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B. D. Steele

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III. *The Measurement of Ionic Velocities in Aqueous Solution, and the Existence of Complex Ions.*

By B. D. STEELE, *B.Sc.*, 1851 *Exhibition Scholar (Melbourne)*.

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As early as 1853 HITTORF ('Pogg. Ann.,' vol. 89, 181, 1853), discussing the results of his experiments, emphasised the fact, that a more detailed study of the movements of the ions during electrolysis would result in an increased knowledge of the constitution of salts in solution.

He himself, in a research extending over a number of years, (*ibid.*, 89, 177, 1853; 98, 1, 1856; 106, 337 and 513, 1859,) determined the ratio of the velocities of the two ions for a large number of salts, and the series of measurements has been further extended by later investigators. (For the original literature on transport number determination, see BEIN, 'Zeitschrift für Phys. Chemie,' vol. 27, 1 (1898)).

The method adopted by HITTORF consisted in the direct determination of the changes in concentration which take place during electrolysis in the neighbourhood of the electrodes, and depends on a recognition of FARADAY'S law. The increase in concentration of the cation at the cathode is proportional to the number of cations carried by the current, and similarly for the increase in anion concentration at the anode, and these numbers are proportional to the velocities of the cation and the anion respectively.

The ratio of the velocity of the anion to the sum of the velocities of the anion and the cation $\frac{V}{U + V}$ is represented by the symbol p , which is called the transport number, "Überführungszahl," of the anion. The corresponding transport number for the cation $= 1 - p = \frac{U}{U + V}$, and hence $\frac{V}{U} = \frac{p}{1 - p}$.

As a result of the examination of simple salts, it has been found that for many salts of the most simple type, *e.g.*, potassium chloride, the transport number is independent of concentration, whereas for a few of this type and for all salts which contain a dyad metal as cation, it varies with the concentration. The direction of

change is different in different cases; for lithium chloride, and the chlorides and sulphates of the alkaline earth metals, p diminishes with increasing dilution, whilst for silver nitrate, the opposite is the case. The measurements of the same salt which have been made by different investigators, although they show considerable differences amongst themselves, nevertheless all point to the same general conclusion; namely, that it is only for a very limited number of salts that the transport number is independent of concentration. These differences are probably due in part to the difficulties of the method, and the very great influence of a small experimental error in the determination of small changes of concentration, and partly also to the fact that, following HITTORF, many workers have employed membranes of one kind or another to separate different portions of the solution, and thus prevent mixing by convection currents, whilst others again have altogether avoided their use. BEIN ('Zeit. Phys. Chem.,' 28, 439, 1898) has shown that the use of certain membranes affects in a very remarkable manner the value of the transport number, and it is probable that a considerable number of the discrepancies are to be traced to this cause. Another serious difficulty consists in the fact that an experiment must only be carried on for such a time that no change in concentration can take place in the middle part of the solution, and for many salts the formation of hydrogen and hydroxyl ions at the electrodes further diminishes this time on account of the great velocity of these ions. The danger from hydrogen ions has been minimised by the use of a cadmium anode, and quite recently NOYES ('Zeit. Phys. Chem.,' 36, 63, 1901) has completely overcome this difficulty by the device of adding small quantities of acid and alkali to the solution in the neighbourhood of the anode and cathode respectively.

The measurements of NOYES are probably the most accurate that have been made, and his results again confirm the statement made above.

The importance of and the need for a measurement of the resistance of aqueous solutions of electrolytes was repeatedly referred to by HITTORF; but it was not until the development by KOHLRAUSCH of his well-known method—in which, by the use of an alternating current, the polarisation effect is neutralised—that this problem could be successfully attacked.

From the measurement of the conductivities of salt solutions, KOHLRAUSCH ('Wied. Ann.,' 6, 1, 26, 213) deduced the law of "the independent wandering of the ions," which states that the molecular conductivity of an aqueous solution of an electrolyte is the sum of two constants, of which one depends only on the nature of the cation, and the other only on the nature of the anion; and he further assumed that these constants are proportional to the velocities of the ions, $\mu \propto U + V$. The values of U and V are obtained from the molecular conductivity, which is the sum, and the transport number, which is the ratio, of the two velocities, or $U \propto (1 - p)\mu$ and $V \propto p\mu$.

It is found further, that with increasing dilution the molecular conductivity increases, until it finally reaches a constant value at very great dilutions. This is

explained by the supposition that in more concentrated solutions only a certain proportion of the molecules are employed at any instant in the carriage of the current, and that with increasing dilution the proportion of active molecules increases until finally all are dissociated, or ionized.

The molecular conductivity of a solution is equal to the sum of the actual velocities of the 2 ions multiplied by the quantity of electricity carried by 1 monad ion; this is equal to 96,450 coulombs. At infinite dilution $\mu_{\infty} = \epsilon(u + v)$, at other dilutions $\mu_x = x \cdot \epsilon(u + v) = \epsilon(U + V)$, and hence $x = \mu/\mu_{\infty}$, where x is the coefficient of ionization, or the proportion of ions (cations or anions) to total molecules. Provided that the specific velocities are independent of the concentration, the actual average velocities at any concentration are $U = xu$ and $V = xv$, u and v are the specific ionic velocities, or the velocities with which the ions move under a driving force of 1 volt per centimetre. The ionic velocities of KOHLRAUSCH are obtained from these by multiplication by ϵ . In all cases the relation $U + V = x(u + v)$ holds good.

Here, as in the case of the transport number, it is found that it is only salts of the simplest type—as, for example, the chlorides and nitrates of the alkali metals—that agree well with theory; salts of the alkaline earth metals and of dyad and triad metals generally present the difficulty that they do not give values for the specific ionic velocities, which are the same when calculated from the measurement of different salts of the same metal.

The idea of measuring directly the velocity of ionic movement by the observation of a boundary originates with LODGE ('Brit. Assoc. Reports,' 1886, p. 389), who, in a large number of experiments, endeavoured to follow the movement of certain ions by their reaction with chemical indicators; thus the passage of the Cl ion through a tube filled with gelatine, was traced by a faint cloudiness caused by its combination with a very little silver salt, which was placed there to mark the progress of the anion. Similarly the passage of the H ion through a gelatine solution was indicated by the discharge of the colour of a very faintly alkaline solution of phenolphthalein. In other experiments the point at which 2 ions travelling from opposite ends of the same tube formed a precipitate, was considered to divide the tube in the ratio of the respective velocities of the 2 ions. Of all these experiments only that in which the H ion was measured gave results in agreement with those of KOHLRAUSCH.

This has been shown by WHETHAM and MASSON to be due to a faulty assumption as to the distribution of potential in the circuit.

KOHLRAUSCH, in his calculations of the absolute velocity, reduces the velocities to that conditioned by a potential fall of 1 volt per centimetre, assuming that the velocity is proportional to the driving force. A knowledge of the potential fall is therefore necessary before any just conclusions can be drawn from the observed velocity of a margin.

In any solution maintained at constant temperature the resistance and hence also

the potential fall depends on the concentration; any changes in which, that may take place during electrolysis will condition corresponding changes in potential fall. The question of concentration changes and the movements of these during electrolysis is discussed by KOHLRAUSCH ('Wied. Ann.,' vol. 62, 209, 1897), in whose calculations it is assumed that the electrodes are far removed from the part of the system under consideration; the effects of ordinary diffusion are also not dealt with.

If we consider the case of electrolysis in a long narrow column of liquid, and neglect the movements that take place in directions at right angles to the length of the tube, dealing only with those in the direction of the axis, KOHLRAUSCH'S general equation takes the form

$$\frac{\partial c}{\partial t} = -i \frac{\partial}{\partial x} \left(\frac{uc}{\mu} \right),$$

where c is the ionic concentration of one species of ion (cation), that of the anion being necessarily the same;

i is the current density;

x is the length of the tube;

u is the velocity of the cation whose concentration is c ;

μ is the molecular conductivity of the solution, if v is the velocity of the anion and

$$\mu = (u + v)c;$$

then

$$\frac{uc}{\mu} = \frac{u}{u+v} = (1-p) = p',$$

where p' is the cation transport number, and the equation takes the form

$$\frac{\partial c}{\partial t} = -i \frac{\partial p'}{\partial x} = -i \frac{\partial p'}{\partial c} \cdot \frac{\partial c}{\partial x}.$$

From this it follows that a change in concentration can be brought about only in the case that there exists an initial concentration change, dc/dx , together with a change in transport number with change in c ; when the solution is originally homogeneous no variation in c is caused even if p' varies with c . If, however, the solution is not originally of the same concentration throughout, a portion, s , of the solution being, perhaps, more dilute than the remainder, then if $\partial p'/\partial c = 0$, or if there is no variation in transport number, s remains stationary, "as many ions leave the section as enter it."

If $\partial p'/\partial c$ is positive, that is, if the cation transport number increases with increasing concentration, then s moves in the direction of the current.

If $\partial p'/\partial c$ is negative, the movement is in the opposite direction.

A sharp margin between a concentrated and a dilute solution of the same salt is

not destroyed or moved by the current if p' is constant.* On the other hand, if p' varies, it will move in the positive or negative direction according as the change in p' is in the one or the other direction; it is further shown that such a sharp boundary may be formed during electrolysis, provided that p' changes in such a way that the following ion moves slower than that in the solution it follows.

The case of the boundary between two electrolytes having a common ion is discussed by KOHLRAUSCH in this paper and also by WEBER ('Sitzungsber. k. Akad. Wiss.,' Berlin, 1897, 936), and MASSON ('Phil. Trans.,' A, 1899, vol. 192, p. 331). KOHLRAUSCH and MASSON arrive independently at the conclusion that the concentration of the two solutions becomes mechanically adjusted during electrolysis, so that

$$\frac{c}{c'} = \frac{p}{p'},$$

where c and c' represent the concentration of the two solutions, and p and p' the transport number of the non-common ions.

MASSON gives experimental proof of this for the case of a solution of copper chloride following potassium chloride.

The stability of such a margin is dependent on the relation between the velocity of the following and the preceding ions. The fact that the boundary between certain pairs of solutions was stable when the current moved in one direction, but showed signs of mixing when sent in the opposite direction, was first explained by WHETHAM ('Phil. Trans.,' A, 1893, p. 337).

Some of the phenomena at the junction of two solutions had been previously observed by GORE ('Roy. Soc. Proc.,' 1880-1881), but were not looked at from the present standpoint.

WEBER shows mathematically that the boundary is stable when the slower ion follows the faster one, and experimental proof of this is given independently by MASSON, who found the relative velocities of the potassium and chlorine ions in potassium chloride to be the same whether the anion was followed by the chromate or the tartaric ion.

For the velocity of the boundary when this condition is fulfilled, WEBER gives the equation

$$\frac{dx}{dt} = \frac{iu}{(u+v)c},$$

where the symbols have the same signification as before. The velocity is hence determined by u and c , the velocity and ionic concentration of the preceding ion. For the anion boundary $\frac{dx}{dt} = \frac{iv}{(u+v)c_1}$; hence if $c = c_1$ the relative velocities of the two margins gives at once u/v .

* Such a margin is obviously lost by diffusion unless some special condition for its maintenance is fulfilled.

If, on the other hand, the following ion has the greater velocity, the velocities of the 2 ions are given by

$$\frac{dx_1}{dt} = \frac{iw^2}{u_1(u_1 + v_1)c}$$

and

$$\frac{dx_2}{dt} = \frac{iu_1}{(u_1 + v_1)c},$$

where u and v are the velocities of the preceding and u_1, v_1 those of the following ions.

The 2 ions no longer move with the same velocities, but a mixing takes place, with the result that no stable boundary is to be expected.

WHETHAM (*loc. cit.*), avoiding altogether the use of gelatine, measured the velocity of the boundary between two electrolytes having a common ion, and by the device of selecting pairs of solutions which possessed the same, or nearly the same, specific resistance, obtained an approximately uniform potential fall for the whole column. He was thus able to convert the observed velocities into those which would be occasioned by a fall in potential of 1 volt per centimetre.

Although, as previously mentioned, the conditions for stability of the boundary are pointed out by WHETHAM, in his experiments the values obtained are the means of two sets of measurements in which the boundary moves alternately in opposite directions, and generally with slightly different velocities.

Most of his figures show a very good comparison with those calculated by KOHLRAUSCH, and the measurements as a whole form the first direct confirmation of the theory. Proof of the fact that the velocity is proportional to the potential fall is also given in this paper.

