301. Activity Coefficients of Nitric and Perchloric Acids in Dilute Aqueous Solution from E.M.F. and Transport-number Measurements.

By A. K. Covington and J. E. Prue.

Precise values have been obtained for the activity coefficients of nitric and perchloric acids in aqueous solutions at 25° up to 0·1M by combining measurements on cells with transport-number measurements. The e.m.f. measurements were made by our recently developed glass-electrode technique and the transport numbers were obtained by the moving-boundary method. The activity coefficients are compared with those of other strong acids.

THERE are no precise values for the activity coefficients γ of nitric and perchloric acids in dilute aqueous solution. The hydrogen electrode cannot be used because of its reducing action and there is a lack of suitable anion-reversible electrodes. However, a technique has recently been developed [1, 2] by which it is possible to obtain results with glass electrodes comparable in precision with those obtained in the most exact work with " classical " electrodes, and we have now used it with nitric and perchloric acids. Measurements on concentration cells of the type :

$$\text{Glass electrode}|HNO_3(m_1)|HNO_3(m_2)|\text{glass electrode}$$

have been combined with transport numbers t^+, t^- obtained by the moving-boundary method. The measurements of e.m.f. of concentration cells were made as previously described for hydrochloric acid.[2] Transport numbers of high accuracy were required and the performance of the apparatus was tested by repeating the measurements of Longsworth [3] on hydrochloric acid.

EXPERIMENTAL

Materials.—" AnalaR " concentrated nitric acid (shown to be free from oxides of nitrogen) and perchloric acid were used without further purification. Solutions were prepared with conductivity water from an ion-exchange column and standardised by weight-titration through sodium borate solution against constant-boiling hydrochloric acid. Conversions from molality to molarity scales were made by using the following equations applicable up to 0·1M :

$$\rho(HNO_3) = 0{\cdot}99707 + 0{\cdot}0332m \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\rho(HClO_4) = 0{\cdot}99707 + 0{\cdot}0573m \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The equations are based on densities (ρ) obtained with a 15 ml. Ostwald pycnometer at 25°. The silver and cadmium used were spectroscopically pure rods supplied by Messrs. Johnson, Matthey and Co., Ltd.

Apparatus.—The moving-boundary measurements were made with an autogenic boundary rising from a cadmium anode in the case of hydrochloric acid and a silver anode in the case of nitric and perchloric acids. Stable boundaries could not be obtained with nitric and perchloric acids with a cadmium anode, and with nitric acid a white solid was deposited on the metal surface. A very small amount of a black sludge was formed at the silver anode, but *X*-ray powder photographs showed that this contained no significant amount of anything other than metallic silver. The anode was cemented into the moving-boundary cell with " Araldite " which is unattacked by hydrochloric acid and only slightly coloured by the oxidising acids. The cell was based on Le Roy and Gordon's design.[4] The graduated tubes were of 3·5 and 3·0

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[1] Covington and Prue, *J.*, 1955, 3696.
[2] Covington and Prue, *J.*, 1955, 3701.
[3] Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2741.
[4] Le Roy and Gordon, *J. Chem. Phys.*, 1938, **6**, 398.

mm. bore graduated every 0·5 cm. over a 20 cm. length; the graduation marks extended on either side of the tube leaving a clear space at front and back, so that the boundary was never obscured by a graduation mark. The method of weighing of mercury was used to calibrate the tube by volume over 10 cm. lengths at 1 cm. intervals. A cathetometer (Precision Tool and Instrument Co.) which could be read to 0·001 cm. was used for measuring the length of the mercury thread. The moving boundary was observed with a system of the kind described by MacInnes, Cowperthwaite, and Huang,[5] the cell being placed in a water thermostat (at 25·00° ± 0·01°) with two glass sides. The motion of the boundary was timed with a " split-second " stop-watch having two second-hands, one of which can be stopped and, after the time has been read, resynchronised with the other hand. The watch was checked against standard time and its error found to be negligible.

