Ionic Velocities

Orme Masson

Phil. Trans. R. Soc. Lond. A 1899 **192**, 331-350
doi: 10.1098/rsta.1899.0007

II.—*Ionic Velocities.*

By Orme Masson, *M.A.*, *D.Sc.*, *Professor of Chemistry in the University of Melbourne.*

Communicated by Professor W. Ramsay, *F.R.S.*

Received December 12,—Read December 15, 1898.

Introduction.

The general theory of electrolytic conduction, involving the laws of Faraday, Hittorf, Kohlrausch, and Arrhenius, may be briefly summed up by the formula

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

where

C is the current,
A is the area of cross-section of the conducting medium,
η is the electro-chemical equivalent of hydrogen or $1/\eta$ is the charge per monad ion,
n is the number of monad equivalents of the electrolyte per unit volume of solution,
U is the average working velocity of the cations,
V is that of the anions,
π is the fall of potential per unit of length (dP/dl), called in the sequel potential slope,
x is the coefficient of ionization,
u is the velocity with which the same cations would travel if, all other things being equal, ionization were complete, and the potential slope had unit value, and
v is the corresponding value for the anions.
u and v are referred to in the sequel as *specific velocities.*

In further explanation it may be pointed out that x may be taken as representing either that fraction of the total dissolved molecules which is at any given moment in the ionized state, or (which is the same thing) that fraction of the total time during which, on the average, any given dissolved molecule is ionized;* and that the relation of the *working velocity* U (or V) to the *running velocity* πu (or πv) is therefore similar to that which holds between the average speed of a train for its whole journey, including stoppages, and its actual average speed between stations. Briefly, $U = \pi x u$ and $V = \pi x v$.

The values of u and v are not necessarily quite the same for the same ions in different strengths of solution, for the running speed, apart from stoppages, may be, and almost certainly is, affected by the concentration. Nor can it be assumed that all ions are equally affected in this manner: more probably each has what may be called its own frictional coefficient. In other words, the value of the ratio u/v for any given electrolyte may be expected to show some variation according to the strength of the solution, though in dilute solutions these variations may practically vanish. At extreme dilution the maximum values u_∞ and v_∞ are attained. Here, also, x attains its maximum value 1; so that

$$U_\infty = \pi u_\infty \quad \text{and} \quad V_\infty = \pi v_\infty;$$

or the working and running velocities are identical.

The history of the study of ionic velocities divides itself naturally into three chapters. The first may be called the Hittorfian chapter, the second the Kohlrauschian, and the third may be associated with the names of LODGE and WHETHAM.

HITTORF, and those who have since adopted his well-known method, studied the changes of concentration in the neighbourhood of the electrodes and deduced from these the ratios $\frac{U}{U+V}$ and $\frac{V}{U+V}$, or (which is the same thing) the ratios $\frac{u}{u+v}$ and $\frac{v}{u+v}$. These ratios, generally called the transport numbers of the cation and anion, may be conveniently represented in the sequel by the symbols $1-p$ and p. They represent respectively the cation share and the anion share of the current.

The classical work of KOHLRAUSCH consists essentially in the measurement of current and potential difference in an electrolytic cell of known dimensions, and containing a uniform solution of an electrolyte of known concentration. Thus all the values in the general equation, as given above, can be observed except $x(u+v)$, and this can be calculated if the truth of the equations be assumed. From this value of $x(u+v)$ and the value of $\frac{v}{u+v}$, as determined by Hittorfian methods, the separate values xu ($= U/\pi$) and xv ($= V/\pi$) for any given concentration may also be calculated. Further, by working with various strengths of solution up to extreme dilution, x is eliminated and $u_\infty + v_\infty$ obtained. But here it is obviously impracticable to determine the Hittorfian ratio by experiment; so that a certain assumption is necessary in calculating the separate values of u_∞ and v_∞. This assumption is that

---

* Compare WHETHAM, 'Phil. Trans.,' A, 1893, p. 340.

the transport numbers determined in dilute solutions are approximately correct for extreme dilution, and that they may be legitimately so far modified as to lead to constant specific velocities, u_∞ and v_∞, in all combinations of the corresponding ions. KOHLRAUSCH's values are thus obtained.

In general, electrolytes composed of monad ions, such as the chlorides of the alkali metals, are those which yield the best and most consistent results, while compounds containing divalent and polyvalent ions, such as Zn or SO_4, do not behave so conformably with the law represented by the equation. This is shown both by the great alteration in the value of the transport numbers produced by change of concentration in many such cases, and by the fact that polyvalent ions do not appear to afford constant values of u_∞ and v_∞ in their different combinations, on which account they are excluded from KOHLRAUSCH's tables of specific ionic velocities. Whatever may be the full explanation of these apparent contradictions of theory, it is probable that in these cases the ionization is not of such a character that the nature and number of ions of either kind can be deduced direct from the known composition of the solution; in other words, the number of active ions of either kind is not related in the usual simple manner to n.

The third chapter in the history of the study of ionic velocities is that which deals with their direct observation and measurement, and was begun by LODGE in 1885 ('Brit. Ass. Reports,' 1886, p. 389). The great value of his work lay in the ingenious conception of the possibility of actually watching the advance of ions whose colour renders their progress through an otherwise colourless solution visible, and of ions which, though themselves colourless, may be detected in progress by their interaction with indicators; and, further, in the introduction for these purposes of solid jellies in place of ordinary aqueous solutions, and the avoidance by this means of various sources of error, such as convection currents due to gravity and to temperature changes. The actual experiments were, however, of a pioneer character; and the interpretation of them seems to have been vitiated by a misunderstanding of the mechanism of the process on which they depended. It is necessary to point this out; first, because the author's experiments cannot be properly discussed unless this be done, and secondly, because most of the recent text-books dealing with electrolysis quote LODGE's experiment on the velocity of the hydrogen ion as affording the first and chief direct experimental verification of KOHLRAUSCH's theory, and do not direct attention to the difficulty in question.

From the general equation and the explanations already given it is obvious that mere direct measurement of U and V, or of both, cannot by itself give results of exact value for comparison with calculated velocities (xu and xv). At best it can afford only an indication of whether something like the right order of magnitude has been arrived at by such calculation. To obtain data for exact comparison not only U or V, or both, but also the potential slope π, causing U or V, must be correctly measured. But the work of LODGE does not show that this latter was determined in any of his experiments; or rather it shows that the value of π was incorrectly assumed. Thus he assumed, in the hydrogen experiment, that the potential slope causing the observed hydrogen velocity was 1 volt per centim., because the tube was 40 centims. long, and there was a difference of potential of 40 volts between the electrodes. It is obvious, however, that this may be a very misleading assumption where the value of π is required in one particular part of a tube which contains quite different electrolytic solutions in different portions of its length. There is, therefore, no exact information to be obtained by comparing LODGE's observed velocity of from ·0024 to ·0029 centim. per second with KOHLRAUSCH's calculated value ·0032. Considerations of temperature and of concentration, though important, are less so than that of correct potential slope, and therefore may be passed over.

