## 504. *Cryoscopic Measurements in Nitric Acid. Part I. The Solutes Dinitrogen Pentoxide and Water. The Self-dissociation of Nitric Acid.*

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The freezing-point diagram of the system N_2O_5–H_2O has been studied over a range of compositions in the neighbourhood of that of HNO_3. From the form of the freezing-point curve on the dinitrogen pentoxide side of the nitric acid maximum, it is concluded that dinitrogen pentoxide in nitric acid is completely dissociated into nitronium and nitrate ions, which are solvated with a total of 4 molecules of nitric acid. From the form of the curve on the water side of the maximum, it is deduced that water in dilute solution in nitric acid is entirely non-ionised, but that each water molecule is solvated with 2 molecules of nitric acid. From the form, and the amount, of the rounding of the freezing-point maximum, it is concluded that nitric acid is considerably self-dissociated, the principal process being the ionic self-dehydration,

$$2HNO_3 = NO_2^+ + NO_3^- + H_2O$$
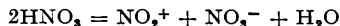
It is estimated that, in analytically anhydrous nitric acid at $-40°$, some $3·4\%$ of the material is dissociated to give $1·2\%$ of nitronium ion, $1·7\%$ of nitrate ion, and $0·5\%$ of water. A further 10% of the nitric acid has to be pictured as being bound in solvates of the self-dissociation products.

(1) *Methods and Results.*

(1.1) *Objects and Background.*—The motive of the present work was to prepare the ground for a general investigation of the cryoscopic behaviour of solutes in solvent nitric acid. The cryoscopic constant of nitric acid having been established by the calorimetric measurements of Forsyth and Giauque (cf. Section 1.3), the primary necessity was to study the self-dissociation of the solvent, and the behaviour of those solutes which are involved in the self-dissociation. This involves measurement of the freezing-point curve of the binary system N_2O_5–H_2O for compositions in the neighbourhood of HNO_3. Such measurements, and the conclusions to be drawn from them, form the subject of the present paper. The work is recorded at this time, because of its close connection with the chemical and physical studies on nitric acid described in several of the accompanying papers (particularly *J.*, 1950, 2400 and paper no. 510).

The only previously published cryoscopic investigations on solutions in nitric acid are those of Pickering (*J.*, 1893, **63**, 436) and of Berl and Saenger (*Monatsh.*, 1929, **54**, 1036) on the system N_2O_5–HNO_3, and of Kuster and Kremann (*Z. anorg. Chem.*, 1904, **41**, 1) on the system HNO_3–H_2O. In both these studies, the freezing points were measured somewhat approximately at widely spaced intervals of composition.

(1.2) *Apparatus and Experimental Procedure.*—The freezing-point cell was the same as that used for the measurements with sulphuric acid; and, in general, the same procedure for making a freezing-point measurement was adopted. The external bath, in which the cryoscope, surrounded by an air-jacket, was supported, consisted of a large Dewar vessel containing alcohol, which could be cooled by pumping alcohol at $-60°$ to $-70°$ through an immersed metal coil, and could be heated electrically when necessary. During a determination, the temperature of the bath was kept constant to $±0·2°$, at about $2°$ below the freezing point, by means of a bimetallic-strip regulator, which controlled the heater, and the pump motor, through a relay.

It was not found possible to seed the solute by touching the outside of the cryoscope with a piece of solid carbon dioxide; and, in consequence, the more direct method of seeding by adding a very small amount of the solid solvent was used. A small quantity of nitric acid was frozen inside a narrow tube, and then pushed out inside the cryoscope so that it fell directly into the solution.

Nitric acid was weighed by means of a weight burette provided with a vacuum jacket which, by preventing condensation on the outside, enabled the nitric acid to be weighed while it was kept below $-30°$. At these temperatures no appreciable decomposition appeared to take place, whereas at room temperature the acid soon acquired a detectable yellow colour.