One of the major difficulties of the moving-boundary method is to maintain a constant current during the electrolysis, since there is a steady change of resistance during an experiment. We required a mains-operated device which would supply a current of between 0·5 and 2·5 mA constant to 0·2% through a load whose resistance changed tenfold in the range 5000—500,000 ohm. The only previous accurate measurements on acid solutions are those of Longsworth[3] who used an elaborate mechanical device. Other workers[4, 6] who have used electronic techniques have only had to contend with changes of 50—100% in the resistance. A satisfactory mains-operated constant-current device was, however, devised and is described elsewhere.[7] After a " warming-up " period on a dummy load, the current was switched to the moving-boundary cell with a double ceramic switch of the " make-before-break " type. Up to 500 v were available for the cell. The current was measured by determining the potential drop across a 100 ohm manganin-wound standard resistance (certified by the N.P.L.) with a vernier potentiometer. The usual precautions in making accurate potentiometric measurements were taken and the positive pole was grounded so that the potentiometer circuit should be near ground potential and the possible effects of electrical leakage minimised.

Procedure.—The moving-boundary cell was rinsed three times with solution and filled through a drawn-out capillary tube. The cell was kept for 1 hr. in the thermostat before the run was started. The motion of the boundary was timed over at least 15 cm. of the tube, time readings being taken at every 5 mm. graduation mark and current readings every 2 mm.

RESULTS AND DISCUSSION

Transport Numbers.—From a plot of current i against time t, the mean value of the current while the boundary was traversing each 5 mm. length between graduations was estimated. Values of the product $i\delta t$ over the same interval were summed over 10 cm. sections of the tube. Some typical values obtained during a run with perchloric acid are given in column 3 of Table 1. Column 4 contains corresponding values of $cF\Delta V$ where c is the concentration of the acid solution, F is the faraday (taken as 96,488 C mole^{-1}) and ΔV is the volume swept through. The ratio of the figures in column 4 to those in column 3 gives values of $t^{+}_{\text{obs.}}$. A mean value was calculated from not less than 11 values in each

TABLE 1.

$[HClO_4] = 0{\cdot}01925_7$ mole l.$^{-1}$. Temp. 25°. $i = 1{\cdot}0131 \pm 0{\cdot}0003$ mA.

Δx (mm.)	ΔV (ml.)	$\Sigma\, i\delta t$ (10^{-3}C)	$cF\Delta V$ (10^{-3}C)	$t^{+}_{\text{obs.}}$
0—100	0·6925	1522·1	1286·7	0·8453
10—110	0·6944	1525·6	1290·3	0·8458
20—120	0·6954	1527·1	1292·1	0·8461
30—130	0·6967	1530·4	1294·5	0·8459
40—140	0·6976	1531·9	1296·2	0·8461
50—150	0·6984	1534·6	1297·7	0·8456
60—160	0·6995	1536·7	1299·7	0·8458
80—180	0·7002	1538·9	1301·0	0·8454
			Mean =	$0{\cdot}8457_5$
			Mean of 17 values =	0·8457

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[5] MacInnes, Cowperthwaite, and Huang, *J. Amer. Chem. Soc.*, 1927, **49**, 1710.

[6] Hartley and Donaldson, *Trans. Faraday Soc.*, 1937, **33**, 457.

[7] Hopkins and Covington, *J. Sci. Instr.*, 1957, **34**, 20.

experiment. The standard deviation for the mean was 0·0001 throughout except for the first entry in Table 2, where it was 0·0002.

A volume correction was applied to the transport numbers to allow for the change in volume behind the boundary at the anode. These small corrections (see Tables 2, 3, and 4) were estimated from partial molal volumes calculated from density data given by International Critical Tables ($CdCl_2$, HNO_3), Longsworth[3] (Cd, Ag, $AgNO_3$), Wirth[8] (HCl), Mazzuchelli and Rossi[9] ($AgClO_4$), and Bigeleisen[10] ($HClO_4$). Because the specific conductivity of the water used was less than 10^{-7} ohm^{-1} cm.$^{-1}$, no solvent correction was necessary.

