859. *The Electrical Conductances of Solutions in Nitric Acid. Part I. Solutions of Dinitrogen Pentoxide, and of Water. The Extent of the Self-dissociation of Nitric Acid.*

By W. H. LEE and D. J. MILLEN.

The electrical conductivities of anhydrous nitric acid, and of solutions of dinitrogen pentoxide, and of water, in nitric acid, have been measured, at −10° and at −20°. On the basis of the self-dissociation, $2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$, the extent of this dissociation has been found. The product of the mole fractions of NO_2^+, NO_3^-, and H_2O, *i.e.*, the classical mole fraction dissociation constant K_x, is found to be $0{\cdot}930 \times 10^{-5}$ at −10°, and $1{\cdot}602 \times 10^{-5}$ at −20°, the molar concentrations of each species being 0·511 and 0·610 at the respective temperatures.

SEVERAL studies of the self-dissociation of nitric acid have yielded a consistent picture of the ionic and molecular species formed. The extent of the process has been estimated from cryoscopic studies by Dunning and Nutt [1] and by Gillespie,[2] both of which apply at the freezing point, −42°.

In the present work, the same self-dissociation process is assumed, *viz.*,

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

and the extent of dissociation is calculated from the change in the electrical conductivity when dinitrogen pentoxide and water are dissolved in nitric acid. Both of these solutes are solvent self-dissociation products, so that a study of their solutions is particularly relevant, and indeed necessary before the conductivities of other solutes in nitric acid can be interpreted.

A number of conductivity studies on solutions in nitric acid have been reported. Veley and Manley [3] measured the conductivities of solutions of water in nitric acid. They observed a conductivity minimum at approximately 2 molal water, which was confirmed by Dalmon [4] and by the present work, though Hantzsch had been unable to find it. Berl and Saenger [5] studied solutions of dinitrogen pentoxide in nitric acid, at 18°. They

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[1] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.
[2] Gillespie, *J.*, 1950, 2552.
[3] Veley and Manley, *Phil. Trans.*, 1898, **191**, 365.
[4] Dalmon, *Mem. Services chim. État*, 1943, **30**, 141.
[5] Berl and Saenger, *Monatsh.*, 1929, **54**, 1036.

reported a maximum conductivity at high solute concentrations, but, as these solutions were yellow, some decomposition must have occurred. Taylor, Lyne, and Follows[6] studied nitric acid solutions of dinitrogen pentoxide, water, and ammonium nitrate, at several temperatures. These previous results show the same general trend as those of the present investigation, but the higher temperatures employed increased the possibility of serious errors due to solvent decomposition.

Very few conclusions were drawn from previous studies, and no attempt was made to deduce the extent of solvent self-dissociation.

EXPERIMENTAL

Measurements were taken at −10° and −20° to avoid, as far as possible, thermal decomposition of nitric acid or dinitrogen pentoxide. The temperature was maintained by a glycol–alcohol bath, cooled by a commercial refrigerator unit, and controlled by a toluene–mercury regulator and subsidiary heaters to within ±0·02°. Resistance was measured by a conventional Wheatstone bridge circuit, supplied by an oscillator with switched frequency control. To obviate catalytic decomposition of the solvent by platinum black, the electrodes were of bright platinum; measurement at different frequencies showed that no appreciable errors due to polarisation were introduced.

Since the solvent and the solutions had very high specific conductances a capillary-tube conductivity cell, of Pyrex glass, having a high cell-constant, was used. The electrodes were about 0·5 cm. square, separated by 20 cm. of capillary tubing. The cell was calibrated at 0° by means of 0·1D-potassium chloride described * by Jones and Bradshaw.[7] The cell constant so obtained was 232·4 at 0°, and this value was also used for measurements made at −10° and −20°, since no calibrating solutions are available for use at these temperatures. It was estimated that contraction of the cell and electrodes could lead to a change in cell constant of about 0·05% at the lower temperature, and this is beyond the accuracy with which the composition of the solutions is known.

Densities of solutions were measured by means of a syphon pyknometer, designed for use with anhydrous liquids (Hennion[8]). It was calibrated with absolute ethanol, at −10°, and had a volume of 2·656 ml.

Preparation of Reagents.—Nitric acid was prepared by static distillation, from a mixture of fuming nitric acid and sulphuric acid, as described by Reed.[9] The product was redistilled in a smaller apparatus, reserved for this purpose. The composition of the product is discussed below.