Weighed amounts of water were added to the acid by means of a weight pipette. When investigating dinitrogen pentoxide, however, the solid solute was not added in separate weighed portions to the nitric acid, because of experimental difficulties. Instead, the cryoscope was charged initially with a solution of dinitrogen pentoxide in nitric acid, and the small weighed amounts of water were added. The solution of dinitrogen pentoxide in nitric acid was prepared by distilling the dinitrogen pentoxide in a stream of ozonised oxygen into nitric acid cooled to $-40°$. By this means, colourless solutions containing quite large amounts of dinitrogen pentoxide could readily be prepared, although attempts to add solid dinitrogen pentoxide directly to the liquid acid always resulted in a yellow solution, probably owing to the heat evolved. No attempt was made to prepare solutions of dinitrogen pentoxide with compositions accurately controlled by weighing, or to estimate the compositions of solutions by analysis. The compositions were found from the total amounts of water that it was necessary to add in order to reach the maximum freezing point, *i.e.*, the composition HNO_3.

A correction for supercooling, $δT$, was added to all the observed freezing points :

$$δT = (C_p{}^l/ΔH_0{}^f)S = 0·011Sθ$$

where S is the amount of supercooling, and θ the total depression of the freezing point. The values of the heat capacity of liquid nitric acid, $C_p{}^l$, and of the heat of fusion of nitric acid, $\Delta H_0{}^f$, that are employed in calculating the above numerical factor, are given in Section 1.3.

(1.3) *Equation for the Freezing-point Depression.*—We shall assume that, in the range of concentrations with which we are concerned, solutions in nitric acid can be regarded as behaving ideally. Suppose that one molecule of a solute A reacts with s molecules of nitric acid to produce a total of v dissolved ions and non-ionised molecules, thus :

$$A + sHNO_3 = pP + qQ + rR + \ldots$$

$$p + q + r + \ldots = v$$
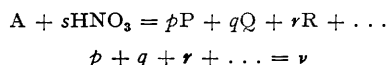
If m_2 is the molality of the solute A, and m_1 the molality of the nitric acid, then the change $\Delta\theta$ in the freezing-point depression, caused by a change Δm_2 in the molality of the solute A, is given by the equation (cf. *J.*, 1950, 2478) :

$$\frac{\Delta\theta}{\Delta m_2} = \frac{RT_0{}^2}{m_1\Delta H_0{}^f}\left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0{}^f}\right)\bar{\theta}\right\}\left\{1 + \frac{(2s - v)\overline{m}_2}{m_1}\right\}$$

Here, $\bar{\theta}$ is the mean depression, and $\overline{m}_2$ the mean molality of the solute A, over the interval of composition to which $\Delta\theta$ and Δm_2 refer.

TABLE I.

Freezing points of solutions of water and dinitrogen pentoxide in nitric acid.

Added H₂O.	Weights (g.). Solution.	Solute.	HNO₃.	Molality of solute.	F. p. (° c.).	Depression ($\Delta\theta$).
Expt. No. 14 :		N_2O_5.		N_2O_5.		
—	102·70	2·298	100·40	0·212	−41·87	0·13°
0·288	102·99	0·570	102·42	0·052	41·78	0·04
		H_2O.		H_2O.		
0·281	103·27	0·186	103·09	0·100	41·74	0·00
0·285	103·56	0·471	,,	0·253	41·84	0·10
0·690	104·25	1·161	,,	0·625	42·34	0·60
0·825	105·07	1·986	,,	1·068	43·21	1·47
0·708	105·78	2·694	,,	1·450	44·14	2·40
0·622	106·40	3·316	,,	1·786	45·13	3·39
Expt. No. 15 :		N_2O_5.		N_2O_5.		
—	117·96	6·578	110·38	0·552	−42·96	1·15
0·182	118·14	5·466	112·67	0·449	42·59	0·78
0·168	118·31	4·458	113·85	0·363	42·27	0·46
0·190	118·50	3·318	115·18	0·267	42·07	0·26
0·199	118·70	2·124	116·58	0·168	41·93	0·12
0·198	118·90	0·936	117·96	0·073	41·84	0·03
		H_2O.		H_2O.		
0·300	119·20	0·144	119·06	0·067	41·81	0·00
0·193	119·39	0·337	,,	0·157	41·83	0·02
0·179	119·57	0·516	,,	0·241	41·85	0·04
Expt. No. 16 :		N_2O_5.		N_2O_5.		
—	86·72	12·098	74·62	1·501	−50·57	8·76
0·402	87·12	9·682	77·44	1·158	47·40	5·59
0·141	87·26	8·836	78·42	1·044	46·37	4·56
0·109	87·37	8·182	79·19	0·957	45·62	3·81
0·084	87·45	7·678	79·77	0·891	45·19	3·38
0·081	87·53	7·192	80·34	0·829	44·64	2·83
0·033	87·56	6·994	80·57	0·804	44·55	2·74
0·085	87·65	6·484	81·17	0·740	44·05	2·24
0·113	87·76	5·806	81·95	0·656	43·55	1·74
0·087	87·85	5·264	82·59	0·589	43·19	1·38
Expt. No. 19 :		H_2O.		H_2O.		
—	88·95	—	88·95	—	−41·78	—
1·388	90·24	1·388	,,	0·867	42·84	1·05
1·117	91·36	2·505	,,	1·565	44·76	2·98
0·894	92·25	3·399	,,	2·123	46·55	4·77
0·786	93·04	4·185	,,	2·614	48·35	6·57

