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On the Velocities of the Ions

W. C. Dampier Whetham

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XIII. *On the Velocities of the Ions.*

By W. C. Dampier Whetham, *M.A., Fellow of Trinity College, Cambridge.*

Communicated by Professor J. J. Thomson, *F.R.S.*

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In a previous communication to the Royal Society ('Phil. Trans.,' 184 (1893), A, p. 337), I have described a method of experimentally determining the velocities of the ions during electrolysis, by observations on the phenomena at the junction of two salt solutions, one at least of which is coloured, when a current of electricity is passed from one to the other.

For the success of the method it is necessary to choose two solutions which (1) are different in density, (2) different in colour, and (3) have nearly equal conductivities at equivalent concentrations, *i.e.*, when the number of gram-molecules dissolved in 1 litre of solution is the same for both. These conditions seriously restrict the number of cases to which the method is applicable, but the results obtained for copper and for the bichromate group (Cr_2O_7) agree well with the values theoretically deduced by Kohlrausch from measurements of the conductivity. Alcoholic solutions of cobalt nitrate and chloride were also used, and the sum of the velocities of the opposite ions, in each case, observed in my experiments, was as nearly as could be expected, the same as their sum calculated from the conductivities by Kohlrausch's method.

In order to extend the method to cases in which there was no colour to be observed, I have returned to the use of solid solutions in agar-agar jelly, by means of which the first direct experimental measurement of the velocity of an ion was made by Dr. Oliver Lodge ('B.A. Report,' 1886), who traced the course of the hydrogen ion as it travelled along a tube filled with a jelly solution of sodium chloride, forming hydrochloric acid, and decolorizing phenol-phthallein as it went. Dr. Lodge tried to determine the velocity of other ions, such as barium, by tracing the precipitates which they formed with suitable reagents, but the results were not satisfactory.

The chief objections to the use of precipitates in jelly solutions are (1) the jelly exudes from the tube under the action of the current; (2) the formation of the precipitate withdraws some of the electrolyte from the solution, and hence changes in conductivity result, which alter the potential gradient, or form surfaces separating liquids of different conductivity, over which distributions of electrification will occur.

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The motion of the jelly as a whole is very slow compared with the speed of the ions, and, if we can measure the velocity while the ions are only moving over a small distance in a short time, it need not affect the result by disturbing the experiment in any other way.

In order to test whether trustworthy observations could be made with jelly solutions, I determined the velocity of the bichromate group when travelling through them. Decinormal solutions of potassium bichromate and potassium chloride were used in the manner presently to be described, and the velocity of the Cr_2O_7 ion under unit potential-gradient (one volt per centimetre) came out 0·00044 centim. per second. In the earlier investigation the same group travelled through an aqueous solution of the same strength with a velocity of 0·00047 centim. per second. The effect of the jelly thus appears to be only slightly to retard the motions. Moreover, ARRHENIUS has shown ('B.A. Report,' 1886, p. 344) that the viscosity of jelly solutions has but a small influence on the conductivity.

The alteration in concentration, due to the formation of a precipitate, appears to have been very considerable in Dr. LODGE's experiments, and may explain his uncertain results. It can, however, be made very small in the following way. Instead of setting up, in contact with each other, two solutions, like barium chloride and sodium sulphate, which completely precipitate each other, the solutions used were barium chloride and sodium chloride, just enough sodium sulphate being added to the latter to enable the motion of the barium ions to be traced by watching the formation of a slight precipitate of barium sulphate. That this did not seriously affect the result was shown by repeating the experiment with less sodium sulphate. The specific ionic velocity then came out 0·000386 centim. per second, a number agreeing with that first obtained, 0·000390, quite as well as the unavoidable errors of experiment would lead us to expect.

The use of jelly solutions, and of precipitates as indicators, being thus justified, many ions could be examined which could not have had their velocity determined by means of a colour boundary. KOHLRAUSCH has lately given corrected values for a number of ionic velocities ('Wied. Ann.,' 1893, vol. 50, p. 385), and, in some cases, tabulated them for solutions of various concentrations. It was, therefore, convenient to determine some of these, and barium, calcium, silver and the SO_4 group, present in sulphates, were chosen as convenient examples.

The apparatus used and the method of measurement were the same as those of the former investigation.