Perhaps the most striking of all LODGE's experiments were those in which he observed the velocities of Cl, Br, or I entering and travelling through a jelly tube from the cathode end, while Sr or Ba travelled in the opposite direction. The original jelly was charged with, among other things, a small proportion of Ag ions to act by partial precipitation as an indicator of the progress of the halogen, and with SO_4 ions to play a similar part towards the new cations. The observed velocities of the former were in all cases approximately double those of the latter; whence LODGE concluded that Cl, Br, and I are, as ions, naturally twice as fast as Sr and Ba. Here again, however, the fact that the observed velocities were caused by unknown, and presumably different, potential slopes necessarily vitiates the conclusion drawn. It will be shown in the sequel that what really determined the interesting and simple velocity ratios observed in this set of experiments was not the specific character of the ions under inspection, but the composition of the intermediate solution into which the Cl and Ba, or similar ions, had not yet penetrated. As, however, this was a mixture, and the indications given of its composition are rather qualitative than quantitative, no results of theoretical value can be deduced.

WHETHAM's method (*loc. cit.*) rendered the use of gelatine unnecessary, as he avoided gravity currents, at all events, by employing a vertical tube in which to observe the rate of migration of the boundary between a coloured solution and a colourless one during the passage of a current, the lighter solution lying above. He also avoided the occurrence of different and unknown potential slopes in different parts of the column by selecting for each experiment a pair of solutions of, as nearly as possible, equal specific resistance. The results so obtained were in very good accord with the calculated velocities (xu or xv) of the same ions in similar solutions of the same concentration, and thus afforded the first exact confirmation of the KOHLRAUSCH theory. But, from the very nature of the method, its application was restricted to a very few cases, as it is obviously not easy to find solutions suitable in all respects.*

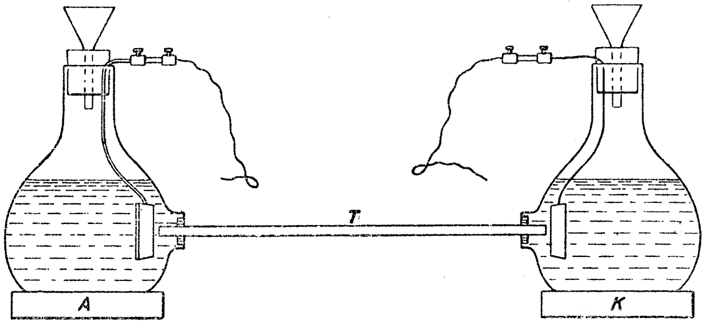
---

* WHETHAM's determination of the velocity of the copper ion, and his comparison of the results with the calculated number, are open to the objection that what he observed was not the copper ion at all, but

New Method of Observing Ionic Velocities.

This method resembles LODGE'S, in so far as it makes use of electrolytic jellies and of visible moving boundaries, but differs from his in its essential principle, as will be explained, and also in the fact that it seeks to avoid such sources of error as change of temperature, the use of mixtures of unknown composition, and the introduction of indicators that react with the ions under observation. The use of gelatine necessarily introduces a small amount of electrolytic impurity which must have some disturbing effect; but the solid gelatine used in making the jellies contains less than ·5 per cent. of its weight of mineral matter, and a plain 12 per cent. jelly was found to have a conductivity so small as to be practically negligible in comparison with those of the salt jellies used for experiment. That this is so is shown by the results obtained; but the fact that the best available gelatine has some conductivity of its own would introduce a real difficulty in any attempt to apply the method to solutions of small concentration.*

Fig. 1.



A sketch of the apparatus is shown in fig. 1. A straight tube of convenient length and uniform narrow bore, the dimensions of which are known, is graduated by

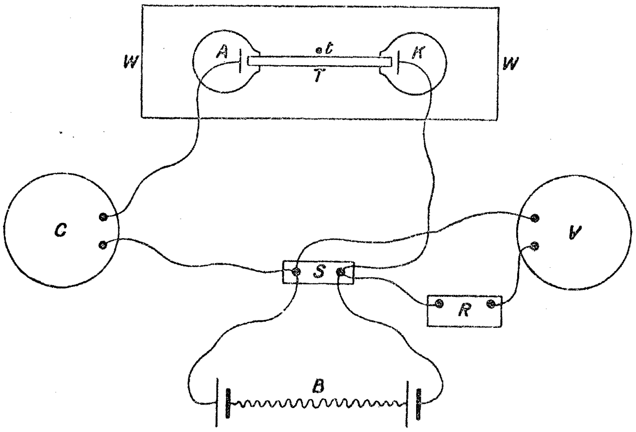
---

a complex cuprammonium ion. He says (*loc. cit.*, p. 344): "The first solutions used were those of copper and ammonium chlorides with just enough ammonia added to each to bring out the deep blue colour of the copper." This is certainly not the colour of the copper ion. In support of this statement it may be mentioned that the deep blue ion of FEHLING'S solution, which has as much right to be called copper as has the deep blue ion of WHETHAM'S experiment, can be proved by direct observation to be a negative ion, which travels towards the anode while its associated K ions carry the current towards the cathode. This observation led the author, in conjunction with B. D. STEELE, to an investigation of the cupro-tartrates, which they propose to communicate to the Chemical Society. Attention is there directed to earlier evidence of the same fact adduced by others.