In a second paper, WHETHAM ('Phil. Trans.,' A, vol. 186 (1895), p. 507) measured the velocity of a number of ions in gelatine solution: in some of these experiments the position of the boundary was indicated by means of chemical indicators. The results show a very good agreement with KOHLRAUSCH's figures.

MASSON (*loc. cit.*), employing a gelatine solution of the salt, compares directly the velocity of the anion and the cation margins, which he shows to be dependent only on the nature of the ions, provided certain conditions are fulfilled; the potential fall although unknown is the same for both boundaries, since between these the concentration, and so also the resistance, is the same at all points. His experiments afford a striking confirmation of the Kohlrausch theory, since he shows that it is possible to calculate the current by measuring the velocity of the two margins.

The general theory of electrolysis is briefly summed up by the equation,

$$C = A \frac{n}{\eta} (U + V) = A \frac{n}{\eta} (u + v) \pi x,$$

since the observed velocities $U = \pi x u$, and $V = \pi x v$.

In this equation,

C = the current as measured by the galvanometer.

A = the sectional area of the conducting medium.

n = the normality of the solution.

η = the electro-chemical equivalent of hydrogen.

U and V = the observed velocity of the cation and anion respectively.

u and v = the specific velocities of the cation and anion.

x = the coefficient of ionization.

π = the fall in potential or potential slope.

In MASSON'S paper it is shown that the ratio $\frac{C\eta}{An(U+V)} = 1$ for a number of salts of the most simple type; but here again salts of the type of magnesium sulphate give values for this ratio (when measured in gelatine) differing considerably from unity, and similarly for more concentrated solutions of potassium, sodium, and lithium sulphates.

Both MASSON and WHETHAM employ as indicators solutions which contain ions having a characteristic colour. The employment of these necessarily limits the method, since there do not exist many coloured anions from which to select, and none which do not give a precipitate with the heavy metals and the metals of the alkaline earth group. WHETHAM'S first method is subject to the further limitation that there are not many pairs of solutions that fulfil all the conditions necessary for its application; it also does not allow for the changes in concentration that will take place, unless the transport numbers as well as the conductivities of the two salts are identical.

NERNST ('Zeitschrift für Electro-chemie,' 3, 308, 1897) has described a lecture experiment, which shows the motion of a coloured margin, that between potassium permanganate and potassium nitrate. The success of the experiment depends on the selection of pairs of solutions whose ions on either side of the boundary possess the same specific velocities, a condition that is fulfilled in the case of the ions MnO_4 and NO_3 .

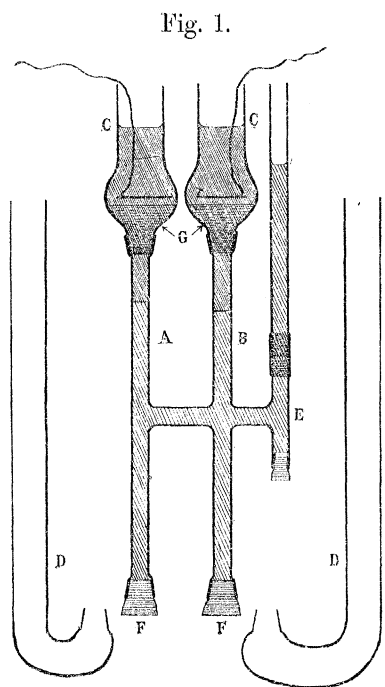
The author (STEELE, 'Chem. Soc. Journ.,' 79, 414, 1901) has succeeded in extending MASSON'S method in two directions.

The first extension consists in the substitution of aqueous for gelatine solutions of the salt to be measured. By this means many salts which will not form solid jellies with gelatine may be investigated. The second depends on the fact that it has been found possible to observe the boundary between two colourless solutions, on account of their difference in refractive index, thus rendering the use of the coloured indicator solutions unnecessary.

The method compares the velocity of the anion and cation, and therefore determines

the ratio $\frac{V}{U}$ or $\frac{V}{U+V}$; as will be seen, it also measures, in the case of salts of the type of sodium chloride, the actual velocity $U = xu$ for any concentration.

The essential feature of the method consists in the imprisonment of the liquid to be measured between two partitions of jelly* containing the indication ions in solutions, thus preventing displacement of the liquid during the course of an experiment.



A large number of different forms of apparatus have been tried, and it has been found that for the measurements of the simplest type of salts, the apparatus shown in fig. 1 is most convenient.†

In the figure, A and B are two carefully selected glass tubes having an even bore, and being both of the same area of cross-section; they are joined by a short piece of tubing of larger diameter. The tube B is also provided with a tube E, by means of which the liquid during measurement is exposed to the atmospheric pressure.

Each tube is fitted at either end with the vessel C, C and D, D which are carefully ground in. For an experiment, two of the vessels (C, C if the indicator solutions are lighter, and D, D if heavier than the measured solution) are taken and filled to a depth of 2.5 centims. with a gelatine solution of the indicator to be employed.

The open ends of the tube having been first closed with rubber stoppers F, the apparatus is filled with the solution and the cells C C placed in position, care being taken not to enclose any air bubbles. The apparatus is then completely immersed in a water-bath, which is provided with parallel walls of good plate-glass, in order that the observations may not be affected by uneven refraction at the surface.

The electrodes are then placed in position, and the current is started by pouring into the cells solutions of the same indicator as that contained in the jelly.

Since the boundaries, at first coincident with those between gelatine and aqueous solutions, advance shortly after the current is started into the tubes A and B, the presence of the jelly can have no influence on their velocities, which are conditioned

* Attempts have been made to use a porcelain membrane instead of gelatine, but it was always found that the liquid was forced through the membrane in the direction of the anode, probably on account of electric endosmose.

† A modification of this form of apparatus may be made by connecting the tube with the electrode cells by means of rubber tubing, as shown in fig. 3.

only by the nature of the preceding ion and by the potential fall, provided certain conditions, which will be described immediately, are fulfilled.

It has been already pointed out that it is not necessary that either the measured or indicator solutions should be coloured, a perfect boundary being rendered visible in most cases by the difference in refractive index of the two solutions.*

The occurrence of such a boundary has been previously noted by LENZ ('Mem. Acad. St. Petersburg,' vii., vol. 30, No. 9, 1882) in the case of cadmium chloride following sodium chloride, and BEIN ('Zeitschrift Phys. Chem.,' vol. 27, 9, 1898) also refers to the same kind of boundary for the same pair of solutions.

The Production and Maintenance of a Good Boundary.

In what follows, by a good boundary will be understood, one which moves with constant velocity under a constant potential fall, or whose change in velocity is proportional to the change in potential fall.†

For the production and maintenance of such a boundary, the following conditions are necessary :—

1. The indicator ions must have a specific velocity slower than that of the ion to be measured.
2. The indicator ion must not be such as to react chemically on the solutions to be examined.
3. During electrolysis the cell solutions must not give rise to any species of ions which would move faster than and overtake the measured ion, thus altering the potential slope within one or both boundaries.
4. The specifically lighter solution should lie over the heavier.
5. The indicator should have a resistance not very much greater than that of the solution it follows.
6. The potential fall should lie within certain limits, which depend on the nature of the solutions forming the boundary.

In addition a tube should be selected of such a size that with the required potential fall the total current does not exceed 0.03 ampere. If this limit is exceeded there is considerable danger of the jellies being melted. It has been found, however, that in a tube of smaller sectional area than 0.08 sq. centim. there is great difficulty in detecting the position of the margin.

Of these conditions, the first three have already been given by MASSON for the measurement in gelatine. In aqueous solutions a refraction boundary may occa-

* This refraction margin may be shown to a large audience, or as a lecture experiment, by means of projection lantern, when it is seen on the screen very clearly and distinctly.

† The best test of a pair of boundaries lies in the fact that if their velocities U and V bear a constant ratio to one another they are probably both good, if the ratio is not constant one or both are bad, and is easy by plotting the velocity curve to see whether the boundary fulfils the required conditions.

sionally be produced even when conditions 1 and 3 are not fulfilled, but, as is seen from the equations of WEBER, already given, its velocity is no longer that of the ion in the intermediate solution. Condition No. 4 is sufficiently obvious, nevertheless it is necessary to point out that it is not sufficient that the difference in density of equimolecular solutions should be known; for, since concentration changes are brought about during electrolysis in the sense that the indicator solution is always (provided condition 1 is fulfilled) of less concentration than the measured solution, it may, and sometimes does, happen that an indicator solution when placed beneath the solution to be measured, and which in equimolecular solutions is more dense than the latter, becomes, through these changes, lighter than and accordingly rises through the overlying solution, with the result that no boundary can be obtained; this behaviour is shown with 2 N potassium chloride solution followed by 2 N copper chloride. According to the relation $c/c' = p/p'$, the concentration of the copper solution becomes reduced to 1.2 N, the density of which = 1.0711, whilst that of 2.0 N potassium chloride = 1.0886. Hence for this reason copper chloride, although its density, as calculated from VALSON'S moduli (see NERNST'S 'Theoretical Chemistry,' p. 333), is much greater than that of potassium chloride, cannot be used as an indicator for the latter from underneath.

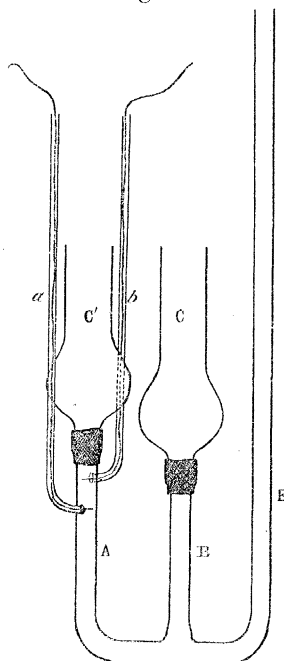
In addition to the experimental evidence of these concentration changes that has been given by MASSON, further qualitative evidence is found in the fact that in an experiment in which lithium or magnesium follows potassium in a solution of potassium chromate, so that there is formed electrolytically a solution of lithium or magnesium chromate overlying one of potassium chromate, the indicator solution is seen to be distinctly lighter in colour than the measured. Since the colour depends only on the anion, this shows the concentration of the latter is less in the indicator solution.

More direct and conclusive evidence was obtained in the following manner:—

An apparatus, shown in fig. 2, was employed. The tubes A and B, instead of having the anode and cathode cells ground in, are provided with pieces of thick, strong, india-rubber tubing, which are firmly bound on with copper wire, into which the cells C and C' can be fitted.

It is found in practice that no displacement of the latter takes place during the course of an experiment, and, in order to reduce the danger of melting the jelly by the current, the necks of the vessels C and C' are made a little larger than the tubes A and B; the tube E serves the double purpose of a support or handle, by means of which the apparatus may be held, and also to allow for any slight contraction or expansion that may take place through unequal heating.

Fig. 2.



a and b are two glass tubes sealed into the tube A, through which enter two platinised platinum wires.

The tube A with the two points serves as an electrode vessel for the measurement of the resistance of the solution to be examined.

The capacity of the apparatus was first determined by the measurement of a solution of known specific resistance. The whole apparatus was then filled with a solution of 0.5 N potassium chloride and the cells placed in position, C' being first filled with a lithium chloride jelly. The resistance of the potassium chloride was then measured, the current was started, and, after the margin had reached a point well below the second platinum point, so that both points were inside the indicator solution, the current was cut off and the resistance again determined. From this the specific conductivity of the lithium chloride was calculated, and from this the corresponding concentration was obtained from KOHLRAUSCH'S tables of conductivities. The concentration of lithium chloride following 0.5 N potassium chloride was thus found to be almost exactly 0.4 N.

The confirmation thus obtained is only qualitative, since according to theory, using HITTORF'S values for the transport numbers, the concentration should be 0.278 N.

The relation between the resistances referred to in condition 5 becomes of importance on account of the distribution of the heating effect of the current; since in any part of the circuit this is proportional to the resistance of that part, it follows that, if in a cylinder of liquid there occurs a short column whose resistance is very much greater than in other parts, the heating will be proportionally greater, convection currents will be set up, and mixing will take place, with the result that the boundary, if not destroyed, will be washed away and will advance more or less rapidly than it should, according as the indicator lies over or under the measured solution. As an example of the great difference in resistance that may occur between the two solutions, the case of the system cadmium chloride following potassium chloride may be taken.

