077	0.084	0.093	0.125	0.157
$P$ (mm. Hg)	13.47	12.99	12.60	12.62	13.27	19.03	27.30

has the same composition as the original solid added. By continuing to plot the overall (solid + liquid) composition on a graph such as Fig. 2, a value for the solubility of the solute can be obtained from the point of intersection of the lines representing the homogeneous and the heterogeneous systems. The solubility values shown in Table 7 were determined in this way.

TABLE 7. Solubilities ( $S$ , in g. per 100 g. of  $HNO_3$ ) in nitric acid, at 0° unless otherwise stated.

Substance	$m_2/m_1$ at intersection	$S$	Substance	$m_2/m_1$ at intersection	$S$	Substance	$m_2/m_1$ at intersection	$S$
$KNO_3$ .....	0.220	35.0	$NaNO_3$ ...	0.068	9.2	$NH_2ClO_4$	0.02	3.7
$KNO_3$ (10°)	0.283	45.1	$KH_2PO_4$ ...	>0.208	>45	$H_3BO_3$ ...	0.404	38.4
$KNO_3$ (20°)	0.339	54.1	$K_2SO_4$ .....	0.134 *	—	$N_2O_5$ .....	0.252	44
$NH_4NO_3$ ...	0.210	26.7						

\* Solid phase =  $KHSO_4$ .

## DISCUSSION

Chédin *et al.*<sup>3</sup> have shown that the vapour-pressure data for the solutes water and potassium nitrate can be interpreted by assuming that the solutions are ideal when solvation has been allowed for. When water is ascribed the solvation number 1 and the nitrate ion 2, the data require that each water molecule yields one particle in solution and each potassium nitrate molecule two particles, as would be expected from little ionization of  $H_2O$  and complete dissociation of  $KNO_3$ . Our thermal measurements<sup>5</sup> and Chédin's more recent considerations<sup>6</sup> indicate that the position cannot be so simple, but this approach provides a basis for classifying the data.

If Raoult's law is obeyed, the mole-fraction of nitric acid in the liquid phase,  $x$ , is related

<sup>5</sup> Lloyd and Wyatt, preceding paper.

<sup>6</sup> Chédin, *J. Chim. phys.*, 1952, **49**, 109.

to its partial pressure,  $p$ , by the expression  $x = p/p^\circ$ . When a solute suppresses the self-dissociation of nitric acid,  $p^\circ$  must clearly refer to the hypothetical (extrapolated) value of the vapour pressure corresponding to undissociated nitric acid, but when a solute does not affect the dissociation of nitric acid (apart from a dilution effect), we may suppose that the extent of this dissociation will be practically unaffected over a moderate range of concentration, and the measured vapour pressure of pure nitric acid would be the better choice for  $p^\circ$  in the ratio  $p/p^\circ$ .

Suppose now that a solution is made from  $m_1$  moles of nitric acid and  $m_2$  moles of the solute, and that each molecule of the solute uses  $s$  molecules of solvent in solvation and reaction to form  $\nu$  particles. Then

$$x = (m_1 - sm_2)/(m_1 - sm_2 + \nu m_2) \quad \dots \quad (1)$$

whence

$$x/(1 - x) = (1/\nu)(m_1/m_2) - (s/\nu) \quad \dots \quad (2)$$

Thus a plot of  $x/(1 - x)$  against  $m_1/m_2$  should be a straight line of slope  $1/\nu$  and intercept  $-s/\nu$ , from which both  $\nu$  and  $s$  can be determined. From a plot of  $p$  against  $m_2/m_1$  (see

