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# DISSOCIATION AND EQUILIBRIA OF PURE LIQUID NITRIC ACID\*

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The freezing point curves of water,  $N_2O_5$ ,  $KNO_3$ ,  $NH_4NO_3$ ,  $HClO_4$ ,  $H_2SO_4$ and acetyl nitrate in 100 % nitric acid have been determined. The course of these curves has been related to the self-dissociation of nitric acid and it is suggested that the nitric acid contains about 8 moles % dissociation products. The following equilibria are suggested to be present :

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5$$
$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$
$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$
$$2HNO_4 \rightleftharpoons H_3NO_5^+ + NO_5^-$$

and possibly

\* The contents of this paper are based on Ministry of Supply Report, No. AC 8230, dated 18th May, 1945.

The mechanisms of nitration and nitrolysis reactions in anhydrous nitric acid have been the subjects of numerous investigations and hypotheses, but little real progress in this field can be expected until the structure of nitric acid and the concentrations and reactivities of the various species of molecules and ions present in it are known. Bennett, Brand and Williams 1 have recently reviewed the allied problem of the nature of the nitrating agent in sulphuric acid, nitric acid, water mixtures -" mixed acid "-and have assembled a convincing argument that the nitronium ion  $NO_2^+$  is the significant species for aromatic nitration. This ion is produced in mixed acid by the reversible reaction,

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

Gillespie, Graham, Hughes, Ingold and Peeling 2 have found a four-fold depression of the freezing point of sulphuric acid by nitric acid, whilst Ingold, Miller and Poole <sup>3</sup> have shown the presence of  $NO_2^+$  and  $HSO_4^$ in these solutions by Raman spectroscopy, thereby confirming Bennett, Brand and Williams' interpretation of Chédin's 4 spectra.

Whilst it must be borne in mind that there are many important differences in the behaviour of mixed acids in aromatic nitration and of anhydrous nitric acid in nitrolytic reactions, it is a reasonable extension of Bennett, Brand and Williams's theory to infer that  $NO_2^+$  is present in pure nitric acid (see ref. (1), p. 872). Hantzsch<sup>5</sup> had suggested that the nitracidium ion  $H_2NO_3^+$  exists in these media, and he isolated two perchlorate salts,  $H_2NO_3^+$ ,  $ClO_4^-$  and  $H_3NO_3^{++}(ClO_4^-)_2$ , from a mixture of anhydrous nitric and perchloric acids. Goddard, Hughes and Ingold <sup>6</sup> have obtained a product of the approximate composition of

$$H_{3}NO_{3}^{++}(ClO_{4}^{-})_{2},$$

but consider it a mixture, since they have succeeded 7 in isolating the compound  $NO_2^+$ .  $ClO_4^-$  from it by fractional crystallization. Whilst these authors do not positively exclude the formation of  $H_2NO_3^+$  they suggest that in an anhydrous nitric acid medium it may be largely converted into  $NO_2^+$ . The main question is to what extent such a reaction takes place, and whether the equilibrium concentration of H<sub>2</sub>NO<sub>3</sub>+ which may be present are kinetically significant.

Measurements of the conductivity of mixtures of nitric acid and water and of nitric acid and nitrogen pentoxide have been made <sup>8</sup> and indicate that the course of the conductivity curve is continuous from the water side to the  $N_2O_5$  side. This, in itself, suggests that water and  $N_2O_5$  are related by a dissociative mechanism to the nitric acid. The conductivity is also found to pass through a minimum at  $2\frac{1}{2}$ % of water, but this minimum cannot be interpreted other than qualitatively until a detailed investigation has been made of the mobilities of those ions which may be concerned.

The following work presents further evidence for the existence of dissociation in pure nitric acid. In this, the species taking part in the dissociation are identified from the shape and course of the freezing point against composition curve, especially at low and high concentrations of the added species.

- <sup>4</sup> Chédin, Ann. chim., 1937, 8, 243.