Dinitrogen pentoxide was prepared by distillation, in a current of ozonised oxygen, from a nitric acid–phosphoric oxide mixture at room temperature. The product was passed through phosphoric oxide drying-tubes before condensation in a trap cooled in alcohol–carbon dioxide.

Good quality, laboratory-distilled water, of specific conductance below 10^{-6} ohm^{-1}, was used.

Solutions were prepared by weight. Dinitrogen pentoxide was re-distilled, through drying-tubes, into a known weight of nitric acid. Water was added from a weight pipette to a known weight of the well-cooled acid. To avoid contamination of solutions during several transfers, the densities were determined on separately prepared solutions.

RESULTS

The specific conductances of the solutions are recorded in Table 1, and densities in Table 2.

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* Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 312) originally defined a demal solution as being one containing 1 mole of solute per cubic decimeter of solution, in air at 0°. For potassium chloride solutions Jones and Bradshaw[7] recommend standard solutions, based on measurements of electrical conductivity of mercury and the international ohm, as follows: D, 71·1352; 0·1D, 7·41913; 0·01D, 0·745263 g. of KCl per 1000 g. of solution *in vacuo*. See Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 1955, Chap. 5.

[6] Taylor, Lyne, and Follows, *Canad. J. Chem.*, 1951, **29**, 439.

[7] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

[8] Hennion, *Ind. Eng. Chem.*, 1937, **9**, 479.

[9] Reed, *J.*, 1950, 2438.

TABLE 1. *Specific conductances of solutions in nitric acid.*

(Concns. are in molarities, and specific conductances in ohm^{-1}.)

$T = -10{\cdot}02°$.

$[N_2O_5]$	$10^4\kappa$	$[N_2O_5]$	$10^4\kappa$	$[N_2O_5]$	$10^4\kappa$	$[N_2O_5]$	$10^4\kappa$
0·085	385	0·3082	441	0·4288	477	0·7061	570
0·1018	390	0·3893	455	0·5033	498	1·279	725
0·2109	413	0·4130	468	0·5502	505	1·880	817

$[H_2O]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$
0·0498	358	0·2886	309	0·3383	297	0·5916	260
0·1503	335	0·3121	301	0·5096	272	1·175	188
0·2225	321						

$T = -20{\cdot}01°$.

$[N_2O_5]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$	$[H_2O]$	$10^4\kappa$
0·1505	366	0·1202	321	0·2266	308	0·3908	283
0·4544	438	0·1788	310	0·2890	295		

TABLE 2. *Densities of solutions in nitric acid.*

$T = -10{\cdot}02°$.				$T = -20{\cdot}01°$.			
$[N_2O_5]$	$d_{soln.}$	$[H_2O]$	$d_{soln.}$	$[N_2O_5]$	$d_{soln.}$	$[H_2O]$	$d_{soln.}$
0·0976	1·5652	0·3988	1·5614	0·1490	1·582	0·1205	1·580
0·1991	1·5663	0·4993	1·5610	0·4498	1·584	0·1792	1·578
0·4001	1·5694	—	—	—	—	0·2897	1·578
0·5981	1·5736	0·7215	1·5590	—	—	0·3917	1·577
0·7262	1·5757	1·9719	1·5544				
1·7297	1·6116						

For the solvent, as prepared by static distillation, the mean values for 20 samples gave the results :

Specific conductance	0·0348 ± 0·0003 ohm^{-1} at −10°
Density	1·5630 ± 0·0002 g. ml.$^{-1}$,,

If the conductivities of solutions of both water and dinitrogen pentoxide are plotted against composition of solution, a smooth curve is obtained, giving no indication of the position of " nitric acid." Addition of dinitrogen pentoxide to nitric acid increases the conductivity; addition of water to nitric acid decreases it. Both solutes, however, produce a freezing-point depression, so that the freezing point–composition graph passes through a maximum at the composition of nitric acid. The properties of the pure acid may thus be unequivocally determined on the liquid of maximum freezing point.

A combined study of the cryoscopy and conductivity of nitric acid has recently been made by Gillespie and Lewis.[10] They find the product of the static distillation to contain 0·10 mole of " excess " water, per litre of nitric acid. The acid of maximum freezing point (−41·64°) has a specific conductance 0·0367 ohm^{-1} at −10°. From our density–composition graph, this acid has a density 1·5644 g. ml.$^{-1}$ at −10°. These values for the pure solvent have been adopted in the interpretation of our results. The concentrations recorded in Tables 1 and 2 have been calculated on this basis.