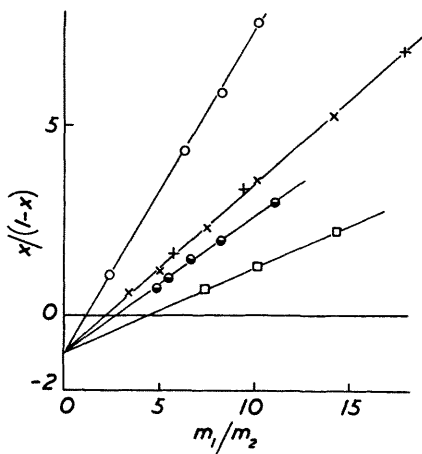


FIG. 1. *The application of Raoult's law to the nitric acid vapour-pressure data.*

○, H<sub>2</sub>O; ×, KNO<sub>3</sub>; +, NH<sub>4</sub>NO<sub>3</sub>; ●, KH<sub>2</sub>PO<sub>4</sub>;  
□, K<sub>2</sub>SO<sub>4</sub>.

below) for H<sub>2</sub>O and KNO<sub>3</sub>, the best extrapolated value for  $p^\circ$  at 0° seemed to be 14.70 mm. Hg. Using this figure for the calculation of  $x$ , we have plotted  $x/(1 - x)$  against  $m_1/m_2$  for several solutes (Fig. 1), and obtained values of  $\nu$  and  $s/\nu$  shown in Table 8. According to current ideas, acetic acid should be omitted from this group since it is regarded as undergoing no change other than solvation and would not therefore repress the dissociation of the solvent.

TABLE 8. *Application of Raoult's law to the vapour-pressure data.*

Solute	H <sub>2</sub> O	KNO <sub>3</sub> and NH <sub>4</sub> NO <sub>3</sub>	H <sub>3</sub> BO <sub>3</sub>	KH <sub>2</sub> PO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> -CO <sub>2</sub> H
$\nu$ .....	1.2	2.25	1.51	2.78	4.47	1.4
$s/\nu$ .....	1.0	1.0	1.0	1.0	1.0	0.8
$\nu/1.125$ .....	1.1	2.0	1.34	2.5	4.0	1.24

The results for the other compounds in Table 8 not only show  $\nu$  values rather higher than expected but show a marked tendency to require the same intercept of  $-1$ . This must be accidental to some extent, since part at least of the value of  $s$  has a very definite meaning when nitric acid is actually removed by reaction (*e.g.*, KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, see below). Nevertheless, this observation suggests that it may be profitable to treat the data in other ways than those involving the assumption of solvation. Our present interest, however, is in the determination of plausible  $\nu$  values, and one obvious approach is demonstrated in the last row of Table 8, where the  $\nu$  values derived from the slopes in Fig. 1 have been divided by a factor such that the final values for KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> become 2.0.

A more direct empirical method follows from the intercepts in Fig. 1 all being about  $-1$ . For this implies that  $\nu = s$ , whence equation (1) can be written as  $x = 1 - \nu(m_2/m_1)$ , which suggests that the observed partial pressure of nitric acid  $p$  should vary linearly with  $m_2/m_1$  and that the slope should depend directly upon  $\nu$ . In Fig. 2 values of  $p$  have been plotted directly in this way, with use of the  $\nu$  values of 1.0 for  $\text{H}_2\text{O}$ ; 2.0 for  $\text{N}_2\text{O}_5$ ,  $\text{KNO}_3$ , and  $\text{NH}_4\text{NO}_3$ ; 2.5 for  $\text{KH}_2\text{PO}_4$ ; and 4.0 for  $\text{K}_2\text{SO}_4$ . At present, comparison with this diagram provides the simplest method for deriving tentative  $\nu$  values for other solutes in nitric acid.

For partial pressures of nitric acid  $p$  below about 13 mm. at  $0^\circ$ , the following empirical formulæ fit the present results:

$$\nu = (14.7 - p)/16.4(m_2/m_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

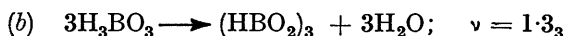
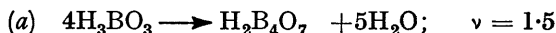
for a solute which suppresses the dissociation of the solvent; and

$$\nu = (14.0 - p)16.4(m_2/m_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for a solute which does not suppress the dissociation of the solvent (*e.g.*, acetic acid).