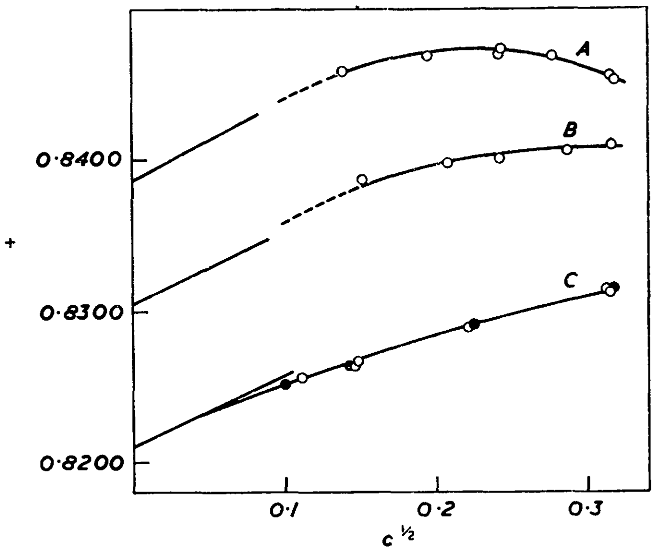

FIG. 1. *A*, $HClO_4$; *B*, HNO_3; *C*, HCl.

The results obtained are given in Tables 2, 3, and 4 and plotted in Fig. 1. The reproducibility of the runs was about 0·0002 in t^+, and we do not believe that the measurements of time, volume, current, or concentration can lead to a systematic error greater than 0·0003 in t^+. The results for hydrochloric acid are in good agreement with those of Longsworth[3] (full circles, ●, in Fig. 1).

TABLE 2. HCl.

c (mole l.$^{-1}$)	$c^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	$t^+_{\text{obs.}}$	Vol. corr.	$t^+_{\text{corr.}}$
0·01231 *	0·1110	0·8255	0·0001	0·8256
0·02144$_7$	0·1464	0·8263	0·0002	0·8265
0·02181 *	0·1477	0·8264	0·0002	0·8266
0·04886 *	0·2210	0·8284	0·0005	0·8289
0·09710$_4$	0·3116	0·8305	0·0009	0·8314
0·09899 *	0·3146	0·8303	0·0009	0·8312

* Obtained with the less satisfactory constant-current device of Bender and Lewis (*J. Chem. Educ.* 1947, **24**, 454).

TABLE 3. HNO_3.

c (mole l.$^{-1}$)	$c^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	$t^+_{\text{obs.}}$	Vol. corr.	$t^+_{\text{corr.}}$
0·02297$_5$	0·1515	0·8385	0·0001	0·8386
0·04306$_9$	0·2075	0·8395	0·0002	0·8397
0·05841$_4$	0·2417	0·8396	0·0004	0·8400
0·08205$_3$	0·2864	0·8400	0·0005	0·8405
0·1002$_2$	0·3163	0·8403	0·0006	0·8409

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[8] Wirth, *J. Amer. Chem. Soc.*, 1940, **62**, 1128.
[9] Mazzuchelli and Rossi, *Gazzetta*, 1927, **57**, 383.
[10] Bigeleisen, *J. Phys. Chem.*, 1947, **51**, 1369.

In Fig. 1 the Onsager theoretical limiting-law slopes have been drawn, the intercepts on the ordinate corresponding to values of the transport numbers at infinite dilution obtained from limiting equivalent conductivities.[11] The results for nitric and perchloric acids approach the limiting slope from above. In this, they resemble nitrates [12, 13] rather than most uni-univalent electrolytes.[13] Values of the transport numbers at rounded concentrations interpolated from a large-scale plot are given in Table 5.