Calculation of the Extent of Self-dissociation.—Evidence for the dissociation of nitric acid according to equation (A) has been summarised by Gillespie and Millen.[11] Cryoscopic evidence shows that dinitrogen pentoxide is completely ionised in nitric acid, but that water is practically un-ionised;[2] and on this basis, the conductivity results in Table 1 may be qualitatively explained.

The increase in conductivity on dissolving dinitrogen pentoxide in nitric acid is a measure of the increased concentration of nitronium and nitrate ions, only partially offset by the repression of solvent self-dissociation. With water as solute, no extra ions are

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[10] T. J. Lewis, Ph.D. Thesis, London, 1954.

[11] Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 282.

added, and the decrease in conductivity is due solely to the repression of self-dissociation. Beyond the broad conductivity minimum, at approximately 2m-water, the hydroxonium ion appears in significant concentration, and, together with the reduced viscosity, this accounts for the increase in conductivity with further addition of water.

The Conductance–Concentration Relation applicable to Solutions in Nitric Acid.—To develop these ideas quantitatively, a relation between conductance and concentration is needed. Preliminary study showed that the dilute-solution law, $\Lambda \propto \sqrt{c}$, was of little value, except that its failure indicated a much higher degree of self-ionisation than is found for other solvents.

It is observed that, for aqueous solutions of a single electrolyte, within the concentration range 0·3—1·0m, the equivalent conductance varies only slowly with concentration; this variation is about 5% (over the range considered) for alkali halides, and about 7% for the nitrates. Thus, within this range, it is a better approximation to take Λ constant, and therefore $\kappa \propto c$, the molarity, rather than $\Lambda \propto \sqrt{c}$. This is equivalent to assuming that there is no change in the ionic mobilities, and that the change in κ is entirely due to the change in the number of ions per unit volume, over this range. The molar concentration of ions in the nitric acid solvent will be shown to be about 0·5; so that, by comparison with aqueous solutions, the relation $\kappa \propto c$ might be expected to apply here, particularly if the dielectric constant of nitric acid is not very different from that of water. There is evidence that this is so, from conductivity measurements of solutions of salts, not containing the nitrate ion, in nitric acid,[12] and from direct measurement by the moving ellipsoid method.[13] We adopt this relation, which, although only approximate, enables all the conductivity results to be combined in finding an accurate value for the extent of the self-dissociation.

Application of the Relationship $\kappa \propto c$ to Conductivities of Solutions in Nitric Acid.—Suppose the molar concentration of each ion, and of water, in anhydrous nitric acid, to be a; then one litre of nitric acid contains $(1000d/M - 2a)$ mole of the species "HNO_3," where d is the density of the acid, and M its molecular weight. The term $(1000d/M)$ has the value 24·825 at −10°, and 25·103 at −20°.

Suppose further that, after the addition of m moles of dinitrogen pentoxide to one litre of nitric acid, there are present n g.-ions of nitrate and nitronium ions. Then we may deduce the amounts of the other species present in the solution, and also the volume of the solution; for convenience, these amounts, together with those present in the pure solvent, are given in Table 3.

TABLE 3. *Number of moles of species present, at −10°.*

System	HNO_3	NO_2^+	NO_3^-	H_2O	Volume of system
Anhydrous nitric acid	$24{\cdot}825 - 2a$	a	a	a	1 litre
1 litre of nitric acid, with m mole of N_2O_5 added	$24{\cdot}825 - 2n$	n	n	$n - m$	$1/D$ litre

The density of the solvent is denoted by d, that of the solution by $d_{\text{soln.}}$ and D is $1000d_{\text{soln.}}/(1000d + 108m)$. Expressions for K_x, the self-dissociation equilibrium constant, with concentrations expressed in mole fractions are:

for the solvent,

$$K_x = \frac{a^3}{(24{\cdot}825 + a)(24{\cdot}825 - 2a)^2} \cdot f_1{}^2 \cdot \frac{f_2}{f_3{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and, for the solution:

$$K_x = \frac{n^2(n - m)}{(24{\cdot}825 + n - m)(24{\cdot}825 - 2n)^2} \cdot \frac{f'_1{}^2 f'_2}{f'_3{}^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where f_1 is the mean ion activity coefficient of $NO_2^+NO_3^-$, f_2 the activity coefficient of water, and f_3 that of nitric acid, all in the pure solvent; and f'_1, f'_2, f'_3 are the corresponding values

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[12] W. H. Lee, Ph.D. Thesis, London, 1953.