<sup>6</sup> Chedni, Ann. chim., 1937, 8, 243.
<sup>6</sup> Hantzsch, Ber., 1925, 58, 941.
<sup>6</sup> Goddard, Hughes and Ingold, Nature, 1946, 158, 480.
<sup>7</sup> Gordon and Spinks, Can. J. Res. B, 1940, 18, 358.
<sup>8</sup> Veley and Manley, Phil. Trans. A, 1898, 191, 365. Berl and Saenger, Monatsh., 1929, 54, 1036. Taylor, Lyne and Follows, Queen's University, Kingston, Canada (unpublished). See also Jones, Thorn, Lyne and Taylor, Nature, 1047. Hep. 162. Nature, 1947, 159, 163.

<sup>&</sup>lt;sup>1</sup> Bennett, Brand and Williams, J. Chem. Soc., 1946, 869, 875, 880.

<sup>&</sup>lt;sup>2</sup> Gillespie, Graham, Hughes, Ingold and Peeling, Nature, 1946, **158**, 480. <sup>3</sup> Ingold, Millen and Poole, Nature, 1946, **158**, 480.

**Theory of the Method.**—The basic principles of the method are well known.<sup>9</sup> The detailed thermodynamic treatment of the method will be given in a subsequent paper,<sup>9a</sup> and it suffices for the moment merely to state the following theorems.

(1) The ideal freezing point law applies if an inert solute is added to solvent with which it does not interact. The freezing point depression is (initially) a linear function of the concentration N of the solute; that is,

$$\left(\frac{\mathrm{d}T}{\mathrm{d}N}\right)_{N\to0} = K.$$

(2a) If the solvent dissociates, then the addition of one of the dissociation products does not (initially) alter the freezing point.

$$\left(\frac{\mathrm{d}T}{\mathrm{d}N}\right)_{N\to 0} = \mathrm{o}.$$

(2b) At sufficiently high concentrations of the added dissociation product, the dissociation of the solvent is practically completely suppressed and the freezing point curve follows the "ideal" line. The extrapolation of this line back to zero concentration gives the freezing point of the hypothetical undissociated solvent. The degree of dissociation can be calculated, if ideality is assumed, from the lowering of the freezing point by the dissociation products. This simple law may be upset if the dissociation products take part in further equilibria, or if the solutions depart seriously from ideality.

(3a) If there is added to a dissociated solvent a solute which itself is completely dissociated and one of these solute products is the same as a dissociation product of the solvent, then initially

$$\left(\frac{\mathrm{d}T}{\mathrm{d}N}\right)_{N\to 0} = (i-1)K$$
$$= iK.$$

instead of

as would have been expected from van't Hoff's *i*-factor argument.

(3b) At sufficiently high concentrations of this solute, the freezing point curve follows that predicted by van't Hoff's argument.

(4) From (2b) and (3b) it is clear that the smaller the degree of dissociation of the solvent, the more easily it will be suppressed and the more rapidly will the freezing point curve approach the "ideal"; that is, the sharper will be the curvature at the origin.

#### Experimental

**Materials.**—The nitric acid used for each experimental run was freshly prepared on the day preceding the experiment. One litre of commercial 70 % nitric acid and 1.26 litres of sulphuric acid were distilled together under reduced pressure at a temperature not greater than 40° C, and the first 250-300 ml. collected in a flask cooled to  $-80^{\circ}$  C. The product was quite colourless and can be stored at  $-80^{\circ}$  C without becoming coloured. Titration usually indicated purities of 99.9 to 100 % nitric acid. This acid was further purified by slowly freezing until half remained as liquid phase which was siphoned away. The solid was remelted and refractionated. All operations were carried out in closed systems.

Nitrogen pentoxide was prepared by adding phosphorus pentoxide slowly and with good stirring to the purified acid at  $-40^{\circ}$  C and then distilling at  $30-40^{\circ}$  C with dry ozonized air. The N<sub>2</sub>O<sub>5</sub> vapour was washed by passing it through colourless, anhydrous nitric acid, over a tray of phosphorus pentoxide and collected in traps at  $-80^{\circ}$  C. Repeated fractional sublimation gave a solid product which was almost snow white.

<sup>9</sup> Stortenbeker, Z. physik. Chem., 1892, 10, 183. van Laar, ibid., 1909, 66, 197. Bray, ibid., 1912, 80, 251, 378. Lewis and Randall, Thermodynamics McGraw-Hill, 1923), pp. 217-220.