The values of the cryoscopic constant $k_f = RT_0{}^2/m_1\Delta H_0{}^f$, and of the factor $\{(2/T_0) - (\Delta C_p/\Delta H_0{}^f)\}$ have been calculated from the following data of Forsyth and Giauque (*J. Amer. Chem. Soc.*, 1942, **64**, 48) : $T_0 = -41\cdot65°$ c. $= 231\cdot51°$ κ., $\Delta H_0{}^f = 2503$ cal. g.-mol.$^{-1}$, and the extrapolated values $C_p{}^l(-41\cdot7°) = 26\cdot74$ cal. g.-mol.$^{-1}$ deg.$^{-1}$, and $C_p{}^s(-41\cdot7°) = 16\cdot56$ cal. g.-mol.$^{-1}$ deg.$^{-1}$. We thus find $k_f = 2\cdot68$ deg. g.-mol.$^{-1}$ kg., and $\{(2/T_0) - (\Delta C_p/\Delta H_0{}^f)\} = 0\cdot0045$ deg.$^{-1}$. The value of m_1 is $15\cdot87$ g.-mol. kg.$^{-1}$. Hence we obtain the following freezing-point equation :

$$\Delta\theta/\Delta m_2 = 2\cdot68\nu\{1 - 0\cdot0045\bar\theta + (2s - \nu)\bar m_2/15\cdot87\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(1.4) *Results.*—The results obtained in several experiments in which the freezing point was measured with the addition of successive small weighed amounts of water to a solution of dinitrogen pentoxide in nitric acid, or to pure nitric acid, are given in Table I.

Forsythe and Giauque (*loc. cit.*) found the freezing point of nitric acid to be $-41\cdot65°$. We have found freezing points of different samples of acid ranging from $-41\cdot71°$ to $-41\cdot81°$. We have assumed that these slightly low values are due to a small amount of decomposition of the acid, because samples with a freezing point appreciably lower than $-41\cdot7°$ had a just perceptible yellow colour. Freezing-point depressions for the solutes water and dinitrogen pentoxide have been calcultated from the observed maximum freezing point of the acid used, and not from the freezing point of the pure acid.

The experimental results are shown graphically in Fig. 1, in association with calculated curves for an ideal non-electrolyte, and an ideal binary electrolyte, with various solvation numbers *s*. The theoretical freezing-point depressions, from which these curves are drawn, are given in Tables II and III. They were calculated from equation (1).

TABLE II.

Calculated freezing-point depressions for solution of a non-electrolyte in nitric acid.

		Depressions.					
		$n = 0.$		$n = 1.$		$n = 2.$	
Molality of solute, $m_2.$	$\Delta m_2.$	$\Delta\theta_0.$	$\theta_0.$	$\Delta\theta_1.$	$\theta_1.$	$\Delta\theta_2.$	$\theta_2.$
0·25	0·25	0·663°	0·663°	0·674°	0·674°	0·685°	0·685°
0·75	0·50	1·291	1·954	1·377	2·051	1·454	2·139
1·25	,,	1·241	3·195	1·407	3·458	1·573	3·712
1·75	,,	1·193	4·388	1·439	4·897	1·682	5·394
2·25	,,	1·145	5·533	1·470	6·367	1·793	7·187
2·75	,,	1·097	6·630	1·501	7·868	1·901	9·088
3·25	,,	1·051	7·681	1·531	9·399	2·005	11·093

TABLE III.

