

V. *Ionic Velocities.*

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Communicated by Professor J. J. THOMSON, F.R.S.

Received October 19,—Read November 24, 1892.

THE most obvious and regular result of passing a current of electricity through the solution of a salt is the simultaneous appearance at the two electrodes of products of chemical decomposition. Since the intervening solution is unaltered, and the products appear only at the electrodes, the motion of the parts of the salt in opposite directions through the solution is a necessary hypothesis, and the idea of ionic velocity is at once suggested.

The facts of ordinary chemical action, as well as those of electrolysis, require us to suppose that a continual molecular interchange of partners is going on, but how this takes place, whether by means of “free ions” or by means of the fractional number of collisions which the mechanical theory teaches us will occur with sufficient violence to bring about separation and possible rearrangement, remains an open question, and one which it is not necessary to consider for our present purpose. The point is that such a motion in opposite directions must occur, and the ions move with a definite average velocity through any given solution. This is independent of any particular hypothesis as to the nature of the active electrolytic molecule, and need not commit us either to the “dissociation” or to the “chemical” theory.

In order to explain the facts of “migration” HITTORF (*Pogg. Ann.*, vols. 89, 98, 103, 106, 1853 to 1859) supposed that the velocities of opposite ions were different, which would produce the observed alterations of concentration round the electrodes according to the obvious and well-known law.

Later, KOHLRAUSCH introduced the idea of a definite specific ionic velocity for each ion, independent of the nature of its combination (*Wied. Ann.*, vols. 6 and 26), except in so far as its motion is affected by the different resistance offered by the different media through which it travels. These differences will disappear at infinite dilution, and the values obtained by extrapolation then show that the specific ionic velocities of the same ion, as deduced from observations on various salts containing it, are, as nearly as can be observed, identical. As it is in examination of this idea that most of the experiments, presently to be described, were made, it will be convenient to reproduce KOHLRAUSCH's theory in some detail. The experimental portion of his

work consisted of a splendid series of determinations of the conductivities of salt solutions. Assuming that all the salt molecules dissolved are actively concerned in conveying the current, from simple notions of convection combined with OHM's law he calculated the relative velocity of the two ions which would be necessary to give the observed conductivity.

Thus (following Dr. LODGE's abstract in the 'B.A. Report,' 1886), let n^3 be the number of active molecules in 1 cub. centim., q the total charge of electricity of whichever kind possessed by the ions of each active molecule, and U the relative velocity with which the opposite ions are sheared past each other by a potential gradient, dv/dx ; we shall then get from considerations of convection n^3qU for the intensity of current (or quantity of electricity conveyed per second through unit area normal to the flow), and from OHM's law $k(dV/dx)$ for the same quantity, where k is the conductivity of the unit cube, therefore

$$k \frac{dV}{dx} = n^3qU.$$

If N be the number of monad gramme equivalents of the active substance present in the unit cube, and η the electro-chemical equivalent of hydrogen

$$N \frac{1}{\eta} = n^3q;$$

therefore

$$\gamma = k \frac{dV}{dx} = n^3qU = \frac{NU}{\eta};$$

therefore

$$U = \frac{k}{N} \eta \frac{dV}{dx} = \frac{\eta}{N} \gamma.$$

Whence the arithmetical sum of the opposite velocities of anion and kation (u and v) when urged by a slope of potential of one volt per centimetre through a solution containing N monad gramme equivalents of active substance per cubic centimetre, and of specific conductivity k , is

$$U = u + v = k/N \times .00010352 \times 10^8 = 10352k/N \text{ centims. per second.}$$

In order to apply this to particular cases KOHLRAUSCH assumes that all the dissolved salt is active, so that N is known from the strength of the solutions. The ratio u/v is taken from HITTORF's migration experiments, and thus the absolute values of u and v can be obtained.

KOHLRAUSCH expresses his experimental results in terms of the specific molecular conductivity (*i.e.*, k/N), and finds that for increasing dilution this tends to a limiting value. Thus, by drawing curves with $N^{\frac{1}{2}}$ (the reciprocal of the average distance

between the molecules) as abscissæ, and k/N as ordinates, he is able to obtain the specific molecular conductivity for infinite dilution. When the values for u and v are worked out for these ideal solutions, it is found that the velocity of any given ion is independent of the nature of the salt of which it forms part, and hence KOHLRAUSCH assigns numbers to various ions which represent their specific ionic velocity.

From a table of these numbers we can at once deduce the conductivity of any given salt solution, and the agreement of the values so obtained with those experimentally observed, furnishes the first confirmation of KOHLRAUSCH's theory. He calculates the conductivity of various salt solutions of strength 0.1 gramme equivalent per litre, and then experimentally determines it for solutions of that strength. Some of his results are as follows :—

Name of salt.	Molecular conductivity calculated from the ionic velocities.	Molecular conductivity observed.
KCl	1060	1047
NH ₄ Cl	1040	1035
NaCl	860	865
$\frac{1}{2}$ BaCl ₂	840	861
$\frac{1}{2}$ ZnCl ₂	780	768
KI	1070	1069
KNO ₃	1000	983
AgNO ₃	900	886
KC ₂ H ₃ O ₂	780	784
HCl	3260	3244
KOH	1950	1986
NaOH	1750	1700

The tabulated numbers are $k/m \times 10^8$ where k is the conductivity in terms of that of mercury, and m is the number of gramme equivalents of salt per litre. The general agreement is very remarkable, though several exceptions show that the law is not of universal application ; for instance, acetic acid should give 2980, while the observed number is 43.

