141. *Automatic Adjustment of Solute Concentration in the "Moving-boundary" Method for the Determination of Transport Numbers.*

By Robert Wright.

The change in concentration of the indicator solution which takes place with the passage of current in the moving-boundary method for the determination of transport numbers has been determined by direct chemical analysis of samples of the solution taken from different parts of the transport apparatus.

The moving-boundary method for the determination of transport numbers has now been carried to a high degree of accuracy, chiefly by American workers (see McInnes and Longsworth, *Chem. Reviews*, 1932, **11**, 171). Although the apparatus required for this method is intricate, the results obtained surpass those of the older Hittorf method in both accuracy and speed.

The method employs solutions of two electrolytes with a common anion, AR and BR, and requires that the less mobile following, or indicator, cation B should at the boundary travel with the same speed as the cation A whose transport number is being determined; in general, this involves a change in concentration of the indicator solution taking place in the neighbourhood of the boundary during the progress of a determination.

This adjustment of indicator concentration has been demonstrated by Cady and Longsworth (*J. Amer. Chem. Soc.*, 1929, **51**, 1656) by observing the change in resistance of the electrolyte as the boundary moved along the tube. A similar method was employed by Drew, Collie, and Hartley (*Trans. Faraday Soc.*, 1934, **30**, 648), who emphasise the irregularities involved by the introduction of subsidiary electrodes into the boundary tube. The results of both these investigations verified the important relationship, first put forward by Kohlrausch (*Ann. Physik*, 1897, **62**, 209), $T_a/T_b = C_a/C_b$, where T_a is the transport number of the leading cation, T_b that of the indicator cation, and C_a and C_b are their respective concentrations at the boundary.

In the present investigation the concentrations of the electrolytes at different parts of the tube were determined by direct chemical analysis. The solutions employed were N/2-hydrochloric acid, followed by a solution of alkali chloride of concentration between N/2 and N/8; the changes in concentration were thus easily determined by titrating samples of the solution with standard sodium carbonate and silver nitrate solutions.

Experimental.

The tube containing the solution was constructed in sections separated from one another by parchment paper. Each section—or cell—consisted of three square pieces of rubber, of 40 mm. edge and 5 mm. thickness, clamped together so as to give a small block 15 mm. thick. Through the centre of each square a circle of 16 mm. diameter was cut, and the middle square of each cell had a slot 5 mm. wide running from the middle of the top edge to the central hole. This slot served for the introduction and withdrawal of solution. The volume of the complete cell (exclusive of the filling slot) was about 3 c.c., thus sufficing for the withdrawal of 2 c.c. of the solution for analysis.

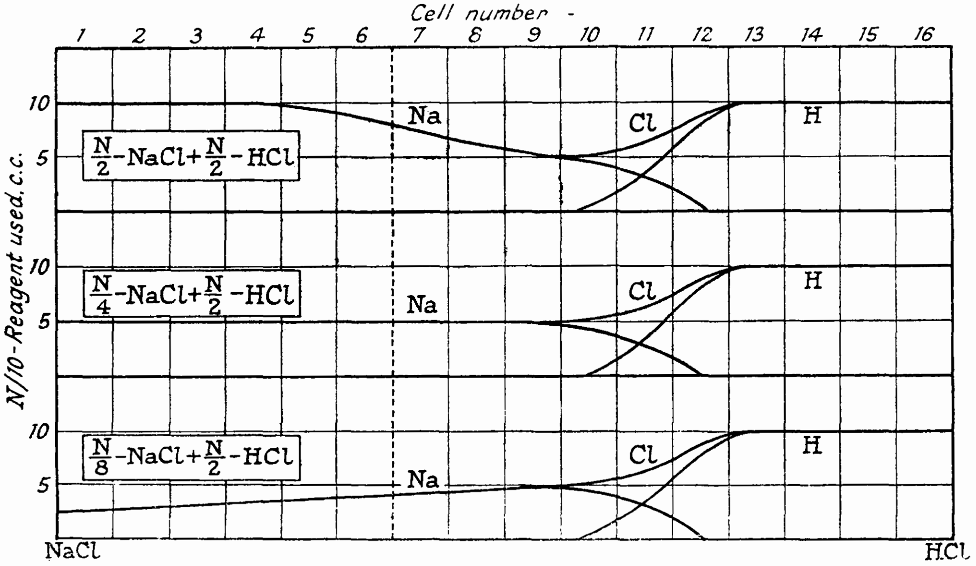
The complete rubber tube of 16 cells with their parchment separators was assembled in a horizontal open-ended wooden trough. At each end of the tube was placed a square of vulcanised fibre, of the same shape and dimensions as the rubber squares. Two 300 c.c. tubulated bottles, with their mouths ground flat, were laid on their sides with the tubulures uppermost and adjusted so that the mouth of each bottle bore against a fibre end-piece of the composite tube, a washer of soft rubber being placed between the bottle mouth and the fibre. The complete assembly of tube and bottles was firmly clamped together by means of a pair of wooden wedges which were inserted between the base of one bottle and a stop fixed to the baseboard of the trough; the second bottle bore against a similar stop at the other end of the apparatus.

