XLVI.—*The Transport Number of very Dilute Solutions.*

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IN discussing the constitution of certain salt solutions, it was recently shown by one of us (Steele, *Phil. Trans.*, 1902, **198**, A, 105) that if the change in transport number which undoubtedly occurs with change in concentration for salts such as magnesium chloride, is assigned to a variation of the specific velocity of the chlorine and magnesium ions into which the salt is assumed to be ionised; and that if u and v represent the specific velocities of cation and anion at a given concentration n, and if u_1, and v_1, represent the values of the velocities of the same ions at the concentration n_1, a similar relation to the following holds for a large number of salts.

In the case of calcium chloride, between $n = 0.01$ and $n = 5.0$ the anion transport number p varies between 0.58 and 0.74. In the dilute solution, $u = \dfrac{42}{58}v = 0.723v$, and in the stronger solution $u_1 = \dfrac{26}{74}v_1$ $= 0.350v_1$, and hence $\dfrac{u}{u_1} = 2.06\,\dfrac{v}{v_1}$, or, assuming the velocity of the anion to remain constant, that of the cation has diminished by more than one-half.

It was also shown that, if the coefficient of ionisation is given even approximately by the relation $x = \dfrac{\mu}{\mu_\infty}$, where μ is the molecular conductivity at the given concentration and μ_∞ that at infinite dilution, then we get the astonishing result that, as the concentration of the calcium chloride increases, the velocity of the Ca ion is steadily diminished, whilst that of the Cl ion is correspondingly increased.

A far more satisfactory explanation of the change in question is that first suggested by Hittorf, who assumed the existence of complex ions

in such salt solutions; a solution of magnesium chloride of which the anion transport number is found to increase with increasing concentration would, according to this conception, consist of a certain proportion of simple chlorine and magnesium ions, and in addition to these a certain number of complex anions ; and since the proportion of the latter increases with concentration, the transport number would, as in the case of cadmium chloride, be greater than unity, provided sufficiently concentrated solutions could be investigated (Hittorf, *Pogg. Annalen*, 1859, **106**, 546).

For a solution containing complex anions of one species only in addition to the simple ions, if u, v, and v' are the specific velocities of the cation, anion, and complex anion respectively, and if c is the io: concentration of the cation, c' that of the complex anion, then $c - v$ is the concentration of the simple anion, and the expression for the anion transport number is

$$p = \frac{(c - c')v + c'v'}{cu + (c - c')v + c'v'} = \frac{cv + c'(v' - v)}{c(u + v) + c'(v' - v)} \quad . \quad . \quad (1)$$

In determining p experimentally by Hittorf's method, the quantity represented by the denominator is correctly measured by means of a silver voltameter ; the numerator, on the other hand, is determined as a concentration change brought about by the migration of the ions, and hence the degree of complexity of the complex anion has to be taken into consideration. If m is the number of monad anions into which the complex would ionise if completely dissociated, then the increase in concentration at the anode is proportional to $(c - c')v + c'mv'$, and the above becomes

$$p = \frac{cv + c'(mv' - v)}{c(u + v) + c'(v' - v)} = \frac{v + a(mv' - v)}{u + v + a(v' - v)} \quad . \quad . \quad (2),$$

where $a = \dfrac{c'}{c}$, or the ratio of complex to total anions. If this expression is put into the form

$$p = \frac{v + a(v' - v) + av'(m - 1)}{v + a(v' - v) + u},$$

it is seen at once that in order that p should be > 1, it is only necessary that $av'(m - 1)$ should be greater than u, a relation which is fulfilled if either a or m is large. For the majority of salts, neither of these factors attains a sufficient magnitude ; but for zinc chloride and cadmium chloride, p is greater than 1 for very concentrated solutions, and the presence of complex anions in solutions of these salts is universally recognised.

Equation 2 shows at once that no constant value for p can be

obtained in solutions of a salt which forms complex ions, since a would vary with the concentration ; for such salts, it is only at dilutions at which a disappears that the equation takes the form given by Hittorf, $p = \dfrac{v}{u+v}$.