If the concentration of the latter solution is 2.0 N, it will have a specific resistance of 5.4 ohms, the concentration of the cadmium chloride becomes 1.0 N and its resistance = 44.6 ohms, or the heating effect in the indicator is 8.25 times as great as in the solution; in consequence of this it has not been found possible to use solutions of cadmium or copper sulphate as indicator for potassium salts.

The formulæ of KOHLRAUSCH and WEBER do not show that the stability of a boundary is in any way dependent on the potential fall. This has, however, been found to be of the greatest importance.

As the result of a great number of observations, it may be stated that, for most pairs of solutions, there is a certain range of potential fall which is capable of producing a good and stable margin; there exists an inferior limit below which no boundary whatever can be detected in the case of colourless solutions; and in the case of one coloured and one colourless solution, a shading out of colour only can

be seen, and a superior limit above which the boundary is rendered useless for observation by the "washing" and "mixing" effect of too great a current density and consequent heating. For a few pairs of solution it has not been found possible to obtain a refraction margin under any conditions that have been tried.

The potential fall in all cases is calculated on the assumption that the solution between the two boundaries is homogeneous, being of the same concentration and specific resistance throughout. Since OHM'S Law holds good for electrolytes, $E = CR$; and from the specific resistance r the resistance of 1 centim. of the liquid column is obtained by dividing by the area of the tube, and hence the potential fall $\frac{d\pi}{dx} = \frac{Cr}{A}$, where C is the current, r the specific resistance, and A the area of cross-section of the column of liquid.

A striking example of the influence of potential fall on the condition of the margin is seen in the case of a normal solution of barium chloride, using the apparatus shown in fig. 1. With magnesium chloride and sodium acetate as indicators the anion boundary is that between barium acetate and barium chloride, and will be represented by $\text{Ba} \frac{\text{Ac}}{\text{Cl}}$, the cation boundary that between magnesium chloride and barium chloride = $\frac{\text{Mg}}{\text{Ba}} \text{Cl}$. Starting the experiment with a potential fall of 1 volt per centim., a fair but not very good anion boundary is produced, but there is no sign of a boundary at the other end; on increasing the voltage to 1.20, the anion margin becomes very sharp and easy to read. At the cation end the gas flame, when viewed through the telescope of the cathetometer, is seen to be slightly distorted, but no boundary has yet appeared. With a voltage of 1.5 the anion boundary shows signs of "washing," whilst that at the cation end is still too indistinct for use. At 2.0 volts it has become good and distinct, whilst from the anion margin little whirlpools are seen to rise, and it has become undulating and sharp as though it were cut with a knife. With further increased potential fall the cation boundary remains good, until about 3.5 volts, when it, in its turn, begins to show signs of "washing" and consequent mixing.

For the determination of the ratio $\frac{V}{U}$ or $\frac{V}{U+V}$ for salts which, like barium chloride, require a different potential fall at the two boundaries, the form of apparatus shown in fig. 3 has been found suitable.

Here the tubes to be used for the measurement are four in number, and are indicated by the letters A, B, and C. The sectional areas of these tubes are different, and each is carefully calibrated, and its area of cross-section determined. Since the potential fall— $\frac{d\pi}{dx} = \frac{Cr}{A}$, it follows that, by selecting tubes of different sizes, any required ratio between the potential falls at the two margins may be easily obtained. It is found in practice that three sizes of tubes are sufficient for all the cases that are

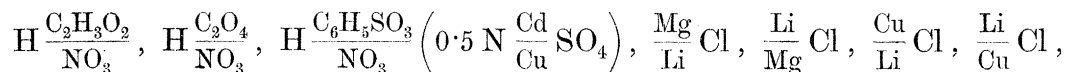
likely to arise, the ratio of the areas of the tubes being approximately 1, : 1.5, : 2.25. In this apparatus, as in that shown, fig. 2, the electrode cells, instead of being ground into the tubes, are connected by means of thick rubber tubing; the tube G serves as a handle by which the apparatus may be held in a clamp, and also, like E in figs. 1 and 2, to allow for expansion of the liquid.

The apparatus shown in the figure permits of the use of the following combinations: The tubes A and B may be used in three ways: with two cells similar to D both indicators may be placed on top; with one vessel, D, and one E, as shown in the figure, one indicator may be used from above and one from underneath; and with two vessels such as E both indicators from underneath. The same combination may be employed with the tubes B and C, whereas with A and C the apparatus can be used only in the second of these three manners; by the use of a second similar apparatus in which the tube C is replaced by B, and *vice versa*. All possible combinations of these three tubes, two at a time, may be obtained.

For the calculation of $\frac{V}{U}$ from the observed velocity, since the latter is proportional to the potential fall, and this inversely as the sectional area of the tubes, it is only necessary to multiply the velocity of the boundary in one tube by the ratio of the two areas. Thus, using the tubes A and C, the sectional areas of which are α and γ , if U' and V' are the actually observed velocities of the two margins, the ratio of the ionic velocities is given by

$$\frac{U}{V} = \frac{\alpha V'}{\gamma U'}$$

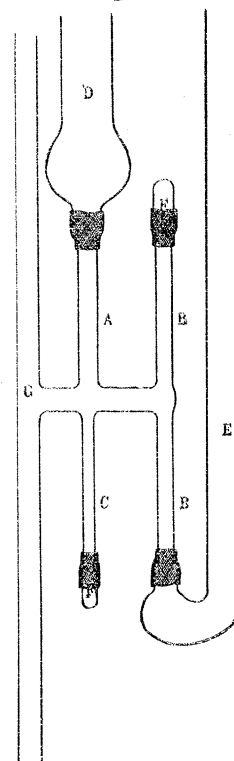
In Table I. are given the potential falls which have been found to give a measurable boundary in the case of thirty-eight different pairs of solutions. In addition to those tabulated, the following have also been examined, but no good margins could be obtained:



and cadmium chloride as indicator following 2N solutions of the chlorides of potassium, lithium, magnesium, and calcium.

In the first column of the table is given the system forming the boundary, thus: $\text{K} \frac{\text{A}}{\text{C}}$ represents the boundary between an acetate and a chloride whose common

Fig. 3.



cation is potassium, and in all cases the indicator ion is placed over the measured ion.

TABLE I.

Margin.	A.	B.	N = 0.5.		N = 1.0.		N = 2.0.	
			A.	B.	A.	B.	A.	B.
K $\frac{Ac}{Cl}$	—	—	0.82	—	—	—	0.84	—
Na $\frac{Ac}{Cl}$	—	—	0.735	—	1.13	—	0.92	—
Li $\frac{Ac}{Cl}$	—	—	1.57-1.98	—	1.06	—	1.94	1.1-2.3
Ba $\frac{Ac}{Cl}$	—	—	1.06	—	1.25	1.1-1.6	1.02	—
Sr $\frac{Ac}{Cl}$	—	—	1.40	—	1.02	—	1.32	1.0-1.6
Ca $\frac{Ac}{Cl}$	—	—	1.2	0.916-1.61	1.18	—	1.2	0.86-1.61
Mg $\frac{Ac}{Cl}$	—	—	1.7	1.55-1.90	1.53	—	1.25-1.41	—
N = 0.2.								
Mg $\frac{Ac}{SO_4}$	2.38	—	2.05	—	2.1	—	2.26	1.1-
Cu $\frac{Ac}{SO_4}$	—	—	1.6	1.14-2.7	1.6	—	1.6	—
K $\frac{Ac}{CrO_4}$	—	—	1.46-1.89	—	—	—	0.935-1.47	—
K $\frac{Ac}{Fe^{III}Ox}$	—	—	2.6-4.25	—	—	—	—	—
K $\frac{Br}{OH}$	—	—	0.81-1.23	0.81	—	—	—	—
Na $\frac{Br}{OH}$	1.40	—	1.02-	1.02-2.10	—	—	—	—
N = 0.1.								
K $\frac{Ac}{Br}$	1.213	—	0.981	—	1.192	—	0.841	—
Na $\frac{Ac}{Br}$	1.07	—	0.906	—	1.04	—	—	—
Li $\frac{Ac}{Cl}$	—	—	0.82	—	—	—	0.84	—
Li $\frac{Ac}{K}$	—	—	0.81-1.23	0.81-	—	—	—	—
Li $\frac{Ac}{K}$	—	—	1.39-2.74	—	—	—	0.89-2.2	-2.3

TABLE I.—*continued.*

Margin.			N = 0.5.		N = 1.0.		N = 2.0.	
	A.	B.	A.	B.	A.	B.	A.	B.
$\frac{\text{Li}}{\text{K}}$ Br	1.21	—	0.981	—	1.192	—	0.85	—
$\frac{\text{Li}}{\text{K}}$ Fe ^{'''} Ox	—	—	2.43	2.15-3.28	—	—	—	—
$\frac{\text{Li}}{\text{Na}}$ Cl	—	—	0.735	—	1.13	—	0.923	—
$\frac{\text{Li}}{\text{Na}}$ Br	—	—	0.906	—	—	—	—	—
N = 0.2.								
$\frac{\text{Ag}}{\text{H}}$ NO ₃	0.48-0.79	—	—	—	—	—	—	—
$\frac{\text{K}}{\text{H}}$ NO ₃	0.70-1.20	—	0.3-0.6	0.238-0.85	—	—	—	—
$\frac{\text{Cd}}{\text{Li}}$ Cl	—	—	2.40	—	1.55	—	—	—
$\frac{\text{Mg}}{\text{Ba}}$ Cl	—	—	2.56	—	2.00	1.60-3.50	2.56	-3.57
$\frac{\text{Mg}}{\text{Sr}}$ Cl	—	—	1.40	—	1.02	—	—	—
$\frac{\text{Mg}}{\text{K}}$ CrO ₄	—	—	2.50-	2.0-	—	—	—	—
$\frac{\text{Mg}}{\text{Ag}}$ NO ₃	—	—	2.02*	—	—	—	—	—
$\frac{\text{Cu}}{\text{Sr}}$ Cl	—	—	—	—	—	—	2.51	—
$\frac{\text{Cu}}{\text{Ca}}$ Cl	—	—	—	—	—	—	2.29	—
$\frac{\text{Cu}}{\text{Mg}}$ Cl	—	—	—	—	—	—	2.05	—
$\frac{\text{Cu}}{\text{Ag}}$ NO ₃	—	—	2.79-3.32*	2.22	—	—	—	—
$\frac{\text{Cd}}{\text{Ca}}$ Cl	—	—	1.13-1.50	—	1.18	—	—	—
$\frac{\text{Cd}}{\text{Mg}}$ Cl	—	—	1.50	—	1.53	—	—	—
$\frac{\text{Cd}}{\text{Mg}}$ SO ₄	2.38	—	2.05	—	2.10	—	2.26	1.1-
$\frac{\text{Cd}}{\text{Cu}}$ SO ₄	—	—	—	—	3.66	—	3.06	2.54
$\frac{\text{Al}}{\text{Cu}}$ SO ₄	—	—	3.04	—	3.36	—	—	—

* Boundary good but jelly melted.

The concentration of the intermediate solution is given at the head of the table, a normal solution, here and throughout the paper, being one which contains 1 gramme equivalent of salt in a litre of solution. In the columns A are given for each concentration of the different boundaries the potential fall which has been found to produce a good and measurable refraction margin. In the columns B are given the limits, where these have been determined, within which such a margin may be expected. Thus, for example, for $0.5 \text{ N Mg } \frac{\text{Ac}}{\text{Cl}}$ the inferior limit is 1.5 volts, the superior 1.9 volts per centim. A very faint and indistinct margin may still be found when the voltage is reduced to 1.39, but its velocity is not constant. Above 1.90 volts the margin becomes "washed."

Although an examination of the table fails to show any regularities of a striking character, it is seen that, generally speaking, the slower the ions forming the boundary the higher the potential fall required. On the other hand, contrary to expectation, it is found that the margin between the same pair of ions varies in the voltage required with the nature of the common ion. This is most clearly shown in the case of the $\frac{\text{Ac}}{\text{Cl}}$ margin; here, with Na as cation, 0.73 volt is more than sufficient to ensure stability, whereas, with Ba, Ca, or Mg as cation, a higher potential fall than this is required before the minimum is reached; the same behaviour is shown by the boundary $\frac{\text{Li}}{\text{K}}$, when Cl is the common anion, 0.82 volt is more than sufficient; with $\text{Fe}^{\text{III}}\text{Ox}$,* on the other hand, the lowest voltage that will give a stable margin is 2.5.

