170. *Transport Numbers of Nitric Acid in Water at 25° from E.M.F. Measurements.*

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The cation transport numbers (t_+) of aqueous solutions of nitric acid ($c = 0.001$ to 0.2 mol./l.) have been determined by combining activity-coefficient data with measurement of the E.M.F. of concentration cells with transport, quinhydrone electrodes being used. The results are compatible with the theoretical limiting value and limiting slope of the t_+–$\sqrt{c}$ curve, agree with the Jones–Dole and the Longsworth equation, but not with the Owen equation, and indicate that, up to 0.2 mol./l., the hydrogen ion mobilities in nitric and hydrochloric acids at the same concentration are equal; the nitrate ion mobilities of potassium nitrate (up to $c = 0.2$) and of silver nitrate (up to $c = 0.1$) are, however, lower than those of nitric acid.

THE only transport-number data reported for aqueous nitric acid are those, almost exclusively from " International Critical Tables " (1929, **6**, 310), quoted in Table I. These values of t_+ (cationic transport number) are plotted against $\sqrt{c}$ in Fig. 1, in which are also shown the straight lines drawn through the theoretical limiting

TABLE I.

Cation Transport Numbers of Nitric Acid in Water.

c (concn., mol./l.)	0·005	0·01	0·02	0·05	0·1	0·2
t_+ at 25° (moving boundary)	—	0·838	0·838	0·840	0·844 *	0·849
t_+ at 18° (moving boundary)	—	—	0·846	—	0·855	—
t_+ at 20° (gravimetric)	0·839	0·840	0·841	0·844	—	—

* MacInnes and Cowperthwaite (*Trans. Faraday Soc.*, 1927, **23**, 400) give 0·8441.

values t_+^0 (for $c = 0$), with slopes equal to the limiting slopes given by Longsworth's equation (*J. Amer. Chem. Soc.*, 1932, **54**, 2741; 1935, **57**, 1185)

$$\underset{c \to 0}{\mathrm{Lt}}\ dt_+/d\sqrt{c} = \beta(2t_+^0 - 1)/\Lambda^0 \quad\quad\quad\quad\quad\quad (1)$$

The value of β, one of the constants in Onsager's conductivity equation (*Physikal. Z.*, 1926, **27**, 388; 1927, **28**, 277)

$$\Lambda' = \Lambda^0 - (a\Lambda^0 + 2\beta)\sqrt{c} \quad\quad\quad\quad\quad\quad\quad (2)$$

is taken as 29·93 in water at 25°. The values of t_+^0 were obtained from the relation

$$t_+^0 = \lambda_+^0/(\lambda_+^0 + \lambda_-^0) \quad\quad\quad\quad\quad\quad\quad\quad (3)$$

and are listed, together with the necessary limiting cationic and anionic mobilities ($\lambda_{H^+}^0$ and $\lambda_{NO_3^-}^0$), in Table II. It appears from Fig. 1 that there is little tendency for the moving-boundary transport numbers at 18° to

TABLE II.

Limiting Ionic Mobilities, Cation Transport Numbers, and Slopes.

Temp.	$\lambda_{H^+}^0$	$\lambda_{NO_3^-}^0$	t_+^0	β	$\underset{c \to 0}{\mathrm{Lt}}\ dt_+/d\sqrt{c}$
18°	315·2 [a]	61·62 [a]	0·8365	25·17	0·04495
20	325·1 [b]	64·42 [b]	0·8346	26·52	0·04557
25	349·72 [c]	71·42 [c]	0·8304	29·93	0·04696

(a) " International Critical Tables," 1929, **6**, 230; (b) interpolated; (c) MacInnes, Shedlovsky, and Longsworth, *J. Amer. Chem.* Soc., 1932, **54**, 2758.

merge into the theoretical limiting slope as c decreases; the agreement is better for the gravimetric values at 20°, and also for the moving-boundary values at 25°, except for the lowest two concentrations in each case. The discrepancies are in the wrong direction and far too great to be ascribed to the omission of the correction for the conductivity of the solvent (Longsworth, *loc. cit.*, 1932); they may possibly be due to the experimental

difficulties inherent in the gravimetric and the moving-boundary method (*idem, ibid.*, 1935, **57**, 1185) at low concentrations. It is clear that further independent measurements are desirable.