Calculated freezing-point depressions for solutions of a binary electrolyte in nitric acid.

|		Depressions.					
		$n = 0.$		$n = 2.$		$n = 4.$	
Molality of solute, $m_2.$	$\Delta m_2.$	$\Delta\theta_0.$	$\theta_0.$	$\Delta\theta_2.$	$\theta_2.$	$\Delta\theta_4.$	$\theta_4.$
0·25	0·25	1·313°	1·313°	1·357°	1·357°	1·398°	1·398°
0·75	0·50	2·483	3·796	2·806	4·163	3·140	4·538
1·25	,,	2·290	6·086	2·940	7·093	3·557	8·095
1·75	,,	2·104	8·190	3·050	10·140	3·897	11·992

(2) *Discussion.*

(2.1) *General Character of the Freezing-point Curve.*—It is immediately obvious from Fig. 1 that there is a considerable difference between the effects of water and dinitrogen pentoxide on the freezing point of nitric acid. The slope of the dinitrogen pentoxide branch of the freezing-point curve is approximately twice as great as that of the water branch, and this indicates that a molecule of dinitrogen pentoxide produces approximately twice as many solute particles as does a molecule of water. The other obvious feature of this freezing-point curve is the very rounded character of the maximum at the composition HNO_3, a clear indication that nitric acid is considerably self-dissociated.

The existence of this large self-dissociation makes it necessary to study solutions at much higher concentrations, and with correspondingly larger freezing-point depressions, than were used in the study of solutions in sulphuric acid (*J.*, 2473, *et seq.*). It is therefore important to know how far solutions in nitric acid can be regarded as behaving ideally in the concentration range

investigated. Unfortunately we have no information about this, except the present freezing-point data, which indicate that the principal deviation from ideal behaviour is that due to solvation, although the possibility of some deviation due to interionic attraction is not excluded. One can, as we shall see, account very satisfactorily for the observed deviations from ideal behaviour by attributing small and plausible solvation numbers to the various dissolved species, completely neglecting any possible deviations due to interionic attractions or other causes.

FIG. 1.

Freezing points of the system dinitrogen pentoxide–water at compositions near that of nitric acid. Of the nearly straight lines which meet at the point O, those on the right are theoretical freezing-point curves for an ideal non-electrolyte with solvation numbers s = 0, 1, 2; and those on the left are theoretical curves for an ideal binary electrolyte with (total) solvation numbers s = 0, 2, 4.
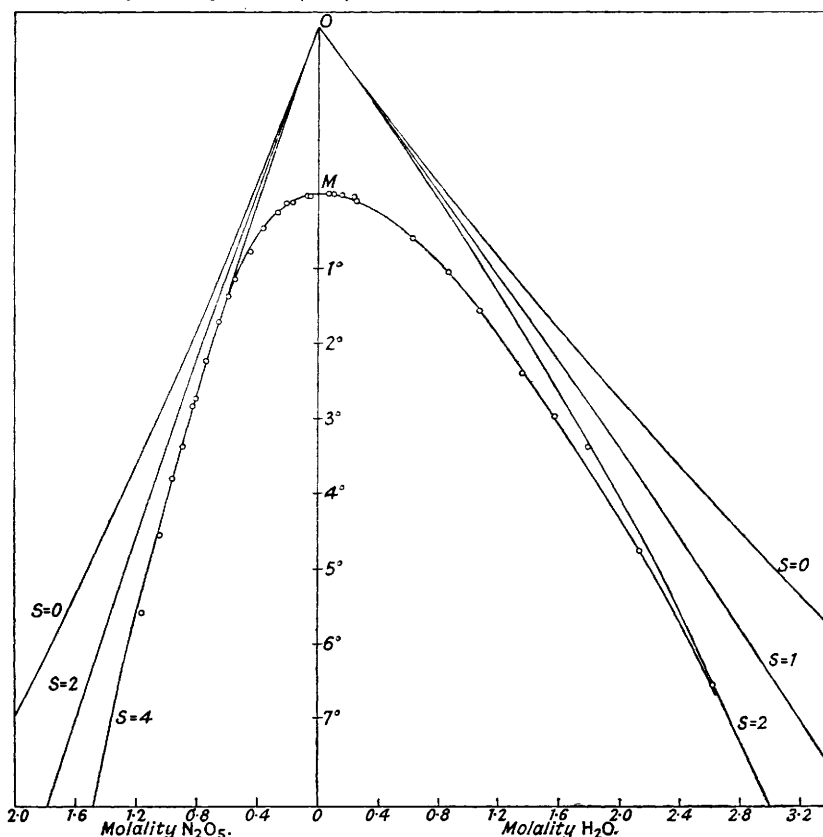
(2.2) *The Dinitrogen Pentoxide Branch of the Freezing-point Curve.*—The slope of the freezing-point curve for dinitrogen pentoxide shows that it forms at least two ions in solution in nitric acid. A resonable mode of ionisation, giving two ions, is the following :