[13] R. F. M. White, personal communication.

for the solution. Similar considerations for solutions of water lead to an analogous equation :

$$K_x = \frac{n^2(n + m)}{(24{\cdot}825 + n - m)(24{\cdot}825 - 2n)^2} \cdot \frac{f''^2_1 f''_2}{f''^2_3} \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

in which n has the same significance as before, but m is now the number of moles of water added to one litre of nitric acid.

Applying the relationship $\kappa \propto c$ previously considered, to the solvent and solution of Table 3, we obtain :

$$\kappa_{\text{soln.}}/\kappa_{\text{HNO}_3} = nD/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

Substituting for a^3, in eqn. (1), and combining it with eqn. (2), we have :

$$(\kappa_{\text{soln.}}/\kappa_{\text{HNO}_3})^3 = \frac{n^3D^3(24{\cdot}825 + n - m)(24{\cdot}825 - 2n)^2}{n^2(n - m)(24{\cdot}825 - 2a)^2(24{\cdot}825 + a)} \cdot \frac{f_1^2 f_2 f'^2_3}{f_3^2 f'^2_1 f_2'} \quad . \quad . \qquad (5)$$

Neglecting the activity coefficient product, we may solve for n, giving :

$$n = m/[1 - D^3(\kappa_{\text{HNO}_3}/\kappa_{\text{soln.}})^3 \,.\, \beta] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

where $\beta = (24{\cdot}825 + n - m)(24{\cdot}825 - 2n)^2/(24{\cdot}825 - 2a)^2(24{\cdot}825 + a)$

Similarly, for solutions of water, n may be evaluated from the equation :

$$n = m/[\beta' D^3(\kappa_{\text{HNO}_3}/\kappa_{\text{soln.}})^3 - 1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

where $\beta' = (24{\cdot}825 + n + m)(24{\cdot}825 - 2n)^2/(24{\cdot}825 - 2a)^2(24{\cdot}825 + a)$

Now β and β' are both functions of a and n, but, since they are only slowly varying functions and do not depart appreciably from unity, equations (6) and (7) may be readily solved by a method of successive approximations; n is effectively constant after three such approximations.

From each value of n, a value of a may be obtained, from $a = nD \,.\, \kappa_{\text{HNO}_3}/\kappa_{\text{soln.}}$. Any dependence of the calculated value of a upon n will indicate departure from the assumptions made concerning the conductance–concentration relation and the neglect of activity coefficients. Variation of a with n is in fact found; but its effect can be overcome by extrapolation to find the value of a as m approaches zero. The form of equation 6 is such that the values of a become less reliable as m decreases. However, since extrapolation is possible for solutions of both water and dinitrogen pentoxide, the procedure reduces to an interpolation of the value of a for that mixture in the N_2O_5–H_2O system corresponding to the composition HNO_3.

The results obtained at −20° may be treated in the same way, by using density factors appropriate to this temperature, the term 24·825 being replaced by 25·103.

The results of these calculations, for solutions of dinitrogen pentoxide and of water at −10°, together with the experimental results, are recorded in Table 4, and those at −20° in Table 5.

TABLE 4.

$T = -10{\cdot}02°$. $10^4\kappa_{\text{HNO}_3} = 368$ ohm⁻¹. $d = 1{\cdot}564$ g. ml.⁻¹.

Molarity of N_2O_5	$10^4\kappa_{\text{soln.}}$	$d_{\text{soln.}}$	n	a	Molarity of H_2O	$10^4\kappa_{\text{soln.}}$	$d_{\text{soln.}}$	n	a
0·1024	390	1·565	0·558	0·523	0·0498	358	1·564	0·573	0·588
0·2057	415	1·566	0·600	0·525	0·1500	335	1·563	0·456	0·499
0·3101	441	1·568	0·661	0·541	0·2002	325	1·562	0·438	0·494
0·4156	468	1·569	0·730	0·560	0·2504	315	1·562	0·416	0·484
0·5224	500	1·571	0·854	0·609	0·3005	305	1·562	0·394	0·472
0·6304	535	1·574	0·868	0·576	0·3505	295	1·561	0·367	0·455
0·7400	574	1·576	0·936	0·575	0·4104	288	1·561	0·364	0·462
					0·5023	273	1·561	0·341	0·456

TABLE 5.

$T = -20{\cdot}01°$. $10^4\kappa_{HNO_3} = 340$ ohm^{-1}. $d = 1{\cdot}582$ g. ml.$^{-1}$.