<sup>9a</sup> Dunning, in course of publication.

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The potassium nitrate and ammonium nitrate were A.R. quality and were crushed and dried *in vacuo* over phosphorus pentoxide for several days before use. The sulphuric acid was also A.R. quality. A perchloric acid solution in nitric acid was prepared by treatment at  $-80^{\circ}$ C of an accurately titrated 60 % aqueous solution of perchloric acid with the theoretical amount of N<sub>2</sub>O<sub>5</sub>. Acetyl nitrate was prepared by the addition of one mole of A.R. acetic anhydride to one mole of N<sub>2</sub>O<sub>5</sub> at  $-80^{\circ}$ C.

The 1:3:5-trinitro-1:3:5-triazocyclohexane which was used was a commercial product; it will be referred to in this paper as Cyclonite.

The chlorbenzene was a commercial product and was repeatedly dried over calcium chloride and fractionally distilled five times until the whole sample came over in the range 131.64 to 131.68°C. It had a density <sup>10</sup> of 1.1117.

**Procedure.**—The freezing points were obtained by measuring the difference between (i) solid nitric acid in equilibrium with a liquid phase of nitric acid plus solute and (ii) solid mercury in equilibrium with liquid mercury. One of the two glass vessels which contained the equilibrium systems is shown in Fig. 1. The mixture A was contained in the vessel B, which had three necks C, D and E. The



solvent and solute were introduced by means of neck E, which was sealed by a ground stopper. The stirrer F and the thermocouple M were mounted on ground glass joints in C and D. An outer jacket H surrounded the vessel and could be evacuated via the tap L; the interior of H and the exterior of B were silvered except for small areas through which the contents of the vessel B could be observed. In use the whole vessel was immersed in a bath of acetone cooled by solid carbon dioxide to the required temperature.

The temperature difference was measured by copper-constantan thermocouples connected to a Moll galvanometer, and the arrangement gave a deflection of about 10 cm. per °C, so that differences of  $\pm$  0.002° C could be measured. Each wire was wound in a close spiral near its junction, and these spirals were below the level of liquid A; in this manner heat conduction along the wires was minimized. The thermocouples and galvanometer were calibrated by two methods. (a) At room temperature: the junctions were standardized against an accurate Beckmann thermometer at room temperature and then, knowing dE/dT for copper-constantan at 15° C and -42° C (0.398  $\mu$ V/°C and 0.345  $\mu$ V/°C respectively <sup>11</sup>), the sensitivity at -42° C could be obtained. (b) A direct method in the temperature range of the experiments:

the temperature difference between the freezing point of mercury and that of a second standard chlorbenzene at  $-45 \cdot 25^{\circ} C \pm 0 \cdot 05^{\circ}$  was used to calibrate the thermocouple directly. The two methods gave figures for the sensitivity that agreed within 1 %, but the value obtained by method (a) was employed, owing to the possibility of impurities being present in the chlorbenzene. The mercury and the acid were transferred to the appropriate flasks and these were submerged in acetone and solid carbon dioxide. To assist the thermologing conduction the incluse H was at atmospheric pressure. When a small

The mercury and the acid were transferred to the appropriate flasks and these were submerged in acctone and solid carbon dioxide. To assist the thermal conduction, the jacket H was at atmospheric pressure. When a small fraction of the material in each flask was seen to be frozen, the jackets were evacuated and the vessels transferred to the cold acetone baths which were maintained within  $\pm \frac{1}{2}$ °C of the freezing points of the contents by the addition of solid carbon dioxide as required.

With the contents stirred continuously, an interval of 15 min. was allowed for the solid and liquid phases to reach equilibrium. The temperature difference was then measured at 10-min. intervals, four or five temperature differences were again recorded. The values so obtained never varied by more than  $\pm 0.005$ °C from the mean, which was taken as the best value. In all cases the contents of the acid vessel were visually observed to ensure that the amount of solid phase was only a small fraction of the total material present, yet enough to establish equilibrium.

<sup>10</sup> Weissberger and Proskauer, Organic Solvents.

<sup>11</sup> Temperature. its Measurement and Control (Reinhold, New York, 1939), p. 210.