The next confirmation of the theory was given by Dr. OLIVER LODGE ('B. A. Report,' 1886), who actually observed the velocity of the hydrogen ion as it travelled along a glass tube and discoloured a solution of phenol-phthallein as it went. The tube contained a jelly in which was dissolved a little phenol-phthallein and common salt, with just enough soda to bring out the colour. The tube joined two vessels filled with sulphuric acid, and when a current was passed between them the hydrogen travelled with it, and liberated HCl as it went along the tube. This decolourized the phenol-phthallein, and could thus be traced. The velocity per unit potential gradient came out as .0029, .0026, and .0024 centim. per second, while KOHLRAUSCH's theoretical number was .0030.

This agreement is striking evidence in favour of KOHLRAUSCH's theory and leads us

carefully to consider the data on which it is based. The only objection which can be raised is to the assumption that all the molecules are active, and on this the accuracy of the results deduced apparently depends, for if we suppose only a part of the salt to be active, it seems necessary to allow a greater ionic velocity *in order that the same current may be carried*. Now the work of ARRHENIUS, VAN'T HOFF, OSTWALD, and others, gives very strong evidence that only a certain fraction of the number of dissolved molecules are active (whatever we may assign as the cause of this activity), and it seems to have been generally supposed that this was quite inconsistent with KOHLRAUSCH's hypothesis (see LODGE, 'B. A. Report,' 1886, p. 391, *et seq.*). I have shown, however, that by examining the matter a little more closely the two ideas can be reconciled. The proof has already been published ('Phil. Mag.,' July, 1891), but it will be convenient to reproduce it here.

Suppose that the ratio of the number of the active to the whole number of molecules, which measures the "ionization" (to use Professor FITZGERALD's convenient name), represents in reality the fraction of each second during which each molecule is on the average active. Each molecule is in turn active, but *at any instant* only a certain fraction of the whole number of molecules are active. (In terms of the dissociation hypothesis this ratio measures the "mean free time" of each ion.) As far as statical effects, such as osmotic pressure are concerned, this is, of course, equivalent to supposing a certain fixed fraction of the whole number of molecules to be active, but when we consider the velocities of the ions the case is different.

KOHLRAUSCH gets the relative velocity of the ions from the relation

$$U_1 = u + v = k/m;$$

but if we suppose that only $1/n^{\text{th}}$ of the molecules are active, we should apparently have to put $U_2 = kn/m$ to get the same current through the solution, which would give $U_2 = nU_1$.

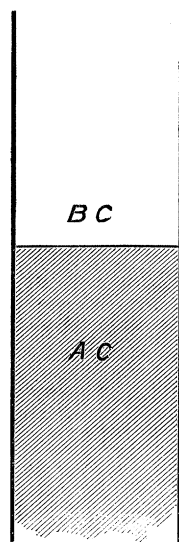
But this U_2 represents the actual velocity of the ions while they are active (or "free"), and if we take a dynamical view of the ionization equilibrium, they are active only for $1/n^{\text{th}}$ part of their time. While inactive (or "combined") they have no relative velocity, and so their average velocity for any *long* time is $1/n^{\text{th}} U_2 = U_1$ —the same as in KOHLRAUSCH's hypothesis. The view that all the salt is active supposes a uniform ionic velocity—the view above detailed supposes a series of rests interposed with a series of intervals during which the ion is moving forward with a velocity which is, while it lasts, on the average $= nU_1$; but the final result is the same, the *effective* velocity is U_1 .

We can, therefore, combine KOHLRAUSCH's theory with the supposition that some of the molecules present in the solution are inactive, the result being that the presence of the inactive or non-electrolytic molecules, which decreases the molecular conductivity of the solution, shows itself by diminishing the effective velocities of the ions.

The agreement between Dr. LODGE's observed value for the velocity of hydrogen and that deduced by KOHLRAUSCH is too close to be accidental, but some further experiments in which the velocities of various ions were determined by watching the formation of precipitates as they travelled along did not give such good results. Thus, Dr. LODGE found $Ba = \cdot 00012$, $Sr = \cdot 00015$, and $Cl = Br = I = \cdot 00024$ centims. per second, while KOHLRAUSCH gives $Ba = \cdot 00033$, $Cl = \cdot 00053$, $I = \cdot 00060$ ('Wied. Ann.,' vol. 6, p. 206).

There are several disadvantages in this method. The greatest appears to be the impossibility of keeping the solutions of a definite strength—the mere fact of producing a precipitate must withdraw a certain amount of salt from the sphere of action, and so reduce the strength of the solution. This will increase the resistance of that portion of the tube in which the precipitate has been formed, and the potential

Fig. 1.



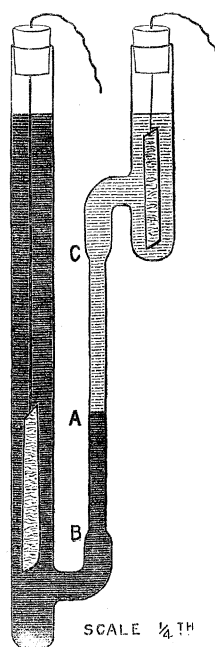
gradient will cease to be uniform and calculable. When jelly is used, the experiments are easy to make, but it has a considerable conductivity of its own, and its great viscosity must offer a high resistance to the passage of the ions through it. Moreover, it gradually exudes from the tube in a direction opposite to that of the current—perhaps owing to electric endosmose. If ordinary liquid solutions are employed, the precipitates cause serious mechanical disturbances which prevent good results, while the use of indicators restricts the experiments to the cases of acids and alkalis and introduces a foreign substance which may itself serve to convey some of the current.

In order to get over these difficulties, and to submit KOHLRAUSCH's important and beautiful theory to adequate experimental tests, I undertook a series of experiments in which the substances used acted as their own indicators. The solutions can then be kept at a definite strength, no third substance need be introduced, no precipitate

need disturb the uniform course of the ions, and no jelly bring in unknown and irregular conditions.