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. One jelly solution was melted and poured into the longer limb till it about half filled it, and was allowed to cool and solidify. The other solution was then poured into the shorter limb, and, when it was solid, the whole was placed in a glass water-bath in front of a window, with a transparent glass scale fixed behind

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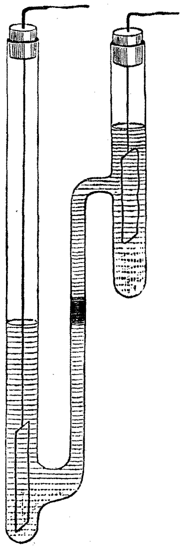
the junction tube. A precipitate formed at the surface of contact between the two solutions, and, when a current was passed from one platinum electrode to the other, the precipitate gradually spread upward or downwards with a velocity which could be measured on the scale by means of a telescope.

Fig. 1.



If the potential gradient at the junction is dV/dx, we have

$$dV/dx = \gamma r/A,$$

where γ represents the total current, r the specific resistance of the solution, and A the area of cross-section of the tube.

If v be the observed velocity, the specific velocity for unit potential gradient is given by

$$v_1 = \frac{v}{dV/dx} = \frac{vA}{\gamma r}.$$

A is determined by filling a known length of the tube with water or mercury, γ is read off on a galvanometer previously graduated, and r is determined by KOHLRAUSCH'S method of a Wheatstone's bridge with alternating currents. In order that the method should be a success, it is necessary that the solutions should be of nearly equal specific resistance, so that a mean value of r may be taken. The slight disturbing effect of any small difference is shown in the former paper to be eliminated if measurements be made when the current is passing in both directions, and the mean taken. But, unlike the colour boundary method, the formation of a precipitate is an irreversible process, so that measurements of the velocity can only be made when the current passes in one direction. All that can be done is to choose solutions of

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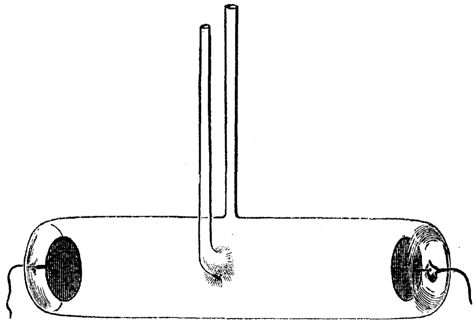
nearly equal specific resistance, so that the uncertainty, which must appear in the result, shall be, at all events, as small as possible.

Barium.—Decinormal* solutions of sodium chloride and barium chloride, the former containing a little sodium sulphate, were made up with agar jelly just strong enough to set. The resistance of each was determined in a cell of the form shown in fig. 2, the constant of which was known, and gave the conductivity of any solution in reciprocals of legal ohms, by dividing 1·5596 by the observed resistance measured in legal ohms.

Fig. 2.



Resistance of sodium chloride solution at 15°·8 = 161·8 ohms.
" barium " " " = 163·0 "
" " " " 13°·4 = 173·0 "

The temperature coefficient of resistance is, therefore, about 2·5 per cent. per degree, and the mean conductivity of the two solutions at 15°·8, $9·60 \times 10^{-3}$.

A small tangent galvanometer was adjusted and graduated by passing the current from a freshly prepared Daniell's cell through it and a box of resistance coils arranged in series. The following readings were obtained—

Resistance.	Reading.	Resistance.	Reading.
ohms.	°	ohms.	°
250	21·6	170	28·7
240	22·1	160	29·8
230	22·9	150	31·3
220	23·8	140	32·7
210	24·5	130	34·5
200	25·4	120	36·1
190	26·4	110	38·4
180	27·5	100	40·6

The resistance of the galvanometer and its leads was 10 ohms.

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* A decinormal solution contains one-tenth of the equivalent weight of the substance in grams in one litre of solution, *e.g.*, $\cdot 1 \times \frac{1}{2} \mathrm{BaCl_2} = \cdot 1 \times \frac{1}{2} (137 + 70\cdot 8) = 10\cdot 39$ grams per litre.

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The solutions were then placed in the velocity apparatus, and measurements taken, the temperature of the water bath being 15°·8.