* Some trials were made with agar-agar in place of gelatine. It proved inferior, however, in respect to freedom from electrolytic impurity; and, though it affords jellies of high melting-point, and otherwise admirable, they have the fatal habit, after setting firm in the tube, of contracting away from its walls and exuding an aqueous solution. It is then easy to blow the whole cylinder of jelly out of the tube by the application of slight pressure at one end. The gelatine jellies used by the author showed no such tendency; nor did any extension from the tube occur in the course of the experiments in the manner described by LODGE. The difference may be due to the use of stiffer jellies, and particularly to the use of a constant temperature bath to prevent heating of the jelly by the current.

an etched scale from end to end. The two ends of the tube can be fitted, water-tight, into the short side necks of two cells of relatively large capacity, so that the tube forms a horizontal connection between them. For an experiment the tube is filled (by means of tubular elbow-pieces and rubber connections) with a molten jelly, which is then allowed to set at the experimental temperature. This jelly contains a known quantity per cub. centim. of the salt, whose ionic velocities it is desired to observe, *e.g.* KCl. The ends of the jelly, after removal of the elbow pieces, are shaped true with a knife; and the tube is then connected with the empty cells, and the whole apparatus is placed in a large bath of water, so that only the mouths of the cells remain above the surface. The temperature of the bath is kept constant at any desired point below the melting-point of the jelly, *e.g.* 18° C. The graduations of the tube are easily read through the water in a good light, and parallax is avoided by having the tube marked both back and front. The electrodes, which have surfaces very large in comparison with the bore of the tube, are placed in the cells and fixed so as to be close to the ends of the tube without touching it. They are connected with a battery of sufficient voltage, as constant as possible. A low-resistance galvanometer serves to register the current, and one of high resistance is arranged in parallel circuit to indicate the voltage. Fig. 2 shows the whole arrangement diagrammatically. The main circuit is completed and the experiment started by filling the cells with aqueous solutions, and a stop-watch is started simultaneously.

Fig. 2.



$W\ W$ = constant temperature bath.
t = thermometer.
T = jelly-tube.
A = anode cell.
K = cathode cell.
C = low resistance galvanometer for current measurement.
V = high resistance galvanometer for voltage measurement.
R = added resistance in voltmeter circuit.
S = mercury connections.
B = battery.

The nature of these cell solutions is all-important to the theory and practice of the method. They may be distinguished as the anode solution and the cathode solution respectively. They must fulfil four conditions, as follows:—In the first place, each must possess a strong and characteristic colour; but the anode solution must owe its colour to its cation, and the cathode solution must owe its colour to its anion. In the second place, the coloured ions must not be such as to act chemically on the salt-jelly, so as to form a precipitate in the tube through which they are to travel. In the third place, the cell solutions themselves must not, during an experiment, undergo such chemical change as to lead to the production of a new sort of cathion (*e.g.*, H ions) in the anode cell, or of a new sort of anion (*e.g.*, OH ions) in the cathode cell. The fourth condition, which will be explained more fully later, is that the coloured ions must be specifically slower than the corresponding ions of the salt-jelly. A suitable anode solution in most cases is made with copper sulphate, provided that the anode be made of copper, to prevent, or at least minimise, the production of free acid, *i.e.*, of H ions. A generally suitable cathode solution is made with potassium chromate and sufficient bichromate to prevent the formation of free alkali, *i.e.* of OH ions.* The cathode should be of platinum. The strength of these solutions should be known, but need not be proportioned to that of the salt in the jelly tube. All that is necessary is that there shall be plenty of coloured ions in the neighbourhood of the electrode and tube for the carriage of the current into the latter.

During the experiment, the procession of the original cations (say K) of the jelly is followed through the tube by a corresponding procession of blue Cu ions, while the opposite procession of original anions (say Cl) is followed by a corresponding procession of yellow CrO_4, or of mixed CrO_4 and Cr_2O_7. Thus the tube is soon seen to contain blue ($CuCl_2$) jelly at one end, colourless (KCl) jelly in the middle, and yellow (K_2CrO_4) jelly at the other end, of which the first and third continually grow in length at the expense of the second, intermediate, part. The ratio of the lengths of blue and yellow is constant, and these eventually meet, to the extinction of the colourless portion. There is no mixing of K with Cu, nor of Cl with CrO_4. The blue and yellow boundaries remain quite clear cut, and may be sharply located at any points in their course, the former marching steadily through the solid jelly towards the cathode, the latter towards the anode, till they meet. It may be mentioned that the blue boundary is always slightly convex in the direction of its migration, while the yellow boundary is always slightly concave, so that each presents a meniscus with its convexity towards the cathode.

At intervals throughout the experiment observations are taken of the positions of the blue and yellow boundaries, of the time, of the current, and of the voltage; also of

---

* The passage of CrO_4 and Cr_2O_7 ions into the jelly-tube, where they meet with K or other cations, does not chemically affect the gelatine. In fact, a transparent orange half-normal bichromate-jelly, containing 12 per cent. of gelatine, may be prepared, solidified, and remelted, without any precipitation of the gelatine; but precipitation occurs on the addition of free mineral acid.

the bath temperature, which should keep constant. With constant E.M.F. the current and the velocities steadily diminish in a manner determined by the nature and strength of the salt-jelly, but they remain in direct proportion to one another. The experiment is terminated when the two boundaries meet, which they do at a point that can always be predicted with very considerable accuracy from the first readings.

The essential principle of the method may now be explained. The visible moving boundaries mark respectively, not only the rates of advance of the foremost Cu and CrO_4, but also those of the rearmost K and the rearmost Cl. These are themselves invisible, but the immediately following coloured ions may be taken as their indicators. Now the intermediate colourless part of the jelly is at the start of uniform composition and remains so throughout the experiment, however much its length may be curtailed by the progress of the blue and the yellow; so that (to use the same symbols as before) n and x have constant values from start to finish and in all parts of the colourless jelly, while π, which diminishes as the experiment proceeds, has yet always the same value there, whether the part near the blue boundary or the part near the yellow boundary be considered. Therefore the rearmost K at the one end and the rearmost Cl at the other are comparable in all respects; and a comparison of their working velocities U and V, made visible by the indicators, gives at once the ratio u/v for the particular concentration employed. Obviously also the result may be put in the form of HITTORF's transport number $\frac{v}{u+v}$ (or p), and may be compared with the values obtained by the indirect Hittorfian method. Of course, the observed U is also that of the copper ions and the observed V that of the CrO_4 ions; but the experiment affords no indication of the corresponding values of π and x, which are certainly very different in the two cases. Hence there is nothing gained by regarding the observations from this point of view, as has already been pointed out in connection with LODGE's experiments.

While the first result is the determination of u/v for the original salt, a second is the testing of the general equation $C = A\frac{n}{\eta}(U + V)$, or, if its truth be assumed, of the efficacy of the method itself. For each quantity is independently determined, and, since all may be expressed in the same (C.G.S.) units, the value 1 should be obtained by dividing the left-hand side by the right.