Hitherto no transport numbers for nitric acid derived from E.M.F. measurements have been reported. This may be because the usual E.M.F. method necessitates the measurement of cells both with and without transport; the former demands two identical electrodes, both reversible to the same ion, either H^+ or NO_3^-, and the latter a pair of non-identical electrodes, one reversible to H^+, the other to NO_3^-. Since, however, accurate activity-coefficient data for nitric acid are available (Hartmann and Rosenfeld, *Z. physikal. Chem.*, 1933, **164**, 377), the second type of cell may be dispensed with. In the absence of any electrode reversible to
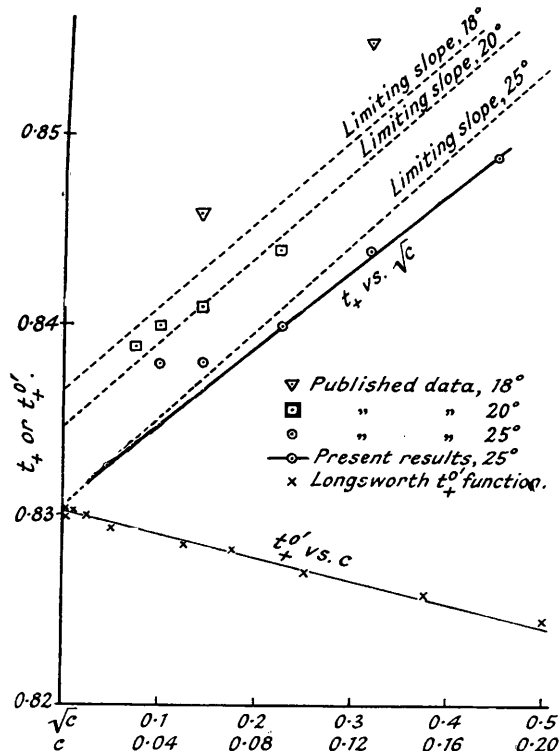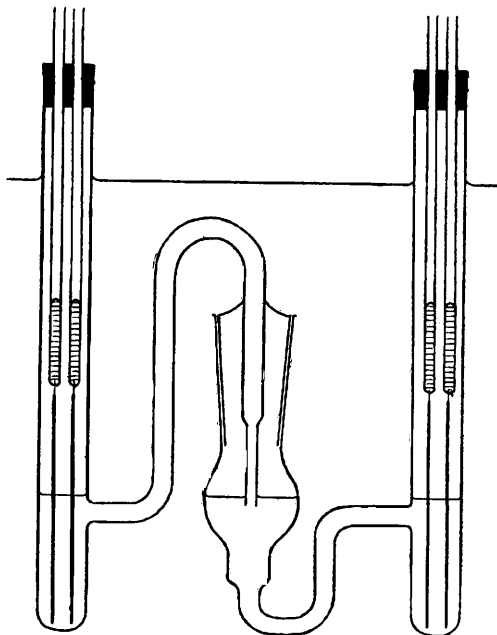
FIG. 1.   FIG. 2.

NO_3^-, there now remains the necessity for an electrode, reversible to H^+, which will function in nitric acid. The hydrogen electrode itself is useless owing to its reducing action on the acid, but the quinhydrone electrode is applicable up to at least 0·2 mol./l., with a known salt error (Stonehill, *Trans. Faraday Soc.*, 1943, **39**, 67). The method therefore adopted was to measure at 25° the E.M.F. of cells with transport of the type Pt|quinhydrone (satd.), HNO_3 (m', fixed)|HNO_3 (m, variable), quinhydrone (satd.)|Pt, which, after correction for the electrode salt error, is given by

$$E = (2RT/F) \int_{m\gamma}^{m'\gamma'} t_- \mathrm{d} \ln m\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where m and m' are molalities (mols./1000 g. of water), and γ and γ' are mean ionic activity coefficients corresponding to this concentration scale. By differentiation of (4), we have

$$(F/2RT)\mathrm{d}E/\mathrm{d} \ln m\gamma = t_- = (1 - t_+) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

EXPERIMENTAL.

The auxiliary apparatus (potentiometer, thermostat, etc.), and the preparation of quinhydrone, stock nitric acid, and cell solutions have already been described (Stonehill, *loc. cit.*). For some preliminary measurements with higher nitric acid concentrations the cell with a ground-glass cap junction (*loc. cit.*) was used; the inner compartment contained the more concentrated of the two acid solutions, and the outside of the inner vessel was rinsed with the more dilute acid solution before assembly of the two compartments; the bubble trap was sealed, and excess of quinhydrone was added to both compartments, which were each provided with a pair of bright gold wire electrodes. The high electrical resistance of the ground-glass junction made it difficult to obtain reliable results for nitric acid concentrations lower than about 0·1 mol./l. Therefore the cell shown in Fig. 2 was used for the main set of measurements, over the concentration range 0·001—0·2 mol./l. This cell consists of two half-cells which connect to form a simple dipping-type liquid junction. The left-hand compartment, while detached from the right-hand section, was filled with the more dilute of the two cell solutions, so that a pendant drop remained at the end of the narrow tube where the liquid junction was to be formed; excess of quinhydrone was added to the test-tube-shaped electrode vessel, and a rubber stopper carrying two bright gold