Time.	Galvanometer.	Scale reading.	Displacement in 10 minutes.
11.14	35·8	24·39	
16	,,	24·28	
18	,,	24·20	
11.24	35·9	23·93	0·46
26	,,	23·83	0·45
28	,,	23·75	0·45
11.34	36·0	23·50	0·43
36	,,	23·40	0·43
38	,,	23·30	0·45
11.44	36·0	23·05	0·45
46	,,	22·95	0·45
48	,,	22·86	0·44
11.54	36·0	22·60	0·45
56	,,	22·51	0·44
58	,,	22·41	0·45
12. 4	36·2	22·16	0·44
6	,,	22·05	0·46
8	,,	21·98	0·43
12.14	36·3	21·71	0·45
16	,,	21·61	0·44
18	,,	21·52	0·46

The velocity of the junction thus kept constant throughout. Its mean value is 0·446 centim. in 10′. The mean galvanometer reading is 36·0, which indicates a current equal to that produced by the electromotive force of one Daniell (= 1·08 volt) working through a resistance of 121 + 10 = 131 ohms. The area of cross section of the tube is 0·430 square centim., and r is the reciprocal of $9{\cdot}60 \times 10^{-3}$. We thus get

$$v_1 = \frac{v\text{A}}{\gamma r} = \frac{0{\cdot}446 \times 0{\cdot}430 \times 131 \times 9{\cdot}60 \times 10^{-3}}{10 \times 60 \times 1{\cdot}08}$$

$$= 0{\cdot}000372 \text{ centim. per second.}$$

Experiments presently to be described gave for the temperature coefficient of the velocity the values 2·78 per cent. at 15°·7, and 2·05 per cent. at 12°·8. The mean of these 2·4 is very near the value, 2·5, found for the temperature coefficient of the conductivity, and justifies us in using the latter value for the small correction necessary to reduce the observations to 18°, the temperature for which KOHLRAUSCH's numbers are calculated.

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We thus find for the specific ionic velocity of the barium ion, travelling through a decinormal solution of barium chloride in solid agar jelly at a temperature of 18°,

$$\mathrm{v}_{\mathrm{Ba}} = \mathbf{0{\cdot}000393\ centim.\ per\ sec.}$$

For an aqueous solution of corresponding strength, KOHLRAUSCH calculates, that, in order to give the observed values to the conductivity and the migration constant, the barium ion must have a specific velocity of

$$\mathrm{v}_{\mathrm{Ba}} = \mathbf{0{\cdot}000366\ centim.\ per\ sec.}$$

New solutions were then set up, the amount of sodium sulphate being only just enough to give a visible precipitate. The voltage used was less—about 24 instead of 40, but otherwise the experiments were similar.

The following mean results were obtained :—

$$v = 0{\cdot}244 \text{ centim. in 10 mins.}$$

Galvanometer = 22·7. Therefore $\gamma = 1{\cdot}08/243$. Mean conductivity of solutions $9{\cdot}57 \times 10^{-3}$ at 16°·9. Temperature of water-bath 16°·9.

Therefore

$$v_1 = 0{\cdot}000376 \text{ centim. per sec.},$$

which gives for the velocity of the barium ion at 18° the value

$$\mathrm{v}_{\mathrm{Ba}} = \mathbf{0{\cdot}000386\ centim.\ per\ sec.}$$

Calcium.—The determination of the velocity of the calcium ion was not quite so satisfactory. The solutions used were decinormal ones of calcium chloride and sodium chloride, sodium carbonate being added to the latter as indicator. The precipitate of calcium carbonate was only visible when a considerable amount of sodium carbonate was present. This would make the change in concentration, due to the precipitation, considerable, and tend to increase the potential gradient at the boundary, and make the observed velocity greater.

The galvanometer had been moved, so that it was re-graduated.

Resistance.	Galvanometer.	Resistance.	Galvanometer.
ohms.		ohms.	
180	27·5	150	31·5
170	29·3	140	33·5
160	30·1	130	35·1

To these resistances 10 ohms must be added for the galvanometer and leads.

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Resistance of calcium chloride solution in cell at 18° = 180 ohms.
" sodium " " " = 170 "

Mean conductivity = $8{\cdot}91 \times 10^{-3}$.

The junction moved the following distances in 10 mins. :

·38, ·38, ·39, ·38, ·38, ·36, ·38, 38, ·40, ·36, ·36, ·36.

Mean = 0·376 centim. Mean galvanometer reading 32·9. Therefore $\gamma = 1{\cdot}08/153$. Temperature of water bath = 18°·1. Area of tube = 0·442.