### Results

Water and  $N_2O_5$  as Solutes.—The purified acid was weighed in the equilibrating vessel by difference, and its freezing point determined. A known quantity of water was introduced from a weight pipette and its freezing point redetermined. The freezing points for a range of water concentrations were obtained in this manner.

To obtain the freezing points of solutions of known concentrations of  $N_2O_5$ in HNO<sub>3</sub> the following procedure was adopted. A solution of  $N_2O_5$  in HNO<sub>3</sub> of suitable known composition was prepared in the equilibrating vessel and its freezing point measured. Water was then added in successive small quantities and the freezing point measured after each addition until the maximum freezing point (corresponding to 100 % HNO<sub>3</sub>) was reached. In some cases sufficient water was added to exceed the stoichiometric equivalent and to pass over and beyond the maximum freezing point.

A close examination of the results for the water and for the  $N_2O_5$  solutions gave indications that the acid used for the preparation of the initial solutions

Series	Mole Fraction $H_2O$ $HNO_3 + H_2O$	Mole Fraction as $N_2O_5$ $\overline{HNO_3 + N_2O_5}$	Freezing Point (°C below f. p. of Hg)	Freezing Point Depression, °C	Mole Fraction as $N_2O_5$ $H_2O_5 + H_2O$
A	(0.00) 0.0020 0.0110 0.0310 0.0510 0.0710		2·785 2·943 3·382 3·905 4·662	0.000 0.000 0.158 0.598 1.120 1.878	(0.500) 0.4990 0.4945 0.4845 0.4845 0.4745 0.4645
В	0.002 0.0210 0.0382 0.0552		2.813 3.071 3.532 4.173	0.000 0.258 0.719 1.360	0·4990 0·4895 0·4809 0·4723
С	   0·0088 0·0244	0.0528 0.0382 0.0258 0.0110 0.0034 	4·334 2·990 2·864 2·785 2·878 3·186	1.554 0.635 0.210 0.084 0.005 0.098 0.406	0.5264 0.5191 0.5129 0.5055 0.5017 0.4956 0.4878
D		0.0812 0.0650 0.0494 0.0342 0.0194 0.0050	7.811 5.898 4.235 3.527 3.036 2.949 3.005	4.871 2.958 1.295 0.587 0.096 0.009 0.065	0.5406 0.5325 0.5247 0.5171 0.5097 0.5025 0.4955
E	  0:0060 0:0184 0:0730	0.0636 0.0186 0.0060  	5·329 3·024 2·901 2·939 3·076 4·954	2·429 0·124 0·001 0·039 0·176 2·054	0·5318 0·5093 0·5030 0·4970 0·4918 0·4635
F	 0·0034 0·0120	0·0260 0·0056 	3·236 3·069 3·057 3·190	0·191 0·024 0·012 0·145	0·5130 0·5028 0·4983 0·4940

TABLE I

contained a trace of water, since the curves of freezing point plotted against the nominal concentration of water or nitrogen pentoxide did not match up, but showed small relative displacements along the direction of the concentration axis. The results were therefore plotted separately for each series on a large scale on transparent graph paper; the papers were superimposed and moved in the direction of the concentration axes until the courses of the curves coincided. This shift of the origin indicated that in some of the solutions there was present in the initial acid about  $0 \cdot 1$  % water, presumably absorbed during the transfer to the vessels. The nominal concentrations were corrected by the appropriate small amounts, and the curves replotted and again superimposed. In this way, the true concentrations of the solutes were obtained and are given in columns 2 and 3 of Table I. In this Table, Series A gives the results for an experiment in which water was added to " white" initric acid, and Series B those in which slightly yellow acid was used. A study of the data for A and B shows that although the initial freezing point of the yellow acid was lower