TABLE 4. $HClO_4$.

c (mole l.$^{-1}$)	$c^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	$t^+_{\text{obs.}}$	Vol. corr.	$t^+_{\text{corr.}}$
0·01925$_7$	0·1388	0·8457	0·0001	0·8458
0·03785$_0$	0·1945	0·8467	0·0001	0·8468
0·05840$_9$	0·2417	0·8467	0·0002	0·8469
0·05905$_2$	0·2430	0·8471	0·0002	0·8473
0·07649$_0$	0·2766	0·8465	0·0003	0·8468
0·09933$_3$	0·3152	0·8451	0·0004	0·8455
0·1011$_2$	0·3180	0·8448	0·0004	0·8452

TABLE 5.

c (mole/l.)	t^+ (HCl)	t^+ (HNO_3)	t^+ ($HClO_4$)
0	0·8210	0·8304	0·8386
0·02	0·8265	0·8377	0·8456
0·04	0·8284	0·8394	0·8471
0·06	0·8296	0·8402	0·8473
0·08	0·8306	0·8406	0·8466
0·10	0·8314	0·8408	0·8452

TABLE 6. HNO_3.

10^3m_2 (mole kg.$^{-1}$)	E (mv)	t^-	$-\Delta\log\gamma$	$\Delta\log\gamma - {}$ $-\Delta\log(\gamma^{\text{st}})^{2\cdot5}$	$\Delta\log\gamma - {}$ $-\Delta\log(\gamma^{\text{st}})^{3\cdot0}$	Δm (mole kg.$^{-1}$)
6·599	20·77$_5$	0·1656	0·06046	−0·00709	−0·01293	0·08540
9·546	17·76	0·1645	0·05460	−0·00682	−0·01227	0·08245
14·28	14·50	0·1633	0·04776	−0·00684	−0·01174	0·07772
21·89	11·10	0·1621	0·03890	−0·00611	−0·01026	0·07011
23·19	10·61	0·1619	0·03945	−0·00782	−0·01185	0·06881
28·89	8·90	0·1614	0·03345	−0·00639	−0·00994	0·06311
44·53	5·50$_5$	0·1603	0·02390	−0·00643	−0·00885	0·04747
48·95	4·79$_5$	0·1602	0·02025	−0·00497	−0·00712	0·04305
64·93	2·64	0·1596	0·01143	−0·00287	−0·00411	0·02707
80·13	1·05	0·1594	0·00431	−0·00088	−0·00139	0·01187
92·00	0	0·1592	0	0	0	0

Cell e.m.f.'s and Activity Coefficients.—The extrapolations necessary to eliminate the effects of asymmetry potentials were similar to those previously used for hydrochloric acid.[2] The results were analysed in the same way, except that a standard value, γ^{st}, of the activity coefficient was defined by

$$\log\gamma^{\text{st}(\sigma)} = -Am^{\frac{1}{2}}/(1 + \sigma m^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the factor σ was not set equal to unity as with hydrochloric acid. If σ is set equal to unity, then plots of $\Delta\log\gamma - \Delta\log\gamma^{\text{st}}$ against Δm are not linear. This is not surprising since the nitrate and perchlorate ions are large and according to the Debye–Hückel theory $\sigma = a/a^\circ$ where a is the closest distance of approach of ions and a° is a constant with the value 3·04 Å at 25°. The results obtained by using values of $\sigma = 2\cdot5$, $3\cdot0$ are shown in Tables 6 and 7. The corresponding plots in Figs. 2 and 3 show that the fit in both cases is slightly better for $\sigma = 3\cdot0$ but, except for one nitric acid point, the

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[11] Robinson and Stokes, " Electrolyte Solutions," Butterworths 1955, p. 452.

[12] MacInnes and Longsworth, *Chem. Rev.*, 1932, **11**, 171.

[13] Longsworth, *J. Amer. Chem. Soc.*, 1935, **57**, 1185.