Since the value for the specific ionic velocity, which is given by the relation $v = p\mu_\infty$ and $u = (1-p)\mu_\infty$, depends on the correctness of Hittorf's equation, it is obvious that, in the case of ions which show a tendency towards the formation of complexes, a constant value for u or v can only be obtained when p is determined for solutions of such dilution that no complexes exist; for more concentrated solutions, $p\mu_\infty = v + x$ and $(1-p)\mu_\infty = u - x_1$ if the change is an increase of p with concentration, and *vice versâ*.

If, however, p can be measured in sufficiently dilute solutions of several salts containing a common ion, then the value for the specific ionic velocity of the latter should be the same, whatever the salt from the measurements of which it is calculated. The problem is, in fact, the determination of the transport number at increasing dilutions until it is found to remain constant.

For the calculation of u and v, it is therefore necessary that we should know both the molecular conductivity at infinite dilution and the "constant" transport number. The former of these is obviously not capable of direct experimental determination ; but from measurements at very great dilutions, which have been carried out by Kohlrausch and others, it can be correctly obtained by extrapolation.

The transport number, on the other hand, if we leave out of consideration salts of the type of potassium chloride and nitrate, for which it is practically constant at all concentrations, has not yet been systematically determined at what may be called "constant" dilutions. To the large class of salts, for which, at ordinary concentrations, considerable variations in p are found to take place, belong all salts of dyad and triad ions, and for only a few of these has the "constant" range of concentration been reached. This is due to the fact that the determination of p for very dilute solutions is, for several reasons, a matter of the greatest difficulty.

In all Hittorfian transport number determinations, it is necessary that a certain portion of the solution between the electrodes should remain unchanged in concentration. In the earliest of these determinations, in order that this might be the case, an experiment could only be carried on for a very limited time, as otherwise, by the migration of the H and OH ions developed at the electrodes, concentration changes took place through the whole column of liquid. This difficulty has been overcome in various ways, the method employed by Hittorf

being the use of a cadmium anode to prevent the formation of H ions ; and to prevent the development of OH ions, the cathode was surrounded with a concentrated acid solution.

Hopfgartner (*Zeit. physikal. Chem.*, 1898, **25**, 115) employed a zinc anode, and at the cathode a concentrated solution of zinc chloride over a mercury cathode.

A further source of error is that due to mixing by diffusion, on account of the large concentration changes that take place during electrolysis in the neighbourhood of the electrodes. This has been eliminated quite recently by Noyes (*Zeit. physikal. Chem.*, 1901, **36**, 63), who adds to the cathode and anode solutions respectively in a **W**-shaped apparatus, solutions of the acid and alkali of which the original salt was composed, and of such a strength that the concentration of the salt at the electrodes remains unaltered. By this means, extremely accurate results were obtained by Noyes, but unfortunately the method cannot conveniently be applied to extremely dilute solutions.

The only measurements of such solutions which have been made, until quite recently, are those of Bein (*Zeit. physikal. Chem.*, 1898, **27**, 1). In all his experiments, however, the amount of matter which was transported did not exceed 9—30 milligrams of chlorine, this being determined as the difference between two very much larger quantities of material. Accurate measurements of dilute solutions have recently been made by Jahn's pupils (*Zeit. physikal. Chem.*, 1901, **37**, 674); the method employed was one in which the development of H and OH ions was prevented by the use of a cadmium anode and a mercury cathode covered by a concentrated solution of copper salt. A very high voltage was employed, and, in the analytical work, the limit of possible accuracy was approached ; in some of the experiments, a very large concentration change at the electrodes took place, apparently without affecting the concentration of the intermediate portion. The method is, however, not applicable for solutions more dilute than about $N/150$.

Jahn criticises the employment of any method which results in the development of gas bubbles at the electrodes, remarking that this gives rise to quite uncontrollable currents, which cause the whole solution to become mixed. Noyes, on the other hand, obtained perfectly concordant results by the use of a properly shaped apparatus, and blank experiments have been carried out by the authors, which will be described immediately, and which show that in an apparatus of the shape of that used by Noyes, absolutely no disturbance of the intermediate portion takes place by the gas development at the electrodes even after 48 hours.

