

## On the Accurate Measurement of Ionic Velocities, with Applications to Various Ions

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XIII. *On the Accurate Measurement of Ionic Velocities, with Applications to Various Ions.*

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ACCORDING to ARRHENIUS' theory of electrolytic dissociation, the conduction of the current in a salt solution is due to the presence of free ions, which, under the influence of an electromotive force, move towards the electrodes with a velocity depending, other conditions being equal, upon the magnitude of the driving force, or fall of potential. This "ionic velocity" can be determined by means of two quite distinct methods, of which one may be termed the indirect and the other the direct method. The former, or indirect method, was evolved by KOHLRAUSCH on his recognition of the law of the independent migration of the ions, which he thus states: "The molecular conductivity,  $\mu$ , of a solution is proportional to the sum of the velocities of the anion and of the cation,  $\mu = \text{constant} \times (u+v)$ ."

The ratio of these velocities,  $u/v$ , had been determined many years previously by HITTORF, whose "Überführungszahl," or transport number,  $p = u/(u+v)$ , for any salt represents the fraction of the total current that is carried by the anion.

The knowledge of this ratio enabled KOHLRAUSCH to calculate the ionic velocities from the molecular conductivity. In order to calculate the velocities of the ions by the indirect method it is, therefore, necessary to know both the molecular conductivity of the solution and its transport number. Although the determination of the former is perfectly easy and straightforward, that of the latter by HITTORF's analytical method is both difficult and laborious, and the method suffers from the great disadvantage that the success or failure of an experiment is known only after the necessary chemical analyses have been completed.

In recent years a method of measuring transport numbers and ionic velocities has been worked out in which the actual rate of motion of the ions is read off by means of a scale and telescope. The first steps in this direction were taken in 1886 by LODGE ('British Assoc. Reports,' 1886, p. 389), whose idea was to make the invisible ion indicate its presence by some characteristic physical or chemical property, such as its colour or the formation of a precipitate with some other ion. For the gradual

development of this idea reference must be made to the original literature;\* but the following is a brief account of the method in its present form:—

It has been shown, both theoretically and experimentally, that if two salt solutions containing a common ion are placed one above the other, and an electric current passed through the system, a stable margin will be formed between the two solutions, provided that the specifically slower non-common ion follows the faster one. Under these circumstances it has been shown that the boundary moves in the same direction as the non-common ions and measures their velocity. In order to observe and measure the velocity of the boundary, advantage is taken of the slight difference in the refractive index of the two solutions, which difference renders the margin quite visible when viewed through a telescope. The method of determining the ratio  $U/V$ , and hence the transport number,  $U/(U+V)$ , for a given salt will be rendered clear by the following considerations:—

Let us suppose that a current flows through the system,

Anode—solution of lithium chloride—solution of potassium chloride—solution of potassium acetate—cathode.

At the margin between the lithium and potassium chloride solutions the slower lithium ion follows the specifically faster potassium ion, and there results a stable margin, the velocity of which is that of the lithium and potassium ions at that point. This, velocity, however, depends on the potential gradient, and it has been proved that the concentration of the lithium chloride becomes automatically adjusted, so that the potential gradient is just sufficiently increased to make the lithium ions keep pace with the potassium ions. In the same way the specifically slower acetate ion follows the faster chlorine ion, at the margin potassium acetate, chloride, and the motion of this margin gives the velocity of the acetate-chlorine ions; but whilst the lithium and acetate ions are moving under the influence of an unknown potential gradient, that which is driving the potassium ion is the same as that driving the chlorine ion—the potassium chloride solution being homogeneous—and, therefore, the velocities of these two ions are strictly comparable. Moreover, the potential gradient in the middle electrolyte can easily be calculated, and hence, also, the average mobility of the ions, or their velocity under a driving force of one volt per centimetre.

The ratio  $U/V$  and the average mobilities of the ions of a number of salts have been determined in this way,† and whilst the agreement between the results so obtained and those obtained by the indirect method is, on the whole, fair, considerable deviations occur in the case of many salts. In the method used for these measure-

\* WHETHAM ('Phil. Trans.,' A, 1893, p. 337; A, 1895, p. 507); MASSON ('Phil. Trans.,' A, 1899, p. 331); KOHLRAUSCH ('Wied. Ann.,' 1899, LXII., p. 209); WEBER ('Sitz. Berliner Akad.,' 1897); STEELE ('Phil. Trans.,' A, 1902, p. 105; 'Zeit. für Phys. Chem.,' 1902, XL., p. 689); ABEGB and GAUS ('Zeit. für Phys. Chem.,' 1902, XL., p. 737); DENISON ('Zeit. für Phys. Chem.,' XLIV., p. 575).