$$N_2O_5 = NO_2^+ + NO_3^-$$

and it is, indeed, difficult to formulate any other mode of ionisation, or any mode at all which would give more than two ions. As can be seen from Fig. 1, the observed slope is somewhat greater than that to be expected for a non-solvated binary electrolyte, but it can be adequately explained by assuming that the total solvation number of the formed ions is 4.

This interpretation of the freezing-point data is in agreement with other information about solutions of dinitrogen pentoxide in nitric acid. It is shown in an accompanying paper (Ingold and Millen, *J.*, 1950, paper no. 510) that the effect on the Raman spectrum of adding, say, 6% of dinitrogen pentoxide to nitric acid is to superpose, on the normal spectrum of nitric acid, the spectra of the nitronium ion and the nitrate ion, but to produce no other spectral appearance, and, in particular, no trace of the known spectrum of molecular dinitrogen pentoxide. This is an

independent demonstration that dinitrogen pentoxide, at concentrations of this order (0·6 molal), is a strong electrolyte, consisting only of nitronium and nitrate ions. The formation of these ions explains the large increase of electrical conductivity which is observed on adding dinitrogen pentoxide to nitric acid (Berl and Saenger, *loc. cit.*); whilst the strong solvation of the ions accounts for their lack of tendency to associate, as is indicated by the negligible effect on the total vapour pressure of adding quantities, even up to 23%, of dinitrogen pentoxide to nitric acid at 0° (*idem, ibid.*).

One would certainly expect the nitrate ion to be strongly solvated in nitric acid. A number of compounds between ammonium, or alkali-metal, nitrates and nitric acid have been described (Ditte, *Compt. rend.*, 1879, **89**, 567; *Ann. Chim. Phys.*, 1879, **18**, 320; Wells and Metzger, *Amer. Chem. J.*, 1901, **26**, 272; Groschuff, *Ber.*, 1904, **37**, 1486; *Z. anorg. Chem.*, 1904, **40**, 1) : they have the general formulæ MNO_3,HNO_3 and $MNO_3,2HNO_3$. Chédin, Leclerc, and Vandoni have found (*Compt. rend.*, 1947, **225**, 734) that the exothermicity of dissolution of potassium nitrate in nitric acid is remarkably large (6 kcals.). Chédin and Vandoni have shown (*Compt. rend.*, 1948, **227**, 1232) that the lowering of the vapour pressure of nitric acid by potassium nitrate can be quantitatively explained, if it is assumed that the dissociated salt has the solvation number 2. The authors attribute the solvation to a tendency of the nitrate ion to form the hydrogen-bonded complex, $(NO_3^-)(HNO_3)_2$; and this idea of the nature of the solvation is supported by Chédin and Fénéant's discovery (*Compt. rend.*, 1949, **228**, 242) that the Raman OH-band of nitric acid near 3400 cm.$^{-1}$ becomes partly replaced by a system of several OH-stretching bands when potassium nitrate is added to nitric acid.