It is worth pointing out that the only salt the transport number

of which has been determined by both Noyes and Jahn is barium chloride, and for this salt the following values were found for p.

$$N/50 \ p = 55{\cdot}69, \ 55{\cdot}81, \text{ and } 55{\cdot}84. \quad \text{Mean} = 55{\cdot}78 \text{ (Noyes)}.$$
$$N/60 \ p = 54{\cdot}2, \ 54{\cdot}4, \text{ and } 54{\cdot}3. \quad \text{Mean} = 54{\cdot}3 \text{ (Jahn)}.$$

These two values differ by about 3 per cent., or about ten times as much as the extreme error in either series. From the fact that by Noyes' method no concentration changes occur during an experiment, his figures should, perhaps, be of the greater value.

The object of the experiments that have been undertaken was two-fold; firstly, to develop a general method by means of which it would be possible to determine the transport number at dilutions comparable with those at which accurate conductivity measurements are made ; and secondly, to test the question as to whether, from the results so obtained, constant values for the migration constant of such an ion as Ca^{++} would be found. The salts of calcium were selected for the experiments, because good measurements of their conductivities have been made at dilutions down to $n = 0{\cdot}0001$.

The concentration of the solutions that have been measured varies between $n = 0{\cdot}00529$ and $n = 0{\cdot}0025$.

It is probably not practicable to work at dilutions greater than the latter on account of the conductivity of ordinarily purified distilled water and the practical impossibility of rigorously purifying such large quantities as are required for the experiments.

In solutions containing so small an amount of salt as those under consideration, it is obvious that, in order to get any considerable quantity of salt carried by the current, it is necessary, either to electrolyse a very large volume of solution, or, using smaller volumes, to carry the experiment for so long a time that a very large change in concentration is brought about. If the usual method is employed, the former of these alternatives requires the use of an apparatus of unmanageable size, whilst the latter is attended with the danger of loss of the experiment on account of the backward diffusion and consequent change in concentration of the middle portion.

The apparatus, shown in Fig. 1 (p. 461), admits of the possibility of electrolysing an unlimited volume of liquid in a vessel of reasonable size.

The electrolysing vessel consists of two U-tubes, A and C, of about 4·0 cm. diameter, one limb of each being bent away at right angles, and the two sealed together at B ; two narrow glass tubes are sealed in at E and E', and two wider ones at D and D', the total length from D to E being about 25 cm. D and D' are connected by means of rubber tubing to the T-piece, F, which in its turn is joined to the large stoppered funnel G ; the small tubes, E and E', are each connected with pieces of long, narrow bore glass tubing which can be brought out

over the edge of the thermostat, these are closed either by stopcocks or by rubber tubes and pinchcocks. The U-tubes, A and C, are each supplied with an electrode vessel which is shown in Fig. 2 (p. 462). This consists of the cup c, about 4 cm. in height and 2·0 cm. in diameter, which is attached to the bent up piece of the broad capillary tube a, the end of which passes through and projects for about 2 cm. into the cup c; the other end of the tube a, after passing through the cork, g, is sealed to the bulb b, and is provided with a stopcock h; through the cork g, passes also the short tube with stopcock d, and the glass tube f, to which is attached the platinum electrode, e, which surrounds the projecting piece of tubing. The cork g' is hermetically sealed with sealing wax into the open end of the tube A (Fig. 1).

To prevent the formation of H and OH ions at the anode and cathode respectively, solutions of alkali and acid are added. Working with such dilute solutions, it was not found convenient to add solutions of sufficient dilution to counter-

FIG. 1.