TABLE II

Solute	Mole Fraction of Solute	Freezing Point below f. p. of Hg, °C	Freezing Point Depression, °C
KNO3	0.000	2·7402	0.000
	0.00795	3·1226	0.382
	0.0104 0.0324 0.0502 0.0693	3.0008 4.6947 6.1754 8.1025	1.955 3.435 5.362
NH4NO3	0.000	2·7440	0·000
	0.0057	2·9844	0·240
	0.01381	3·3492	0·605
	0.02615	4·2146	1·471
	0.04241	5·5211	2·777
	0.05367	6·5889	3·845

than that of the pure acid, the shapes of the freezing point against composition curve are similar. It appears, therefore, that the presence of small amounts of impurities arising from decomposition is not significant. Similarly, Series C to E were carried out by adding water progressively to colourless  $N_2O_5 + HNO_3$ solutions and Series F by addition to slightly coloured  $N_2O_5 + HNO_3$  solutions. The results shown in Table I (columns 5 and 6) are plotted in Fig. 2 as freezing point depression on the  $H_2O + N_2O_5$  phase diagram. They are concordant with the results of Küster and Kremen <sup>12</sup> and of Berl and Saenger.<sup>8</sup>

Potassium Nitrate and Ammonium Nitrate as Solutes .- Weighed quantities of these salts were added to a weighed amount of pure nitric acid and the freezing points determined. The results are given in Table II and Fig. 3.



TABLE III

Solute	Mole Fraction of Solute	Freezing point of Solution below f. p. of Hg, ° C	Freezing point Depression, °C
HClO4	0.000	2·7340	0.000
	0.002965	2·8715	0.137
	0.005745	3·0019	0.268
	0.01620	3·6036	0.060
	0.02069	4·1034	1·369
	0.02619	4·6230	1·889
	0.03104	4·8991	2·165
	0.03366	5·1063	2·372
	0.03750	5·6866	2·053
	0:03979	5·9054	3·171
	0:04485	6·4708	3·637
H <sub>2</sub> SO <sub>4</sub>	0.000	2·7921	0.000
	0.01497	3·6376	0.846
	0.02951	5·1164	2.324
	0.04362	7·0533	4.261

<sup>&</sup>lt;sup>12</sup> Küster and Kremann, Z. anorg. Chem., 1904, 41, 1.

**Perchloric Acid and Sulphuric acid as Solutes.**—Small quantities of a solution of perchloric acid in nitric acid were added to pure nitric acid and the freezing points determined. Similarly, sulphuric acid was added to nitric acid and the freezing points of the resulting solutions obtained. Table III gives the data, which are illustrated in Fig. 4.

Potassium Perchlorate, Cyclonite and Acetyl Nitrate.—Since potassium perchlorate is not very soluble in nitric acid, the freezing point of only one

Solute	Mole Fraction of Solute	Freezing point of Solution below that of Hg, °C	Freezing point Depression ° C
KClO <sub>4</sub>	. 0.000	2·7705	0.000
	0.0046	3·1718	0.401
Cyclonite .	. 0.000	2·7722	0.000
	0.00269	2·9264	0.1542
	0.01352	3·3 <sup>8</sup> 73	0.6151
	0.02563	3·8466	1.0744
	0.03759*	4·6523	1.8801
Acetyl nitrate	. 0.000	2·7704	0·000
	0.00648	3·0800	0·3096
	0.02362	4·3851	1·6147
	0.04516	7·5827	4·8123

TABLE IV

\* Variable, probably near the saturation limit.

solution was obtained. A series of points for Cyclonite and for acetyl nitrate were obtained and these results are given in Table IV and illustrated in Fig. 5.



Freezing Point of Pure Nitric Acid. Consideration of the results quoted in the Tables and those of unreported experiments indicated that the purest anhydrous nitric acid used in these experiments had a freezing point not more than  $2\cdot73^{\circ}$  C below that of mercury. Using  $-38\cdot89^{\circ}$  C as the freezing point of mercury, this indicates that the freezing point of pure nitric acid is  $-41\cdot62^{\circ}$ C. The error in the absolute value of the sensitivity of the thermocouple was less than 2%, so that the accuracy of the above value of the freezing point is of the order  $\pm 0\cdot05^{\circ}$ C. This value of  $-41\cdot62 \pm 0\cdot05^{\circ}$ C compares well with that of Forsythe and Giauque <sup>13</sup> who report a value of  $-41\cdot58^{\circ}$ C.