If we accept the value 2 for the solvation number of the nitrate ion, then the assumption of the reasonable solvation number of 2 for the nitronium ion will suffice to account for the freezing-point curve. General confirmation of the strong solvation of dinitrogen pentoxide follows from Chédin, Leclerc, and Vandoni's observation that the exothermicity of dissolution of water in a dissolution of dinitrogen pentoxide in nitric acid is very much smaller than the exothermicity of solution of water in pure nitric acid (*loc. cit.*). It follows that the destruction of dissolved dinitrogen pentoxide by hydration involves a strongly endothermic process, which can only be the desolvation of strongly solvated ions. On the whole, it seems that our interpretation of the freezing-point curve on the basis that dinitrogen pentoxide is a strong electrolyte, forming stably solvated nitronium and nitrate ions in nitric acid, is in agreement with a variety of other observations.

(2.3) *The Water Branch of the Freezing-point Curve.*—As can be seen from Fig. 1, the slope of the freezing-point curve for water is somewhat greater than that to be expected for a non-solvated non-electrolyte, but much smaller than that of a binary electrolyte. Therefore one might try to interpret the observational curve by assuming that water behaves as a weak binary electrolyte, ionising to a rather small extent according to the equation :

$$H_2O + HNO_3 = H_3O^+ + NO_3^-$$
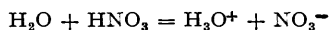
However, it can be seen from Fig. 1 that the observed freezing-point curve agrees quite well with that to be expected for a non-electrolytic solute with a solvation number of 2, *i.e.*, with the assumed formation, by the added water, of the non-ionised complex $(H_2O)(HNO_3)_2$. It is not possible to interpret the cryoscopic observations quite unambiguously; however, a considerable body of evidence can be cited to the effect that water is very little ionised in dilute solution in nitric acid, but that, on the other hand, water is quite stably solvated by nitric acid.

Investigations of the effect of added water on the Raman spectrum of nitric acid (Chédin, *Ann. Chim.*, 1937, **8**, 295; Rao, *Indian J. Physics*, 1941, **15**, 185; Redlich and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1883) have shown that the strongest line belonging to the nitrate ion, the line at 1050 cm.$^{-1}$, remains very weak, much as it is in pure nitric acid, until about 10% by weight of water has been introduced. Even in an equimolecular mixture of nitric acid and water, containing 22% by weight of water, the proportion of material ionised, as indicated by the intensity of the nitrate ion line, is no more than 2%. It seems impossible, therefore, that the first few units % of added water could produce sufficient ions to account for the deviation of the freezing-point curve from that of a non-solvated non-electrolyte. The same conclusion follows from studies of the electrical conductivity of mixtures of nitric acid and water (Veley and Manley, *Phil. Trans.*, 1898, **191**, *A*, 365; Dalmon, *Mem. Serv. chim. de l'État*, 1943, **30**, 191). The conductivity of nitric acid containing as much as 10% by weight of water is not substantially greater than that of anhydrous nitric acid; and the addition of the first few units % of water to nitric acid causes a fall in conductivity.

The fact that water, although it forms very few ions, does form a stable solvate with solvent

nitric acid has been shown by Chédin in several ways (Chédin and Fénéant, *Compt. rend.*, 1947, **224**, 930; Chédin, Leclerc, and Vandoni, *loc. cit.*; Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722). The partial vapour pressures of water over a solution of water in nitric acid are exceedingly small at all concentrations up to 20% by weight of water. The exothermicity of dissolution of water in absolute nitric acid is very considerable (3 kcals.). The effect of adding up to 20% by weight of water to nitric acid on the Raman OH-band near 3400 cm.$^{-1}$ is gradually to replace it by a group of several bands. This shows that water, like the nitrate ion, forms with solvent nitric acid a stable hydrogen-bond complex.