Consider the boundary of two salt solutions of slightly different density, which have one ion in common, but are of different colours (fig. 1). Let us denote the salts by AC and BC. When a current passes across the boundary there will be a transference of C ions in one direction (*against* the current, if we suppose the C's to be acid radicles, and, therefore, anions), and of A and B ions in the other (in the case supposed, *with* the current). Since the colour in this case depends on the kation A or B, the colour boundary will move with the current, and its velocity will indicate that of the ion causing the change in colour.

Fig. 2.



Postponing for the present the consideration of certain complications which may arise, I will describe the method of working and some preliminary observations. As small quantities of gas may be evolved at the electrodes they could not be sealed up, and finally a very simple apparatus was found to be the best (fig. 2). Two vertical glass tubes about 2 centims. in diameter were joined by a third, considerably narrower, which was bent parallel to the others for the greater part of its length. The longer tube was filled with the denser solution to about the level A, and then the lighter solution was run into the other tube from a burette, till it just began to trickle over the shoulder and run down to A. The proper solutions were then run into the two limbs at rates just sufficient to keep the junction near A; after some practice this could be done quite well, and the tubes filled without much disturbing the junction.

The current was passed from platinum electrodes, which could be connected with a battery of twenty-six accumulators by means of platinum wires passing through the

corks. The corks fitted loosely, and a vertical groove, filed in each, allowed any gas which might be evolved to escape. The junction tube had a length, from B to C, of 12.6 centims., and a diameter of about 1.2 centims. If we add one-half the diameter as a correction for each end we get 13.8 centims. as the effective length of the tube, which must be divided into the total difference of potential between the electrodes to give the potential gradient.

The advantages of such an apparatus are shortly as follows :—

1. Any gas evolved at once escapes without interfering with the experiment.
2. Since the liberation of ions and decomposition of salt occur only at the electrodes, it is (in general) only near them that alterations of concentration occur. Since they are surrounded by a large mass of liquid, these alterations will not appreciably change the resistance of the tube as a whole, and will be entirely without effect on the resistance of the column of liquid in the narrow tube, which is the important point.
3. Changes in density at the electrodes will not appreciably accelerate or retard the velocity of the junction. Take the case of copper chloride when the current is passing down as a fairly typical example. The average current was $\frac{1}{2550}$ in C.G.S. units. The quantity of electricity which passed in one hour was, therefore, $\frac{60 \times 60}{2550}$, and the weight of copper deposited,

$$31.5 \times \frac{60 \times 60}{2550} \times 10^{-4} = .0045 \text{ grm.}$$

Supposing that all this copper comes from the kathode vessel, and that when deposited it occupies no volume (both of which suppositions would increase the disturbing effect we are considering), half this weight of solution would pass from anode to kathode to bring the liquids in the two tubes to their original levels. The area of cross-section of the tube is 0.430 sq. centim. (see p. 347). Therefore the passage of .0023 cub. centim. of solution from anode to kathode in one hour would mean a velocity of .0054 centim. per hour. The actual velocity observed in this case, due to the ionic velocities, was 1.6 centims. per hour. The correction for differences in density is thus utterly negligible.

4. A more important objection was pointed out by Professor J. J. THOMSON. With salt solutions of equivalent strength there is, in general, a difference of specific resistance, although this is small in most cases. At the junction there will thus be a discontinuity of potential gradient, and, therefore, a distribution of electricity, which will be acted on by the electric force and introduce disturbances at the boundary. By a little consideration we shall see that this is a non-reversible effect, and should be eliminated by reversing the current and taking the mean of observations in each direction. Suppose that the current is passing in the direction which gives a distribution of positive electricity over the boundary. This will tend to make the

boundary move under the influence of the electric forces in the same direction as the current. Suppose the current reversed. It will now cause a distribution of negative electricity over the boundary, which will tend to move it in the direction opposite to that of the current. But the current has now also been reversed, and, therefore, the boundary tends to move in the same direction relatively to the tube as at first. This effect is therefore eliminated by reversing the current, and when the velocity is observed to be the same in each direction, within the limits of experimental error, it shows that the effect we are considering is negligible.

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. Their strength was about 0.18 gram. equivalent per litre.

The current was first sent upwards from the copper to the ammonium solution—the junction travelled upwards, with the current. The following readings of its position were made by a kathetometer :—

Voltmeter at grade 23.8.	Time.	Position.
8.8	12.45	27.20
	2.15	23.58
8.8	3.55	19.49
		$\left. \begin{array}{l} 27.20 \\ 23.58 \\ 19.49 \end{array} \right\} = 3.62 \text{ in } 90' = .0402 \text{ in } 1'$ $\left. \begin{array}{l} 23.58 \\ 19.49 \end{array} \right\} = 4.09 \text{ in } 100' = .0409 \text{ in } 1'$

The current was then reversed—the junction travelled downwards.

Voltmeter at grade 23.8.	Time.	Position.
7.5	12.30	20.74
7.7	3.10	26.83
		$\left. \begin{array}{l} 20.74 \\ 26.83 \end{array} \right\} = 6.09 \text{ in } 160' = .0381 \text{ in } 1'$

If we calculate this for the same E.M.F. as before we get .0441 centim. per minute for the velocity coming down. The mean is .0423 centim. per minute.

The E.M.F. as measured by a voltmeter comes out $\frac{88}{23.8} \times 10.2 = 37.7$ volts, which makes the potential gradient 2.73.

The velocity of the copper ion, under a potential gradient of 1 volt per centimetre, and through a solution of strength 0.18 gram. equivalent per litre, at a temperature of 15° C., comes out

0.00026 centim. a second.

The value deduced by KOHLRAUSCH from theory for a solution of infinite dilution at 18° C. is ('Wied. Ann.,' vol. 6, p. 206)

0.00031 centim. a second.