wire electrodes was fitted into place. The right-hand compartment was then filled with the other solution to about the middle of the bulb below the ground-glass joint, quinhydrone added, and a stopper with two gold wire electrodes fitted; the cell was then assembled, so that at the liquid junction the denser solution was below the other. The ground-glass joint was lubricated with light vacuum grease to resist leakage of thermostat liquid (kerosene) into the cell. It was necessary to ensure that no quinhydrone diffused into the liquid junction region, otherwise variable results were obtained. The cell was also tested for interdiffusion of the solutions by placing potassium permanganate solution on one side and water on the other; no colour diffused into the neighbourhood of the water-filled electrode vessel in 48 hrs. Cells were measured at 25° ± 0·01° for 6—12 hrs. Equilibrium ensued in about 2—3 hrs. for intermediate concentrations, rather longer for the more dilute, and shorter for the more concentrated solutions; in the latter, however, rapid drifts were observed after about 2 hrs., due to interaction of quinhydrone and nitric acid (Stonehill, *loc. cit.*); for this reason, no reliable values could be obtained for concentrations above about 0·2 mol./l. Duplicate cells were measured in all cases, and agreed within 0·03 mv. or rather better for the more dilute solutions; the two electrodes in each half-cell generally agreed to within 0·01—0·03 mv. With a given pair of solutions, both the old and the new cell gave the same results.

Results.—The values of the nitric acid concentration (c mols./l. of solution, or m mols./kg. of water), the observed E.M.F. ($E_{obs.}$), and log γ are given in Table III. The fixed solution in one half of the cell had concentration $c' = 0·1038$.

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TABLE III.

*Experimental E.M.F. Results.**

c.	m.	$-\log \gamma$.	$E_{obs.}$.	ΔE.	$E_{corr.}$.	E'.
0·2040	0·2058	0·1242	4·56	0·54	5·10	21·36
0·1530	0·1542	0·1158	2·74	0·27	3·01	21·62
0·1020	0·1027	0·1034	0·00	0·00	0·00	21·90
0·09184	0·09236	0·1001	− 0·78	−0·05	− 0·83	21·93
0·08164	0·08209	0·0966	− 1·55	−0·11	− 1·66	22·05
0·06123	0·06152	0·0879	− 3·69	−0·22	− 3·91	22·14
0·05103	0·05126	0·0825	− 4·99	−0·27	− 5·26	22·27
0·04082	0·04099	0·0762	− 6·71	−0·32	− 7·03	22·32
0·03061	0·03073	0·0685	− 8·90	−0·38	− 9·28	22·43
0·02041	0·02048	0·0584	−12·00	−0·43	−12·43	22·61
0·01021	0·01024	0·0439	−17·53	−0·49	−18·02	22·77
0·005102	0·005118	0·0324	−23·17	−0·51	−23·68	22·92
0·002042	0·002048	0·0212	−30·81	−0·53	−31·34	23·02
0·001021	0·001024	0·0154	−36·70	−0·53	−37·23	23·04

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* All values of E in millivolts, and with European sign convention (Stonehill, *loc. cit.*).

Values of m for a given c were obtained from the equation (Stonehill, *loc. cit.*, p. 72)

$$m/c = 1·00298 + 0·029855c + 0·001142c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and values of γ for a given m were obtained from a large-scale graph of γ against $\sqrt{m}$ plotted from the data of Hartmann and Rosenfeld (*loc. cit.*). The correction for the salt error of the quinhydrone electrodes was obtained by adding

$$\Delta E = (c' - c) \times (0·00529 \pm 0·00005)\text{v.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

to $E_{obs.}$, thus giving $E_{corr.}$. The probable error in the second factor in equation (7) causes a maximum uncertainty of 0·005 mv. in $E_{corr.}$, which is less than the experimental error.