Greater regularities and a possible explanation of the difficulty of obtaining a margin in certain cases are found by considering, instead of the potential fall in the measured solution, the change of potential slope on passing from indicator to solution, or the difference between the potential fall in the two parts of the system. To obtain this a knowledge of the resistance in the indicator is necessary, and this can be calculated very approximately from the transport numbers of the two ions, which condition the concentration change, and from KOHLRAUSCH'S conductivity tables.

Table II. contains the differences in potential for a few boundaries for which the data exist for the required calculation. The numbers under "Potential Fall (A)" give the voltage used for the production of the particular boundary, and in the few cases where the minimum fall is known, this is given in the fourth column under B. In the last column $E_i - E_s$ are given the differences in potential fall between indicator and solution for the voltage under A and B.

* This symbol has been used as an abbreviation to indicate the complex anion of the ferric oxalates.

TABLE II.—Potential Fall.

Margin.	N.	A.	B.	$E_i - E_s$.
$\frac{K}{H} NO_3$	0.574	—	0.20	1.18
$\frac{Li}{K} Cl$	0.5	0.82	—	1.16
$\frac{Li}{K} Br$	0.5	0.98	—	1.10
$\frac{Li}{Na} Cl$	0.5	0.73	—	0.45
$\frac{1}{2} \frac{Mg}{Li} Cl$	2.0	2.00	—	0.01
$\frac{1}{2} \frac{Mg}{Ba} Cl$	1.0	—	1.60	0.65
$\frac{1}{2} \frac{Mg}{Sr} Cl$	1.0	—	1.02	0.28
$\frac{1}{2} \frac{Cd}{Ca} Cl$	0.5	1.15	—	1.69
—	2.0	0.65	—	1.92
$\frac{1}{2} \frac{Cd}{Mg} Cl$	1.0	1.53	—	2.82
—	2.0	1.25	—	2.67
$\frac{1}{2} \frac{Cd}{Li} Cl$	0.5	1.06	—	1.04
$\frac{1}{2} \left(\frac{Cd}{Mg} SO_4 \right)$	0.5	2.04	—	0.47
—	—	1.00	—	0.23
$\frac{1}{2} \left(\frac{Cd}{Cu} SO_4 \right)$	0.5	6.95	—	0.30
$K \frac{Ac}{Cl}$	0.5	0.82	—	0.98
$Mg \frac{Ac}{Cl}$	0.5	—	1.39	1.13
$Ca \frac{Ac}{Cl}$	0.5	—	0.916	0.98
$K \frac{Br}{OH}$	0.5	0.81	—	1.32

From this table it is seen that a very different electrical tension across the boundary is required for some pairs of solutions than for others. On the other hand, for the same pair of ions, a different value for the potential fall in the intermediate solution corresponds to approximately the same change in potential slope. This is shown by the $\frac{Ac}{Cl}$ margin with K, Mg, and Ca as common cation. Looked at from this standpoint, it seems that the change in potential fall required is some function of the velocities of the ions, and it is most probable that a connection will be found to exist

between this and the Nernst theory of liquid cells. To establish the relation, however, it is necessary that a very much larger number of experiments should be carried out. In the table only five of the experiments correspond to the minimum potential fall. This follows from the fact that the investigation had for its first aim the production of a margin, and not the determination of the limits of voltage within which this may be produced.

Two of the boundaries previously referred to for which no satisfactory conditions could be found are the $\frac{\text{Li}}{\text{Mg}}$ Cl and $\frac{\text{Mg}}{\text{Li}}$ Cl. From Table II. it is seen that for this pair of solutions no change in potential slope is brought about. The densities and refractive indices of the two solutions, however, differ very considerably. Perhaps it is on this account that it is possible to obtain an indistinct and undulating refraction margin whether the Li follows Mg or Mg Li; but in neither case is the velocity constant. This is undoubtedly due to the fact that, since there exists no difference in potential fall at the two sides of the margin, there is no controlling force which shall prevent the faster ion diffusing into the slower, or *vice versa*. Diffusion therefore takes place, the resistances become slightly altered, and so also the potential fall and velocities. A similar case is that of the $0.5 \text{ N } \frac{\text{Cd}}{\text{Cu}} \text{ SO}_4$ margin. Here, with a low voltage, a mixed colour boundary, which cannot be located nearer than perhaps 1–2 millims., results; but when the voltage is increased, a sharp colour boundary ultimately appears at about 6.5 volts, and from the table it is seen that even with 7 volts the change in potential slope only amounts to 0.30 volt. That no refraction margin can be detected with this pair of solutions at this concentration (such a margin is obtained in more concentrated solutions) is explained by the circumstance that the refractive indices of the two solutions lie very close together. NERNST, in describing the experiment previously quoted, refers to the necessity for a high voltage that will allow the experiment to be completed in a comparatively short time, as the margin would otherwise be lost by diffusion. This is another case in which there is no change in potential slope on passing from one solution to the other, the velocities of the NO_3 and MnO_4 ions being practically identical.

The case of cadmium chloride as indicator following 2 N solutions of the chlorides furnishes examples of another difficulty. Here the boundaries obtained are the most distinctly to be seen of any that have been investigated, but the motion is always irregular and much too slow. These irregularities are probably due to a mixing by convection currents set up as previously described by the greater heating in the indicator solution; they may, however, be in some way connected with the nature of the anions in the cadmium chloride solution, which according to HITTOFF, are not simple Cl ions, but something more complex.

For the systems $\frac{\text{Li}}{\text{Cu}}$ Cl and $\frac{\text{Cu}}{\text{Li}}$ Cl also an undulating refraction results in both cases; but in the former case the copper lags behind the margin, and the

resulting lithium chloride solution shows throughout the entire length of the column a uniform blue colour. In the latter case, when Cu is the following ion, it encroaches on the intermediate solution and advances ahead of the refraction margin from 0·5 to 1·0 centim., the colour gradually fading away.

The only case in which no boundary whatever has been obtained occurred in the attempt to measure the velocity of the NO_3 ion in nitric acid.* Three indicators (the acetic, oxalic, and phenylsulphonic ions) were tried in different experiments, always without success. It may be mentioned that with such excellent conductors as the acids the use of a high voltage is practically impossible on account of the great heat development. An apparatus was, however, constructed by means of which a potential fall of 2·0 to 3·4 volts was obtained at the anion boundary; under these conditions the whole column of liquid was seen to be mixed by rapid convection currents.

It has been occasionally noticed that with the same boundary the inferior limit apparently differs according to the direction from which it is approached; thus for the $\frac{\text{K}}{\text{H}} \text{NO}_3$ margin, when an experiment is started with a low voltage and this is gradually increased, no margin can be detected at 0·29 volt, whereas starting with 0·4 volt and diminishing, the boundary does not entirely disappear until a potential fall of 0·17 volt is reached. This is due to the fact that with a lower potential fall a longer time is required before the stationary condition is reached than with a higher one, and if before an experiment is started a little diffusion takes place at the point where gelatine and aqueous solutions are in contact, it is possible that the margin may have travelled right through the tube before it has become visible.

The production of a refraction boundary in the case that the slower ion precedes the faster, has been noticed for a few cases, *e.g.*, $\frac{\text{Li}}{\text{Mg}} \text{Cl}$, $\frac{\text{Li}}{\text{Cu}} \text{Cl}$, and $\frac{\text{Mg}}{\text{Cu}} \text{Cl}$. In the majority of instances, however, no boundary is obtainable under these circumstances. But if at the beginning of such an experiment the concentrations of the two solutions are proportional to the transport numbers of the respective cations (or anions), then a stable boundary results which travels with the current. Such a ratio of concentration is automatically brought about during electrolysis, when the slower ion follows the faster, and once this condition is established the margin so produced may be made to move backwards by altering the direction of the current, and this may be repeated a number of times without losing the boundary, although its velocity has been proved by experiment to be less in the backward than in the forward direction. The stability of this margin is easily understood from the fact that the potential slope in

* For the investigation of acids and bases it is impossible to employ gelatine solutions in the cathode and anode cells respectively, as these are immediately destroyed by the H and OH ions; for these, therefore, a partition of earthenware was substituted at the one end, and in order to prevent as far as possible movements of the solution through the membrane, the open limb of the apparatus (E, fig. 1) is dispensed with.

the two solutions is so adjusted that the velocities of the two ions is the same. This is, however, only strictly true for what may be called the reverse direction, for the first moments after reversal of the current, since the change in potential slope no longer hinders diffusion between the two solutions, but aids it, and hence the resistances become altered, and so also the potential fall and the velocity. The boundaries that have been investigated in this direction are $\frac{\text{Li}}{\text{K}} \text{Cl}$ and $\text{Cu} \frac{\text{Ac}}{\text{SO}_4}$, and both of these are quite permanent when the current is reversed, and are not lost even after 2 hours, their velocities becoming, however, steadily less.

The Influence of Hydrolysis in the Indicator.

It is necessary that the indicator solution should not be such as has undergone hydrolysis; when this is the case, the H and OH ions overlap the boundary, and entering the intermediate solution, thus reduce the resistance and so also the velocity at that end.

Provided an experiment in which one of the indicators undergoes hydrolysis is not carried so far that the H or OH ions reach the second boundary, the ratio of the velocities remains perfectly constant, but is quite different to the ratio obtained with an indicator which is not hydrolysed.

This is clearly seen by a comparison of the transport number of copper sulphate as obtained with aluminium sulphate, and with cadmium sulphate:

Indicators =	$\text{Al}_2(\text{SO}_4)_3$ and $\text{NaC}_2\text{H}_3\text{O}_2$.	CdSO_4 and $\text{NaC}_2\text{H}_3\text{O}_2$.
CuSO_4 0·5 N	0·749	—
1·0 N	0·842	0·660
2·0 N	—	0·730

The influence of the H ions formed by hydrolysis of the $\text{Al}_2(\text{SO}_4)_3$ solution, in reducing the velocity of the $\frac{\text{Al}}{\text{Cu}} \text{SO}_4$ margin, is strikingly shown.

The Gelatine Solutions.

For the preparation of the indicator jellies the best commercial gelatine was employed, which had been purified by diffusion in distilled water in the manner described by LOBRY DE BRUYN ('Rec. Trav. Chim.,' 1900, 19, 236). Gelatine solutions containing half an equivalent weight in grammes of indicator salt were used for the $\frac{n}{2}$ solutions, containing two equivalent weights for the N and 2 N solutions. The strength of the jellies in gelatine was always, where possible, 12 per cent.

Certain regularities in the behaviour of the different jellies used may be noted.

Good firm jellies suitable for use in the experiments are obtained with the following salts, using 12 per cent. gelatine : Potassium chloride, bromide, fluoride, and chromate, sodium acetate, the sulphates of magnesium, copper, and cadmium, and half-normal silver nitrate.

To obtain a sufficiently solid jelly of lithium or magnesium chloride, it is necessary to use 20 per cent. gelatine.

0.5 N potassium iodide and 2.0 N cadmium bromide, do not form solid jellies even with 23 and 25 per cent. of gelatine.

It is not possible to prepare a 0.5 N aluminium sulphate jelly containing 12 per cent. gelatine, as it becomes coagulated and semi-solid even at 100° ; with 5 per cent. gelatine a good solution is obtained, which solidifies to a very fine jelly of high melting point.

By the electrolytic formation of the following gelatine solutions, the jellies are melted even with very small heating by the current :*

Copper or magnesium nitrate formed by the passage of NO_3 anion into 12 per cent. jellies of 2 N copper or magnesium sulphate. In only one experiment the copper nitrate jelly so formed was not melted.

The passage of Br ions into a lithium chloride jelly results in its melting with a current density which would be quite safe, with no formation of lithium bromide.

The entrance of bichromate ions into a lithium chloride jelly invariably occasions the melting of the latter; and H or OH ions, so dilute as 0.2 N, immediately destroy any jelly they enter.

From these observations, which are entirely qualitative, the statement seems to be justified that the influence of the salt on the melting point of a jelly depends on the nature of the ions, that, among anions the lowering effect increases as we pass down the series SO_4 , Cl, Br, to NO_3 , Cr_2O_7 and I, and similarly for the cations as we pass down the series K, Na, Cu, Cd, Li, and Mg.

The sulphates of all these readily form jellies of high melting point; with the chlorides the melting point falls as we pass from potassium and sodium to Mg, and so for the others. A quantitative investigation of the influence of salts on the melting points of gelatine solutions should yield instructive and interesting results.

As indicators, normal solutions of the following salts have been used :—

Cation Indicators.

CuSO_4 , with copper anode, to minimise the formation of H ions.