The next solutions were chosen to show the motion of the acid radicles, and potassium chloride and potassium permanganate were taken. The junction in this case, depending on the acid radicles, should, if its motion really shows the course of the ions, travel against the current. Such was found to be the case. The solutions had a strength of about .046 gm. equivalent per litre.

Voltmeter at grade 23·8.	Time.	Position.
10·8	4.11	21·42 } ·93 in 10' = ·093 in 1'
	4.21	20·35 } ·62 in 5' = ·124 in 1'
	4.26	19·73 }
10·8	4.40	20·89 } ·55 in 5' = ·110 in 1'
	4.45	20·34 } ·57 in 5' = ·114 in 1'
	4.50	19·77 }

A downward current from chloride to permanganate thus gives an upward velocity to the junction of 0·110 centim. per minute.

CURRENT reversed.

Voltmeter at grade 23·8.	Time.	Position.
10 8	4.28	19·72 } ·61 in 5' = ·122 in 1'
	4.33	20·33 } ·58 in 5' = ·116 in 1'
	4.38	20·91 }

The downward velocity of the junction is thus 0·119 centim. per minute.

The mean of the two is therefore 0·115 centim. per minute.

The potential gradient is 3·36, which makes the velocity for unit gradient

0·00057 centim. per second.

As the red permanganate disappears its place must be taken by chlorine, and hence this ought to give an indication of the velocity of the chlorine ion. For this KOHLRAUSCH gives

0·00053 centim. per second.

Solutions of one-tenth this strength were then set up (.0046 gm. equivalent per litre).

	Centim. per minute.
Average upward velocity	= ·1195
„ downward velocity	= ·1205
Mean	= ·120
Voltmeter, 10·9.	
Therefore specific ionic velocity	
= 0·00059 centim. per second,	

which is appreciably greater than for the stronger solutions.

The success of these preliminary determinations and the closeness of their agreement with theory led me to consider whether any improvement in the method was possible, by which further and more accurate results could be obtained.

In order to eliminate entirely the effect of the discontinuity of potential gradient it is necessary to use pairs of salts which have the same specific resistance for the same strength of solution. This very much limits one's choice, but an example will be found below. In such cases as that of copper and ammonium chlorides where the velocities in opposite directions are sensibly the same, it is fair to conclude that this effect is negligible, but it was worth while to find one case at any rate where it could not in the least affect the result.

The next improvement was in devising a means of getting over the necessity of directly estimating the potential gradient.

Consider the kation of one salt AC at the junction. Let its specific ionic velocity be v_1 , and its actual velocity v , under a slope of potential $= dV/dx$. Let r be the specific resistance of the solution. Let γ be the total current passing, and R the total resistance of the column of liquid from the anode to the junction.

Then we have $v = v_1 dV/dx$.

Since γ is constant along the tube we get by OHM's law

$$v = v_1 \gamma \frac{dR}{dx}.$$

Now since the tube is of uniform bore near the junction $dR/dx =$ the increase of resistance which would occur if we supposed the column of liquid from the electrode to the junction, whose resistance we have called R , to be increased in length by unity.

This increase of resistance $= r/A$, where A represents the area of cross-section of the tube at the junction.

Therefore

$$\frac{dR}{dx} = \frac{r}{A},$$

and we get

$$v = v_1 \gamma r/A,$$

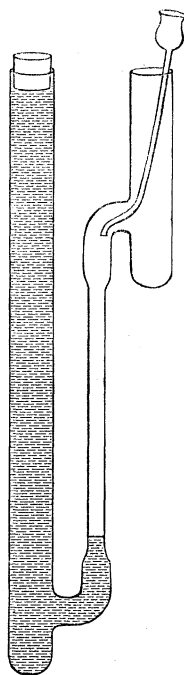
or

$$v_1 = vA/\gamma r.$$

Now in this equation A can be determined once for all, γ can be read off in a graduated galvanometer of proper sensitiveness, r can be measured by separate experiments for the solution in question, and v , the velocity of the junction, is directly observed. Hence v_1 , the specific ionic velocity, can be deduced without estimating the potential gradient directly, and introducing all the consequent uncertainties.

The method was first employed for the case of copper and ammonium chlorides, where the differences in specific resistance are not great, so that the velocities in opposite directions are approximately equal, and the correction for discontinuity is not important. The area of cross-section of the tube was determined as follows.

Fig. 3.



The longer limb was corked up so as to be air-tight, and filled with water till the surface stood just above the beginning of the narrow part of the junction tube. Its level was read off on the kathetometer. A flask containing water was then weighed, and liquid from it poured into the junction-tube through a weighed thistle-tube, till the surface nearly reached the top of the narrow part. The level was then again read off, giving the length of the column of liquid added, and the volume of water used was estimated by weighing the flask again, a correction for the small quantity retained on the walls of the thistle-tube being obtained by noticing the increase in its weight. Two determinations of the area of cross-sections by this section gave (1) 0.4300 sq. centim. and (2) 0.4297 sq. centim. Mean 0.4299, or correct to three places, **0.430** sq. centim.

The solutions were prepared by weighing out 0.670 gm. of pure cupric chloride and 0.534 gm. of ammonium chloride into two 100 cub. centims. flasks, and dis-

solving them in about 70 cub. centims. of water. An aqueous solution of ammonia was then added to the copper solution till the deep blue colour was formed. The same volume of ammonia was next run into the ammonium chloride solution, and both were made up to 100 cub. centims. This gave solutions whose strengths were 0.1 monad grm. equivalent per litre. Their specific resistances were found by the method used by KOHLRAUSCH and FITZPATRICK, and came out 157×10^9 (for the CuCl_2) and 117×10^9 (for the NH_4Cl) in C.G.S. units for the cubic centimetre.