*Behaviour of Solutes in Nitric Acid at  $0^\circ$ .*—Water and dinitrogen pentoxide are generally supposed to have  $\nu = 1$  and 2, respectively. The points for dinitrogen pentoxide in Fig. 2 are rather anomalous over part of the concentration range, though the nearest whole number for  $\nu$  is 2. Potassium and ammonium nitrates with  $\nu = 2$  agree well with water if this is assigned  $\nu = 1$ .

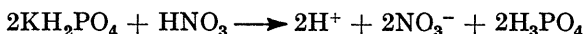
*Boric acid.* At least two interpretations are possible:



Of these, (a) seems the more likely chemically, but  $\nu = 1.33$  gives better agreement with the other solutes at higher concentrations. Both require the production of water in the solution, which is confirmed by analysis of the vapour (see Table 3).

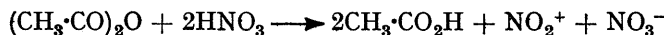
*Phosphoric acid.* Since no excess of water was detected in the vapour, orthophosphoric acid cannot be greatly dehydrated in nitric acid solutions. On the other hand,  $m_2/m_1$  must be greater than 0.5 before formation of 1 mole of  $\text{H}_2\text{O}$  per mole of  $\text{H}_3\text{PO}_4$  could be detected in this way, in view of the low volatility of water in nitric acid solutions stronger than 90% by weight. The  $\nu$  values, however, which are always less than 1 and decrease towards 0.5 at the highest concentrations, suggest polymerization rather than poly-acid formation with elimination of water, and an equilibrium constant of 10 for the formation of a dimer can be shown to give nitric acid partial pressures which agree with those observed to within 1–2% over the  $m_2/m_1$  range of 0.024–0.442.

*Potassium dihydrogen phosphate.* The observed  $\nu$  value of 2.5 could be explained at the higher concentrations by the reaction



since  $\nu$  for  $\text{H}_3\text{PO}_4$  then approximates to 0.5. It is probable therefore that phosphoric acid is weak enough for its salts to be completely solvolysed in nitric acid.

*Acetic acid, acetic anhydride, and acetyl nitrate.* These all appear to behave as would be expected from labile equilibria in the  $\text{N}_2\text{O}_5\text{-H}_2\text{O-(CH}_3\text{CO)}_2\text{O}$  system; as acetic acid is the only one of the three that gives no excess of dinitrogen pentoxide in the vapour, we can formulate the reactions of the other two thus:

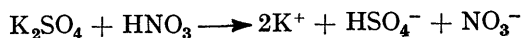


Our results do not support Dunning and Nutt's view<sup>2</sup> that acetyl nitrate is effectively nitronium acetate in nitric acid solution. Apart from the unlikelihood of the presence of

the acetate ion in such an acid medium, this interpretation does not account for the presence of dinitrogen pentoxide in the vapour, which shows up directly in the vapour-pressure method.

The minima in the total pressures for the acetic anhydride and acetyl nitrate systems (see Tables 5 and 6) do not seem to have been recorded before (see, *e.g.*, Vandoni and Viala <sup>7</sup>), and the azeotrope in the acetic acid-nitric acid system, which has previously been observed in boiling-point studies,<sup>8</sup> is now clearly reflected in the vapour pressure (Table 4).