Molarity of N_2O_5	$10\kappa^4_{soln.}$	$d_{soln.}$	n	a	Molarity of H_2O	$10^4\kappa_{soln.}$	$d_{soln.}$	n	a
0·1505	366	1·582	0·645	0·593	0·1202	321	1·580	0·637	0·672
0·4544	438	1·584	0·790	0·605	0·1788	310	1·578	0·562	0·613
					0·2890	295	1·578	0·538	0·614
					0·3908	283	1·577	0·528	0·630

The Figure shows a plot of the calculated values of a against m. It is seen, that although there is a slight dependence of the value for a on m, there is no difficulty in obtaining the interpolated value of a at $m = 0$. Also shown in the same diagram is a plot of the calculated values of n against m. It will be seen that the curves intersect satisfactorily at $m = 0$. This intersection is very dependent on the value used for the specific conductance of the solvent and affords a sensitive test for the correctness of the value taken.

Graphical interpolation to obtain values for a, the molarity of water, nitrate, and nitronium ions in anhydrous nitric acid. All concentrations are expressed in molarities. ○, *n at* −10·02°. ×, *n at* −20·01°. □, *a at* −10·02°. △, *a at* −20·01°.

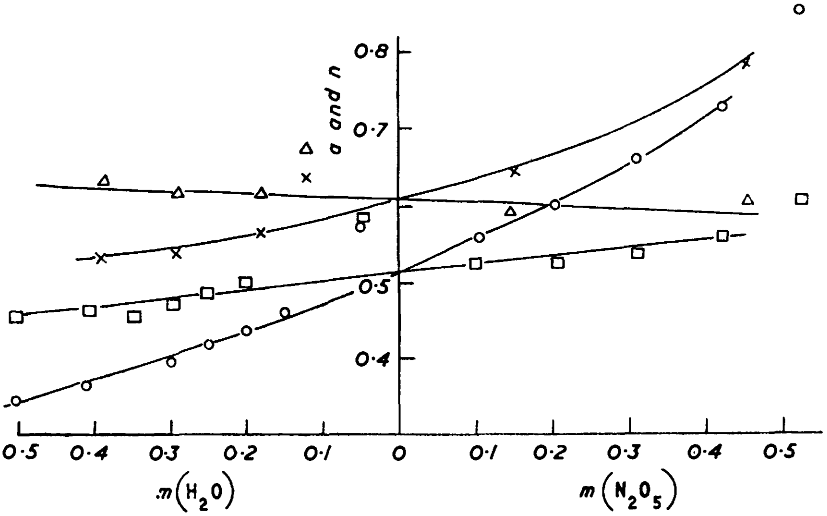

Table 6 records the values of a obtained for the two temperatures, the mole fractions of nitronium ion $x_{NO_2^+}$ ($= x_{NO_3^-} = x_{H_2O}$), and also the values of the classical mole fraction dissociation constants.

TABLE 6.

	a	$x_{NO_2^+}$	$x_{HNO_3^-}$	10^5K_x
At −10·02°	0·511	0·0194	0·942	0·930
At −20·01°	0·606	0·0227	0·932	1·602

TABLE 7. *The classical self-dissociation constant for nitric acid at various temperatures.*

Temp.	10^5K_x	Ref.
−40°	2·44	1, 10
−20	1·602	Present work
−10	0·930	,,
+25	0·280	6

By similar calculations from the conductance data of Taylor *et al.*[6], K_x has been found at 25°. These values are summarised in Table 7, together with a value for a temperature of −40° obtained cryoscopically.

The variation of K_x may account in part for the temperature-dependence of the specific conductance of nitric acid, which shows a maximum at about 25°; this result [6] has been confirmed in the present investigation. Thus, despite a continuous decrease in viscosity, the specific conductance falls above 25°, because there is an even greater effect due to the decrease in the number of ions present. Other factors which may contribute are changes in solvation of the ions and variation in the dielectric constant, with temperature, and it is hoped to investigate these later.

The equivalent conductance of nitronium nitrate, given by $\Lambda = l_{NO_2^+} + l_{NO_3^-} = 1000\kappa/c$, is found to have the values, 55·7 at −20°, 71·9 at −10°, and 107·4 at 25°, for the solutions corresponding to anhydrous nitric acid. The corresponding values for the pure solvents, water and sulphuric acid, at 25° are 536 and 166·3. The low value obtained for the ions produced by the self-ionisation of nitric acid may be due in part to the high concentration of ions in this case. However, the main cause of the higher values for water and sulphuric acid is probably the chain-conductance mechanism which operates in both of these cases; [14] as will be shown later, no such mechanism has been observed in nitric acid.

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[14] Gillespie and Wasif, *J.*, 1953, 970.