The solutions were carefully run into the velocity tubes, and the current sent through them and a low-resistance galvanometer in series. The galvanometer had previously been graduated by sending the current from a single freshly-prepared Daniell cell through it and through a known resistance, and noticing the deflections as the resistance was varied from 11,000 ohms to 150 ohms.

GRADUATION of Galvanometer. Zero $1^\circ 9$.

Ohms.	Deflection.	Ohms.	Deflection.
11,000	$= 5.8$	1,600	$= 39.5$
10,000	6.1	1,400	42.5
9,000	6.7	1,200	45.9
8,000	7.4	1,000	49.8
7,000	8.2	900	52.1
6,000	9.8	800	54.5
5,000	11.5	700	57.0
4,000	15.4	600	59.9
3,500	18.7	500	63.2
3,200	21.0	400	67.1
3,000	22.9	350	69.1
2,700	25.6	300	71.7
2,500	28.0	250	74.1
2,200	31.3	200	76.8
2,000	33.7	150	79.4
1,800	36.6		

The resistances were then again increased to 400 ohms $= 67^\circ 1$, 1200 $= 45^\circ 9$, and 3500 $= 18^\circ 7$ —numbers identical with those first obtained.

COPPER and Ammonium Chlorides. Velocities. Current upwards.

Galvanometer.	Time.	Position.
74.7	10.50	$\left. \begin{array}{l} 32.4 \\ 32.2 \end{array} \right\} 32.3$
	4.0	$\left. \begin{array}{l} 23.4 \\ 23.5 \end{array} \right\} 23.5$
		} 1.70 centims. per hour.

CURRENT reversed at 4.0 downwards.

Galvanometer.	Time.	Position.
74.9	6.25	26.9 } 27.0 = 1.45 centims. per hour. 27.2 }
72.8	11.30 12.45	27.2 } 29.2 } 1.65 centims. per hour.
	1.30 1.45	30.5 } 30.9 } 1.70 " "

CURRENT upwards.

Galvanometer.	Time.	Position.
73.9	2.0 4.15	30.9 } 27.3 } 1.53 centims. per hour.
73.0	5.0 7.15	26.3 } 23.0 } 1.43 " "

Means going up G. = 73°·9 $v = 1.57$ centims. per hour.

" " down 73°·9 1.60 " "

Means of all observations G. = 73°·9

 $v = 1.59$ centims. per hour.

We get γ from the table of graduations to be $\frac{1}{2.55}$, and find from our equation (p. 346)

$$v_1 = \frac{vA}{\gamma r} = \frac{1.59 \times .430 \times 255}{157 \times 10^9 \times 60 \times 60} = 3.09 \times 10^{-12}.$$

This is for unit potential gradient on the C.G.S. system, and gives for a gradient of 1 volt per centim. a velocity of

$$3.09 \times 10^{-4} = 0.000309 \text{ centim. per second.}$$

This is the velocity of the copper ion in a solution of 0.1 gram. equivalent per litre, while KOHLRAUSCH deduced for infinite dilution

$$0.00031 \text{ centim. per second.}$$

The next case I shall describe is that of a pair of salts whose 0.1 gram. equivalent solutions have specific resistances which are nearly the same. Mr. FITZPATRICK kindly supplied me with a long list of conductivities reduced to comparable units,

and from those I was able to select two solutions which fulfilled the necessary conditions (*viz.*, (i.) different colours; (ii.) different specific gravities; (iii.) nearly equal specific resistances). Potassium bichromate has a specific molecular conductivity (*i.e.*, k/m) of 9.10×10^{-12} (LENZ), and potassium carbonate 9.34×10^{-12} (KOHLE-RAUSCH), a difference of less than 3 per cent.

I thought it better to use solutions of slightly different strengths and exactly equal conductivities to get rid of even this small variation, and therefore adjusted the strength of the carbonate till its resistance just equalled that of the bichromate. Thus, in the resistance cell which I used, the bichromate gave 1485 ohms and 1490 ohms at $17^{\circ}.4$, and the carbonate 1475 ohms and 1480 ohms at $17^{\circ}.5$.

The first point I investigated with these solutions was the influence of change of potential gradient on the velocity. These should, on KOHLRAUSCH's theory, obviously be proportional to each other.

When the current was passed downwards, so that the junction travelled up the tube, two distinct surfaces of separation appeared, one between the orange of the strong bichromate and the yellow of that portion of the carbonate solution into which a little bichromate had passed by diffusion, and the other between this and the colourless carbonate. These kept fairly distinct and travelled upwards at equal rates. I append full particulars of the first series of observations.

VELOCITIES.—Potassium Bichromate and Carbonate. Current Downwards, Movement Upwards.

	Galvanometer.	Time.	Position.	Velocity in centims. per hour.
Orange	35.0	11.45 .46 .47	24.70 .65 .60	
Yellow	35.1	11.48 .49 .50	23.03 22.92 .85	
Orange	35.1	12.0 .1 .2	23.80 .74 .69	} 3.63
Yellow	35.1	12.3 .4 .5	22.18 .08 .00	} 3.39
Orange	35.4	12.15 .16 .17	22.89 .83 .77	} 3.65
Yellow	35.6	12.18 .19 .20	21.32 .28 .23	} 3.24

Mean upward velocity . . . = 3·48 centims. per hour.
 „ galvanometer reading . . = 35°·3.

In the same way the observations of downward velocity came out 3·28 and 3·55 for galvanometer readings of 35·2 and 35·1, and when new solutions were set up 3·45 for 36·4.

Mean downward velocity . . . = 3·43 centims. per hour.
 „ galvanometer reading . . = 35°·6.