To carry out the differentiation indicated in (5), the slope of the graph to be plotted was first reduced by subtracting $(RT/F)\,t_-^0 \ln(m\gamma) = 20·058 \log(m\gamma)$ (in mv.) from $E_{corr.}$, giving E', so that instead of equation (5) there now remained

$$\frac{F}{2RT}\frac{dE'}{d\ln m\gamma} = \frac{1}{118·3}\frac{dE'}{d\log m\gamma} = \frac{d(E_{corr.} - 20·058 \log m\gamma)}{118·3\,d\log m\gamma} = t_- - t_-^0 = t_+^0 - t_+ \quad . \quad . \quad . \quad (8)$$

where $E_{corr.}$ and E' are in mv. Thus the values of E', given in Table III, were plotted against $\log m\gamma$, and the slope of the smooth curve drawn through the points so obtained was determined at intervals of 0·1 in $\log m\gamma$ by the use of Rutledge's derivative function (*Physical Rev.*, 1932, **40**, 262); this method is equivalent to fitting a fourth-degree equation to successive sets of five equispaced ordinates at various positions along the curve. From these slopes values of t_+ were obtained by using equation (8). These preliminary t_+ values were then plotted against E', and smoothed by drawing a smooth curve as evenly as possible through the plotted points. The average deviation of the latter from the smoothed curve was 0·0005 (compare the average deviation of 0·005 in the similar treatment of the results of Harned and Dreby, *J. Amer. Chem. Soc.*, 1939, **61**, 3113, for hydrochloric acid in water). Smoothed values of t_+ for values of E' corresponding to round values of c (read off a graph of E' against $\sqrt{c}$) were read off; these are listed in Table IV, col. 3. Account being

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TABLE IV.

Experimental Cation Transport Numbers for Nitric Acid at 25°, and Various Extrapolation Functions.

c.	$\sqrt{c}$.	t_+ (expt.).	$1/(1 + t_+)$.	$t_+^{0'}$.	t_+ (eq. 12).
0·001	0·03162	0·8321	0·54584	0·8303	0·8318
0·002	0·04472	0·8327	0·54564	0·8300	0·8324
0·005	0·07071	0·8336	0·54539	0·8302	0·8335
0·01	0·1000	0·8348	0·54503	0·8300	0·8346
0·02	0·1414	0·8366	0·54450	0·8294	0·8360
0·05	0·2236	0·8400	0·54348	0·8286	0·8384
0·07	0·2450	0·8408	0·54324	0·8283	0·8386
0·10	0·3162	0·8437	0·54241	0·8271	0·8402
0·15	0·3873	0·8466	0·54154	0·8259	0·8410
0·20	0·4472	0·8492	0·54078	0·8246	0·8413

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taken of the average deviation in the smoothing process, and of the average experimental error of 0·02 mv. in E', which produces by the Rutledge method an average error in t_+ of 0·0008, the probable error in t_+ is of the order $\pm 0·0008$. The correction for solvent conductivity is negligible, being $-0·0004$ at $c = 0·001$, and less for higher concentrations.

DISCUSSION.

The final values of t_+ are plotted against $\sqrt{c}$ in Fig. 1 as an unbroken curve. This merges into the limiting slope and limiting value $t_+^0 = 0·8304$ satisfactorily, indicating that the present results at concentrations below $c = 0·02$ are better than the values from " International Critical Tables." Above $c = 0·02$, the latter values and the present ones agree quite well within the uncertainty limits of $\pm 0·001$.

Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1073) proposed the equation

$$t_+ = A/(1 + B\sqrt{c}) - 1 \text{ or } 1/(1 + t_+) = 1/A + B\sqrt{c}/A \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

for extrapolating t_+ against $\sqrt{c}$ in order to obtain t_+^0. If this equation holds, a plot of $1/(1 + t_+)$ against $\sqrt{c}$ should be linear. Values of $1/(1 + t_+)$ from the present results are given in Table IV, col. 4; when plotted against $\sqrt{c}$ they lie fairly well on a straight line which upon extrapolation gives an intercept $1/A = 1/(1 + t_+^0) = 0·54624$, and thus $t_+^0 = 0·8307$. The agreement with the known value $t_+^0 = 0·8304$ is gratifying though perhaps fortuitous in view of the probable uncertainty in the t_+ values.

Longsworth (*loc. cit.*, 1932) proposed the equation

$$t_+ = t_+^0 + (2t_+^0 - 1)\beta\sqrt{c}/\Lambda' + Ac(1 + 2\beta\sqrt{c}/\Lambda') \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where A is an empirical parameter, and Λ' and β are connected by Onsager's equation (2), in which α and β are constants having the respective values 0·2277 and 29·93 in water at 25°. From equation (10) Longsworth derived an extrapolation function

$$t_+^{0'} = (t_+\Lambda' + \beta\sqrt{c})/(\Lambda' + 2\beta\sqrt{c}) = t_+^0 + Ac \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which, when plotted against c, should give a straight line extrapolating to t_+^0. Values of $t_+^{0'}$ calculated from the present t_+ values are listed in Table IV, col. 5, and plotted against c in Fig. 1; apart from one or two values, they lie on a straight line with slope $A = -0·030$ and intercept $t_+^0 = 0·8302$. The agreement with the known value $t_+^0 = 0·8304$ is again better than might have been expected.