The experiment, as carried out, also affords data for the determination of the working velocities per unit potential slope, viz., of $U/\pi = xu$ and $V/\pi = xv$. For the total resistance for each position of the boundaries is given by the readings of voltage and current; and, as the increase of total resistance is directly proportional to the diminution of the length of the colourless jelly, and as a constant correction can be introduced for the resistance of the galvanometer, and approximately also for that of the solutions between the electrodes and the ends of the tubes, the resistance of the tube full of the colourless jelly, and therefore of $x(u+v)$, follows. Obviously the same result can be obtained by separate measurement of resistance by KOHLRAUSCH's method, and this has certain advantages. Arrangements are also possible for the direct measurement of π in the various parts of the tube during the progress of an experiment by means of wires sealed through the walls of the tube, but this would introduce considerable complication. The velocities per unit potential slope, obtained as above, are not dealt with in the present paper; but it may be mentioned that they show (in accordance with conductivity results obtained by ARRHENIUS and others) a considerable percentage reduction in solid jelly as compared with aqueous solutions, but a reduction which is, at all events approximately, the same for different salts. The values of the relative velocities of the different ions should, therefore, be fairly comparable with those found by the older methods.

It is clear that any value which the method may have must depend on the justice of the assumption that the observed velocities of the boundaries are determined by, and may be taken as indicative of, those of the intermediate colourless ions, or that no mixing of these with their coloured pursuers occurs. In support of this there are both experimental facts and theory.

At the end of an experiment in which the tube was originally full of a strong chloride jelly, the author has frequently melted out the yellow part (without disturbing the blue, which consists of $CuCl_2$), and tested it for chlorine without finding more than, at most, a barely perceptible trace. After one experiment with KCl, in which a wide tube was employed, so that the quantities were considerable, only a doubtful trace of potassium could be found in the blue part, after separation of the copper by H_2S, evaporation with sulphuric acid, and ignition to destroy organic matter.

Less direct, but no less striking, evidence to the same effect is afforded by the fact, established by preliminary experiments, that the ratio of velocities of the blue and yellow boundaries is practically the same in different experiments with the same concentration of the same salt, no matter how the dimensions of the tube be varied. There is also the fact, already stated, that this ratio in any one experiment remains practically constant from first to last. Very slight variations, it is true, do occur, attributable most probably to the presence of impurities in the gelatine or in the salts employed, or to slight heating by the current in spite of the constant temperature bath. But such small deviations from perfect constancy need not be considered at present.

A third line of evidence is found in the fact that, while it is possible to greatly vary the relative velocities of the same indicators by using different salt-jellies, it is found that the relative rates of advance of the two boundaries remain the same with different indicators and the same salt-jelly. The latter part of this statement has, however, so far been tested only by the substitution of potassium ferrocyanide, and by that of a tartrate solution, for the usual chromate in experiments with potassium sulphate and sodium chloride. In the tartrate experiment the indicator was, of course, quite invisible in itself, but it met the copper and formed a visible precipitate across the tube at the exact point calculated from previous experiments made in the usual way. The relative velocities of Na and Cl were thus given the same value, whether Cu and CrO_4 or Cu and $C_4H_4O_6$ were used as indicators.*

Besides these experimental indications that there is no commingling of the ions at the blue and yellow boundaries, there are theoretical reasons in favour of the same conclusions, *provided that the coloured ion is specifically slower than the one it is following.* This has been already mentioned as one of the requisite characters of a satisfactory indicator. Imagine naturally slow Cu ions travelling behind naturally faster K ions, with Cl ions travelling past both in the opposite direction. If Cu lag behind K, or K run away from Cu, a region will be established where cations are deficient, a state of affairs that must immediately correct itself by reason of the consequent E.M.F. If, on the other hand, they keep pace with one another, as in fact they do, it must be by virtue of a steeper potential slope in the blue. If now some K ion accidentally lags behind its fellows, it will find itself in this region and be at once hurried forward again; while any ambitious Cu ion, trying to penetrate

---

* The precipitates formed across the tube by the meeting of Cu ions with CrO_4 ions and $Fe(CN)_6$ ions are of the nature of the semi-permeable membranes used by TRAUBE and PFEFFER in the study of osmotic pressure. An interesting fact has been observed with both these membranes. They are first seen as fine transverse films across the tube, but, if the experiment be not stopped, they rapidly thicken up till they form discs about half a millim. wide. Simultaneously the galvanometer shows a rapid fall of current, which becomes almost nil within a very few minutes of the first meeting. If now, or later, the current be reversed, the galvanometer deflection rapidly goes up almost to its previous value, though the membrane remains apparently quite unaffected even when the reversed current is maintained for hours. By again reversing it the phenomena may be repeated, though the current does not now fall off immediately. The explanation suggests itself that the membrane is impervious to the ions (Cu and CrO_4 or $Fe(CN)_6$) which have produced it, but not to other ions such as K and Cl. Before the first reversal of the current, only Cu ions can reach the membrane from the anode side and only CrO_4 (or $Fe(CN)_6$) from the cathode side, and these cannot pass. After reversal, K and Cl, or other corresponding ions respectively, carry their charges to and through the membrane. These are now on the wrong side; so that when the current is again reversed, it is some time before the original state of affairs is restored and the current again cut down. If, after the membrane is first completely formed, the circuit be broken and everything left *in situ* for 24 hours or so, it is found that, on re-connecting without reversal, a very fair current will pass; but it does not last long. In all probability this is due to simple diffusion through the membrane, by which a little K and a little Cl find their way across to the parts of the tube previously free from them.

It is a curious fact, no certain explanation of which has yet been arrived at, that when the intermediate salt is a sulphate instead of a chloride, the copper and chrome ions do *not* form a membrane on meeting, but simply intermix with production of a greenish colour; nor is the current cut down. This difference of behaviour has been consistently manifested in all the experiments recorded in this paper. Yet copper sulphate and potassium chromate solutions precipitate copper chromate when mixed. The usual membrane was, however, obtained with a K_2SO_4 jelly and Cu and $Fe(CN)_6$ indicators.

The making of osmotic pressure apparatus might be improved by depositing the membrane electrolytically in the walls of the pot, previously charged with a potassium chloride jelly. Current readings would give a sure indication of the condition of the membrane during and after its formation.

the K region, will find itself forced to drop back. This explanation of the sharpness of certain margins was advanced by WHETHAM (*loc. cit.*), but bears repetition here. It comes to this—that the boundary will possess stability if the necessary condition be fulfilled, but not otherwise. As a matter of fact it has been found by experiment that the colourless SO_4 ion following the yellow CrO_4 ion through a jelly tube overtakes it continuously, so that there is *no* boundary visible, but only a gradual fading out of colour. A similar result was got also by following the blue Cu ions with colourless Zn ions through the tube: again there was *no* boundary, but the colour gradually faded out. These cases probably illustrate the non-fulfilment of the condition that the foremost ion must be by nature the faster.

