

(3×10^{-11}) of the C.G.S. electrostatic unit of quantity. Other estimates of the amount of this remarkable unit of electricity have since been made, and do not materially differ from the above. Here, then, we have all the machinery required. The motions which go on actively within chemical atoms can scarcely fail to wave about these electrons which are so closely associated with them; and we know that the waving about of such of these charges of electricity as for the time happen to be undisguised, must generate in the ether exactly such electro-magnetic waves as those revealed to us in the spectra of gases (see 'Transactions of the Royal Dublin Society,' vol. 4 (1891), p. 583).

V. "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. Received May 2, 1895.

(Abstract.)

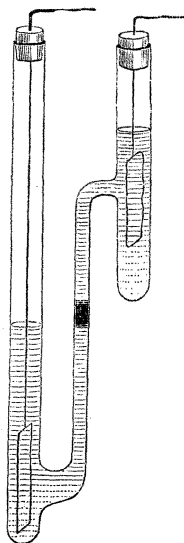
In a previous communication to the Royal Society ('Phil. Trans.,' 184, (1893), A. p. 337), I have described a method of experimentally determining the velocities of the ions during electrolysis, by observations on the phenomena which occur when a current of electricity is passed across the junction of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

The results obtained agreed, within the limits of experimental error, with the numbers deduced by Professor F. Kohlrausch from measurements of the conductivities. The method is, however, seriously restricted by the conditions necessary for its success. The two solutions must be of different densities, of different colours, and of nearly equal conductivities at equivalent concentrations.

In order to extend the method, I have used solid solutions in agar-agar jelly, tracing the motion of the ion by the formation of a precipitate. Jelly solutions were employed by Dr. Oliver Lodge, but, although he got a good result for hydrogen with phenol-phthallein as an indicator, when he tried to measure the velocity of barium and strontium by watching the formation of precipitates, the experiments were not very successful. This was probably due to the fact that, when a precipitate forms, it removes some of the electrolyte from solution, and so increases the specific resistance and the local potential-gradient. In order to eliminate this disturbing cause, instead of setting up two solutions which completely precipitate each other, like barium chloride and sodium sulphate, use was made of 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 the

formation of a slight precipitate of barium sulphate. That this did not seriously affect the result was shown by making two determinations of the velocity of the barium ion, much more sodium sulphate being present in the first case than in the second. The numbers obtained for the specific ionic velocity were 0.000385 and 0.000390 cm. per second respectively.

The influence of the jelly was examined by determining the velocity of the bichromate group (Cr_2O_7) with solid solutions of potassium bichromate and potassium chloride—the motion being indicated by the change in colour. The result was 0.00044 cm. per second. In the former paper the velocity of the same ion, measured by means of aqueous solutions of these salts, came out 0.00047 cm. per second. The influence of the jelly thus appears to be small, as is also indicated by Arrhenius' experiments on the conductivity of such solutions ('B. A. Report,' 1886, p. 344).



The apparatus used and the method of measurement were the same as in the former investigation. Two vertical glass tubes, about 2 cm. in diameter, were joined by a third, considerably narrower, which was bent parallel to the others for the greater part of its length. In this tube the jelly solutions came in contact with each other, and formed a slight precipitate at the junction. When a current was passed from one solution to the other, this precipitate spread, and the rate at which its advancing surface moved, was measured on a glass scale placed behind it, the observations being made through a telescope.

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 is 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 by means of a Daniell cell and a box of resistance coils, and r is determined by Kohlrausch's method of a Wheatstone's bridge with alternating currents.

The solutions must be of nearly equal conductivities, so that a mean value of r may be taken. This is the more important because, unlike the colour-boundary method, the formation of a precipitate is an irreversible process. Measurements cannot, therefore, be made with the current flowing in both directions, which, in the former paper, was shown to get rid of the disturbing effect of any remaining difference in conductivity. All that can be done is to choose solutions whose conductivities are very nearly equal, so that the uncertainty which must appear in the result shall be, at all events, as small as possible.

The apparatus was immersed in a water bath, and the results all corrected to a temperature of 18°C ., in order that they might be comparable with Kohlrausch's calculated values.

The following results were obtained :—

Barium.—Solutions used: decinormal barium chloride and sodium chloride, a little sodium sulphate being added to the latter.

Temperature, 15.8° . Mean conductivity at 15.8° in reciprocals of legal ohms, 9.60×10^{-3} . Mean current, $1.08/131$ ampère. Area of cross-section of tube, 0.430 sq. cm. Mean velocity of precipitate, 0.446 cm. in 10 minutes.

$$v_1 = vA/\gamma r = 0.000372 \text{ cm. per sec.}$$

The temperature coefficient was found to be 2.5 per cent. per degree, so that we get 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° ,

$$v_{\text{Ba}} = 0.000393 \text{ cm. per sec.}$$

For an aqueous solution of this strength Kohlrausch gives ('Wied. Ann.,' vol. 50, p. 385)

$$v_{\text{Ba}} = 0.000366 \text{ cm. per sec.}$$

With new solutions, containing only just enough sulphate to give a visible precipitate, the result was

$$v_{\text{Ba}} = 0.000386 \text{ cm. per sec.}$$

Calcium.—Solutions used: decinormal calcium chloride and sodium chloride, the latter containing a considerable amount of sodium carbonate, in order to get a visible precipitate; this increases the disturbing effect of the precipitation.

Temperature, 18.1° . Mean conductivity at 18.1° , 8.91×10^{-3} .