The exact composition of the complex is, however, open to some doubt. The only known solid compounds of water and nitric acid are $(H_2O)_3(HNO_3)$ and $(H_2O)(HNO_3)$, and, of these, the latter at most could be of possible importance in the range of composition in which we are interested (cf. Kuster and Kremann, *loc. cit.*). Chédin, Fénéant, and Vandoni have deduced from the partial vapour pressures of water and nitric acid above their solutions that the complex $(H_2O)(HNO_3)$ is produced (*loc. cit.*). Their data refer to solutions containing from 20% to 5% by weight of water. Our freezing-point results indicate the complex to be $(H_2O)(HNO_3)_2$. However, our data relate to solutions containing from 5% to 0% by weight of water. The two conclusions are not necessarily inconsistent. The simpler solvate, probably the hydrogen-bond complex, H_2OHONO_2, is apparently rather stable; but when many nitric acid molecules are in competition for each water molecule, the latter may form a second similar bond to give the complex $H_2O(HONO_2)_2$, thus completing the co-ordination shell of its oxygen atom.

(2.4) *The Rounding of the Freezing-point Maximum.*—This feature of the freezing-point curve indicates that the self-dissociation of nitric acid is extensive. If there were no self-dissociation, the dinitrogen pentoxide and the water branch of the freezing-point curve would meet in a point, as do the theoretical curves for the two solutes. The presence of the products of self-dissociation depresses the freezing point of the pure solvent below the value it would have if it did not undergo dissociation. The addition to the pure solvent of limited amounts of either dinitrogen pentoxide or water causes a partial recombination, and therefore a disappearance, of self-dissociation products; and thus the added solutes at first exert considerably less than their normal depressing effects on the freezing point. When, however, sufficient of either solute has been added to repress the self-dissociation completely, then a further portion of the solute will exert its normal depressing effect. Thus the freezing-point curve has a rounded maximum, and only the lower portion of either branch of the curve is expected to agree with the theoretical curve for the relevant solute.

These principles have been applied in constructing Fig. 1. First, the theoretical curves were drawn. Then the experimental curve was plotted, and so placed that its maximum fell vertically beneath the origin of the theoretical curves, whilst its two branches ran as nearly as possible asymptotically to two of the theoretical curves. The interval between the origin O of the theoretical curves and the maximum M of the experimental curve is 2·20°. It represents the amount by which the products of self-dissociation of the solvent reduce its freezing point.

The simplest type of self-dissociation that we could contemplate would be the autoprotolysis

$$2HNO_3 = H_2NO_3^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
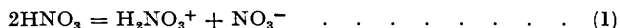
However, the shape of the freezing-point curve shows that the self-dissociation cannot, in fact, be as simple as this. For we have seen that, whilst dissolved dinitrogen pentoxide supplies nitrate ions, small amounts of added water produce scarcely any nitrate ions. The auto-protolysis represented above should therefore be repressed effectively by added dinitrogen pentoxide, but scarcely at all by added water; and thus the freezing-point curve should be rounded on the dinitrogen pentoxide side of the maximum, but should descend sharply on the water side.

The second possibility is that the dissociation is a self-dehydration :

$$2HNO_3 = N_2O_5 + H_2O$$
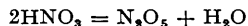
Since, as we have already seen, dinitrogen pentoxide is fully dissociated into solvated ions, whilst water, though also solvated, is scarcely ionised, the complete ionic self-dehydration can, apart from solvation, be approximately represented thus :

$$2HNO_3 = NO_2^+ + NO_3^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad (2)$$
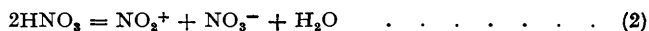
This equation would interpret the qualitative features of the freezing-point curve. Water is a product of this form of dissociation, as well as the ions of dinitrogen pentoxide; and hence the freezing-point curve should be rounded on both sides of the maximum, as, in fact, it is. Further,

dinitrogen pentoxide supplies two of the three products of dissociation, whereas water provides only one; hence dinitrogen pentoxide should be more effective than water in repressing the dissociation of the solvent; and hence dinitrogen pentoxide should begin to exert its full effect in depressing the freezing point at a lower concentration than should water, as, in fact, is found.