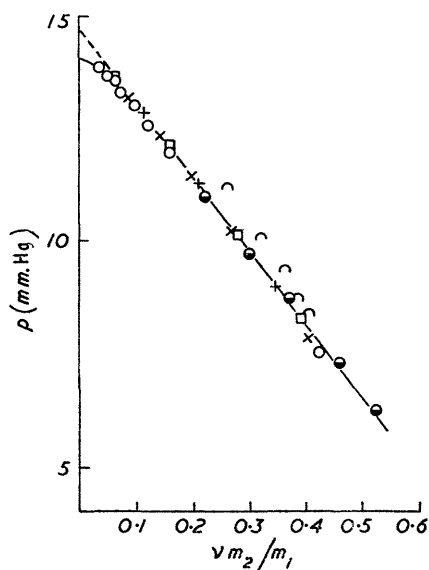
*Potassium sulphate.* In view of the weakness of the hydrogen sulphate ion as an acid in aqueous systems, potassium sulphate should be completely solvolyzed into a mixture of the hydrogen sulphate and nitrate:



This explains the observed  $\nu = 4$  and also the fact that the solid in equilibrium with the solution after saturation was found by analysis to have the composition of anhydrous potassium hydrogen sulphate. Further additions of potassium sulphate after saturation

FIG. 2. *The empirical determination of  $\nu$  values for solutes in nitric acid.*

○, H<sub>2</sub>O with  $\nu = 1$ ; ×, KNO<sub>3</sub> with  $\nu = 2$ ; +, NH<sub>4</sub>NO<sub>3</sub> with  $\nu = 2$ ; ●, KH<sub>2</sub>PO<sub>4</sub> with  $\nu = 2.5$ ; □, K<sub>2</sub>SO<sub>4</sub> with  $\nu = 4$ ; ∩, N<sub>2</sub>O<sub>5</sub> with  $\nu = 2$ .



produced (after equilibration) depressions of the vapour pressure equivalent to those to be expected from potassium nitrate. Some modification to this simple interpretation may be necessary at higher concentrations, since preliminary measurements indicate that potassium hydrogen sulphate dissolved in pure nitric acid yields a vapour containing an excess of dinitrogen pentoxide. Further work is in progress.

*Sulphuric acid.* Our results agree well with Vandoni's <sup>9</sup> in this region of composition. No overall straight line is obtained when the data are plotted as in Figs. 1 and 2, indicating that changes occur in the extent of some reaction as the concentration of sulphuric acid is increased (see, *e.g.*, Fénéant and Chédin <sup>10</sup> for one possibility). Since the nitrate and nitronium ions are supposed to exist together near the composition of pure nitric acid, a shift in the position of the equilibrium



<sup>7</sup> Vandoni and Viala, *Mém. Services chim. État*, 1945, **32**, 80.

<sup>8</sup> Taylor and Follows, *Canad. J. Chem.*, 1951, **29**, 461.

<sup>9</sup> Vandoni, *Mém. Services chim. État*, 1944, **31**, 87.

<sup>10</sup> Fénéant and Chédin, *Comp. rend.*, 1956, **243**, 41.

must occur in some range of the nitric acid–sulphuric acid system, but it is difficult to reconcile changes of this kind with our present method of determining  $\nu$ . It is, however, significant that the results for perchloric acid are similar to those for sulphuric acid.

*The Self-dissociation of Nitric Acid.*—The straight line in Fig. 2 projected back towards the pressure axis reached the vapour pressure of the pure solvent at a value of  $m_2/m_1$  corresponding to the total concentration of dissociation products in the pure acid. From the results for water and potassium nitrate the total mole-fractions of dissociation products at 0°, 10°, and 20° were found to be 0.040, 0.033, and 0.028, respectively, indicating that the extent of dissociation decreases with increasing temperature, as has also been deduced from conductance<sup>11</sup> and thermal data.<sup>12</sup> If the dissociation reaction is represented as  $2\text{HNO}_3 \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}$ , the mole-fractions of the nitronium ion in the pure acid at the three temperatures become 0.013, 0.011, and 0.009, which are slightly lower than would be expected from the values at other temperatures summarized by Lee and Millen.<sup>11</sup>

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<sup>11</sup> Lee and Millen, *J.*, 1956, 4463.

<sup>12</sup> Wyatt, *Trans. Faraday Soc.*, 1956, 52, 806.

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