balance the concentration changes, as was done by Noyes, on account of the very large volumes of such solutions that would be required; small quantities of half normal solutions were therefore used instead. The experiment is carried out in the following manner. The apparatus is first placed in position in a large water-bath, and the two tubes attached to E and E' are brought out over the edge. All the stopcocks are then closed. G is next filled with
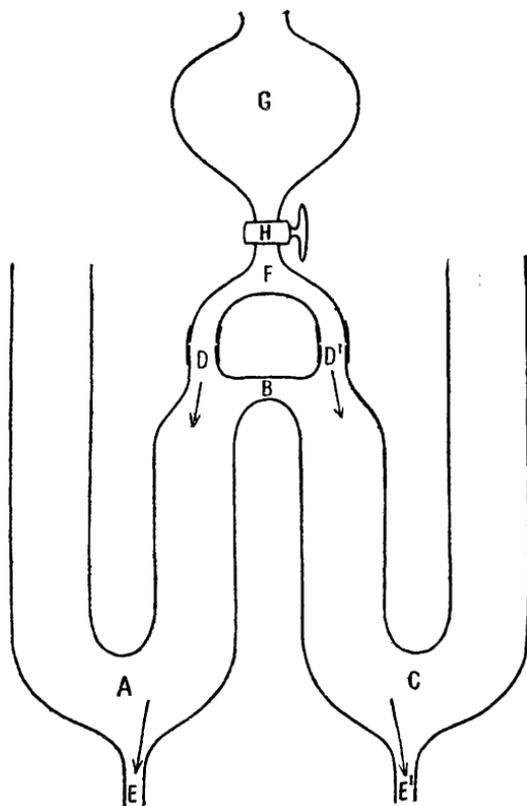
the solution to be electrolysed, and this is allowed to run into
the apparatus, more solution being added to G as required. When the
last bubbles of air in F have been got rid of (by suction if necessary),
the stopcocks, d, are cautiously opened, and the liquid allowed to
rise in the outer limbs of A and C to a point about 2 or 3 cm. above
the electrode vessel, c. The stopcocks, d, are then closed. The
solutions of acid and alkali are next added. If the solution of both
electrodes is to be subsequently analysed, it is necessary to know exactly
the quantity of each solution which is added;
in all the experiments tabulated, the cathode
solution only was analysed, and therefore the
acid only was weighed. This was done by means
of a glass weighing pipette of about 30 c.c.
capacity, which was weighed before and after
each experiment. After weighing the pipette,
about 1 c.c. of the acid is transferred to the bulb
b ; all the stopcocks but d being closed, the acid
is allowed to run in slowly by carefully opening
the stopcock h ; the acid runs in through the
tube a, and since its density is very much greater
than that of the solution, falls over and around
the electrode e and lies at the bottom of the cup c.
A similar quantity of alkali is added in the same
manner to the anode. In order to judge when
the reagent becomes exhausted, small quantities
of an indicator are added simultaneously. In
the majority of cases, methyl-orange was the
indicator employed. From time to time during
the experiment, fresh quantities of acid and alkali
are added in the same manner when they are
shown to be required by the reaction of the in-
dicator. The electrodes are connected with the
terminals of the battery, a silver voltameter whose
platinum cathode had an area of about 1 sq. cm.
being placed in circuit, and the experiment is
started by inserting the cathode. Under ordinary
circumstances, an experiment arranged in this manner could not
be allowed to run more than 60 to 80 minutes with a voltage of
60 volts without concentration changes reaching the portion B ;
but in that time very small quantities of salt will have been trans-
ported. About every twenty minutes the portion of solution con-
tained in the inner limb of the ∪-tube is removed as follows. To
remove the portion from A, all the stopcocks being closed, H is first
opened, and then very carefully the stopcock attached to E ; the solu-

FIG. 2.

tion then flows in the direction of the arrows marked (1), and is collected in a suitable vessel and weighed ; on now closing E and opening E' the current flows in the directions indicated by the arrows (2), and the solution from C is thus removed. Unless it is desired to analyse this portion also it is not collected, but is allowed to run off.

The duration of experiments varied according to the voltage used from 7 to 36 hours ; in the later ones, with a voltage of 170 to 180, 7 to 8 hours was usually sufficient, but with the earlier ones, using 70 volts only, the experiment was allowed to run overnight with a low voltage, to prevent danger of mixing in B. To test the question as to whether mixing occurs due to gas development at the electrodes, the apparatus was arranged as described, a small quantity of phenolphthalein being added to the whole volume of solution. No liquid was removed, but the circuit was closed for short periods every half-hour or so, so as to start the convection currents in the outer limbs of the apparatus. After a lapse of 48 hours, no trace of alkali could be detected as having found its way into the portion B of the apparatus. A similar experiment with litmus failed to detect either acid or alkali at B.