Therefore

$$v_1 = 0{\cdot}000350 \text{ centim. per sec.},$$

which gives for the specific velocity of the calcium ion, moving through a decinormal solution of calcium chloride in agar jelly at 18°C., the value

$$\mathbf{v}_{\mathrm{Ca}} = \mathbf{0{\cdot}000349} \textbf{ centim. per sec.}$$

For the corresponding aqueous solution KOHLRAUSCH gives

$$\mathbf{v}_{\mathrm{Ca}} = \mathbf{0{\cdot}000290} \textbf{ centim. per sec.}$$

The temperature coefficient of the velocity was determined for these solutions by cooling the water-bath to 13°·2.

Mean conductivity at 13°·2 = $7{\cdot}90 \times 10^{-3}$.

Velocity = ·34, ·30, ·34, ·32, ·34, ·32, ·32, ·32, ·32. Mean = 0·324 centim. in 10 mins.

Mean galvanometer reading = 29·7. Therefore $\gamma = 1{\cdot}08/175$.

Therefore

$$v_1 = 0{\cdot}000305 \text{ centim. per sec.},$$

which gives a temperature coefficient, at a mean temperature of 15°·7, of 2·78 per cent. per degree.

Silver.—Decinormal jelly solutions of silver nitrate and sodium nitrate, the latter containing a little sodium chloride, gave in the resistance cell

Silver nitrate at 17°·4 = 171 ohms.
Sodium " " 17°·4 = 177 "

Therefore mean conductivity at 17°·4 = $8{\cdot}96 \times 10^{-3}$.

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Velocity = ·46, ·48, ·48, ·48, ·46, ·49, ·50, ·49, ·48. Mean = 0·480 centim. in 10 mins.

Mean galvanometer reading = 31·0. Therefore $\gamma = 1{\cdot}08/164$.

Temperature of water-bath, 17°·4. Area of cross-section of tube = 0·442 square centim.

Therefore

$$v_1 = 0{\cdot}000481 \text{ centim. per sec.}$$

Thus the specific velocity of the silver ion, moving through a decinormal solution of silver nitrate in agar jelly at 18°, is

$$\mathbf{v_{Ag} = 0{\cdot}000488 \text{ centim. per sec.}}$$

For the corresponding solution in water, KOHLRAUSCH gives

$$\mathbf{v_{Ag} = 0{\cdot}000462 \text{ centim. per sec.}}$$

The temperature coefficient was determined by cooling the water-bath to 8°·2.

Mean conductivity at 8°·2 = $7{\cdot}12 \times 10^{-3}$.

Velocity = ·37, ·37, ·39, ·40, ·40, ·40, ·41, ·43, ·40. Mean = 0·397 centim. in 10 mins.

The electromotive force applied being the same as before, we can compare this with 0·480 centim. in 10 mins., the velocity at 17°·4. The temperature coefficient at the mean temperature of 12°·8 is thus **2·05 per cent. per degree.**

The Sulphate Group.—As an example of an anion the velocity of the SO_4 group was determined by the use of decinormal jelly solutions of sodium sulphate and sodium chloride, barium chloride being added to the latter as indicator.

The galvanometer was re-graduated, the following readings being enough for our purpose. To the resistances 10 ohms must be added for the galvanometer.

70 ohms	50°·8,	230 ohms	23°·8,
80 ,,	47°·6,	250 ,,	22°·1.

Resistance of sodium chloride solution in cell at 14°·6 = 151·5.

,, ,, sulphate ,, ,, 14°·6 = 175·5.

Therefore mean conductivity at 15°·2 = $9{\cdot}69 \times 10^{-3}$.

Velocity = ·24, ·24, ·26, ·26, ·26, ·27, ·27, ·27, ·25, ·24, ·25, ·27, ·27, ·26, ·24, ·25, ·27, ·26. Mean = 0·257 centim. in 10 mins.

Mean galvanometer reading = 23·3. Therefore $\gamma = 1{\cdot}08/246$.

Temperature 15°·2. Area of cross-section of tube = 0·430 square centim.

Therefore

$$v_1 = 0{\cdot}000406 \text{ centim. per sec.}$$

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This gives for the specific ionic velocity of the SO_4 ion, when travelling through a decinormal solution of sodium sulphate in agar jelly at 18°,

$$V_{SO_4} = 0\cdot000434 \text{ centim. per sec.}$$

KOHLRAUSCH finds for decinormal potassium sulphate solution in water

$$V_{SO_4} = 0\cdot000492 \text{ centim. per sec.}$$

Another determination was then made in another tube having a larger area of cross-section = 0·746 sq. centim.