Theory of the Moving Boundary.

It is easy to deduce the behaviour of the ions on each side of a moving boundary from the fundamental equation given at the beginning of this paper, and from the fact that the visible (coloured) ion keeps pace with the invisible (colourless) ion in front of it.

Let the boundary in question be that between visible and invisible cations travelling with the current and matched by invisible anions, all of one kind, travelling against it. Let the symbols be used with the same meaning as before, but let those applying to the coloured part of the jelly be marked with dashes to distinguish them from those applying to the colourless jelly on the other side of the boundary.

Since equal currents cross all sections of the tube at the same time,

$$n'(U' + V') = n(U + V).$$

But

$$U' = U.$$

Hence

$$\frac{n}{n'} = \frac{U'}{U' + V'} \times \frac{U + V}{V} = \frac{1 - p'}{1 - p}.$$

Also

$$\frac{V'}{V} = \frac{n}{n'} \times \frac{V'}{U' + V'} \times \frac{U + V}{V} = \frac{p'(1 - p)}{p(1 - p')}.$$

Thus the concentrations of the salts in the two portions of the jelly are directly as the corresponding cations' transport numbers; and the working velocities of the common anion on the two sides of the boundary are directly as its own transport numbers, and inversely as those of the corresponding cations. Since $\frac{p'(1-p)}{p(1-p')} = \frac{uv'}{u'v}$, and since v and v' may be considered for practical purposes as of equal value, the second of these rules may be put more simply, though not quite so correctly, in the form $V'/V = u/u'$; or the working velocities of the common anion are inversely as the specific velocities of the corresponding cations.

It is possible to test the foregoing conclusions by analytical experiments conducted as follows:—The exact ratio of the velocities of the K and Cl ions having been first found by experiments with two coloured indicators in the usual manner, a tube of suitable length and considerable capacity is marked with a file at the place where these (or other) indicators should meet. It is then filled with the KCl jelly and connected with the cells, in *both* of which is placed copper sulphate solution. A copper anode and a platinum cathode are used. During the progress of the experiment, two boundaries travel as usual, though only one is visible, viz., that between KCl and $CuCl_2$. It will, however, meet the other, *viz.*, that between KCl and K_2SO_4, at the mark previously made; and the circuit must be broken when the blue boundary reaches this point. The cathode will have gained in weight by as many milligramme equivalents of copper as there were milligramme molecules of KCl originally present in the whole tube; and this may be taken as a test of the correctness of the experiment. That it is so, is evident from the fact that there will have travelled across that section of the tube, where the meeting of the margins occurred, all the K ions originally present on one side of it, and all the Cl ions originally present on the other, but nothing else. These are together equal in number to the total K, or to the total original KCl molecules. The tube is cut in two at the mark as soon as the experiment is over, and the contents of each part are then analysed separately, Cl and Cu being estimated in the part nearest the anode, and SO_4 and K in the other. The results may be checked by estimating the Cl that has escaped into the anode cell, and the K that has escaped into the cathode cell. The results give the value of n' directly for each end of the tube, with which the value of the original n may be compared. The relative specific velocities (u/v) for Cu and Cl, and for K and SO_4 follow from consideration of the exchanges at the anode end and the cathode end respectively; and, as those of K and Cl are already known, as determining the meeting point, the specific velocities of all four ions may be compared with one another.

One such experiment has been carried out, but the accuracy of the analytical results was, to some extent, spoilt by unforeseen difficulties that cropped up in the course of the work, due in part to the presence of gelatine in the solutions of the tube-contents, and in part to the formation of cup*rous* chloride in the *anode* cell and on the anode. This formation of cuprous chloride has since been observed in other experiments. It may be seen on the anode as a white crust after it has been washed with water, alcohol, and ether; and its formation there causes the anode to lose *less* than the calculated weight instead of more, as is usual. It is intended to repeat the experiment described above, taking all precautions to ensure accuracy. In the meantime it may be said that the results, though rough, tended entirely towards the confirmation of the theory. Thus they showed, as might be expected, that very little change of concentration or of K velocity occurs across the KCl/K_2SO_4 boundary, but that at the blue boundary the Cl approximately doubles its velocity and reduces its concentration to about two-thirds. These figures (which are only rough approximations) agree, according to the formulæ already given, with a chlorine transport number (p') in $CuCl_2$ of ·67, taking its value (p) in KCl as ·5. The author is not aware of any Hittorfian experiments with $CuCl_2$; but, to judge from those made with other chlorides and with other copper salts, this value for p' can not be far wrong.

Experimental Details.

The following facts, in addition to those already stated, may be recorded concerning the series of experiments, the results of which are tabulated in this paper.

Gelatine.—The small conductivity of this has been already referred to. As additional evidence that its impurities are unimportant, it may be mentioned that practically no difference is observed in the value of u/v got for the same concentration of the same salt, whether the jelly contain, as usual, 12 per cent. of gelatine or only half that amount.

Salts.—The salts used were all re-crystallized, and were what is generally called pure; but no very special purification was attempted, as the present object was rather to test the method in a preliminary manner than to get the most accurate quantitative results attainable.

Jellies.—These were made as follows. The required quantity of the salt was weighed into a beaker, dissolved in water, and washed into a stoppered 50 cub. centim. flask containing 6 grammes of gelatine in small pieces. The flask was warmed till the gelatine had dissolved, water was added to the mark, and the contents mixed and cooled. The exact volume was then made up with water and, after re-warming and thoroughly mixing, the jelly was ready for use. It was always made fresh for each experiment. For the experiments with lithium chloride, which is very deliquescent, the calculated quantity of carbonate was dissolved, with all precautions, in slight excess of hydrochloric acid, and the chloride was obtained neutral in reaction by evaporation and drying at about 150° C. The jellies were all clear when solid and were transparent in the tube; except the twice-normal lithium sulphate one, which was, in bulk, very slightly opalescent. The melting-points were by no means all the same, but all were completely solid at the temperature employed.

Temperature of the Bath.—This was in all cases very close to 18° C., the average in each experiment lying below rather than above that point. The extreme variation during any experiment did not exceed ·5° on either side of 18°, and was generally less.

Cell-solutions.—These were always of normal strength, *i.e.*, the anode cell contained $\frac{1}{2}$ $CuSO_4$ gramme per litre, and the cathode cell contained $\frac{8}{18}$ $K_2CrO_4 + \frac{1}{18}$ $K_2Cr_2O_7$ gramme per litre. Each cell contained 100 cub. centims.