The means in each direction are

$$v = 3·45 \quad G = 35^{\circ}·4,$$

which gives

$$v_1 = \frac{vA}{\gamma r} = \frac{3·45 \times .430 \times 129 \times .00910}{60 \times 60} \\ = 0·00048 \text{ centim. per second.}$$

The galvanometer was too sensitive, and had to be shunted and regraduated with a Daniell cell.

Resistance.	Resistance.
70 = 49·0	140 = 32·7
75 = 47·7	150 = 31·9
80 = 46·1	160 = 30·0
85 = 44·9	180 = 26·9
90 = 43·7	200 = 23·8
95 = 42·3	230 = 20·2
100 = 41·1	260 = 17·3
110 = 38·9	300 = 14·1
120 = 36·9	320 = 12·7
130 = 35·1	350 = 11·4

Resistance of battery + galvanometer + wires = 1 ohm.

An E.M.F. of about one-third that used above was then applied with the following results :—

CURRENT upwards. Movement downwards.

Galvanometer.	Time.	Position.	Galvanometer.	Time.	Position.	Result.	Centims. per hour.
12·5	12.30	23·65	12·5	12.45	24·04	·39	} 1·48
	.31	·67		.46	·04	·37	
	.32	·70		.47	·05	·35	
12·7	1.4	24·92	12·7	1.19	25·27	·35	} 1·39
	.5	·95		.20	·30	·35	
	.6	·98		.21	·32	·34	

CURRENT Downwards. Movement Upwards.

Galvanometer.	Time.	Position.	Galvanometer.	Time.	Position.	Result.	Centims. per hour.
14·0	11.40	24·14	14·0	11.55	23·81	·33	} 1·28
	.41	·10		.56	·78	·32	
	.42	·07		.57	·76	·31	
13·8	3.25	24·14	13·7	3.55	23·46	·68	} 1·37
	.26	·11		.56	·43	·68	
	.27	·10		.57	·41	·69	
13·6	4.20	22·04	13·1	4.50	21·44	·60	} 1·23
	.21	·02		.51	·39	·63	
	.22	·00		.52	·38	·62	

Means—Downward velocity = 1·44 centims. per hour.

G. = 12°·6

Upward velocity = 1·29 centims. per hour.

G. = 13°·7

This gives

$$v = 1·37 \quad G = 13°·2,$$

and

$$v_1 = vA/\gamma r = 0·00047 \text{ centim. per second.}$$

Thus the value obtained for the specific ionic velocity is independent of the E.M.F. applied, *i.e.*, the velocity of the ions is proportional to the potential gradient.

New solutions were afterwards set up and the experiments with the large E.M.F. repeated. The results were—

Movement upwards :

$$v = 4·98, 4·84, 4·62, 4·66, 4·62.$$

$$G = 43·8, 43·8, 43·0, 43·2, 43·2.$$

Means :

$$v = 4·74 \quad G = 43·4 \quad v_1 = 0·00044.$$

Movement downwards :

$$v = 5·02, 5·16, 4·78, 4·70, 4·66.$$

$$G = 42·5, 43·4, 43·0, 43·0, 42·8.$$

Means :

$$v = 4·86, \quad G = 42°·0, \quad \text{therefore, } v_1 = 0·00049.$$

Mean of v_1 in both directions = 0·00046.

Taking the mean value deduced from all three series of separate experiments, we get

$$v_1 = 0.00047 \text{ centim. per second,}$$

as the specific ionic velocity of the bichromate group.

This is not given by KOHLRAUSCH, but we can calculate it by his method from known observations. Thus, LENZ has found the specific molecular conductivity of the solution to be 9.10×10^{-12} , and the migration constant was determined by HITTORF, and came out .502.

By KOHLRAUSCH's theory (see p. 338),

$$\begin{aligned} U &= u + v = 10352 \frac{k}{N} \\ &= 10352 \times 9.10 \times 10^{-8} = .000942, \end{aligned}$$

therefore,

$$\begin{aligned} v &= .000942 \times .502 \\ &= 0.000473. \end{aligned}$$

This close agreement between theory and observation led me to examine a case in which the specific resistances of the solutions were not the same, in order to see whether the method could be used when no solutions could be found with the exact resistance needed. I used potassium bichromate and potassium chloride, whose conductivities are 9.10×10^{-12} and 11.13×10^{-12} respectively. If the extension of method is practicable, these solutions should give the same velocity for the bichromate group as the former pair—bichromate and carbonate. The galvanometer was moved, and, therefore, had to be regraduated.

Resistance.	Resistance.
60 = 54.0	90 = 45.4
65 = 52.4	100 = 43.0
70 = 51.0	110 = 40.7
75 = 49.4	120 = 38.6
80 = 48.0	130 = 36.5
85 = 46.7	

The following results were obtained—

CURRENT Downwards. Motion Upwards.				
$v = 4.04$	4.18	4.18	4.22.	Mean, 4.15.
$G = 40.0$	40.0	40.2	40.2.	„ 40.1.

Therefore

$$v_1 = 0.000516.$$

CURRENT Upwards. Motion Downwards.

$v = 5.19$	5.18.	Mean, 5.19.
$G = 50.5$	49.2.	„ 49.9.

$$v_1 = 0.000394.$$

Thus, the effect of the discontinuity of potential gradient is to increase the velocity in one direction and to decrease it in the other, as it should do (see p. 343). The mean of the two numbers comes out

$$v_1 = 0.000455 \text{ centim. a second,}$$

a value which, though it is of the same order of magnitude as the one obtained from the other pair of solutions, is appreciably less. A second series of observations gave

$$0.000483 \quad \text{and} \quad 0.000402. \quad \text{Mean, } 0.000443.$$

These results show that the mean value of the velocities in opposite directions gives a number which is nearly, but not quite, the same as that obtained from a pair of solutions whose specific resistances are equal to each other. We may, therefore, use solutions whose resistances are not identical, to give, at any rate, some indication of the value of the specific ionic velocity, provided the differences are not great. But this extension of the method must be used with caution.