The apparatus being assembled and made watertight by means of the wedges, one bottle and the six cells adjoining it were filled with the alkali chloride solution, the remaining cells and the second bottle with N/2-hydrochloric acid. The liquid in the neck of each cell was now removed by temporarily inserting a glass rod into the cell so that some liquid overflowed, and this surplus was removed by mopping with cotton wool; this clearing of the cell neck was necessary, as the solution in that part of the cell would not be affected by the passage of the current. An amalgamated zinc anode was now placed in the bottle containing the solution of the alkali chloride, and a platinum cathode in the acid solution. A current of 50 milliamps., hand-regulated by means of a series resistance, was passed through the solution for 4 hours. After this passage of 200 milliamp.-hours, 2 c.c. of solution were removed from each cell and titrated first with N/10-sodium carbonate and then with N/10-silver nitrate; from these titrations, which are shown in the table against H and Cl, the concentrations of acid and alkali salt were found. At least two determinations were carried out in each case, the two titres for any one cell being often identical and seldom differing by more than 0·2 c.c.

Anode soltn.*		Cell number.															
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
N/2-KCl	H	—	—	—	—	—	—	—	—	—	0·4	2·6	8·2	10	10	10	10
	K	10	10	10	9·5	9·0	8·6	7·5	6·9	6·5	5·6	4·3	0·8	—	—	—	—
	Cl	10	10	10	9·5	9·0	8·6	7·5	6·9	6·5	6·0	6·9	9·0	10	10	10	10
N/4-KCl	H	—	—	—	—	—	—	—	—	—	0·5	2·9	8·0	10	10	10	10
	K	5·0	5·0	5·0	5·2	5·5	5·9	6·1	6·4	6·6	6·3	4·3	1·0	—	—	—	—
	Cl	5·0	5·0	5·0	5·2	5·5	5·9	6·1	6·4	6·6	6·8	7·2	9·0	10	10	10	10
N/8-KCl	H	—	—	—	—	—	—	—	—	—	0·6	3·4	7·9	10	10	10	10
	K	2·5	2·7	3·0	3·2	3·5	4·2	4·8	5·5	5·8	5·5	3·8	1·0	—	—	—	—
	Cl	2·5	2·7	3·0	3·2	3·5	4·2	4·8	5·5	5·8	6·1	7·2	8·9	10	10	10	10
0·3N-KCl	H	—	—	—	—	—	—	—	—	—	0·6	3·7	8·5	10	10	10	10
	K	6·0	6·0	6·0	6·0	6·0	6·0	6·0	6·0	6·0	5·6	3·4	0·8	—	—	—	—
	Cl	6·0	6·0	6·0	6·0	6·0	6·0	6·0	6·0	6·0	6·2	7·1	9·3	10	10	10	10
N/2-NaCl	H	—	—	—	—	—	—	—	—	—	0·4	3·1	8·6	10	10	10	10
	Na	10	10	10	10	9·3	8·4	7·2	6·0	5·4	4·6	3·2	0·4	—	—	—	—
	Cl	10	10	10	10	9·3	8·4	7·2	6·0	5·4	5·0	6·3	9·0	10	10	10	10
N/4-NaCl	H	—	—	—	—	—	—	—	—	—	0·3	3·0	8·7	10	10	10	10
	Na	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	4·6	3·0	0·3	—	—	—	—
	Cl	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	4·9	6·0	9·0	10	10	10	10
N/8-NaCl	H	—	—	—	—	—	—	—	—	—	0·3	3·0	8·7	10	10	10	10
	Na	2·5	2·5	2·7	2·9	3·4	4·0	4·2	4·4	4·7	4·7	3·0	0·3	—	—	—	—
	Cl	2·5	2·5	2·7	2·9	3·4	4·0	4·2	4·4	4·7	5·0	6·0	9·0	10	10	10	10