CdSO_4 , with cadmium anode.

LiCl, with Li_2CO_3 suspended in the solution.

* This difficulty of the melting of the gelatine would be overcome by substituting an earthenware partition, as has been done for the acids and alkalies.

MgCl₂, with MgO, suspended in the solution.

KCl, containing dissolved K₂CO₃.

AgNO₃, with silver anode.

Al₂(SO₄)₃, with Al₂(OH)₆ suspended in solution.

Anion Indicators.

NaAc, with HAc to prevent formation of OH ions.

KF, containing a small quantity of HAc.

K₂CrO₄, with K₂Cr₂O₇.

The current was obtained from a battery of thirty storage cells, and the total voltage used in different experiments varied from 20 to 70 volts.

The temperature of the experiments was that of the room ; it was constant to 0°·5 throughout any experiment, but varied in different experiments between 14° and 19°.

The Accuracy of the Measurements.

The apparatus having been prepared as already described, shortly after the current is started, the boundaries having advanced into the tube ; their rate of motion is measured by means of a cathetometer, a small gas jet when placed behind the tube being seen to be cut by a dark line at the point where the two solutions are in contact. Each tube has etched on it a horizontal line, which serves as a fixed point from which measurements are made. At frequent intervals the time, the current, and the distance moved over are measured ; the ratio of the distances moved over by the anion and the cation boundaries gives directly $\frac{V}{U}$, from which $\frac{V}{U+V}$ is at once obtained.

The cathetometer employed was capable of giving readings correct to the tenth of a millimetre, but from various causes the accuracy with which the position of the margin can be read is about one-third of this. The difference in the values of p obtained in the various readings of the same experiment amounts in some cases to 2 per cent., but the error here arises in nearly every case from the fact that in the earlier measurements, where the distance moved over by the boundary is often less than 0·5 centim., a small error in reading the cathetometer has a very much greater influence than later when the distance is more, hence it is found always that the last few readings agree much better among themselves than do the earlier ones.

All the readings from an experiment are therefore averaged in the following manner :—

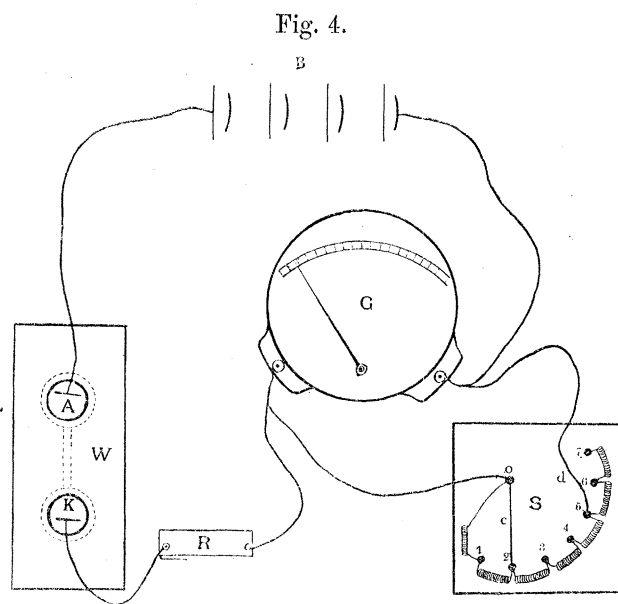
Each value for p is multiplied by the distance moved over by one of the boundaries since the beginning, the numbers thus obtained are added together and divided by the sum of the multiplicands. When averaged in this manner, it is

found that for salts of simple type, the difference in transport number of the same salt, as determined in different experiments, is exceedingly small: thus six experiments with 2 N, KCl gave 0.492, 0.490, 0.494, 0.488, 0.488, and 0.489, and two experiments with N, KBr gave 0.473 and 0.474.

For salts of less simple type than these, only two duplicate measurements have been made; these are, for magnesium sulphate 0.5 N, 0.693 and 0.694, and for a 0.2 N solution of the same salt 0.649 and 0.646.

For the measurement of the current, a galvanometer with the resistance of about 100 ohms was employed; it was far too sensitive for the amount of current used, and was therefore always connected with a shunt. Provided the total deflection of the needle amounted to at least 70 scale divisions, readings correct to 1 part in 200 could be made; to ensure accuracy in the measurements, therefore, it was necessary that, whatever the strength of the current, the deflection should be not less than about 50 scale divisions.

Since the current varied greatly in different experiments, a series of shunts was prepared by the use of which widely varying values could be given to the scale divisions. The apparatus is shown in fig. 4, where G is the galvanometer and S the



box of coils, one or all of which can be used as a shunt. In the figure the three coils between 2 and 5 are connected with the binding screws of the galvanometer, and by moving the connecting wire *c* and the wire *d* to different mercury cups, a large number of different values can be given to the shunt. The value in amperes of each scale division was determined by direct measurement when the various coils were connected with the galvanometer, and by this means it was possible, however the amount of current varied, to ensure in all cases a deflection of from 80 to 100

scale divisions. Fig. 4 shows, also diagrammatically, the arrangement of the whole apparatus for an experiment. B represents the battery. W is the water-bath, in which is immersed the apparatus, of which A and K are the anode and cathode cells respectively. R is a very large and easily varied resistance placed in circuit, by means of which the voltage between A and K can be varied as required.

EXPERIMENTAL RESULTS.

The independence of the margin velocity on the nature of the indicator, provided the latter fulfils the required conditions shown by MASSON, has been confirmed by the measurement of magnesium sulphate with three pairs of indicators—copper sulphate and potassium chromate, cadmium sulphate and sodium acetate, copper sulphate and sodium acetate—and by the fact that practically the same result has been obtained for the velocity of the hydrogen ion when measured with silver nitrate or with potassium chloride as cation indicator.

The negative case has been proved by a large number of experiments, all of which show that, when the faster ion follows the slower, in cases where a boundary is produced at all, the ratio of its velocity to that of the boundary at the opposite end of the solution is quite inconstant.

Table III. contains the results obtained during the research.

In column 1 are given the formulæ of the salts measured. In the second column is given the concentration of each salt.

In column 3, under $\frac{V}{U}$, is given the ratio of the velocity of the anion to that of the cation, this being calculated directly from the observation in the manner previously described.

In columns 4, 5, and 6, under $\frac{V}{U+V}$, are given for comparison the values of the anion transport number. Under S are given the numbers obtained by the author, under (MASSON) those obtained by MASSON by direct measurement in gelatine, and under (HITTORF, &c.) are given those obtained by different investigators by the indirect method of HITTORF. The latter numbers are taken from KOHLRAUSCH and HOLBORN ('Leitvermögen der Electrolyte').

A comparison of the figures in the fourth and fifth columns shows that for potassium and sodium chloride there is a very close agreement between the numbers obtained by direct measurements in water and in gelatine, whilst for lithium chloride and magnesium sulphate no such agreement exists. For 2 N magnesium sulphate there is given in brackets (column 5) the number 0.688, obtained by the author for the value of p in gelatine; this measurement being made for purposes of comparison. For this salt the gelatine results agree among themselves, as also do the aqueous; whereas the two sets of measurements show no such agreement as

TABLE III.

Salt.	N.	$\frac{V}{U}$	$\frac{V}{U+V}$			Indicators.	
			S.	(MASSON.)	(HITTORF, &c.)	Cation.	Anion.
KCl. . .	0.5	0.96	0.490	0.495	—	LiCl	NaAc
	1.0	0.955	0.488	0.490	0.515	—	—
	2.0	0.955	0.489	0.483	—	—	—
NaCl . .	0.5	1.48	0.597	0.598	0.626	LiCl	NaAc
	1.0	1.45	0.591	0.595	0.637	—	—
	2.0	1.44	0.590	0.587	0.642	—	—
KBr . . .	0.1	0.935	0.483	—	—	LiCl	NaAc
	0.5	0.920	0.478	—	0.513	—	—
	1.0	0.900	0.473	—	—	—	—
	2.0	0.880	0.468	—	—	—	—
NaBr . .	0.5	1.47	0.595	—	—	LiCl	NaAc
LiCl. . .	0.5	2.52	0.716	0.687	0.73	CdSO ₄	NaAc
	1.0	3.02	0.751	0.680	0.745	—	—
KOH . .	0.574	2.71	0.730	—	0.738	LiCl	KBr
AgNO ₃ . .	1.15	0.943	0.486	—	0.495	CuSO ₄	KF
BaCl ₂ . .	0.5	1.36	0.576	—	0.615	MgCl	NaAc
	1.0	1.62	0.619	—	0.640	—	—
	2.0	1.73	0.633	—	0.657	—	—
SrCl ₂ . .	0.5	1.67	0.625	—	—	MgCl ₂	NaAc
	1.0	1.98	0.665	—	—	—	—
	2.0	2.44	0.709	—	—	CuSO ₄	—
CaCl ₂ . .	0.5	2.14	0.681	—	0.675	CdSO ₄	NaAc
	1.0	2.30	0.697	—	0.686	—	—
	2.0	2.51	0.715	—	0.700	CuSO ₄	—
MgCl ₂ . .	0.5	2.39	0.705	—	0.690	CdSO ₄	NaAc
	1.0	2.60	0.722	—	0.709	—	—
	2.0	2.84	0.740	—	0.729	CuSO ₄	—
MgSO ₄ . .	0.184	1.82	0.646	—	0.660	CdSO ₄	NaAc
	0.5	2.26	0.693	0.684	0.700	—	—
	1.0	2.50	0.715	0.703	0.740	—	—
	2.0	2.80	0.737	0.693	0.750	—	—
	—	—	—	(0.688)	—	—	—
CuSO ₄ . .	1.0	1.94	0.66	—	0.696	CdSO ₄	NaAc
	2.0	2.71	0.73	—	0.720	—	—
K ₂ CrO ₄ . .	0.5	0.807	0.447	—	0.512	LiCl	NaAc
	2.0	0.677	0.403	—	—	—	—
KFe ^{'''} Ox .	0.603	0.495	0.331	—	—	LiCl	NaAc

do those for potassium chloride. The explanation of this behaviour is rendered more difficult by the fact that the transport number for magnesium sulphate has been determined by HITTORF'S method, using a gelatine partition to separate the anode and cathode portions of the solution. Two experiments made in this manner gave 0.732 and 0.744 for the anion transport number, numbers which agree well with the older determinations and with the figures in column S. It is worth pointing out that whilst p for these salts, when determined in water, shows a considerable change with concentration, in gelatine on the other hand p is approximately constant.

TABLE IV.

	Group I.				Group II.		
	$n = 0.5$.	$n = 1.0$.	$n = 2.0$.		$n = 0.5$.	$n = 1.0$.	$n = 2.0$.
Li	0.716	0.751	—	Mg	0.705	0.722	0.740
Na.	0.597	0.591	0.590	Ca.	0.681	0.697	0.715
K	0.490	0.488	0.489	Sr	0.625	0.665	0.709
				Ba.	0.576	0.619	0.633

A point that is shown with great clearness by a consideration of the figures in the fourth column is the periodicity of the transport number of the same anion with different cations belonging to the same group. Table IV. shows the periodicity in question for the chlorides of the elements of Groups I. and II. as far as these have been studied. Tables III. and IV. bring out very clearly the difference, referred to in the earlier part of this paper, between salts of the type of potassium chloride and those of the type of barium chloride and magnesium sulphate. For the former, p is practically independent of the concentration; for the latter, p changes with the concentration.

A comparison of the figures in the fourth and sixth columns shows that for potassium and sodium chlorides the values obtained by the two methods are both nearly constant, although not coincident with one another. For the other salts a general agreement is seen to hold between the two sets of figures; the variation in p is also in the same sense and of approximately the same magnitude.

In referring to the individual experiments it may be mentioned that for the measurement of potassium hydroxide only one gelatine partition was used.

The experiment with silver nitrate is probably the least accurate of all those tabulated, as the potential fall employed for the anion margin was very near the inferior limit for a good boundary, in order to prevent melting of the jelly on entrance of the NO_3 ion.

Many unsuccessful attempts have been made to measure solutions of sodium

bromide and silver nitrate of different concentrations to those given in the table. In the former case, the $\frac{\text{Li}}{\text{Na}}$ Br and in the latter the $\frac{\text{F}}{\text{NO}_3}$ Ag boundary could not be made to move with a constant velocity or without "washing" under any of the varied conditions tried. For the first salt, no other indicator has as yet been used; for the second, no other anion whose silver salt was soluble has suggested itself for trial.