After the three salts of calcium had been measured, the method as above described was slightly modified, with the result that subsequent experiments with potassium choride gave much more closely agreeing figures. This is probably due partly to the fact that the modification eliminates certain very small sources of error, and partly also to the fact that chlorine is capable of far more accurate determination as silver chloride than calcium as calcium sulphate. The modification consists in the attachment of long capillary tubes to E and E', so that, instead of periodically removing the solution, it is allowed to flow through the apparatus in a steady but very slow stream during the whole course of the experiment. At the conclusion of an experiment, all the stopcocks are closed, and the current is disconnected by removing the cathode from the silver voltameter ; the cathode is immediately washed in distilled water and dried with alcohol. The T-piece, F, is then disconnected from the tubes, D and D', and the solution from B, and to a depth of about 4 cm. in A, is removed through D by means of a large pipette ; this portion is weighed for analysis, as the middle portion. On opening now the stopcock attached to E', the solution from C is run out. The apparatus is then lifted from the water-bath, and the remaining solution from the cathode limb, A, is removed through E, and finally the whole of this limb, the bulb, b, and the cup, c, rinsed out several times with small quantities of the original solution, all the rinsings being added to the cathode solution for analysis. If it is required to analyse the solution from the anode, the limb, C, must of course be treated in the same manner.

For analysis, the solutions were in all cases evaporated to a small bulk; this was done as each portion of liquid was removed from the apparatus.

The calcium salts were in all cases estimated as sulphate; in the case of the chloride and nitrate, the solution was evaporated over a water-bath in a large porcelain evaporating basin, the evaporation being continued until the solution to be analysed, which varied between 2 and 3 litres, was reduced to about 100 c.c.; it was then transferred to an accurately weighed platinum basin of about 250 c.c. capacity, a very slight excess of sulphuric acid was added, and the solution evaporated to dryness on the water-bath, the basin being finally ignited at a dull red heat.

In the earlier experiments, the basin was covered during ignition with a piece of ashless filter paper, which was afterwards burnt, and the ash weighed separately, but as in no case was a weighable quantity of ash so obtained, the basin, in subsequent experiments, was simply covered during ignition with a clean clock-glass.

The analysis of the calcium sulphate solution could not be carried out in the same manner on account of the separation of the calcium sulphate, and the impossibility of transferring this without loss from the porcelain to the platinum basin. It was therefore necessary to evaporate in a vessel which could be afterwards weighed.

The evaporation of 3 litres of solution in a basin of 250 c.c. capacity was an operation too slow to be attempted; a large platinum basin holding about half a litre, and weighing 300 grams, was therefore employed, and the solution after weighing was transferred directly to this, and the solid calcium sulphate weighed in it. The difficulty of performing analytical operations of great accuracy under these conditions probably accounts for the greater variations found for the transport number of calcium in calcium sulphate.

In the experiments with potassium chloride, the chlorine was estimated as silver chloride, the solution being, as before, evaporated to a comparatively small bulk, usually about 150 c.c.*

The precipitate was collected in a Gooch crucible and weighed, after thorough washing and drying, at a temperature of 180°. An attempt was made to estimate the potassium chloride by direct evaporation and weighing the residue, but this led in all cases to results far too low, pointing either to volatilisation of the salt in steam from concentrated solutions, or, what seems more probable, to loss from

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* If it is desired, as in transport number determinations, to estimate the chlorine to the nearest tenth of a milligram, this concentration is necessary; for, since the solubility of silver chloride in water at 18° amounts to 1·5 mg., corresponding to 0·4 mg. chlorine per litre, the estimation in very large volumes of dilute solutions is attended with a constant error of considerable magnitude.

spirting, even when no higher temperature than that of a water-bath is employed.

The calculation of the results will be best rendered clear by the following example, that of calcium nitrate. In this experiment, these were passed through the cathode limb of the apparatus, weighed, and evaporated, 2702·94 grams of solution, including 26·20 grams of nitric acid, added to the electrode during electrolysis. Deducting the latter, the weight of solution analysed was 2676·74 grams, which before the experiment would yield 0·8932 gram of calcium sulphate. On analysis afterwards, it was actually found to yield 1·0205 grams of calcium sulphate.