The Tube.—This was the same in all the experiments tabulated. Its ends were ground smooth, and its bore uniform. Its length was 15 centims. and its area of cross-section (A), which was determined carefully by the weight of its mercury contents, was ·0378 sq. centim. It was divided into half centims. on both sides to avoid parallax, and the scale divisions were picked out with red. They were easily seen through the water against the white porcelain bottom of the bath. It was quite possible to divide by eye to less than half a millim.; but only the readings made when the boundary was crossing a scale division have been used in drawing the curves. The walls of this tube were rather thicker than is advisable, since it is important to maintain free thermal communication between the jelly and the bath. Nearly 1½ centims. at each end of the tube were hidden in the cell neck, so that readings, after the start, could not be made till the boundaries reached that mark.

The Battery employed consists of 48 cells of zinc | potash | copper oxide, arranged in one series and giving about 40 volts. It is very constant, whether in use or not, even many months after setting up. The current, in the experiments quoted, varied from about 2 to about 13 milliamperes.

The Time for an experiment, from the starting of the current till the meeting of the boundaries, varied from nearly three hours to over seven. The tube was under constant observation. Time readings were made to the nearest quarter-minute.

TABLE I.—Experimental Results.

Salt.	n	$\frac{u}{v}$	$\frac{v}{u+v}$	p	$\frac{C\eta}{An(U+V)}$
NH_4Cl	1	1·041	·490	·508 – ·517 (H)	1·005
KCl	·5 1 3	1·021 1·041 1·069	·495 ·490 ·483	·503 – ·516 (H)	1·017 1·032 1·014
NaCl	·5 1 2	·671 ·681 ·703	·598 ·595 ·587	·622 – ·648 (H)	1·023 1·013 1·022
LiCl	·5 1	·456 ·471	·687 ·680	·674 – ·773 (K)	1·004 1·013
½ K_2SO_4	·5 1	1·143 1·143	·467 ·467	·498 – ·499 (H)	1.002 ·951
½ Na_2SO_4	·5 1	·765 ·765	·567 ·567	·634 – ·641 (H)	1·005 ·950
½ Li_2SO_4	·5 1 2	·538 ·508 ·515	·650 ·663 ·660	·595 – ·649 (K)	1·021 1·006 ·907
½ $MgSO_4$	·5 1 2	·463 ·422 ·442	·684 ·703 ·693	·656 – ·762 (H)	·942 ·861 ·807

Experimental Results.

In Table I., the first column gives the salt used, the formula specifying the quantity required, in grammes per litre, for a normal solution, *i.e.*, for one in which $n = 1$. The values of n given in the second column refer to the number of gramme formula weights per litre. In the third column are given the ratios, u/v, these being the values calculated from the observed meeting points of the blue and yellow boundaries. In one case, however, viz., that of half normal KCl, this final reading was rejected and the ratio calculated from the readings immediately preceding it; for the experiment, otherwise one of the best as regards constancy of u/v, was spoilt just at the end by a disturbance that had a very visible effect on the meeting point, spoiling the boundaries and shifting the film formation 1 millim. This was the only case of the kind. In the fourth column the results are expressed as $\frac{v}{u+v}$, the transport numbers of the anions; so that they may be compared with the corresponding values obtained for aqueous solutions by the indirect Hittorfian method. These latter are given, under p, in the fifth column, where the experimenter's name (HITTORF or KUSCHEL) is signified by its initial letter. To be strictly comparable, these values should be for the same concentrations; but, as such data are not in most cases available, the extreme values of p are given, the most dilute value being placed first. For most of the salts these extreme values of p refer to concentrations outside those employed in the jelly-tube experiments, so that they may be taken as including the values for corresponding concentrations. Two points may be noticed. The first is that, while the author's results for lithium and magnesium salts fall within the p limits, those found by him for sodium, potassium, and ammonium salts give smaller anion transport numbers than the smallest value obtained by HITTORF. The second point is that the new values for the chlorides tend to decrease slightly as the concentration increases, whereas the opposite tendency is manifested by the Hittorfian values. There is, however, a general similarity that is evident on comparing the two columns. The last column of the table gives the values of $\frac{C\eta}{An(U+V)}$, for the calculation of which all the quantities were expressed in C.G.S. units. As already explained, the approximation of this value to unity may be taken as a test of the method, and it is evident that the result is, on the whole, satisfactory. Only the stronger sulphate solutions give too small values; and it is notable that magnesium sulphate, which contains two divalent ions, is abnormal even in the most dilute solution employed, though it would evidently behave normally with greater dilution. It has already been pointed out that it is salts of divalent and polyvalent ions that have always proved least consistent with theory.

For the calculation of the numbers in this last column it was necessary to obtain strictly comparable current and velocity values. Now those directly obtained in an experiment are not comparable, those of C referring to current at given instants and those of U and V to average velocities for a long period of time; and it has been already told how both current and velocity steadily diminish at a rate determined by the nature and strength of the jelly. Either, then, an average current value must be obtained, or velocity values at definite points. Both methods have been used. For the former, since the quantities involved were too small to admit of the use of a voltameter, the average current was calculated from the area of the time-current curve. This was done for all the experiments except those with lithium and magnesium sulphates; and it was found in all cases that the average current value was attained at a point very close to that at which the indicators had travelled half their distance. With lithium and magnesium sulphates the current and velocities were so nearly constant that an appreciable error could hardly occur by assuming this as the correct point. The numbers given in the table were calculated in this manner.*

The other mode of calculation, which is a more rigid test of the experimental method, was applied to only two cases, but with satisfactory results. The values of U + V at intervals throughout the experiment were deduced by drawing tangents to a curve got by plotting the added lengths of the coloured portions of the tube against the time. The current-time curve gave the corresponding current values. Numerous values of the ratio $\frac{C}{U+V}$ were thus obtained, which in the case of half-normal KCl were constant to within 1 per cent. of their mean value, and in the case of twice-normal KCl were nearly, but not quite, so consistent. These mean values corresponded