Temperature 11°·3. Mean conductivity $= 8\cdot79 \times 10^{-3}$.

Velocity = ·38, ·40, ·41, ·44, ·47, ·44, ·48, ·44, ·42, ·44, ·44, ·50. Mean = 0·438 centim. in 10 mins.

Mean galvanometer reading = 48°·4. Therefore $\gamma = \frac{1\cdot08}{77\cdot5 + 10}$.

Therefore

$$V_1 = 0\cdot000388 \text{ centim. per sec.},$$

which at 18° gives us

$$V_{SO_4} = 0\cdot000458 \text{ centim. per sec.}$$

The numbers thus obtained all agree with those deduced from theory, to an accuracy which must be considered to be as great as the unavoidable experimental errors would lead us to expect.*

Certain substances, such as ammonia and acetic acid, are known to have abnormally low conductivities, as long, at all events, as the aqueous solutions containing them are not exceedingly dilute. It seemed of great interest to examine whether the velocities were, in these cases, proportionately reduced. The result of an investigation on acetic acid, in which phenol-phthallein was used as indicator, has already been published ('Philosophical Magazine,' October, 1894), and gave the velocity of the hydrogen ion travelling through an agar jelly solution containing 0·07 gram.-equivalent of sodium acetate per litre, as

$$V_{H_1} = 0\cdot000065 \text{ centim. per sec.}$$

Now the value given by KOHLRAUSCH for the specific velocity of the hydrogen ion in a solution of hydrochloric acid of this concentration is

$$V_H = 0\cdot0030 \text{ centim. per sec.},$$

so that, when travelling through acetates, its speed is reduced in the ratio of 1 to 46.

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* It is worthy of remark that the velocities of all the kations measured come out larger than theory requires, while that of the one anion (SO_4) comes out less. It is possible that this may be due to the presence of the jelly.

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The ratio of the conductivity of a solution of acetic acid, containing 0·07 gram.-equivalent per litre, to that of an equivalent solution of hydrochloric acid is 1 to 62. Thus the velocity of the hydrogen ion is reduced in about the same proportion as the conductivity.

In order to examine the velocity of the acetate ion ($C_2H_3O_2$) of acetic acid, some substance was needed to serve as indicator. With ferric salts, acetates give a deep red colour, which is also produced if the solid ferric acetate is dissolved in water.

It is well known that solutions of ferric chloride undergo decomposition into soluble ferric hydroxide and hydrochloric acid, to an amount which increases as the dilution gets greater, and as the temperature rises. The hydrochloric acid can, in fact, be separated from the hydroxide of iron by dialysis through a membrane of parchment paper.

The electrical conductivity of an aqueous solution of ferric acetate shows that, in this case also, a similar reaction goes on, for it has an abnormally low conductivity, comparable with that of equivalent solutions of acetic acid, just as a solution of ferric chloride has an abnormally great conductivity owing to the presence of hydrochloric acid.

The molecular conductivity of an aqueous solution of ferric acetate, containing one-tenth of a gram.-equivalent of iron in one litre, was determined by measuring its resistance in another cell, whose constant was found by filling it with standard solutions of silver nitrate and barium chloride. The conductivity of any solution could be found by dividing the constant, $1·604 \times 10^{-9}$, by its observed resistance in legal ohms. A volume of 10 cub. centims. of this solution was then taken, and made up to 100 cub. centims. in a graduated flask.

This process was repeated three times, with the following results :—The first column, headed n, gives the concentration of the solution in gram.-equivalents of iron per litre; the second, R, gives the observed resistance in the cell; the third, T, shows the temperature; in the fourth are put the values of k_0, the conductivity in C.G.S. units, that of the water being subtracted, reduced to a temperature of 18°, and the fifth gives k_0/n, the molecular conductivity.

n.	R.	T.	k_0 at 18°.	k_0/n at 18°.
·1	2455	16·3	$7·03 \times 10^{-13}$	$70·3 \times 10^{-13}$
·1	2180	21·2		
·01	12600	17·9	$1·25 \times 10^{-13}$	125 ,,
·001	49700	17·7	$2·99 \times 10^{-14}$	299 ,,
·0001	177000	16·6	$6·74 \times 10^{-15}$	674 ,,