Mean current, 1.08/153 ampère. Area, 0.442 sq. cm. Mean velocity, 0.376 cm. in 10 minutes.

$$v_{\text{Ca}} = 0.000349 \text{ cm. per sec.}$$

Kohlrausch gives $v_{\text{Ca}} = 0.000290 \text{ cm. per sec.}$

Silver.—Solutions used: decinormal silver nitrate and sodium nitrate, the latter containing a little sodium chloride.

Temperature, 17.4° . Mean conductivity at 17.4° , 8.96×10^{-3} . Mean current, 1.08/164 ampère. Area, 0.442 sq. cm. Mean velocity, 0.480 cm. in 10 minutes.

$$v_{\text{Ag}} = 0.000488 \text{ cm. per sec.}$$

Kohlrausch gives $v_{\text{Ag}} = 0.000462 \text{ cm. per sec.}$

The Sulphate Group (SO_4).—Solutions used: decinormal sodium sulphate and sodium chloride, the latter containing a little barium chloride.

Temperature, 15.2° . Mean conductivity at 15.2° , 9.69×10^{-3} . Mean current, 1.08/246. Area, 0.430 sq. cm. Mean velocity, 0.257 cm. in 10 minutes.

$$v_{\text{So}_4} = 0.000434 \text{ cm. per sec.}$$

Another determination in a tube whose area of cross-section was 0.746 sq. cm. gave

$$v_{\text{So}_4} = 0.000458 \text{ cm. per sec.}$$

Kohlrausch gives $v_{\text{So}_4} = 0.000492 \text{ cm. per sec.}$

The general result goes to show that the ionic velocities thus measured agree, within the limits of experimental error, with Kohlrausch's numbers.*

It has already been shown ('Phil. Mag.', October, 1894) that when travelling through acetates whose concentration is 0.07 normal, the velocity of the hydrogen ion is about 0.000065 cm. per second,

* It is worthy of note that all the results for kations are slightly larger than indicated by theory, while the only measurement made for an anion gives a value which is slightly less. This may possibly be a result of the use of jelly.

whereas in other solutions, such as chlorides, it is about 0·0030, that is, about 46 times as great. Now acetic acid at the concentration mentioned above has an abnormally low conductivity, only the $1/62$ part of that of an equivalent solution of hydrochloric acid, so that, in such cases, the *immediate* cause of the low conductivity appears to be a reduction in the ionic velocities.

An attempt was made to complete the investigation of acetic acid by measuring the velocity of the acetate group $C_2H_3O_2$. I thought the red colour, which acetates give with ferric salts, might be used as indicator, and for this purpose set up solutions of ferric chloride and ferric chloride coloured red by ferric acetate. These ferric salts are said to be decomposed in solution into ferric hydroxide and the acid. Besides the chemical reasons in favour of this hypothesis, it is supported by the conductivities. Ferric chloride, which gives hydrochloric acid, is known to have abnormally great conductivity, and measurements I have carried to great dilution show that the molecular conductivity reaches a maximum at a certain concentration, and, as the dilution is pushed further, sinks again. This behaviour is characteristic of the solutions of acids. In the case of ferric acetate, acetic acid is produced, and the molecular conductivity is abnormally low. It seemed likely, then, that the red colour produced by acetates, when added to solutions of ferric salts, might be used as a means of measuring the velocity of the acetate group in acid solutions. When the experiment was made, however, it was found that the colour boundary travelled in the wrong direction for an anion, viz., with the current, the specific velocity being 0·00028 cm. per second. Now it is unlikely that an ion should behave thus, and an experiment on the migration phenomena of a solution of acetic acid showed that there was no accumulation of acid round the kathode. The result of further investigation was to show that the red colour of such solutions is due to the presence of soluble ferric hydroxide, and that, under the influence of a current, this is transported through the solution without decomposition in the direction of the current. Among other experiments, a direct measurement of the velocity of the transport was made. If a solution of ferric chloride be dialysed through parchment paper, hydrochloric acid escapes, while a red solution of soluble ferric hydroxide, known as "dialysed iron," remains. This was used to colour a solution of ferric chloride, which was set up in contact with an ordinary aqueous solution of ferric chloride of the same concentration. The specific velocity of the hydroxide could thus be determined by observing the motion of the colour boundary, and came out 0·00033 cm. per second in the direction of the current. It is evident that this is what we were measuring in the case of the acetate described above.

The conductivity of the dialysed iron solution is very low, and an

investigation on its value for solutions of different concentration led to the conclusion that, in such solutions, the whole work of carrying the current is done by the residual ferric chloride, which is itself probably decomposed to some extent into hydroxide and acid, though perhaps the proportion decomposed is not so large as in solutions without an excess of ferric hydroxide, which is one of the products of the decomposition.

An experiment on the migration of acetic acid showed that the velocity of the acetate group ($C_2H_3O_2$) was, at all events, very small, so that, as in the case of mineral acids, the conductivity is mainly 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 centimetres 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 „ $CoCl_2$...	—	0·000026	„
Nitrate group „ $Co(NO_3)_2$	—	0·000035	„

The values are calculated from Kohlrausch's theory for the same strength of solution as that used for the direct observation. In the case of copper, in decinormal copper chloride solution, there are no migration data for this. The velocity of the copper ion *at infinite dilution* is given by Kohlrausch as 0·00031. The sum of the ionic velocities of cobalt nitrate in alcohol, as calculated from the conductivity, comes out 0·000079, and that for cobalt chloride 0·000060. These numbers are to be compared with the sum of the observed velocities given above, namely, 0·000079 and 0·000048 respectively.

The Society adjourned over the Whitsuntide Recess to Thursday, June 13.