#### Discussion

The relationship between the freezing point depression and the change in the chemical potential of the HNO<sub>3</sub> with addition of solute is given by

$$\frac{\mathrm{d}T}{\mathrm{d}N} = \frac{T}{L_s} \cdot \frac{\mathrm{d}\mu_s}{\mathrm{d}N}, \quad . \qquad (1)$$

where N is the mole fraction of the solute and  $L_{\epsilon}$  the molar heat of fusion of the

solid nitric acid. For water as solute, it can be shown <sup>96</sup> that

$$\frac{\mathrm{d}\mu_{s}}{\mathrm{d}N_{w}} = -\frac{N_{w}}{1-N_{w}} \left\{ \left( \frac{\partial\mu_{h}}{\partial N_{w}} \right)_{0} + \left( \frac{\partial^{2}\mu_{h}}{\partial N_{w}^{2}} \right)_{0} \cdot N_{w} \right\} \qquad . \qquad (2)$$

<sup>13</sup> Forsythe and Giauque, J. Amer. Chem. Soc., 1942, 64, 48.

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and

$$\frac{\mathrm{d}T}{\mathrm{d}N_{w}} = -\frac{T}{L_{s}} \cdot \frac{N_{w}}{\mathrm{I} - N_{w}} \left\{ \left( \frac{\partial \mu_{h}}{\partial N_{w}} \right)_{0} + \left( \frac{\partial^{2} \mu_{h}}{\partial N_{w}^{2}} \right)_{0} \cdot N_{w} \right\} \qquad (3)$$

where  $\mu_s$  and  $\mu_h$  are the chemical potentials of the species HNO<sub>3</sub> and  $H_2O$  respectively and  $N_w$  is the mole fraction of added water. It is clear from (3) that  $dT/dN_w$  is zero when  $N_w$  approaches zero, if  $(\partial \mu_h / \partial N_w)_0$  is finite. It is apparent from Fig. 2 that the freezing point composition curve for nitric acid and water or pentoxide has a flat maximum for  $N_w$  and  $N_p$  equal to zero. This indicates (Theorem 2a) that anhydrous nitric acid is dissociated into these two components,

(a) 
$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O_5$$

This conclusion is, of course, without prejudice to possible participation of these dissociation products in further equilibria. From the curve for pentoxide as solute, it is apparent that at high concentration the asymptote to the curve has a slope greater than that corresponding to an ideal solute with a van't Hoff *i* factor of I, and is close to, but slightly greater than that for *i* equals 2. This would indicate that the  $N_2O_5$  is itself largely dissociated in the nitric solution, and

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

would seem to be the most likely equilibrium, taking into consideration the conductivity data of Berl and Saenger<sup>8</sup> and of Taylor, Lyne and Follows.<sup>8</sup> The latter authors have also discussed these equilibria. Their evidence, together with that of Chédin and his collaborators <sup>14</sup>*a* are in agreement with this conclusion.

It will also be noted that the curve for water approaches an asymptote corresponding to i equals 1. This seems to indicate that the water exists mainly as  $H_2O$  molecules at these concentrations. This is at first sight a rather surprising conclusion, but it is known that nitric acid in aqueous solution is not a strong but a medium acid. This finding is in agreement with the relatively high partial pressure of water over these concentrations of acid <sup>14</sup> and with the work of Chédin and his collaborators.<sup>144</sup> It would seem, then, that the equilibrium constant of

(c) 
$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$

is such that water exists mainly as  $H_2O$ . It is necessary to point out at this stage that the asymmetry of the curve in Fig. 2 requires that the conditions be expressed as these two equilibria, which should not be added together to give a single equilibrium as in

(d)  $3HNO_3 \rightleftharpoons NO_2^+ + 2NO_3^- + H_3O^+$ .

Fig. 3 shows that both the nitrates give points which fall on a single curve. This curve is tangential to the line, i equals 1 for small concentrations, which indicates that nitrate ion is involved in the nitric acid dissociation, in accordance with Theorem 3a. At higher concentrations of the added nitrate salts, the slope of the curve approaches that for i equals 2; at this stage the self-dissociation of the nitric acid is suppressed to a large extent (Theorem 3b).

The curves in Fig. 4 are also interesting. Here a similar behaviour is found for perchloric acid and sulphuric acid as solutes. These at once indicate that hydrogen ion in some form is participating in the reaction. Either the added acids are reacting with water to form oxonium ions and driving back the equilibrium (b) to conserve the concentration of HNO<sub>3</sub>, or other modes of dissociation of the nitric acid are present such as

(e) 
$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$
.