For equivalent solutions of acetic acid, KOHLRAUSCH (‘Wied. Ann.,’ 26, p. 197) gives the following results :—

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n.	k_0/n.
·1	46×10^{-13}
·01	140 ,,
·001	404 ,,
·0001	1058 ,,

It is, therefore, probable that, just as ferric chloride decomposes into ferric hydroxide and hydrochloric acid, thus :

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl,$$

so ferric acetate gives ferric hydroxide and acetic acid, thus :

$$Fe(C_2H_3O_2)_3 + 3H_2O = Fe(OH)_3 + 3(H.C_2H_3O_2).$$

In each case most of the work of carrying the current is done by the acid.

An attempt was made to use the red colour of the ferric acetate as an indicator to show the presence of the acetate group. A decinormal solution of ferric chloride was placed in one limb of the apparatus, and a similar solution, coloured red by a little ferric acetate, in the other. It was thought that, by the motion of the colour boundary, the acetate group could be traced, and, since the current is almost exclusively carried by the free acid, that the velocity thus measured would be that of the anion of acetic acid in dilute solution.

When the current was applied, however, it was at once seen that the colour boundary moved in the same direction as the current—not against it as an anion should. The following measurements were obtained :—

Resistance of ferric chloride solution in a third cell at 18°·8 = 363 ohms.

,, ,, ,, + acetate solution in Cell No. 2 at 18°·9 = 384·5 ohms.

Cell constant = 2·356.

Therefore mean conductivity at 19°·2 = $6·35 \times 10^{-3}$.

Velocity.—Half-hour intervals. Current upwards. Displacement upwards :

·9, ·9, ·8, ·8, ·8, ·8, ·7, ·8, ·9.

Current downwards. Displacement downwards :

·9, ·9, ·9, ·8, ·8, ·8.

Mean velocity = 0·833 centim. in 30 minutes.

Mean galvanometer reading = 46°·2. Resistance of galvanometer = 218 ohms.

Graduation with a Daniell cell :

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200 ohms . . .	30·7	30 ohms . . .	45·5
170 ,, . . .	32·7	0 ,, . . .	49·3.

therefore

$$\gamma = 1{\cdot}08/243,$$

therefore

$$v_1 = -\ 0{\cdot}000284 \text{ centim. per second,}$$

which, reduced to 18°, gives

$$-\ 0{\cdot}000276 \text{ centim. per second.}$$

If this really represents the velocity of the acetate group in an acid solution, it is evident that, if a measurement be made of the migration constant of acetic acid, the concentration round the kathode must increase, since the acetate group travels in the same direction as the hydrogen.

The current from twenty storage cells was passed for some hours through a decinormal solution of acetic acid. The liquid was contained in an apparatus consisting of two upright glass tubes, in which the platinum electrodes were placed. These tubes were connected below the level of the top of the solution by a horizontal tube, made of india-rubber for part of its length, in order that it might be closed by a screw pinch-cock. After the passage of the current, the two vessels could thus be isolated from each other, and the contents of each examined.

A current of 0·0014 ampère was passed for 5 hours, at the end of which time the solution round each electrode was titrated with decinormal soda solution with the following results:—

Original solution . . .	10 cub. centims.	require	10·0	cub.	centims soda.
Anode ,, . . .	,,	,,	10·4	,,	,,
Kathode ,, . . .	,,	,,	9·9	,,	,,

This preliminary observation, therefore, gives no evidence of accumulation of acid at the kathode.

The experiment was repeated. A current, whose average strength was 0·00178 ampère, was passed through decinormal acetic acid solution for 38½ hours.

Original solution . . .	10 cub. centims.	require	9·8	cub.	centims. soda.
Anode ,, . . .	,,	,,	9·85	,,	,,
Kathode ,, . . .	,,	,,	9·4	,,	,,

Now it is possible that an accumulation round the kathode might be masked by the reduction of the acetic acid by the hydrogen there liberated, but, if such an accumulation occurred, it would mean that all the acid decomposed must be taken from the anode vessel, as well as some which migrates unchanged through the liquid. The numbers given above seem to show conclusively that the amount of acid round the anode does not decrease, but that, if anything, a slight increase occurs.