The difference, 0·1273 gram, gives the actual amount of calcium, calculated as sulphate, which had been brought to the cathode by the current. During the experiment, 0·4517 gram of silver had been deposited on the cathode of the voltameter ; if 108 is the atomic weight of silver, and 68 the equivalent weight of calcium sulphate, the expression $\dfrac{0 \cdot 1273 \times 108}{68 \times 0 \cdot 4517} = 1 - p$ gives at once the transport number of the calcium ion in $CaSO_4$. In making the calculation for more concentrated solutions, a further correction is required for the volume changes brought about by the movement of the ions during electrolysis ; but at the dilutions dealt with in the present paper this correction is quite negligible.

In the table are given the values found for the transport numbers, and also the data from which these are calculated ; in the first column are given under N the concentration of the solutions in gram equivalents per litre ; the second column gives the weight of the solution analysed, these are the actual weights of solution removed from the cathode less the weight of acid added during the experiment. The next two columns give the salt contents of this quantity of liquid, under "original" being tabulated the contents calculated from analyses made on the original solution, and under "final" the actual weight of salt found to be present after electrolysis. The difference between these is given in the next column as salt transported. In the case of the calcium salts, all the figures refer to calcium sulphate found on analysis, reduction to weight of calcium nitrate and chloride for these salts being unnecessary. In the case of potassium chloride, all the figures refer to the weight of silver as calculated from the silver chloride weighed. In the seventh, eighth, and ninth columns are tabulated the results of the analyses of the middle portion for the various experiments ; three of these were unfortunately lost.

A comparison of the results given above with those obtained by previous investigators cannot be made for calcium sulphate and nitrate. For calcium chloride, values for the transport numbers have been found

by Hittorf, Bein, and others, which are gathered together and tabulated by Kohlrausch as follows :

$N =$	10	5	2	1	0·2	0·05	0·02	0·01
$1 - p =$	0·21	0·263	0·30	0·314	0·34	0·39	0·41	0·42

which approach with diminishing concentration the value found by us for $N = 0·004$.

Our value for potassium chloride is in agreement with all the best determinations, and is confirmatory of Kohlrausch's fundamental assumption as to the constancy of the transport number for this class of salt with increasing dilution.

The Specific Ionic Velocities.

From the figures given above, it is possible to calculate, by the aid of the conductivity, the migration constants of the ions $\frac{1}{2}Ca$, K, $\frac{1}{2}SO_4$, Cl, and NO_3; the results so obtained are grouped together in the following table :

Salt.	$\mu_\infty.$	$1 - p.$	Ion.	$u.$	$v.$
$CaSO_4$	122·0	0·441	$\frac{1}{2}Ca$	53·8	
			$\frac{1}{2}SO_4$		68·2
$Ca(NO_3)_2$	115·5	0·450	$\frac{1}{2}Ca$	52·0	
			NO_3		63·5
$CaCl_2$	118·7	0·438	$\frac{1}{2}Ca$	52·0	
			Cl		66·7
KCl	131·5	0·495	K	65·1	
			Cl		66·4

To which may be added, for purposes of comparison and discussion, Noyes' figures for K_2SO_4 :

K_2SO_4	135·5	0·496	K	67·2	
			$\frac{1}{2}SO_4$		68·3

Of the above, the figures for K and Cl from KCl merely confirm the accepted values. It is further seen at once, by a comparison of the figures for Cl from calcium and potassium chlorides, that, at the dilutions at which p has been determined for these salts, calcium chloride dissociates in such a manner as to form chlorine ions having the same velocity as those formed by the dissociation of potassium chloride ; the dissociation at these dilutions is therefore normal. Looking next at the velocity of the calcium ion, this is seen to be identical for solutions of the nitrate and chloride ; very dilute solutions of these salts seem therefore strictly to obey the law of the independent wandering of the ions and to be comparable with potassium chloride in more concentrated solutions. If, however, these two salts are