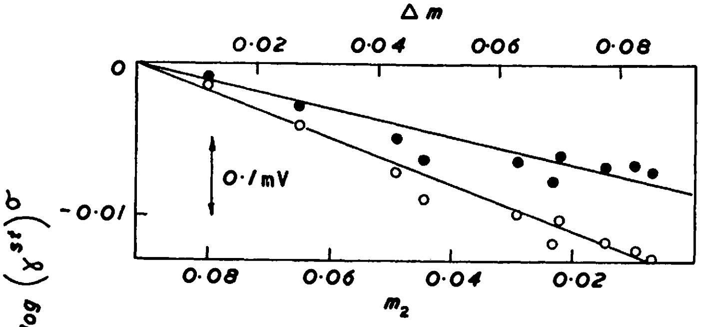

FIG. 2. ●, $\sigma = 2{\cdot}5$; ○, $\sigma = 3{\cdot}0$.

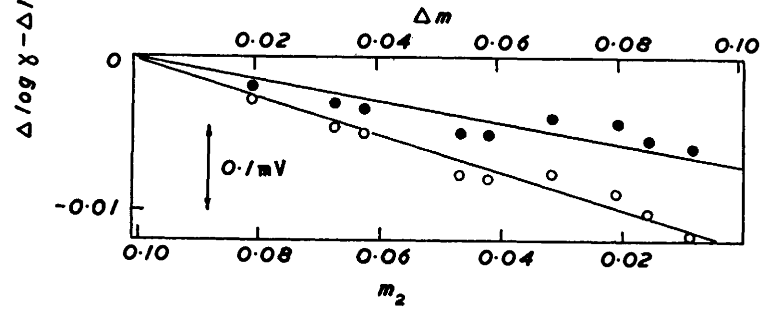

FIG. 3. ●, $\sigma = 2{\cdot}5$; ○, $\sigma = 3{\cdot}0$.

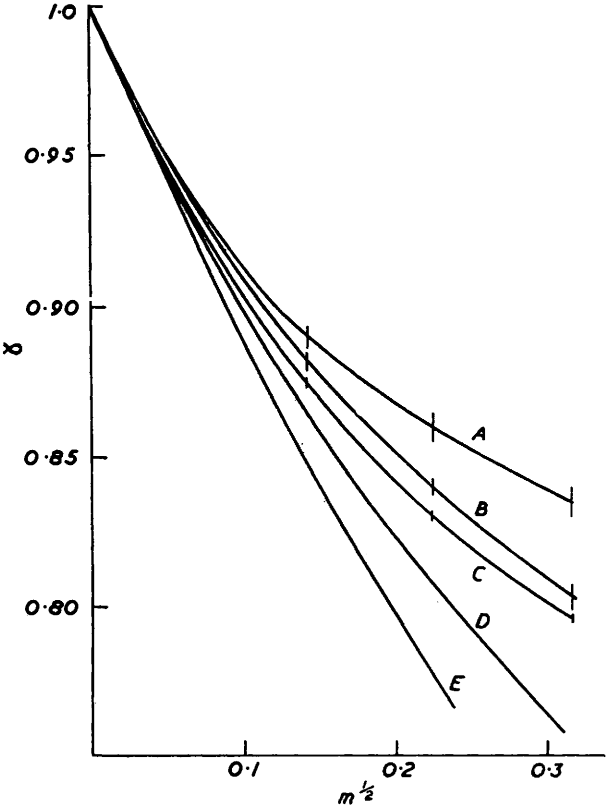

FIG. 4. *A*, HI; *B*, HBr, HNO_3, $HClO_4$; *C*, HCl; *D*, $\sigma = 1$, $B' = 0$; *E*, limiting law.

TABLE 7. $HClO_4$.

