712. *Transport Numbers of Sodium and Potassium Iodides from Electromotive Force Measurements.*

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The electromotive forces (e_T) of the cells Ag–AgI|MI(c_R)|MI(c)|Ag–AgI, where M = Na or K, in the concentration range 0·1—0·5N, at 25° were measured. Electromotive forces (e) of the corresponding cells without transport were computed from existing activity coefficients, and the cation transport numbers obtained from the curve of e_T against e.

MEASUREMENTS of the e.m.f. of concentration cells with transport, in conjunction with those of the same cells without transport, are convenient for determining transport numbers, although the results are not as accurate as is possible with the moving-boundary method. Transport numbers of sodium and potassium iodides were determined [1] from

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[1] Torto, Ph.D. Thesis, London University, 1947.

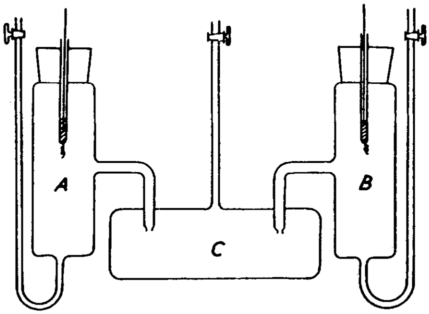
measurements of e.m.f. of the cells Ag–AgI|MI(c_R)|MI(c)|Ag–AgI, the electrolytes being the aqueous iodides. The e.m.f. of the corresponding cells without transport was obtained from Harned and Douglas's [2] activity coefficients for potassium and Robinson's [3] for sodium iodide. The cation transport numbers were obtained by applying Rutledge's differentiation procedure [4] to the curve obtained by plotting e_T for cells with transport against e for cells without transport.

EXPERIMENTAL

Materials.—" AnalaR " potassium iodide and sodium iodide were recrystallised thrice and four times, respectively, from distilled water, and dried at 120°. Solutions were boiled in a vacuum, allowed to cool in an atmosphere of purified hydrogen, and the iodide content determined gravimetrically or by titration with potassium iodate. Concentrations determined by the two methods agreed to within 0·05%.

Electrodes.—The silver–silver iodide electrodes were prepared as previously,[5] and with the rigid exclusion of oxygen from solutions and cell it was possible to obtain reproducibility of the order of 0·03—0·05 mv.

Cell and Filling Technique.—The cell is shown in the Figure. The electrodes, sealed into glass tubes, were mounted in well-fitting rubber bungs which were sealed in position with paraffin wax, the latter then being painted with collodion or cellulose acetate. The stopcocks were greased with petroleum jelly which had been boiled for several hours with frequently changed distilled water. In filling the cell, one limb *A* was rinsed with the lighter of the two solutions, forced in by hydrogen pressure, the limb *B* and the remainder of the cell being rinsed in a similar manner with the heavier solution. Purified hydrogen was then passed through the cell for about 30 min. With the cell inverted the lighter solution was forced into limb *A*, and the compartments *B* and *C* similarly filled with the heavier solution after turning the cell upright. The cell was placed in a thermostat at 25° (±0·02°); the thermostat and the potentiometer and its accessories stood on an equipotential metal foil surface.[6] The e.m.f. was measured at intervals of 10 min. until equilibrium was reached, usually in about 1 hr. To allow for the asymmetry between the electrodes, each measurement was repeated with the positions of the two electrodes in the two solutions reversed, and the two readings, which agreed to within 0·05—0·08 mv, averaged. Since the e.m.f. of this type of cell depends only on the solutions surrounding the electrodes, and not on the distribution of concentration gradients in the connecting solution, diffusion across the boundary between the two solutions should not affect the equilibrium e.m.f., which should therefore remain constant for considerable periods. (It remained constant for 36 hr. or more.) Moreover, replacement of the solution in compartment *C* in a cell set up in the normal way with *ca.* 0·2 and 0·3M-potassium iodide solutions with a solution containing approximately equal amounts of the two solutions had no effect on the equilibrium e.m.f. of 9·45 mv.



DISCUSSION

Potassium Iodide.—The e.m.f. for solutions ranging between 0·05 and 0·5N was measured against a reference 0·1992N-solution. The lower concentration limit was fixed by the available activity-coefficient data, and the upper limit by the increasing solubility of silver iodide in iodide solutions [7] above 0·5N. The experimental e.m.f.s are given in Table 1*A*, and those for round concentrations obtained by interpolation are shown in

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[2] Harned and Douglas, *J. Amer. Chem. Soc.*, 1926, **48**, 5095.

[3] Robinson, *ibid.*, 1935, **57**, 1161.

[4] Rutledge, *J. Math. Phys. M.I.T.*, 1929, **8**, 1; *Phys. Rev.*, 1932, **40**, 262.

[5] Partington and Torto, *J.*, 1948, 216.

[6] White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011.

[7] Bates, *ibid.*, 1938, **60**, 2983.

column 4, Table 1*B*. The e.m.f.s of the corresponding cells without transport were obtained from Harned and Douglas's activity coefficients;[3] molalities were converted into molarities,[8] and activity coefficients at round concentrations read from a plot of f against $-\log c$. The values obtained (column 2, Table 1*B*) were employed in the expression $e = -0{\cdot}1183 \log (c_1f_1/c_2f_2)$ to give the values of e in column 3, Table 1*B*.