---

[*] A rather frequent occurrence in these experiments may be mentioned here. It is one which, at first sight, looks as if it must be fatal to them, but which has been proved to be really unimportant. Flaws, having the appearance of small bubbles or cracks, are apt to appear in the jelly towards the end of an experiment. They seldom occur till the boundaries have done most of their journey, and they generally appear near the centre of the tube. In many experiments they do not appear at all, but when a flaw does come it is apt to extend in a rather curious manner. This occurrence of flaws at once causes a reduction of current, and it is easy to locate their first appearance in the time-current curve, even were it not noted at the time, as was always done. It has, however, very little, if any, effect on the velocities of the boundaries; and the ratio of these (u/v) is absolutely unaffected. It is indeed striking to watch the calm indifference with which these flaws are treated by the travelling colour boundaries, and to contrast the behaviour of the latter with that of the galvanometer needle. The facts are explicable on the assumption that the flaws reduce the current by reducing the value of A, leaving the current density (C/A), and therefore the actual velocities, as well as their ratio, unaffected. It is obvious that, in such a case, the experiment must be regarded as finished as soon as flaws appear, where the object is to test the truth of the equation involving the original, and only known, value of A; but that, for the determination of u/v (or of p), the experiment may be continued as usual till the boundaries meet. These rules have been observed in all cases. The occurrence of flaws of the kind described was noticed by LODGE (*loc. cit.*). Their cause has not been ascertained. Whether they will occur or not in any given experiment almost seems to be decided by caprice.

respectively to the figures 1·015 and 1·002 for $\frac{C\eta}{An(U + V)}$, in place of 1·017 and 1·014, found by the other method and given in the table.

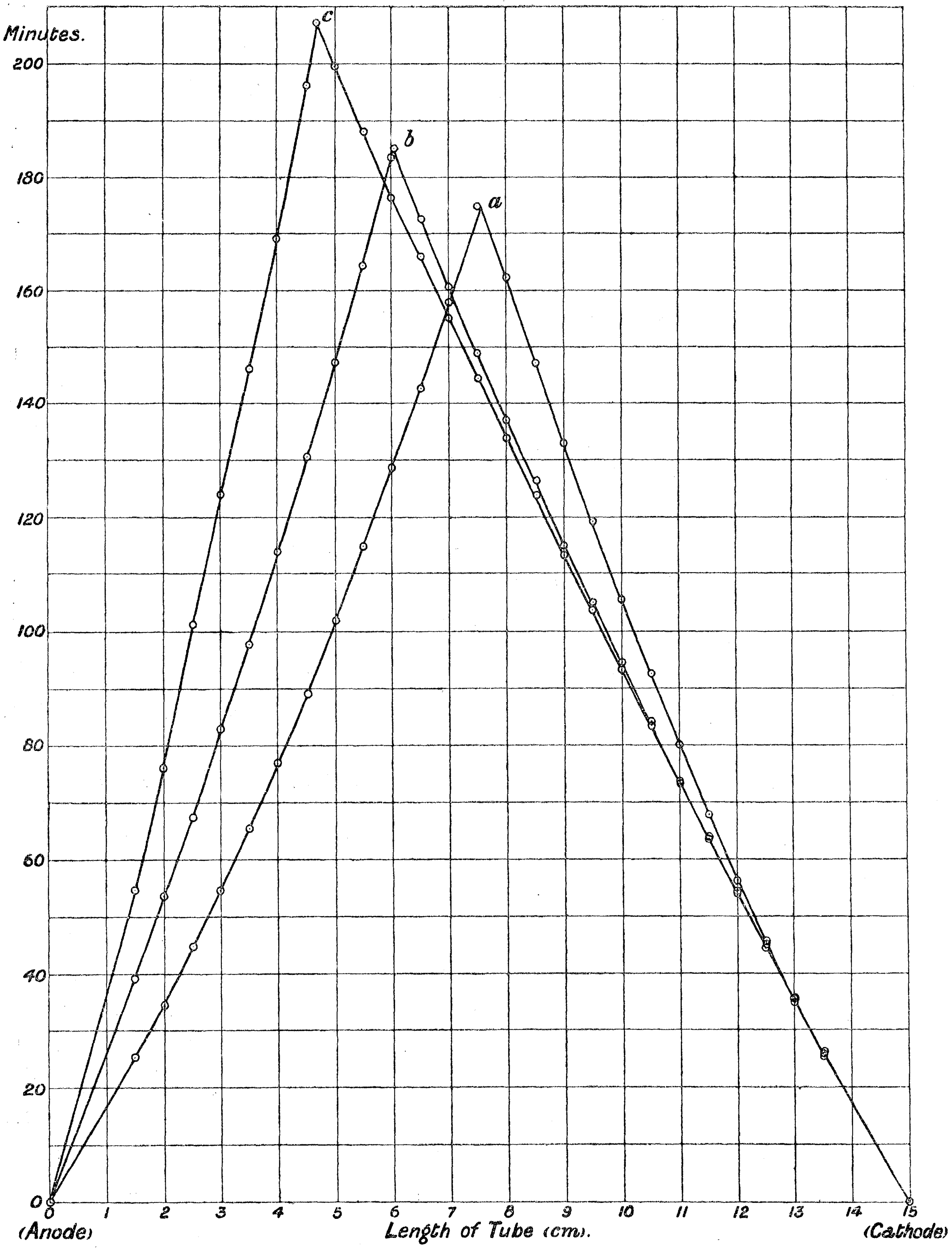
TABLE II.—Relative Velocities of the Ions.

	Chlorides.			Sulphates.			KOHLRAUSCH.		
	n = ·5.	n = 1.	n = 2.	n = ·5.	n = 1.	n = 2.	1879.	1885.	1893.
K	100	100	100	100	100	...	100	100	100
Na	65·7	65·4	65·8	66·9	66·9	...	65	62	68
Li	44·7	45·2	...	47·1	44·4	45·2	44	46	55
NH_4	...	100	...	...	...	...	98	96	100
$\frac{1}{2}$Mg	...	...	...	40·5	36·9	38·7	...	...	...
Cl	97·9	96·1	93·6	...	...	...	102	104	105
$\frac{1}{2}SO_4$	...	...	...	87·7	87·7	87·7	...	...	...

In Table II., the results of the same experiments are given in such a form that the specific velocities of the different ions may be compared with one another and with those calculated for the same ions by KOHLRAUSCH. From the found values of $\frac{u\,(\mathrm{K})}{v\,(\mathrm{Cl})}$ and $\frac{u\,(\mathrm{Na})}{v\,(\mathrm{Cl})}$, the value of $\frac{u\,(\mathrm{Na})}{u\,(\mathrm{K})}$ may evidently be deduced, and so with the others. By making $u\,(\mathrm{K})$ at each concentration equal to 100, comparable values are obtained. These are given for the chlorides and sulphates employed. Under KOHLRAUSCH's name are given, in parallel columns, the relative values of his specific velocities for the same ions, also reduced to the basis $u\,(\mathrm{K}) = 100$. The figures in the first of these columns correspond to the specific velocities calculated by him in 1879 ('Ann. Phys. Chem.,' vol. 6, p. 172) by extrapolation to extreme dilution from experiments with solutions the strength of which was not less than half normal. The figures in the second column correspond to the velocities given by him in 1885 ('Ann. Phys. Chem.,' vol. 26, p. 214) for solutions one-tenth normal, while the figures in the last column correspond to his well-known specific velocities at infinite dilution, calculated in 1893 ('Ann. Phys. Chem.,' vol. 50, p. 408) by extrapolation from his later work with exceedingly dilute solutions.