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We must, therefore, look for some other explanation of the velocity phenomena. If ferric hydrate be dissolved in ferric chloride solution, a red liquid is obtained. When it is remembered that the ferric acetate solution contains ferric hydrate, it is evident that a motion of the colour boundary would be obtained if this ferric hydrate were carried through the solution, either by its being attached to the kation, or by a motion similar to that observed in the case of light non-electrolytic particles suspended in water.

Ferric hydrate can be obtained in a soluble form by *dialysing* a solution of ferric chloride. The ferric chloride solution is placed in a glass cylinder, the lower end of which is covered by a sheet of parchment paper. The cylinder is then suspended in such a manner that the lower end is just below the surface of a large volume of distilled water. At the end of several days, nearly all the hydrochloric acid is found to have passed into the water, leaving the iron behind as a brown solution of ferric hydrate. A solution prepared in this manner was found to have a concentration of 0·0044 gram.-equivalent per litre of chlorine, and 0·0652 gram.-equivalent of total iron. Its conductivity was, in C.G.S. units, $7{\cdot}83 \times 10^{-13}$, which gives for the iron a molecular conductivity of 120×10^{-13}, a value much below the normal. If, however, we suppose that it is only the ferric chloride remaining in the solution which is active, and calculate the molecular conductivity from the amount of chlorine, we get 1780×10^{-13}—a number nearly equal to that for the ordinary ferric chloride solution of equivalent strength.

A series of conductivity measurements of this solution was made at different dilutions, and then two similar sets for ferric chloride. In the following Table the results are compared.

Dialysed iron.		Ferric chloride.	
Concentration in gram.-equivalents of chlorine per litre.	Molecular conductivity at 18°.	Concentration in gram.-equivalents per litre.	Molecular conductivity at 18°.
		0·00968	1445×10^{-13}
0·0044	1780×10^{-13}		
0·00088	2255 ,,		
		0·000353	2575 ,,
0·000176	2580 ,,	0·000131	2690 ,,
		0·0000968	2747 ,,
		0·0000506	2250 ,,
0·0000352	1267 ,,		
0·0000176	1016 ,,		
		0·00000968	915 ,,

The molecular conductivities are corrected for the conductivity of the re-distilled water used ($2{\cdot}97 \times 10^{-15}$), and reduced to 18°.

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The two series of numbers correspond with each other within the limits of experimental error, and this indicates that the conductivity of the solution of dialysed iron is due, in great part, at any rate, to the presence of residual chloride. Whether the conductivities of these two solutions are accurately equal or not, it would need a thorough investigation to decide, and this was unnecessary for the immediate purposes of this paper. One would imagine that, if the conduction is entirely done by the chloride, the conductivity of the dialysed iron solution would be a little reduced, for the residual chloride, finding itself in presence of a large excess of ferric hydroxide, one of the products of its decomposition, would be less completely resolved into hydroxide and acid than in its ordinary solutions, and would, therefore, have a molecular conductivity more nearly equal to that of common salts than in the usual case.

It is interesting to observe that the molecular conductivity, in both these cases, reaches a maximum as the concentration decreases, and then, as the dilution is pushed still further, again falls. This is a characteristic property of the solutions of free acids and alkalis, and confirms the hypothesis that decomposition into ferric hydroxide and hydrochloric acid occurs. We may take it, then, that the ferric hydroxide, into which solutions of iron salts are partially decomposed, is electrolytically nearly inactive, the conductivity being almost entirely due to the acid formed. It is the large quantity of this hydroxide present that gives the dark red colour to ferric acetate solutions, and it is the motion of the ferric hydroxide which is measured by observations on the movement of the colour boundary in the velocity experiment.

In order to examine this conclusion, 10 cub. centims. of a solution of ferric chloride were run into some dialysed iron solution, and made up to 100 cub. centims. Another volume of 10 cub. centims. of the same ferric chloride was made up to 100 cub. centims. with water. These two solutions were placed in the velocity apparatus, and a measurement of the velocity of the red colour boundary made. It travelled in the same direction as the current.

Resistance of ferric chloride in cell, 818 ohms at 18°·4.

„ „ „ + hydroxide, 607 ohms at 16°·8.

Mean conductivity in reciprocals of legal ohms at 16°·2 = $2{\cdot}12 \times 10^{-3}$.

Velocity.—Temperature 16°·2. Mean galvanometer reading = 27·5. Current upwards. Upward displacement during successive intervals of 10 minutes each. Boundary kept quite sharp.

·64, ·63, ·65, 65, ·68, ·64.