Owen (*J. Amer. Chem. Soc.*, 1935, **57**, 2441) proposed the equation

$$t_+ = t_+^0 + (2t_+^0 - 1)\beta\sqrt{c}[1 - (1 - \alpha\sqrt{c})\sqrt{2c}]/\Lambda' \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is equivalent to equation (10) if we put

$$A = -\beta\sqrt{2}(2t_+^0 - 1)/\Lambda^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the quantities Λ^0, Λ', α, and β having the same significance as in equations (2) and (10). Owen's equation has the advantage that only t_+^0, without any arbitrary parameter, is required in order to calculate t_+ values. The equation was tested by calculating values of t_+ from it for various round concentrations. The values obtained are given in Table IV, col. 6, and are seen to diverge increasingly from the present values as c increases above 0·01. Owen's equation thus fails for nitric acid. This could be seen at once by comparing the experimental value of A, viz., $-0·030$, with the value required by equation (13), viz., $-0·066$.

MacInnes and Cowperthwaite (*Trans. Faraday Soc.*, 1927, **23**, 400) showed that at concentration $c = 0·1$ mol./l. the value of $t_+ \Lambda = \lambda_{H^+}$ was approximately the same for both hydrochloric and nitric acid in water at 25°. By using the present values of t_+ for nitric acid and more recent values of the equivalent conductivities (Λ) of both acids and of t_+ for hydrochloric acid, the validity of this relation for concentrations up to 0·2 mol./l. was tested. The details are given in Table V. The agreement of the hydrogen-ion mobilities of the two acids

TABLE V.

Hydrogen-ion Mobilities in Nitric and Hydrochloric Acids at 25°.

c.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	References.
Λ^{HNO_3}	411·2	407·3	402·8	394·0	386·0	376·1	I.C.T., 1929, **6**, 242
$t_+^{HNO_3}$	0·8334	0·8348	0·8366	0·8398	0·8437	0·8488	Present results.
$\lambda_{H^+}^{HNO_3}$	342·6	340·0	337·0	330·9	325·7	319·2	
Λ^{HCl}	415·7	411·9	407·1	399·0	391·2	381·3	I.C.T., 1929, **6**, 242; Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411
t_+^{HCl}	0·8239	0·8251	0·8266	0·8292	0·8314	0·8337	Longsworth (*locc. cit.*)
$\lambda_{H^+}^{HCl}$	342·5	339·9	336·5	330·9	325·2	317·9	

is reasonably good up to $c = 0·1$, and possibly up to $c = 0·2$ if allowance is made for the uncertainty in the values of t_+ for nitric acid and the unknown probable error in the values of Λ for nitric acid, which are not so precise as those for hydrochloric acid. It appears, then, that Kohlrausch's law of independent ion mobilities holds here up to $c = 0·2$, and that up to this concentration at least nitric acid must be regarded as completely

dissociated if hydrochloric acid is assumed to be so. A similar comparison of values of $\lambda_{NO_3}-$ in nitric acid, potassium nitrate, and silver nitrate at 25° (Table VI) amplifies the results for $c = 0.1$ obtained by MacInnes and Cowperthwaite (*loc. cit.*), and confirms their conclusion that the two salts are incompletely dissociated.

TABLE VI.

Nitrate-ion Mobilities in Nitric Acid, Potassium Nitrate, and Silver Nitrate at 25°.

$c.$	0·01.	0·02.	0·05.	0·1.	0·2.	References.
$\lambda_{NO_3^-}^{HNO_3}$	67·3	65·8	63·1	60·3	56·9	See Table V
Λ^{KNO_3}	135·8	132·4	126·8	120·4	113·3	Shedlovsky, *loc. cit.*; I.C.T., 1929, **6**, 242
$t_-^{KNO_3}$	0·4916	0·4913	0·4907	0·4897	0·4880	Longsworth, *loc. cit.*, 1935
$\lambda_{NO_3^-}^{KNO_3}$	66·8	65·1	62·2	59·0	55·3	
Λ^{AgNO_3}	124·72	121·37	115·20	109·10	—	Shedlovsky, *loc. cit.*
$t_-^{A\,NO_3}$	0·5352	0·5348	0·5336	0·5318	—	MacInnes and Cowperthwaite, *Chem. Rev.*, 1932, **11**, 171
$\lambda_{NO_3^-}^{AgNO_3}$	66·74	64·91	61·48	58·01	—	