10^3m_2 (mole kg.$^{-1}$)	E (mv)	t^-	$-\Delta \log \gamma$	$\Delta \log \gamma - \Delta \log (\gamma^{st})^{2\cdot5}$	$\Delta \log \gamma - \Delta \log (\gamma^{st})^{3\cdot0}$	Δm (mole kg.$^{-1}$)
8·390	18·66	0·1570	0·05803	−0·00589	−0·01185	0·09253
15·50	$13{\cdot}93_5$	0·1553	0·04676	−0·00529	−0·01016	0·08540
20·77	11·72	0·1544	0·04038	−0·00423	−0·00884	0·08013
31·60	8·57	0·1534	0·03130	−0·00386	−0·00755	0·06930
42·43	6·35	0·1528	0·02590	−0·00501	−0·00793	0·05847
47·00	5·59	0·1528	0·02346	−0·00493	−0·00755	0·05390
62·55	3·50	0·1528	0·01505	−0·00327	−0·00500	0·03835
67·13	2·98	0·1529	0·01309	−0·00302	−0·00451	0·03377
81·06	1·60	0·1535	0·00734	−0·00189	−0·00272	0·01984
100·9	0	0·1548	0	0	0	0

deviations from the straight lines are always less than 0·03 mv. The straight lines drawn correspond to the values

$$HNO_3\ \text{(i)}\ \sigma = 2{\cdot}5, B' = -0{\cdot}092;\ \text{(ii)}\ \sigma = 3{\cdot}0, B' = -0{\cdot}154$$
$$HClO_4\ \text{(i)}\ \sigma = 2{\cdot}5, B' = -0{\cdot}070;\ \text{(ii)}\ \sigma = 3{\cdot}0, B' = -0{\cdot}123$$

in the equation

$$\log \gamma = -Am^{\frac{1}{2}}/(1 + \sigma m^{\frac{1}{2}}) + B'm \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Values of γ corresponding to the alternative values of the parameters in equation (4) are given in Table 8. They would be changed by 0·001 or 0·002 by a systematic error of 0·0003 in the transport numbers. The concentration-cell results which Stonehill[14] obtained for nitric acid with the quinhydrone electrode when analysed with our transport-number data are found to be in approximate agreement with our own.

The smoothed values of the activity coefficients of nitric and perchloric acids are compared in Table 8 with those obtained by other workers for hydrochloric, hydrobromic, and hydriodic acid. In the cases of hydrochloric and hydrobromic acids the γ values are also uncertain by 0·002 to 0·003 according to the smoothing function used and the weighting of the points for the most dilute solutions. The activity coefficients are plotted in Fig. 4, the values from different smoothing formulæ and the possible errors being shown by the vertical bars on the Figure. The limiting-law curve and the curve corresponding to $\sigma = 1$, $B' = 0$ are also shown. We see that the activity coefficients of hydrobromic, nitric, and perchloric acids are very similar and lie in a sheaf together above those of hydrochloric acid. We note that as the size of the anion increases the standard activity equation with $\sigma = 1$, $B' = 0$ becomes increasingly unsatisfactory; we saw earlier that in the cases of nitric and perchloric acids the deviations from it cannot be represented by the addition of a linear term in m.

TABLE 8.

m (mole kg.$^{-1}$)	HCl[a]	HBr[b]	HNO_3 (i)	HNO_3 (ii)	$HClO_4$ (i)	$HClO_4$ (ii)	HI[c]
0·01	0·904	0·906	0·909	0·911	0·909	0·911	0·91
0·02	0·875	0·879	0·881	0·884	0·882	0·885	0·89
0·05	0·830	0·838	0·838	0·840	0·841	0·843	0·86
0·10	0·796	0·805	0·796	0·798	0·800	0·804	$0{\cdot}83_5$

[a] Hills and Ives, *J.*, 1951, 318. [b] Harned, Keston, and Donelson, *J. Amer. Chem. Soc.*, 1936, **58**, 989. [c] Calc. from Pearce and Fortsch, *ibid.*, 1923, **45**, 2852.

We thank the Department of Scientific and Industrial Research for a grant to one of us (A. K. C.), Dr. K. Robinson for taking the *X*-ray powder photographs, and Mr. D. T. Hopkins for the design of the constant-current device.

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[*Received, October 24th,* 1956.]

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[14] Stonehill, *J.*, 1943, 647.