Current downwards. Downward displacement during successive intervals of 10 minutes.

·81, ·81, ·77, ·69, ·67, ·66, ·68, ·70, ·66.

The first three measurements of the latter series are much larger than the rest,

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and after them the velocity kept constant. It is probable that the extra value was due to some disturbance at the boundary introduced by the first current, which gradually got reversed and eliminated when the current was reversed. These three observations were therefore neglected. The others give a mean velocity of 0·68 centim. in 10 minutes. We thus get for the velocity with which ferric hydroxide is transported in the direction of the current through a dilute solution of ferric chloride, by a potential gradient of 1 volt per centim., at a temperature of 16°·2, the value 0·000315 centim. per second, and at 18°

0·00033 centim. per second.

This is the same, within the limits of experimental error (which with these badly conducting solutions are considerable) as the value deduced by experiments with ferric acetate solutions of rather greater concentration, which was

0·00028 centim. per second.

It seems clear, then, that what we were measuring in that case, was not the velocity of the acetate group, but the velocity with which the soluble ferric hydroxide was transported through the solution without undergoing any decomposition.

In order further to examine this explanation, a migration experiment was made with the dialysed iron solution. A current of 0·003 ampère was passed through the liquid for five hours, at the end of which time the red colour had become much paler round the anode, while a precipitate of ferric hydroxide appeared at the bottom of the vessel containing the kathode.

The volume of liquid in each vessel was 30 cub. centims., and in 30 cub. centims. of the original solution the weight of ferric oxide was 0·0780 gram.

In the anode vessel the weight of oxide in solution was 0·0438 gram.

The kathode vessel contained 0·0720 gram. in solution, and 0·0158 gram. precipitated; total, 0·0878 gram.

Thus the anode vessel contains less iron, and the kathode vessel more, than an equal volume of the original solution. This, also, is consistent with the hypothesis that unaltered ferric hydroxide is carried through the liquid in the direction of the current.

A similar experiment, made with ferric acetate solution, also showed an accumulation of iron in solution near the kathode, both as estimated by the colour of the liquid, and as determined by analysis.

Our attempt to measure directly the velocity of the acetate group ($C_2H_3O_2$) in acetic acid solutions has therefore failed, but the migration experiment, described on p. 518, at any rate showed that no great change of concentration occurred in the neighbourhood of the anode, towards which the acetate group travelled. Its velocity is, there-

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fore, very small, and, as in the case of common mineral acids, the conductivity is chiefly due to the motion of the hydrogen.

The following table gives the velocities of all ions which have been experimentally determined.

Name of ion.	Specific ionic velocity in centims. per second.		Observer.
	Calculated from KOHLRAUSCH'S theory.	Directly observed.	
Hydrogen (in chlorides)	0·0028	0·0026	O. J. LODGE
,, (in acetates)	0·000048	0·000065	W. C. D. WHETHAM
Copper	..	0·00031	,,
Bichromate group (Cr_2O_7)	0·00047	0·00047	,,
Barium	0·00037	0·00039	,,
Calcium	0·00029	0·00035	,,
Silver	0·00046	0·00049	,,
Sulphate group (SO_4)	0·00049	0·00045	,,
Cobalt (in alcoholic $CoCl_2$)	..	0·000022	,,
,, (,, $Co(NO_3)_2$)	..	0·000044	,,
Chlorine (in alcoholic $CoCl_2$)	..	0·000026	,,
Nitrate group (NO_3) (in alcoholic $Co(NO_3)_2$)	..	0·000035	,,

The values in the second column are calculated from KOHLRAUSCH'S theory for solutions of the same concentration as those used for the direct observations. LODGE does not give the strength of his solution, but, as the molecular conductivity of dilute hydrochloric acid does not alter much with change of concentration, the number given, which is calculated for a decinormal solution, is, probably, fairly comparable with that observed. The velocity of copper was measured in chlorides, and the data for the calculation from theory are not known for this salt. The specific ionic velocity of copper, *at infinite dilution*, is given by KOHLRAUSCH as 0·00031 centim. per second. The sum of the ionic velocities of cobalt chloride in alcohol, as calculated from the conductivity of the solution, is 0·000060 centim. per second, and that of cobalt nitrate is 0·000079. These numbers are to be compared with the sums of the observed velocities given in the table, namely, 0·000048 and 0·000079 respectively.