In Table V. is given the ratio of the current, as measured by the galvanometer, to that calculated from the margin velocities. For potassium and sodium chlorides, potassium and sodium bromide, potassium hydroxide, and 0.5 N lithium chloride, this ratio is, as required by theory, within the limits of experimental error, equal to unity. On the other hand, this is not the case for all the other salts examined, the closest agreement with theory being shown by the more dilute solutions; for example, 0.5 N magnesium chloride and 0.2 N magnesium sulphate. Only for one salt have duplicate measurements been made, namely, for 0.5 magnesium sulphate, but here the results are in accordance.

TABLE V.

Salt.	N.	$\frac{C_\eta}{AN(U+V)}$	Salt.	N.	$\frac{C_\eta}{AN(U+V)}$	Salt.	N.	$\frac{C_\eta}{AN(U+V)}$
KCl . .	0.5	0.984	BaCl ₂ .	0.5	0.956	MgSO ₄ .	0.183	0.980
	2.0	1.009		1.0	0.944		0.5	0.949
NaCl . .	1.0	0.989		2.0	0.956		0.5	0.951
	2.0	1.004	SrCl ₂ .	0.5	0.870		1.0	0.977
KBr . .	0.1	0.978		1.0	0.916		2.0	0.956
	0.5	1.000		2.0	1.080		2.0	0.807*
	1.0	1.031	CaCl ₂ .	0.5	1.04		2.0	0.814†
	2.0	0.998		1.0	1.03	CuSO ₄ .	1.0	1.06
NaBr . .	0.5	1.001		2.0	0.973		2.0	0.965
LiCl . .	0.5	1.006	MgCl ₂ .	0.5	1.01	K ₂ CrO ₄ .	0.5	0.965
	1.0	1.070		1.0	1.05		2.0	0.910
KOH . .	0.57	1.02		2.0	0.968			

* MASSON, in gelatine.

† STEELE, in gelatine.

MASSON has found that for this salt the ratio as measured in gelatine is considerably less than 1. Under 2.0 N, MgSO₄, are given in the table the values found by the author in aqueous and in gelatine solution, and also MASSON'S number found in gelatine; a difference is here to be noted corresponding with that already pointed out for the transport number.

For the calculation of the current the average is taken, this being obtained from the area of the time-current curve, and for the velocities the total distance moved over divided by the time in seconds.

TABLE VI.

Salt.	N.	Conductivity.		U = <i>xv.</i>		V = <i>xv.</i>	
		Measured.	Calculated.	KOHLRAUSCH.	Found.	KOHLRAUSCH.	Found.
KCl . .	0·5	102·3	104·5	0·000512	0·000553	0·000543	0·000529
	2·0	92·6	91·0	0·000466	0·000483	0·000494	0·000458
NaCl. .	1·0	74·4	74·5	0·000285	0·000318	0·000485	0·000452
	2·0	64·8	64·6	0·000250	0·000274	0·000418	0·000395
KBr . .	0·5	105·7	104·5	0·000542	0·000568	0·000553	0·000516
	1·0	102·0	99·5	0·000522	0·000542	0·000532	0·000484
	2·0	97·4	97·3	0·000500	0·000538	0·000510	0·000471
KOH . .	0·576	192·0	190·0	0·000530	0·000535	0·001450	0·001435
LiCl . .	0·5	70·3	67·0	0·000196	0·000191	0·000535	0·000483
	1·0	62·8	58·8	0·000173	0·000141	0·000480	0·000450
BaCl ₂ . .	0·5	77·6	75·2	0·000310	0·000330	0·000494	0·000450
	1·0	70·3	71·5	0·000264	0·000283	0·000465	0·000457
	2·0	60·3	60·7	0·000213	0·000231	0·000411	0·000398
SrCl ₂ . .	0·5	80·4	81·0	0·000312	0·000316	0·000512	0·000524
	1·0	73·6	75·2	0·000255	0·000261	0·000507	0·000519
	2·0	54·1	50·9	0·000164	0·000152	0·000396	0·000374
CaCl ₂ . .	0·5	74·7	67·6	0·000252	0·000224	0·000521	0·000476
	1·0	67·8	64·2	0·000220	0·000201	0·000482	0·000464
	2·0	58·0	55·0	0·000180	0·000162	0·000420	0·000408
MgCl ₂ . .	0·5	71·0	64·2	0·000229	0·000196	0·000508	0·000468
	1·0	63·0	56·9	0·000189	0·000163	0·000463	0·000427
	2·0	53·0	51·6	0·000149	0·000139	0·000400	0·000396
MgSO ₄ . .	0·18	44·0	45·4	0·000155	0·000167	0·000301	0·000304
	0·5	35·4	36·8	0·000111	0·000117	0·000257	0·000264
	1·0	28·9	29·4	0·000078	0·000087	0·000221	0·000217
	2·0	21·4	23·1	0·000054	0·000061	0·000168	0·000178
CuSO ₄ . .	1·0	25·8	22·7	0·000082	0·000080	0·000186	0·000155
	2·0	20·1	19·9	0·000058	0·000055	0·000150	0·000151
NaOH . .	0·2	---	---	---	---	0·00152	0·00158
KOH . .	0·576	192·0	190·0	0·000540	0·000535	0·00145	0·001435
HNO ₃ . .	0·2	---	---	---	---	0·00280	0·00282*
	0·2	---	---	---	---	0·00280	0·00272†

* With AgNO₃ as cation indicator margin = $\frac{\text{Ag}}{\text{H}} \text{NO}_3$.

† With KNO₃ as cation indicator margin = $\frac{\text{K}}{\text{H}} \text{NO}_3$.

The correctness of the assumption that the velocity of the boundary is in reality that of the preceding ion is capable of being tested by the calculation of the conductivity of the intermediate solution from the observed velocity. For this purpose it is necessary to first reduce the latter to that which would be produced by a potential fall of 1 volt per centimetre. From the sum of the velocities thus obtained the conductivity is obtained by multiplication by ϵ , where ϵ is the quantity of electricity carried by 1 ion = 96,500 coulombs. Table VI. contains a comparison of the conductivities so calculated with those given by KOHLRAUSCH. In the last four columns are given the values of the velocities, calculated from KOHLRAUSCH'S tables, at the concentrations indicated in the second column, and those reduced from the author's measurements.

Since the sum of the velocities is proportional to the conductivities, the sum of U and V must show the same agreement with the sum of U and V from KOHLRAUSCH'S figures, as is shown in columns 3 and 4; that U and V singly do not show such an agreement is due to the fact that the velocity $U = \frac{\mu}{\epsilon} p$, and hence if the Hittorian p is used in the calculation, a different value for U will be obtained than if the author's p is used. In columns 5 and 7 the p that is used is HITTORF'S; in columns 6 and 8 that obtained during the present research, and hence the want of agreement. The fact that by the use of the latter the figures in question would be brought into much greater concordance, speaks strongly in favour of their greater accuracy.

The Existence of Complex Ions.

With the three electrolytic measurements that have been considered, it has been found that it is only in the case of a few salts of the most simple type that experiment and theory are in agreement. In the case of all other salts, in the first place the transport number, whether measured by the older method of HITTORF or by the direct method, described in the present paper, is not independent of the concentration; secondly, from the measurements of the conductivity it is not possible to assign any specific ionic velocity to such ions as Mg, which is constant in different salts of the same cation; and finally, the current as measured by the galvanometer is not the same as that calculated from the observed velocity of the margin.

For the change in transport number two explanations only seem possible, since in the majority of instances the influence of hydrolysis is practically negligible.

The first of these is that with change in concentration there occurs a variation in the specific velocity occasioned by the electrolytic friction, and that the influence of the latter is greater for some ions than for others, and usually greater for the cation than for the anion.

If we assume that at a given total concentration the specific mobilities of the ions are

represented by u and v , and the ionic concentration by c , then for the transport number we have

$$p = \frac{cv}{c(u+v)} = \frac{v}{u+v}.$$

For any other total concentration n the mobilities are u_1 and v_1 , and the ionic concentration c_1 :

$$p_n = \frac{c_1 v_1}{c_1(u_1 + v_1)} = \frac{v_1}{u_1 + v_1}.$$

In order that p_n should be greater than p it is necessary either that v_1 increase faster than u_1 , that u_1 diminish faster than v_1 , or that u_1 decrease and v_1 increase with increase of concentration; the latter case may be excluded from its great improbability. Further, since in all cases the fluidity of a solution decreases with addition of salt, it is not probable that the ionic mobility will be greater in the more viscous solution.*

Assuming, then, that no increase in u_1 or v_1 takes place, for a variation in p u_1 must decrease very much more rapidly than v_1 . To take the case of barium chloride, the anion transport number changes between $n = 0.01$ and $n = 2.0$ from 0.56 to 0.66.

In the dilute solution $u = \frac{0.44}{0.56} v = 0.786 v$,

in the stronger solution $u_1 = \frac{0.34}{0.66} v_1 = 0.514 v_1$,

and hence $\frac{u}{u_1} = 1.53 \frac{v}{v_1}$,

or between these concentrations u has diminished in velocity 1.53 times as much as v .

For calcium chloride a similar calculation gives the relation

$$\frac{u}{u_1} = 2.94 \frac{v}{v_1}.$$

Such a large difference in the influence of concentration change on the actual velocities of the two ions seems hardly to be expected.

It is also difficult to explain by any change in u and v the fact that if we consider solutions up to 0.1 N of potassium nitrate and chloride and barium nitrate and chloride, in the case of the three former no change in p occurs; whilst for the latter

* The conclusions of JAHN ('Zeitschrift für Phys. Chem.,' 33, 545, 1900; 35, 1, 1900) point to the fact that with increasing concentration, up to $\frac{N}{30}$ the velocity of the ions increases in solutions of potassium, sodium, and hydrogen chloride, the ratio of the velocities, however, remaining constant. (See also ARRHENIUS, *ibid.*, 36, 28, 1901, and SACKUR, 'Zeit. für Electrochemie,' 1901, No. 34.)

it does; this would mean, either that the Ba ion has its velocity diminished more than the anion in solution of the chloride but not in the nitrate, or, that the NO_3 ion is diminished in velocity in the barium salt, but not in the potassium salt. Further, the variation in p for potassium sulphate points to the fact that the potassium ion is retarded more than the sulphate, but not more than the chloride. Any of these conclusions are of course possible, but improbable, and the more so since all the facts are far more simply explained by the supposition that complex ions exist in certain salt solutions.

The variation in p with N , which is found by direct measurement in aqueous solution, seems to point to the correctness of the assumption of a variation in u and v . But for this class of salts it has been demonstrated for a few cases, and is probably true for all, that a change in concentration of the solution occurs within the anion boundary. Such a change does not occur with potassium chloride, and it is not clear how it can be brought about in a system containing only simple ions. And here again a more reasonable explanation is afforded by the theory of complex ions.

The form of the equation given by MASSON for the relation between current and margin velocity is not altered by supposing a variation in u and v , hence no explanation is afforded by this assumption of the divergence from unity of the ratio of the current as measured by the galvanometer to that calculated from the observed velocities.

The difficulty in assigning values to the specific ionic velocities finds here, also, a possible explanation. For a given solution the conductivity is $\lambda = \epsilon c (u + v)$, where ϵ is the quantity of electricity carried by one monad ion, and u , v , and c have the same signification as before. The molecular conductivity $\mu = \frac{\lambda}{n} = \epsilon \frac{c}{n} (u + v)$, where n is the total concentration of the solution.

For infinite dilution, $c = n$ and $\mu_\infty = \epsilon (u_\infty + v_\infty)$, where u_∞ and v_∞ are the specific velocities at infinite dilution. Hence $\frac{\mu}{\mu_\infty} = \frac{c}{n} \cdot \frac{u + v}{u_\infty + v_\infty}$. Here $\frac{c}{n}$ = the ratio of ionic to total concentration, or the coefficient of ionization.

Therefore
$$x = \frac{\mu}{\mu_\infty} = \frac{u_\infty + v_\infty}{u + v},$$

and since
$$\mu_\infty = \epsilon (u_\infty + v_\infty) \text{ therefore } x = \frac{\mu}{\epsilon (u + v)},$$

or the coefficient of ionization is given by the ratio of the molecular conductivity to the product of ϵ into the sum of the specific velocities at the same concentration, and is only equal to $\frac{\mu}{\mu_\infty}$ when $(u + v) = (u_\infty + v_\infty)$.