14 Wilson and Miles, Trans. Faraday Soc., 1940, 36, 356.

<sup>14a</sup> Chédin, Leclerc and Vandoni, *Compt. rend.*, 1947, **223**, 734. Chédin and Fénéant, *Compt. rend.*, 1947, **224**, 930. Chédin and Vandoni, *Compt. rend.*, 1948, **226**, 1722.

The perchloric or sulphuric acids would in this case form the nitracidium ion,

(f) 
$$HNO_3 + HClO_4 \rightleftharpoons H_2NO_3^+ + ClO_4^-$$

and thereby suppress this dissociation. From the curves for sulphuric or perchloric themselves it would not be possible to decide whether nitracidium or nitronium ions are the principal product, since either equilibrium (f) or (g)

(g)  $HNO_3 + 2HClO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2ClO_4^-$ 

would give a value of i equals I at zero concentration of perchloric acid and a value of i equals 2 for the asymptote at higher concentrations. The curves in Fig. 4 are seen to have slopes appreciably greater than i equals 2 for the higher concentrations and further, these slopes are different for the two acids. It is possible that the second dissociable hydrogen of the sulphuric acid may be taking some part, or the increased slope may be due to a large heat of dilution or other lack of ideality.

In the same way, the small discrepancies in the slopes at higher concentrations in other Figures such as Fig. 2, 3 and 5 may be due to the presence of terms relating to the heats of dilution or other forms of nonideality. The values of the heat of dilution of nitric acid by water have been given by Berthelot <sup>15</sup> and Thomsen, <sup>16</sup> but the acid they start with is not anhydrous, and so the contribution of the heat of dissociation would probably be lacking if an extrapolation were relied upon.

If the asymptotes in Fig. 2 were known, then their point of intersection with the temperature ordinate at

$$N_w = N_p = 0$$

should give the freezing point of a hypothetical nitric acid in which there is no dissociation, and the length of the intercept on this ordinate could be considered as the depression of the freezing point of this hypothetical acid by adding the dissociation products in the concentrations corresponding to the equilibrium conditions in the pure acid. An extrapolation of the tangents to the curves in Fig. 2 will be found to intercept the ordinate at widely different points. An exploratory calculation based on the two equilibria

$$2HNO_3 \rightleftharpoons NO_2^+ + H_2O + NO_3^-$$
$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$

in which suitable equilibrium constants were taken showed that the curves would be asymmetrical about this ordinate and that the equilibrium is suppressed much more quickly on the pentoxide side than on the water side. Thus, the tangents to the experimental curves do not represent the asymptotes. This calculation also indicated that the intercept made by the tangent on the pentoxide side is closer to the true value of a hypothetical melting point than on the water side. If we bear in mind the unsatisfactory nature of this procedure, we may take the length of this intercept, and it is found that the melting point of the hypothetical acid has been depressed to an extent which corresponds to the presence of about 8 moles % dissociation products.

In Fig. 5 the freezing points of acetyl nitrate solutions in anhydrous nitric acid have been plotted. This is of some interest, since it indicates that acetyl nitrate is not merely a solution of pentoxide in acetic anhydride. Were this so, the slope at small concentrations would be that for i equals  $\frac{1}{2}$ , since the concentration scale is based on the formula, CH<sub>3</sub>COONO<sub>2</sub>. Both the slope at low concentration and the slope at high concentration suggest that acetyl nitrate dissociates as

$$CH_{3}COONO_{2} \rightleftharpoons CH_{3}COO^{-} + NO_{2}^{+}$$
.

<sup>16</sup> Berthelot, Ann. Chim. Phys. (5), 1875, 446.
<sup>16</sup> Thomsen, Ber., 1873, 6, 697.

The very steep slope at higher concentrations may again be due to heat of dilution or other forms of non-ideality, but it seems excessively steep for this. In this figure there are also shown the points for Cyclonite and KClO<sub>4</sub>, which indicate that for an inert solute (Cyclonite) *i* equals 1, and that strong electrolytes (KClO<sub>4</sub>) are dissociated in nitric acid.

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