There is good evidence in the Raman spectrum of nitric acid for the presence of the three products of ionic self-dehydration. The nitronium ion is identified by the weak, but sharp, Raman line at 1400 cm.$^{-1}$, first found by Chédin in absolute nitric acid, whilst the nitrate ion has been proved to be the source of the weak frequency 1050 cm.$^{-1}$. Ingold and Millen (*J.*, 1950, paper no. 510) have estimated, from the intensities of these two lines, that absolute nitric acid is about 0·22 molal with respect to nitronium ion, and about 0·24 molal with respect to nitrate ion. The presence of water in anhydrous nitric acid is qualitatively established by Chédin and Fénéant's investigation of the high-frequency Raman bands (*Compt. rend.*, 1947, **224**, 930). In addition to the strong band at 3400 cm.$^{-1}$, representing the OH-stretching frequency of nitric acid, the absolute acid exhibits two exceedingly weak bands, at 2980 and 3550 cm.$^{-1}$, which become greatly intensified on the addition of small amounts of water, and are certainly to be attributed to a hydrogen-bonded solvate of water.

From all this evidence it seems clear that the ionic self-dehydration of nitric acid (2) is at least the chief mode of its self-dissociation. What is not clear is whether any appreciable proportion of autoprotolysis (1) occurs simultaneously. Any such autoprotolysis would produce nitric acidium ion, and would lead to a total concentration of nitrate ion in excess of that of nitronium ion. It is not an argument against the presence of the nitric acidium ion, $H_2NO_3^+$, that no evidence for it is found in the Raman spectrum. The simple hydroxonium ion, H_3O^+, in aqueous solution cannot be detected by the Raman effect; and whatever may be the cause of this might apply equally to the nitric acidium ion in nitric acid solution. Bauer suggests that the life-periods of individual hydroxonium ions are too short to produce sharp energy levels (*J. Chim. physique*, 1948, **45**, 242). Again, it is true that an approximate equivalence of nitronium and nitrate ions in absolute nitric acid has been established on the basis of Raman intensities; but the equivalence has not yet been established accurately enough to exclude the possibility that some minor but appreciable proportion, such as 10 or 15%, of the total dissociation may consist of autoprotolysis. Hughes, Ingold, and Reed have shown by a kinetic method (*J.*, 1950, 2400) that autoprotolysis is an actual step on the way to ionic self-dehydration. Thus, autoprotolysis must occur in principle, and the question now at issue is essentially the quantitative one of the proportion in which its immediate products survive in equilibrium. This matter will be probed further.

In the meantime let us calculate the self-dissociation at equilibrium on the assumption, which at least is approximately true, that it consists wholly of ionic self-dehydration. Then $[H_2NO_3^+] = 0$, and $[NO_2^+] = [NO_3^-] = [H_2O]$. From the temperature interval between the origin of the theoretical freezing-point curves and the observed maximum freezing point of nitric acid, we find

$$[NO_2^+] + [NO_3^-] + [H_2O] = 2 \cdot 20/2 \cdot 68 = 0 \cdot 82 \text{ molal}$$

and therefore

$$\left.\begin{array}{lll} [NO_2^+] = 0 \cdot 27 \text{ molal} = 1 \cdot 2\% \text{ by weight} \\ [NO_3^-] = 0 \cdot 27 \quad ,, \quad = 1 \cdot 7\% \quad ,, \quad ,, \\ [H_2O] = 0 \cdot 27 \quad ,, \quad = 0 \cdot 5\% \quad ,, \quad ,, \end{array}\right\} \text{Total dissociated} = 3 \cdot 4\%$$

Since we have estimated that each of the three products is solvated with two molecules of nitric acid, a further 10% of the nitric acid has to be pictured as being bound in solvates of the 3·4% of self-dissociation products. The value of the equilibrium constant for ionic self-dehydration is

$$K_{id} = [NO_2^+][NO_3^-][H_2O] = 0 \cdot 020 \text{ g.-mol.}^3 \text{ kg.}^{-3}$$

Granted the basic assumption that the amount of autoprotolysis is small enough to be neglected, these values are expected to be more accurate than the estimates derived from Raman intensities. On the other hand, exact agreement could not be expected, even if both methods were quite accurate, because the present values apply to the temperature −40°, while the spectroscopic values relate to the temperature −15°.

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