N.	Solution from cathode.			Salt transported.	Silver deposited in voltameter.	Middle portion.			Cation transport number.	Mean.
	Weight of solution.	Salt contents.				Weight of solution.	Salt contents.			
		Original.	Final.				Original.	Final.		
Calcium sulphate, CaSO$_4$.										
0·0047	2307·67	0·7377	0·8159	0·0782	0·2854	—	—	—	0·435	
0·0047	1664·75	0·5328	0·6163	0·0841	0·2925	246·52	0·0782	0·0785	0·456	
0·00448	2505·52	0·7639	0·9069	0·1430	0·5298	—	—	—	0·429	
0·00423	1994·64	0·5739	0·6859	0·1120	0·3920	203·28	0·0584	0·0566	0·448	
0·00423	2467·33	0·7138	0·7995	0·0857	0·3182	193·19	0·0547	0·0555	0·448	
0·00455	2458·60	0·7625	0·8572	0·0947	0·3502	231·05	0·0716	0·0712	0·430	0·441
Calcium nitrate, Ca(NO$_3$)$_2$.										
0·00485	2799·22	0·9218	1·0657	0·1439	0·5023	234·31	0·0772	0·0789	0·455	
0·00435	2655·16	0·7853	0·8883	0·1030	0·3693	227·72	0·0677	0·0683	0·448	
0·00491	2676·74	0·8932	1·0205	0·1273	0·4517	222·09	0·0741	0·0744	0·448	0·450

N.	Weight of solution.	Solution from cathode. Salt contents.		Salt transported.	Silver deposited in voltameter.	Weight of solution.	Middle portion. Salt contents.		Cation transport number.	Mean.
		Original.	Final.				Original.	Final.		
Calcium chloride, CaCl₂.										
0·00529	2279·24	0·8211	0·9408	0·1197	0·4402	231·24	0·0831	0·0835	0·432	0·438
0·00421	2370·44	0·6783	0·7991	0·1209	0·4316	224·61	0·0643	0·0641	0·445	
0·00419	2470·39	0·7029	0·8226	0·1197	0·4342	228·94	0·0652	0·0660	0·438	
Potassium chloride, KCl.										
0·0025	3084·0	0·83320	0·70859	0·12461	0·2452	168·61	0·04502	0·04553	0·491	0·495
0·0025	2392·0	0·64625	0·48554	0·16071	0·3161	178·6	0·04768	0·04825	0·492	
0·0046	2541·3	1·26030	1·00689	0·25341	0·5019	183·27	0·09089	0·09080	0·495	
0·0037	2398·9	0·96748	0·81809	0·14939	0·2984	170·50	0·06876	0·06880	0·499	
0·0034	3157·9	1·15263	0·98489	0·16774	0·3342	173·13	0·06318	0·06353	0·498	
0·0041	2737·4	1·20884	1·03865	0·17019	0·3377	174·3	0·07697	0·07708	0·496	
0·0036	2229·5	0·85315	0·67477	0·17838	0·3522	—	—	—	0·494	
0·0036	3164·0	1·21075	0·98475	0·22600	0·4473	214·2	0·08213	0·08197	0·495	
0·0027	2915·5	0·85162	0·70021	0·15141	0·3009	206·0	0·06017	0·06067	0·497	

considered in less dilute solutions, entirely different values are obtained for u and v; thus, for $N/50$ calcium chloride, $1 - p = 0\cdot41$, and accordingly, $u = 487$ and $v = 700$.

The complex present in this solution is therefore one which diminishes the apparent cation velocity and increases the apparent anion velocity, since, by the dissociation of the complex, the latter cannot presumably be diminished below the value it has in salts such as potassium and sodium chloride. The dissociation of the complexes in calcium chloride, and also in the nitrate, appears to be complete.

The value for u, calculated from calcium sulphate, however, is found to be $3\cdot46$ per cent. higher than in either of the other salts. This behaviour would appear to be in some way connected with the presence of the sulphate ion, for the value for K, calculated from the potassium sulphate figures, is also higher than that calculated from the chloride or the nitrate, and, as a coincidence, it may be noted that the percentage increase is about the same ; further, the value of v for SO_4, obtained from the potassium and the calcium salts, is practically identical.

It is conceivable that this may be due to a very small amount of hydrolysis occurring in very dilute solutions of sulphates, which at very great dilutions becomes of sufficient magnitude to give too high values for the molecular conductivity, and thus increase both u and v. It is certainly difficult to see how otherwise such enhanced values can be obtained.