While working with solutions of different resistances it was often observed that when travelling in one direction the boundary got vague and uncertain, and when travelling in the other hard and sharp. Similar phenomena at the junction of liquids through which a current is passing have been previously described (see GORE, 'Roy. Soc. Proc.,' 1880 and 1881). Many of them can be explained as follows:—

Suppose that the coloured solution has greater resistance than the other, and that the junction is travelling from the coloured to the colourless solution. Any wandering ion which happens to be in advance of the main body, finds itself in a region where the potential gradient is less. It is therefore gradually overtaken, and the boundary becomes sharp. When the current is reversed, so that the junction travels in the opposite direction, any straggling ion, which lags behind the retreating column and so gets into the region of smaller potential gradient, finds itself left further and further behind, while others are continually falling out of the ranks. In this way the boundary becomes vague. If the coloured solution has less resistance than the other, a solitary ion is acted on by a *greater* potential gradient, and the order of these phenomena is reversed.

As far as I am aware, no attempt has hitherto been made to apply KOHLRAUSCH's theory to the case of solutions of salts in solvents other than water. The conductivity of alcoholic solutions is much less than that of the corresponding aqueous ones, and the question whether KOHLRAUSCH's theory still held good seemed of great interest.

The method described above can easily be applied, but the comparison of the results with theory offered some difficulty, as no data for the migration constants are

available. In order to prevent the necessity of experimentally determining these constants, I thought it better to observe the velocities of both ions of a salt and compare their sum with the value deduced from the conductivity. The salts used were (i.) the chloride and nitrate of cobalt (the colours of which in alcoholic solutions are blue and red respectively) giving the velocity of the acid radicles, and (ii.) cobalt and calcium chlorides (blue and colourless) and cobalt and calcium nitrates (red and colourless), giving the velocity of the cobalt ion.

It was found that the observed velocities were very small, and in order to increase them a shorter tube was used of rather greater cross-section. This enabled a greater potential gradient to be applied. The area of cross-section was determined as before and came out 0.746 sq. centim.

A series of solutions of cobalt chloride and cobalt nitrate of different strengths was made up and the specific resistances determined. They were then placed in pairs of equivalent strength in the velocity apparatus, and a long investigation made on their behaviour. It was found that with weak solutions, whose strength was below 0.08 gm. equivalent per litre, the phenomena were quite regular. The junction travelled against the current, as it ought, since the change of colour depends on the acid radicles. As the strength of solution increases new phenomena appear. When the concentration reaches 0.1 gm. equivalent per litre the junction sometimes divides into two parts, which often travel in opposite directions, producing a broad purple band between the red and the blue solutions.

The junction sometimes seems to travel entirely the wrong way, but there is always either a fainter band which goes the right way, or, if this cannot be seen, the colour of the solution in that direction gradually changes. These phenomena more and more disturb the normal course of the experiment as the concentration of the solutions becomes greater, and with the strongest solutions which can conveniently be used (0.15 gm. equivalent) are very marked indeed.

In order to examine the applicability of the theory to these cases, it is necessary to choose solutions so dilute that the motion of the ions is normal, but still strong enough to show their colours plainly, and give an appreciable difference of density. The best solutions to use were found to be those whose strength was about 0.05 gm. equivalent per litre.

Solutions of cobalt nitrate and cobalt chloride in alcohol of .05 strength were, therefore, set up in the velocity tube, and the following results were obtained:—

CURRENT from red to blue. Temperature, 17°.8.

$v =$.39	.35	.43	.43.	Mean,	.40 centim. per hour.
$G =$	49.5	49.4	48.8	48.5.	„	49°.1

CURRENT from blue to red.

$v =$.42	.41.	Mean,	.42 centim. per hour.
$G =$	49.1	48.6.	„	48°.9

2 z 2

CURRENT from red to blue.

$v =$.50	.47	.41	.40.	Mean,	.44 centim. per hour.
$G =$	49.8	49.8.			„	49°8

CURRENT from red to blue.

$v =$.41	.45	.48	.47	.34	.43.	Mean,	.43 centim. per hour.
$G =$	49.6	49.1	48.8	49.0	48.7.		„	49°0

Thus the velocity is practically the same in both directions, and the mean values are $v = 0.42$ centim. per hour and $G = 49.2$.

The conductivity of the chloride was found by FITZPATRICK'S method to be 2.86×10^{-13} C.G.S. units, which gives

$$v_1 = vA/\gamma r_1 = 0.000026 \text{ centim. per second}$$

for the velocity of chlorine in this solution. We see at once from this result, that conductivity and specific ionic velocity for different solvents are, at any rate approximately, proportional to each other. The conductivity of these alcohol solutions is about one-tenth, or rather less, that of an aqueous solution of a neutral salt of equivalent strength, and we see that the ionic velocity of chlorine is reduced to rather less than one-tenth of its usual value for aqueous solution. This confirms the result at which we have already arrived, viz., that all the molecules are concerned, at any rate in turn, in the process of electrolysis, and that the cause of the increased resistance is a decrease in the *average* ionic velocity.

In order to obtain the velocity of the cobalt ion, solutions of cobalt and calcium chlorides were set up of strength 0.05 gm. equivalent.

CURRENT upwards.

$v =$.30	.26	.20	.24.	Mean,	0.25.
$G =$	45.8	45.4	45.6	45.4.	„	45°6.

CURRENT downwards.

$v =$.26	.24.	Mean,	0.25.
$G =$	46.9	48.0.	„	47°5.

CURRENT upwards.