From a large-scale plot[9] of $(e - e_T)$ against e, values of e_T were obtained at 5 mv intervals of e, and the function de_T/de evaluated by means of the Rutledge differentiation.[5] The values of de_T/de were plotted against e, and from this curve smoothed values of transport number n_c at round concentrations were obtained. As a check on the accuracy of this smoothing of the transport numbers the integral $\int_{c_R}^{c} de_T = e_T = \int_{c_R}^{c} n_c de$ was evaluated graphically from the plot of n_c against e. The values of e_T thus obtained are shown in column 5, Table 1*B*, and the deviation of these values from the experimental values under Δe_T. Apart from the value corresponding to $c = 0{\cdot}5$, Δe_T is within the limits of experimental error. The mean deviation of the plotted points from the smooth curve is less that ±0·002, and this can be taken as a rough estimate of the mean error in the final transport numbers.

The final transport numbers are given in Table 1*C* together with the values obtained by Longsworth[10] by the moving-boundary method, and those obtained by Gelbach by the electromotive-force method.[11]

TABLE 1*A*.

c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)
0·06502	−26·46	0·1103	−13·52	0·1992	0·00	0·3862	+15·34
0·07080	−23·76	0·1203	−11·70	0·2306	+ 3·50	0·4352	+18·00
0·08302	−20·08	0·1355	− 8·86	0·2733	+ 7·29	0·4721	+19·93
0·09321	−17·47	0·1832	− 1·92	0·3401	+12·27	0·5007	+21·16

TABLE 1*B*.

c	f	e	e_T (exp.)	e_T (calc.)	Δe_T
0·7089	0·797	−48·57	−23·81	—	—
0·10	0·775	−32·26	−15·83	−15·82	0·01
0·15	0·748	−13·25	− 6·50	− 6·50	0·00
0·1992	0·729	0·00	0·00	—	—
0·25	0·715	+10·67	+ 5·27	+ 5·24	0·03
0·30	0·703	+19·17	+ 9·46	+ 9·42	0·04
0·35	0·694	+26·43	+12·99	+13·01	0·02
0·40	0·686	+32·69	+16·10	+16·06	0·04
0·45	0·681	+38·37	+18·81	+18·82	0·01
0·50	0·677	+43·48	+21·19	+21·29	0·10

TABLE 1*C*.

c	n_c	n_c (Longsworth [10])	n_c (Gelbach [11])
0·10	0·490	0·4883	0·4940
0·15	0·490	—	—
0·20	0·491	0·4887	0·4917
0·25	0·490	—	—
0·30	0·489	—	—
0·35	0·487	—	—
0·40	0·486	—	—
0·45	0·486	—	—
0·50	0·485	—	0·4878

Within the limits of the error inherent in our results, the agreement with the moving-boundary results is fair, and the slight increase in the transport number with concentration up to 0·2M found by Longsworth[10] is reproduced in our results.

Sodium Iodide.—The variable solutions had concentrations between 0·09 and 0·6N, and the reference solution was 0·1281N. The limits of concentration were fixed by similar considerations as in the previous case. The e.m.f.s of cells without transport were computed from Robinson's activity coefficients[4] obtained by the isopiestic vapour-pressure method. The manipulation of the data was carried out as for potassium iodide, and the results are given in Tables 2*A* and 2*B*, the figures having the same significance as those in corresponding columns of Tables 1*A* and 1*B*. The average value of Δe_T is 0·03 mv. As in the previous case the mean error in the final transport numbers, shown in column 1, Table 1*C*, is probably ±0·002.

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[8] Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, New York. 1943, 556.

[9] Harned and Dreby, *J. Amer. Chem. Soc.*, 1939, **61**, 3113.

[10] Longsworth, *ibid.*, 1935, **57**, 1185.

[11] Gelbach, *ibid.*, 1933, **55**, 4857.

TABLE 2*A*.

c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)	c (moles/l.)	e_T (mv)
0·08713	−7·00	0·1906	+ 7·23	0·2991	+15·40	0·4478	+22·79
0·1031	−3·84	0·2031	+ 8·30	0·3425	+17·93	0·5106	+25·16
0·1281	0·00	0·2478	+12·01	0·4017	+20·69	0·5884	+27·81
0·1534	+3·18			0·4201	+21·61		

TABLE 2*B*.

c	f	e	e_T (exp.)	e_T (calc.)	Δe_T
0·09935	0·788	−12·07	− 4·52	− 4·53	0·01
0·1281	0·773	0·00	0·00	0·00	0·00
0·1500	0·765	+ 7·54	+ 2·84	+ 2·84	0·00
0·1980	0·752	+20·95	+ 7·85	+ 7·85	0·00
0·2500	0·743	+32·32	+12·14	+12·09	0·05
0·2959	0·737	+40·57	+15·18	+15·16	0·02
0·3500	0·732	+48·84	+18·27	+18·22	0·05
0·4000	0·729	+55·49	+20·75	+20·68	0·07
0·4897	0·726	+65·67	+24·38	+24·31	0·07
0·6807	0·729	+82·81	+28·35	—	—

TABLE 2*C*.

c	n_c	n_c (Denison [12]) at 18°
0·05	—	0·381
0·10	0·375	0·376
0·15	0·375	—
0·20	0·374	—
0·25	0·373	—
0·30	0·371	—
0·35	0·368	—
0·40	0·364	—
0·45	0·359	—
0·50	0·354	—

It is obvious from Table 2*C* that the transport numbers increase as the solutions become more dilute, but approach a limiting value at high dilutions. In the absence of values at concentrations lower than 0·10N, it was not considered desirable to extrapolate the data to infinite dilution.

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[12] Denison, *Trans. Faraday Soc.*, 1909, **5**, 165.