From what has been already said, the probability is that if u and v change, $u + v$ is less than $(u_\infty + v_\infty)$, and hence the real value of x is greater than $\frac{\mu}{\mu_\infty}$.

Now, taking as an example solutions of calcium chloride, if we assume that v is not diminished in velocity, u only being affected, and assign such a value to x that the absolute velocity of the chlorine ions at the various concentrations = 0·000690 centim. second, the value given by KOHLRAUSCH for the specific velocity, then we find that for

$$N = 0\cdot5, x = 0\cdot756; N = 1\cdot0, x = 0\cdot697; \text{ and } N = 2\cdot0, x = 0\cdot610.$$

For the corresponding solutions of sodium chloride, the figures are

$$0\cdot737, 0\cdot678, \text{ and } 0\cdot590,$$

or, solutions of calcium chloride are more dissociated than solutions of sodium chloride of the same concentration. If we assume, instead of this, that the ratio $\frac{\mu}{\mu_{\infty}}$ gives the correct values for x , and calculate the specific ionic velocities for the anion and the cation at different concentrations, we obtain the following figures for solutions of calcium chloride :—

N = 0·5	. . .	$u = 0\cdot000401$	$v = 0\cdot000830$
1·0	. . .	386	845
2·0	. . .	372	867

v for Cl from KCl or Na Cl at all concentrations = 0·000690.

Thus we find that, unless calcium chloride is much more dissociated than sodium chloride, the velocity of the anion steadily increases, and that of the cation steadily decreases with rise in concentration; and the same is shown by all the chlorides referred to in this paper whose transport number increases with increasing N .

The assumption of a variation in specific ionic velocity does not in itself seem to be sufficient to afford a probable explanation of the difficulties in question.

The second explanation that we shall consider is one that was advanced in 1859 by HITTOFF, who says ('Pogg. Ann.,' 106, p. 385, 1859): "Die Verhältnisse, welche von der Zunahme des Wassers abhängen, und bei den Verbindungen der Metalle aus der Magnesia-gruppe auf die Ueberführungen so wesentlich einwirken, müssen bei den Kalium und Ammoniumsalsen so gut wie fehlen. Dadurch werden wir auf chemische Veränderungen der Constitution unserer Electrolyte, die mit der wachsenden Menge des Wassers eintreten, hingewiesen." In the case of the chlorides of zinc and cadmium, and of cadmium iodide, the change in p is so great that the ratio $\frac{V}{U+V} > 1$, as measured by HITTOFF, or there is more current carried by the anion than the total current—a conclusion which is obviously absurd. To explain these cases, he supposes that ionization takes place not only into the simple ions $\overset{++}{\text{Cd}}$ and $\overset{-}{\text{I}}$, but also, at least

partly, into complexes of the nature of $(\text{Cd} \bar{\text{I}}_2 \bar{\text{I}}_2')$, and that a portion of the current being carried by these, the change in concentration in the neighbourhood of the anode becomes increased by the amount of neutral salt carried by this complex anion. Referring again to the variation in p for other salts, he says (*ibid.*, p. 546-7):

“Die bedeutende Abhängigkeit der Ueberführungszahlen von der Concentration der Lösung erklärt sich in derselben Weise, wie bei dem Doppelsalze ($\text{ICd} + \text{IK}$). Mit der Zunahme des Wassers zerfallen die Doppelatome in immer wachsender Zahl in die einfachen, der Strom wird daher immer mehr von den einfachen geleitet, welche bei stark Verdünnung allein vorhanden sind.

“Nur durch diese Deutung vermag ich den Thatsachen gerecht zu werden, und stehe nicht an, dieselbe auf das Verhalten sämmtlicher Salze, welche zur Magnesia-gruppe gehören, zu übertragen. Die schon früher für einen Theil derselben angegebenen Ueberführungen sind ebenfalls in hohem Grade von der Concentration abhängig und würden, wenn noch concentrirtere Lösungen in hinreichender Ausdehnung untersucht werden könnten, für das Anion ebenfalls die Einheit übersteigen.”

More recently BREDIG ('Zeit. f. Phys. Chemie,' vol. 13, 262, 1894) has pointed out the possibility of explaining this difficulty by means of complex ions, and NOYES (*loc. cit.*) assumes the existence of complex anions BaCl_3^- or BaCl_4^{--} in solutions of barium chloride so dilute as $\frac{N}{10}$.

The most natural assumption that can be made as to the manner in which such a salt as magnesium chloride would ionize, is that there would be first formed the two ions MgCl^+ and $\bar{\text{Cl}}$, and that on further dilution the former of these would dissociate into the simple ions Mg^{++} and $\bar{\text{Cl}}$. NOYES ('Zeitschr. f. Physik. Chemie,' 9, 618), from a study of the solubilities of such salts, concludes that this is the case, but the formation of such ions (complex cations) would lead to a change in p exactly the opposite of that which actually occurs, and it is possible that his results could be as well explained by the supposition of complex anion, *e.g.*, $(\text{MgCl}_2 \bar{\text{Cl}}_2)$. The tendency towards the formation of complex ions is discussed fully by ABEGG and BODLÄNDER ('Zeitschr. f. Anorg. Chemie,' vol. 20, 471, 1899), who show that these are formed always by the combination of a free electrically charged ion with an electrically neutral molecule, the latter may be of the nature of a salt or not. As an example of the former, the complex $\text{K}_3\text{Fe}(\text{Cn})_6$ is formed of the simple cation K and the complex anion $\text{Fe}(\text{Cn})_6'''$, which latter is formed from the neutral part $\text{Fe}(\text{Cn})_3$ and the simple anion $\bar{\text{Cn}}$.

Similarly, the complex anion of the periodides $\bar{\text{I}}_3$ is formed by the union of the anion $\bar{\text{I}}$ with the neutral molecule I_2 . This definition also includes the case of the double salts, which differ only from the ferrocyanides and others in the greater tendency of the complex to dissociate into its component parts when dissolved in water.

It is only with the weaker ions that this tendency to the formation of stable complexes is manifested, and according to the theory put forward by ABEGG and BODLÄNDER, this tendency is a measure of the electro-affinity or the ability of an atom to combine with unit charge of electricity to form an ion. "The weaker an ion is, the more it seeks to form complexes by the addition of a neutral part." The nature of the complex that will be formed, whether cation or anion, depends on the question whether the simple anion or cation has the greater electro-affinity.

"The weaker of the two ions will combine with the neutral molecule to form the complex."

Thus the complexes that are formed in solutions of the chlorides of the alkaline earth group are anions, the comparatively strong cations showing less tendency to combine with the neutral salt than does the chlorine. On the other hand, in solutions of silver nitrate, where the cation is a very weak one, and the anion one of the strongest known, complexes, if formed at all, should be cations, and, as a matter of fact, HITTORF'S measurements show that for this salt p changes in the opposite direction to that for the other salts considered.

With the very strong ions K and Na there is shown no tendency towards the formation of such complex bodies, and consequently no change in transport number with increasing concentration, whereas with the weaker ions of the second group, a very marked change in p occurs, and for the still weaker ions, such as Cu and Zn, the change in p is still more marked.

If now we apply this explanation to our three difficulties, we shall find that it is able to afford at least a qualitative explanation without involving any improbable conclusions.

If we assume that in a given solution dissociation takes place in such a manner that there are formed in addition to the simple ions only one species of complex (for example, complex anions) then, if c is the ionic concentration of the cations, and c' that of the complex anions, $(c - c')$ is the ionic concentration of the simple anions, and if u , v , and v' are the specific ionic velocities of the cation, simple anion, and complex anion respectively, the total amount of current carried is proportional to

$$cu + (c - c')v + c'v',$$

the amount of current carried by the anions to the anode is equal to

$$(c - c')v + c'v',$$

and hence

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

Since v will be most probably greater than v' , this equation seems to show that, by the formation of complexes, p should become diminished and not increased; but in the Hittorian experiments, whilst the current, as determined by the silver voltameter, is

correctly represented by $c(u + v) + c'(v' - v)$, the numerator in the above fraction is determined by a measurement of concentration change, and the amount of this will depend on the type of complex that is formed.

If u , v , and v' represent the velocity of that quantity of matter which carries 1 unit charge of electricity, u and v will be associated with the passage from one part of the solution to another of single equivalents, but this is not the case with v' . If m is the number of monad anions into which the complex would fall if completely dissociated, then the change in concentration that would be produced by the movements of the complex is proportional to mv' ; hence the increase in concentration at the anode is proportional to $(c - c')v + c'mv'$, and the Hittorfian

$$p = \frac{cv + c'(mv' - v)}{c(u + v) + c'(v' - v)} = \frac{v + \alpha(mv' - v)}{u + v + \alpha(v' - v)},$$

where $\alpha = c'/c$, or the ratio of complex to total anions.

Now since, as we have before remarked, v' is probably less than v , the denominator becomes diminished, and unless m is very small, $mv' > v$, and so the numerator increases with formation of complexes, or the anion transport number as determined in this manner increases with formation of complex anions, that is, with concentration, and the change is in the opposite direction if complex cations are present. If the above equation is put into the form

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

it is seen at once that for the case $p > 1$ it is only necessary that $\alpha v'(m - 1)$ should be $> u$, a relation which is fulfilled if either α or m is very large. In the case of the cadmium and zinc salts the anions are probably more complex than in the magnesium group.

For the relation of the coefficient of ionization to μ we have the following. Let us define by the coefficient of ionization the ratio of total cations or anions to the total number of molecules; then, if c is the ionic concentration of the cations and n the total concentration, $c/n = x$.

The conductivity of the solution is

$$\begin{aligned} \lambda &= \epsilon(c(u + v) - c'(v - v')), \\ \text{or if } \frac{c'}{c} &= \alpha, \\ &= \epsilon c [(u + v) - \alpha(v - v')]. \end{aligned}$$

For any other concentration

$$\lambda_1 = \epsilon c_1 [(u + v) - \alpha_1(v - v')].$$

Since the molecular conductivity $\mu = \frac{\lambda}{n}$, we get

$$\frac{\mu}{\mu_1} = \frac{\frac{c}{n} [(u+v) - \alpha(v-v')]}{\frac{c_1}{n_1} [(u+v) - \alpha_1(v-v')]}.$$

At infinite dilution $c = n$ and $\alpha = 0$,

and
$$\frac{\mu}{\mu_\infty} = \frac{x[(u+v) - \alpha(v-v')]}{u+v}$$

$$= x - \alpha x \frac{v-v'}{u+v},$$

or
$$x = \frac{\mu}{\mu_\infty} + \alpha x \frac{v-v'}{u+v}.$$

Hence, only in the case that $v = v'$ or $\alpha = 0$ do we obtain the true coefficient of ionization from the conductivities.

Further, from the conductivities and transport number we are not able to determine the values of the specific ionic velocity for any one species of ion, unless the transport number is determined at such a dilution that no complexes exist. With other values of p we obtain instead

$$U = xu - \alpha xv'(m-1)$$

and
$$V = xv + \alpha x(mv' - v),$$

and therefore the apparent velocity of the anion becomes increased and that of the cation decreased by increasing concentration, and consequent increase in α . To determine the specific ionic velocities, therefore, of such cations as Ba, Ca, Cu, &c., it is necessary to know the value of p at very great dilutions, much greater than any at which this important physical constant has been hitherto determined.

It is of interest to point out that the values for p recently determined by NOYES for 0.02 N solution of barium chloride and nitrate are such as give to Ba the same absolute velocity in solutions of the two salts

$$\begin{aligned} \mu_{\infty/\epsilon} \times (1-p) \text{ for BaCl}_2 &= 0.000564 \\ &\text{for BaNO}_3 = 0.000562. \end{aligned}$$

Since the total amount of current crossing unit area of the conducting medium in unit time under a potential fall of π volts per centim. = $\epsilon\pi c[(u+v) - \alpha(v-v')]$, the amount of current passing across a section of area A in a solution of concentration N is given by

$$C = A\epsilon\pi x[(u+v) - \alpha(v-v')]N,$$

since
$$x = \frac{c}{N}.$$

Thus the equation in the form given by MASSON no longer holds good for solutions which contain complex ions, a conclusion which is verified by the irregular values for the ratio $\frac{C}{Ane(U + V)}$ shown for these salts in Table V.