$v =$.30	.21	.26	.28.	Mean,	0.26.
$G =$	47.9	47.0			„	47°4.

(After this, the velocity began to fall off, and the kathode solution (CaCl_2) got thick and faintly blue, perhaps indicating that some current is conveyed by the water of crystallisation of the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, which deposits a hydrate when it meets the calcium, and that some cobalt goes faster than the rest and colours the solution. Finally, the junction went the wrong way, and other secondary actions occurred. All this shows that the effect of too great concentration has not yet been eliminated.)

Taking the mean velocity while it remained constant we get $G = 46^\circ.8$, $v = 0.25$ centim. per hour.

Therefore $v_1 = vA/\gamma r = 0.000022$ centim. per second.

Adding this to the velocity of the chlorine (viz., 0.000026) we get

$$V = u + v = 0.000048 \text{ centim. per second.}$$

The conductivity is 2.86×10^{-13} , and on KOHLRAUSCH's theory this gives

$$V = 10352 \frac{k}{N} = 0.000060 \text{ centim. per second.}$$

Considering the difficulties of the method and the effect of too great concentration, these numbers must be considered to agree within the limits of experimental error.

The conductivity of the nitrate of cobalt is rather greater than that of the chloride. This means that the number of active molecules is larger, and that the salt more nearly approaches the normal state. We should therefore expect the agreement to be closer than in the case of the chloride.

The velocity of the cobalt was found by using cobalt and calcium nitrate solutions, the first being red, the second colourless.

Upward velocity—Means: $G = 50^\circ.3$ $v = 0.44$.

Downward „ „ $G = 43^\circ.6$ $v = 0.41$.

Means of both directions: $G = 46^\circ.9$ $v = 0.43$.

No irregularities (such as reversals, &c.) were detected with these salts. This is what would be expected from the better conductivity.

The result is

$$v_1 = vA/\gamma r = 0.000044 \text{ centim. per second.}$$

The velocity of the NO_3 group can be calculated from the numbers in p. 356. The conductivity is 3.80×10^{-13} , and this gives

$$v_1 = 0.000035 \text{ centim. per second.}$$

Therefore

$$V = u + v = 0.000079 \text{ centim. per second.}$$

From KOHLRAUSCH's theory we can calculate

$$V = 10352 \frac{k}{N} = 10352 \frac{3.80 \times 10^{-13}}{.05} = 0.000079 \text{ centim. per second.}$$

From the close agreement of these numbers, it is, I think, fair to conclude that KOHLRAUSCH's theory holds good in the case of alcoholic solutions, at all events when they are moderately dilute.

The case of the chloride, where the agreement is not so good, seems even more interesting than that of the well-behaved nitrate, and to be worthy of closer examination. The irregularities only appear when the concentration of the solutions is considerable, and we may assume that the agreement with theory would be closer for more dilute solutions if the difficulties of observing them could be surmounted. But how are we to explain the phenomena shown by strong solutions? The velocity of the junction becomes uncertain, several distinct lines often appear, bounding different shades between red and blue, and some of these may travel in the opposite direction to that indicated by theory and actually observed in the case of dilute solutions. On any theory of ionic charges, it seems impossible that an ion, as such, should travel in a direction against the electric forces, and we are forced to the supposition that the part of the salt which we see travelling thus is composed of non-electrolytic molecules, and is in reality attached to the opposite ion to form a complex structure which moves with the electric forces. The only other possible explanation seems to be the supposition that there is a proper motion of the solvent on which the ionic velocities are superposed, and that in some cases the motion of the solvent in one direction is greater than that of the ion in the other. Even neglecting the mechanical disturbances which would then appear, this view is untenable, firstly, because a motion of the solvent is disproved by another series of experiments, which I hope soon to publish, and, secondly, because the reversed motion is observed in strong solutions of both cobalt nitrate-cobalt chloride, and cobalt chloride-calcium chloride. The motion of the boundary in these two cases is in opposite directions with reference to the current, hence we cannot explain matters by a motion of the solvent in one direction.

The hypothesis of complex ions, advanced to explain the abnormal migration constant of cadmium iodide in alcohol must, therefore, be extended to these solutions. The cases are not quite parallel, for the phenomena shown by cadmium iodide can be explained if we imagine molecules of CdI_2 joined to the anion only, while in our case, since both pairs of solutions used show reversed motion when sufficiently strong, we must suppose that molecules of undecomposed salt are connected both to the anion and to the kation.

I hope soon to be able to publish an account of some further experiments bearing on the question of complex ions, and of others connected with several points in the subject of electrolysis.

The following table shows at a glance the results of this paper, and the figures obtained by calculation from KOHLRAUSCH'S theory :—

SPECIFIC Ionic Velocities.

I. Aqueous Solutions.

Ion.	Velocity observed.	Velocity calculated from KOHLRAUSCH'S theory.
Copper	$\left. \begin{array}{l} \cdot 00026^* \\ \cdot 000309 \end{array} \right\}$	$\cdot 00031$
Chlorine	$\left. \begin{array}{l} \cdot 00057^* \\ \cdot 00059^* \end{array} \right\}$	$\cdot 00053$
Bichromate group (Cr_2O_7) . .	$\left. \begin{array}{l} \cdot 00048 \\ \cdot 00047 \\ \cdot 00046 \end{array} \right\}$	$\cdot 000473$

II. Alcoholic Solutions.

Salt.	Velocity of anion (observed).	Velocity of kation (observed).	Sum of velocities (observed).	Sum of velocities (calculated).
Cobalt chloride .	$\cdot 000026$	$\cdot 000022$	$\cdot 000048$	$\cdot 000060$
„ nitrate .	$\cdot 000035$	$\cdot 000044$	$\cdot 000079$	$\cdot 000079$

* Preliminary determinations.