N/2-LiCl	H	—	—	—	—	—	—	—	—	—	1·0	4·2	8·0	9·5	10	10	10
	Li	10	10	10	10	9·0	8·1	6·3	5·3	4·3	3·5	1·6	0·4	0·1	—	—	—
	Cl	10	10	10	10	9·0	8·1	6·3	5·3	4·3	4·5	5·8	8·4	9·6	10	10	10
N/4-LiCl	H	—	—	—	—	—	—	—	—	—	0·8	4·4	8·5	10	10	10	10
	Li	5·0	5·0	5·0	5·0	5·0	5·0	4·6	4·2	4·0	3·3	1·6	0·2	—	—	—	—
	Cl	5·0	5·0	5·0	5·0	5·0	5·0	4·6	4·2	4·0	4·1	6·0	8·7	10	10	10	10
N/8-LiCl	H	—	—	—	—	—	—	—	—	—	0·8	4·0	8·4	9·6	10	10	10
	Li	2·5	2·6	2·7	2·9	3·1	3·3	3·5	3·8	4·0	3·4	2·0	0·3	0·2	—	—	—
	Cl	2·5	2·6	2·7	2·9	3·1	3·3	3·5	3·8	4·0	4·2	6·0	8·7	9·8	10	10	10
N/5-LiCl	H	—	—	—	—	—	—	—	—	—	1·0	3·7	7·3	9·0	10	10	10
	Li	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	3·4	2·0	0·5	0·2	—	—	—
	Cl	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·4	5·7	7·8	9·2	10	10	10
		Salt solutions at start.						Acid solutions at start.									

* The cathode solution in every case was N/2-HCl.

Considering the results for the sodium chloride–acid transference (see fig.) we find that when both solutions are N/2 there is a fall in saline concentration at the neighbourhood of the boundary, but when N/8-sodium chloride is used an increase in the salt concentration results; with N/4-salt and N/2-acid the concentration of the salt solution remains constant at the boundary. With potassium chloride the concentration of this unchanging solution is 0·3N, and with



lithium chloride 0·2N. These figures represent approximately the concentrations of the salt solutions which do not require adjustment at the boundary in contact with N/2-hydrochloric acid, and therefore should agree with the equation $T_a/T_b = C_a/C_b$. Now the values of the cation transport numbers for the different solutions are: 0·5N-HCl, 0·840; 0·3N-KCl, 0·493; 0·2N-NaCl, 0·385; 0·2N-LiCl, 0·304 (International Critical Tables), and hence we have

	T_a/T_b.	C_a/C_b.		T_a/T_b.	C_a/C_b.		T_a/T_b.	C_a/C_b.
H/K	1·70	1·66	H/Na	2·18	2·00	H/Li	2·76	2·50

The agreement is only approximate, as the experimental method does not indicate with sufficient exactness the concentration of indicator solution in equilibrium at the boundary.

The measurements were not, however, undertaken for the determination of transport numbers, but to observe the changes in concentration at different parts of the tube produced by the passage of the current. In contrast to the methods of Cady and Longsworth and of Drew, Collie, and Hartley, the present method indicates the concentrations existing at different parts of the tube at the same instant, and not the change in concentration at the same part of the tube at different times due to the passage of the boundary.

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