The conclusions arrived at by KOHLRAUSCH, and given in the early part of this paper, as to the movements during electrolysis of a portion of an electrolyte which differs from the remainder in concentration, these movements being conditioned by a change in transport number, receive a simple explanation by the assumption of complex ionization. Let us imagine such a solution having initially a section which differs from the remainder in concentration, and first let us assume no complexes to be present, that is, p constant. Then since only the simple ions carry the current, that portion of the salt which is not ionized remains stationary (neglecting diffusion), and no movement is brought about. Next let us assume complexes to be present, that is, p variable; then, in addition to the motion of the completely ionized salt, a portion at least of the remainder of the salt is carried by the current, and movements of the section take place. If the complexes are cations, that is, p decreases with increasing concentration, the movement is in the positive direction; if, on the other hand, p increases, or the complexes are anions, in the negative direction, in complete agreement with KOHLRAUSCH'S conclusions.

This behaviour of such a section explains at once the change in p that is found when the velocities of the two boundaries are measured; for, assuming that the margins are those between indicator and simple ion, there occurs simultaneously and independently the migration of the complex, by means of which the whole column of salt solution (cations and anions) is carried along and in the positive or negative direction, according as the complex ions are cations or anions, and hence the apparent velocity of the one boundary is diminished and that of the other increased. The influence of the presence of such complexes on the velocity of the margin between two solutions is a question of considerable importance, and one that is worthy of strict mathematical investigation. It is, however, not considered by either KOHLRAUSCH or WEBER in the papers previously cited.

It is possible that, at the anion boundary, where the indicator is following two ions which differ in velocity, the concentration of the solution within the margin may become slightly altered.

Such a change undoubtedly occurs at the anion boundary of solutions of magnesium sulphate and copper sulphate, and the change is in the direction of a diminution of concentration at this point. This corresponds with an increased resistance, and accordingly a higher potential fall, and hence a greater velocity for this margin, a result which would also help to explain the increase in p with more concentrated solutions.

Experimental evidence of the changes referred to has been obtained in the following manner :—

The apparatus previously described, and shown in fig. 2, is filled with the solution to be measured, and the cells C and C' with the indicator jellies are placed in position for the investigation of the anion margin. The cell C' contains the anion indicator. After the current is started the resistance of the solution between the points *a* and *b* is measured.*

If the concentration is the same right up to the margin, the resistance will remain constant up to the time when the margin reaches the wire *b*, when it will suddenly increase, and continue to do so until both the points *a* and *b* are well within the indicator.

In fig. 5 are drawn the curves for the conductivity between the points *a* and *b* and for the neighbourhood of the anion margin for solutions of magnesium and copper sulphates. As abscissæ are plotted the position of the margin at the time of observation, the position of the platinum points being indicated by two small circles on each curve. As ordinates are plotted the conductivity of the column of liquid lying between the two points.

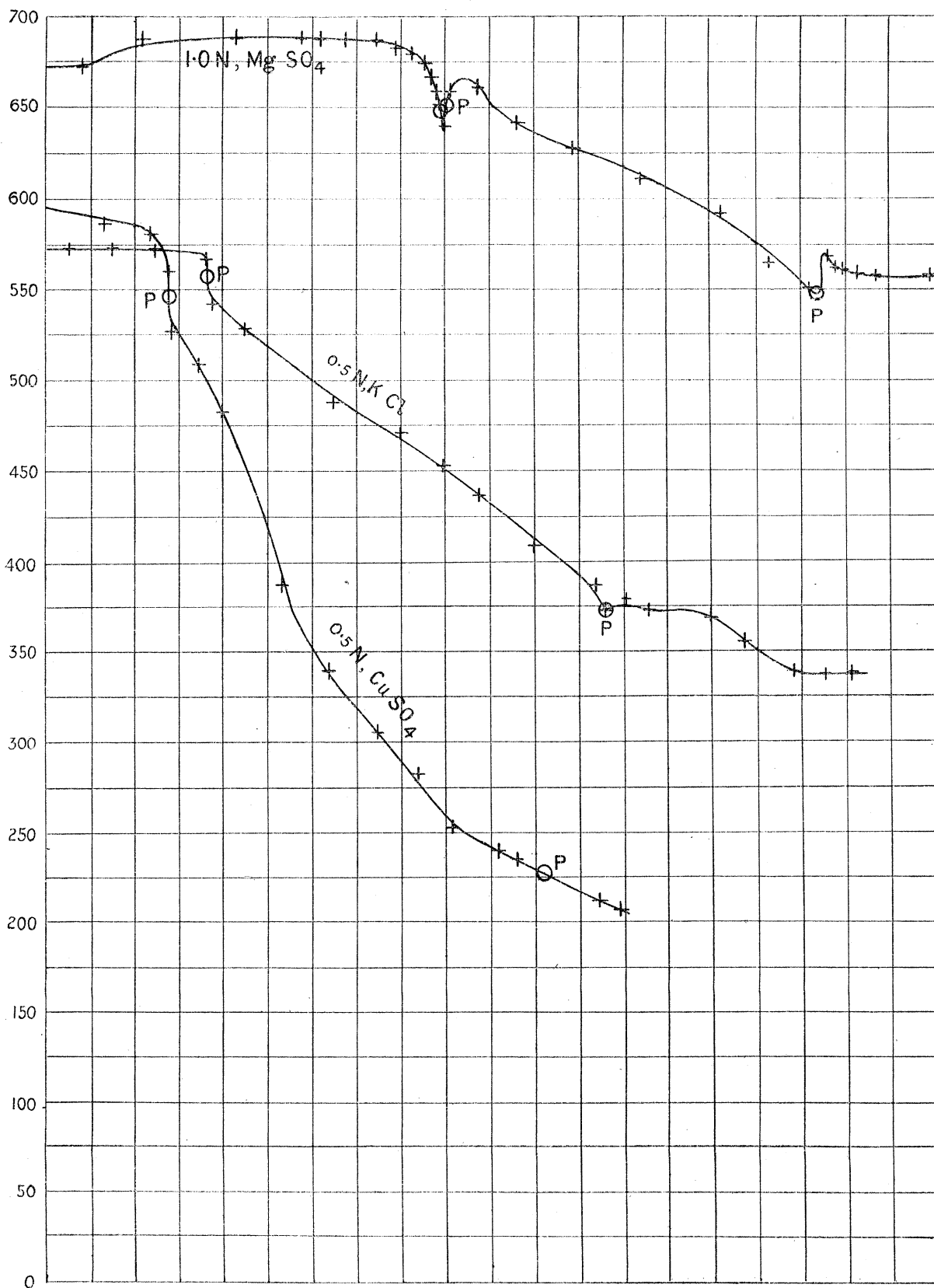
The similarly obtained curve for potassium chloride is also shown. Following this curve from left to right, it is seen that the conductivity, and so also the concentration, is constant as long as the two points are within the solution, a sudden and great fall in conductivity taking place after the point *b* is passed by the boundary. This fall continues, and the concentration is not constant again until the two points are both well within the indicator solution. The curves for the magnesium and copper sulphates show no such constancy in conductivity within the boundary. On the contrary, it is seen that just as the margin approaches the point *b* a very considerable change is indicated.

The cation boundary of magnesium sulphate has been examined by the same method, but only a very slight conductivity change was shown; this was, however, in the opposite direction to that detected at the anion end.

Further and very striking evidence of the dilution that occurs at the anion margin for the solution of copper sulphate, is obtained by simple observation of the solution during an experiment. Using sodium acetate as indicator there results a system in which a dark-blue solution of copper acetate lies over the lighter blue solution of the sulphate; a perfect boundary is produced, and one at which the refraction and colour margins are absolutely coincident; but the solution immediately beneath the indicator is much lighter in colour than that a $\frac{1}{2}$ centim. lower, thus indicating a diminution in copper concentration. This difference in colour has been

* It is necessary that the platinum points should be so near together that the difference in potential between them is not sufficient to overcome the decomposition tension of water and so to cause an evolution of hydrogen and oxygen gases, which would result in a mixing of the two solutions. A very curious phenomenon has been noticed in measuring the resistances in this apparatus: in all cases the resistance as measured during the passage of the current is less than that found when it is measured with no current passing, and this is the case whether the latter is sent in the one direction or in the opposite.

Fig. 5.



noticed in every experiment which has been made with copper sulphate as intermediate solution, and it is always much more noticeable in the more concentrated solutions.

A few experiments have been carried out which show that complex ions of a different kind to those hitherto considered do undoubtedly exist. The most striking of these is the measurement of the transport number of a solution of potassium ferric oxalate; for this salt it was possible to obtain a very good margin with the acetic ion as anion indicator. At the other end of the tube, where the complex entered the cation indicator, there is formed a solution of lithium ferric oxalate, and the ion penetrated the lithium chloride jelly for about 1.0 centim. on its way to the anode as a complex anion.

In another experiment, evidence of the constitution of the periodides was obtained.

The apparatus shown in fig. 1 was filled with a 0.5 N solution of potassium iodide containing iodine, the indicators being sodium acetate and lithium chloride.

At the cathode end, where the $\frac{\text{Ac}}{\text{I}}$ Na boundary was formed, a precipitation of iodine occurred, doubtless on account of the fact that the I_3 ion being slower than the I ion, some of the former would be left behind in a portion of the system, where the equilibrium between KI, I_2 , and KI_3 was disturbed, and therefore nearly the whole of the iodine was thrown out of the solution. The existence of complex I_3 ions is conclusively proved by the behaviour of the solution at the anode end; here a $\frac{\text{Li}}{\text{K}}$ I margin travels away from the gelatine solution of lithium chloride, and simultaneously the I ions enter the latter, forming lithium iodide, but not only I ions enter the jelly, but I_3 also, and the jelly for a length of about 1 centim. becomes coloured a deep red by the solution of LiI_3 that is produced. The entrance of the iodine is far too rapid to be explained by diffusion, and a blank experiment that was carried out showed that in the same time the distance covered by diffusion of the iodine amounted to only about 1 millim., and showed no such sharp line of demarcation between the coloured and colourless portions of the system.

Previous evidence of the existence of the compound KI_3 is given by LE BLANC and NOYES ('Zeitschrift für Phys. Chem.', 13, 359, 1894, and 20, 19, 1896), JAKOWKIN (*ibid.*, 6, 385, 1890), and NOYES and SIEDENSTICKER (*ibid.*, 27, 357, 1898), whilst DAWSON ('Chem. Soc. Jl.', 79, 238, 1900) discusses the dissociation of the compound KI_3 into the ions K and I_3 .

Yet another series of experiments may be described which tend to show in the same manner the presence of complexes in solutions of copper sulphate. When a solution of this salt is followed by the three indicator ions Cd, Mg, or Li, a great difference in behaviour is to be noticed. Cd as indicator fulfils the condition that it is slower than the Cu, and consequently the solution behind the boundary remains quite colourless; with the other two ions this condition is not fulfilled. When Mg

follows Cu the latter falls behind the margin, and the colour does not entirely disappear until a point about 2 centims. behind the boundary is reached ; no copper, however, is found to enter the MgSO_4 jelly.

With Li as indicator the copper also lags behind the boundary, but as has been previously mentioned, the colour shows no sign of entirely fading out, and when there exists a column 6 centims. long of Li_2SO_4 solution, the blue colour of the copper left behind is perfectly uniform, but lighter in colour than the measured solution. On examining the lithium chloride jelly after the experiment, it was found that copper had entered it for a distance of between 3–3·5 millims., thus indicating the passage of the copper to the anode as complex anion. This behaviour is possibly associated with the fact that the double sulphates of copper belong to the class $\text{M}'_2\text{Cu}(\text{SO}_4)_2$, and hence a complex $\text{Cu}(\text{SO}_4)_2$ will be stable in the presence of a monad cation such as Li, but not if the cation is of the type of Mg.

The method described in the preceding pages gives a simple and accurate means of determining the transport number of the simplest type of salts ; in its present form it is applicable only to more concentrated solutions. It is hoped to modify it in such a manner as to permit of the measurement of more dilute solutions. For salts of the dyad metals, more doubt attaches to the accuracy of the method, in consequence of our want of exact knowledge as to the mechanism of the changes that may take place at the margin, on account of the presence of complexes.

The existence of these may be considered to be established with a probability amounting almost to certainty, but the evidence is, as yet, qualitative only ; by the solution of the problem, as to exactly how the margin velocity is influenced by the presence of complexes, and their dissociation outside the margin, it is possible that a means of determining quantitatively the proportion of complex to simple ions in a given solution may be indicated.

In conclusion, it is the author's very pleasant duty to express his indebtedness to Professor ABEGG for the help he has received from him during the course of the work.