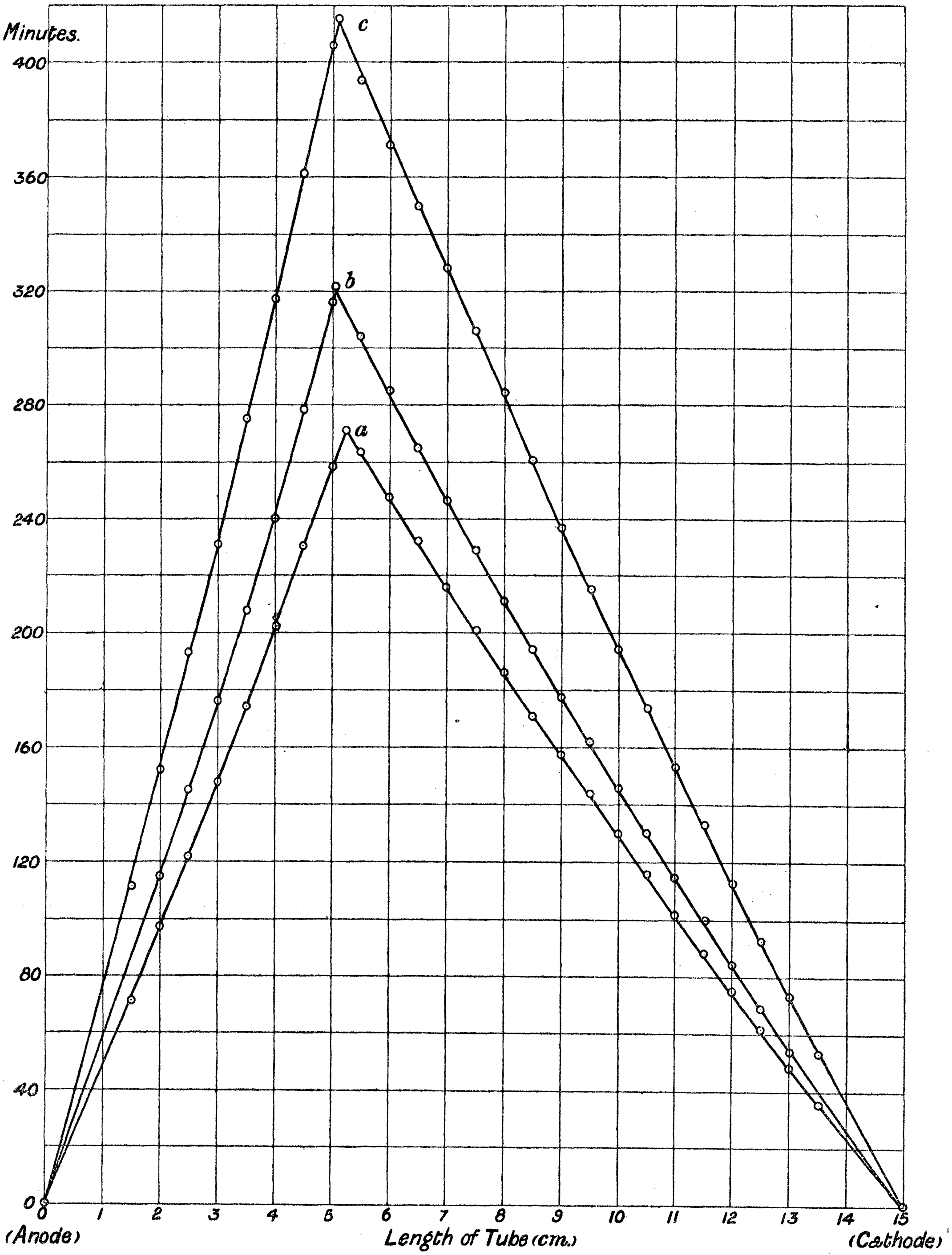
The theoretical considerations advanced in the earlier part of this paper show that no exact agreement need be expected between the values for the same ion in the various columns of this Table. A general agreement might, however, be expected; and it is

Fig. 3.



Half-normal KCl (a), NaCl (b), LiCl (c) jellies.

Fig. 4.



Half-normal (a), normal (b), and twice-normal (c) Li_2SO_4 jellies.

certainly seen to exist. Moreover, one would naturally expect the author's results to show better agreement with KOHLRAUSCH'S 1879 values than with his later ones, as the former were deduced from the conductivities of normal and half-normal solutions. This is notably the case, and is conspicuous in the lithium values. The only striking difference is that seen when the relative values of cation and anion are compared, which would be still more pronounced were one to include SO_4 in the KOHLRAUSCH columns; but he himself excludes it. This difference is, however, but a repetition of what has been already noticed in the comparison of the results obtained with HITTORF'S transport numbers; for KOHLRAUSCH bases his calculations on HITTORF'S value of p in KCl.

The character of the observations on which the author's values are based will be best judged by inspection of the specimen curves shown in the accompanying plates.

In fig. 3 are shown the curves for half-normal chlorides of potassium, sodium, and lithium; and in fig. 4 the curves for the three strengths of lithium sulphate. In all of these figures the right-hand curve represents the progress of the yellow boundary, *i.e.*, of the anions, while the left-hand curve represents the simultaneous progress of the blue boundary, *i.e.*, of the cations. The gradual narrowing of the figure enclosed by the right-hand and left-hand curves represents the colourless jelly originally filling the whole tube, and becoming curtailed till it vanishes at the apex. The curvature, which corresponds to diminishing velocity (and current), is seen to depend on the nature of the salt used—to be most marked in the case of the best conductor (KCl), and to nearly disappear in that of the worst (Li_2SO_4). Fig. 4 shows the regular result of increased concentration, which decreases the ionization (x), and therefore the values of the working velocities (U and V).

The displaced point at the apex of the half-normal KCl curve, already described, is shown in fig. 3; and in fig. 4 it may be noticed that the later readings of the yellow boundary were slightly inaccurate, this being due to the fact that the experiment, which was a long one, had to be finished by gas light.

In conclusion, the author desires to express his great obligation to his colleague, Professor T. R. LYLE, for much kindly suggestion and practical aid.