† MASSON (*loc. cit.*); STEELE (*loc. cit.*).

ments the solution to be measured was separated from the solutions containing the slower indicator ions by two partitions of a gelatine solution of the same indicators, and in this way it was possible to place the solutions in position without any appreciable mixing taking place at the surfaces of contact.

It has been shown by DENISON (*loc. cit.*) that the deviations referred to are due, largely, if not entirely, to the occurrence of electric endosmose at the gelatine partitions. DENISON measured the amount of endosmose, and applied the correction to the ratio  $U/V$  with satisfactory results in the case of many salts.

The present research has been undertaken with the object of devising a method by means of which the solutions could be superposed without mixing, and which would avoid the use of membranes of any sort during the progress of the experiment.

The use of gelatine especially was to be avoided, not only on account of electric endosmose, which would be caused by any membrane, but also on account of the ease with which it melts on the passage of even small currents, and on account of the impossibility of obtaining it free from saline impurities. Even the purest obtainable gelatine contains a quantity of saline matter which is an appreciable fraction of the concentration of a moderately dilute salt solution, and this is probably the reason why our previous attempts to measure such solutions have been unsuccessful, and it appears to be impossible to measure transport numbers in dilute solutions in a system containing gelatine. Now we know that it is only in the case of the simple salts of the alkali metals that the transport number is practically independent of concentration; with other salts the general tendency is for the anion transport number to increase with increasing concentration. This gives, of course, different values for the velocity of the same ion at different dilutions, and, moreover, the velocity of one and the same ion is found to be different for the same concentration when measured in different salts. These differences, however, vanish in dilute solution\* in which, in accordance with the theory of KOHLRAUSCH and ARRHENIUS, a given ion has the same velocity in different salts. Hence an extension of the direct method of measuring ionic velocities to dilute solutions is much to be desired on account of its great simplicity and ease of manipulation.

Before this could be accomplished, however, it was necessary to devise some means of observing the margins. If gelatine be employed as membrane, the margins become invisible in solutions more dilute than about 0.2 N.

It was thought that an electrical method could be used to indicate the position of the boundary by taking advantage of the difference in conductivity of the indicator and measured solutions. This method, however, proved impracticable. Coloured salt solutions could not be used as indicators, as in solutions of about 0.02 normal the colour of solutions of salts such as copper sulphate, cobalt sulphate, nickel sulphate, &c., is much too faint to be serviceable. The intensely coloured ions of some of the organic dyes were tried, but, although certain acid dyes are excellent anion indicators,

\* STEELE and DENISON, 'Journ. Chem. Soc.,' 1902, LXXXI, p. 456.

no basic dye was found sufficiently free from hydrolysis to be of any use as a cation indicator. It was ultimately found that, by the use of very high voltages, distinctly visible refraction margins could be obtained in solutions as dilute as 0.02 N.

*Method of Experiment.*

The placing of the two indicator solutions in contact with the middle electrolyte without appreciable mixing taking place, and without using gelatine or other membrane during the experiment, presented considerable difficulty. The ordinary method of pouring the one solution upon a thin piece of cork floating on the other solution was found to be quite unsatisfactory. The problem was finally solved by the use of the apparatus shown in figs. 1 and 2. It consists of two parts which are

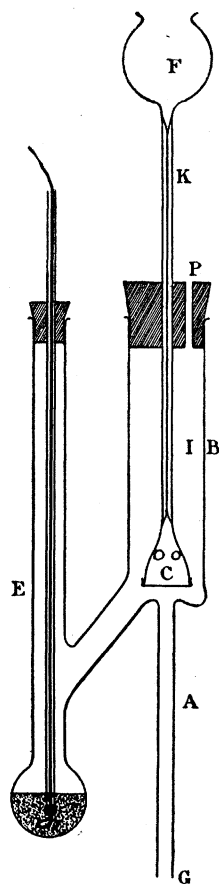


Fig. 1.

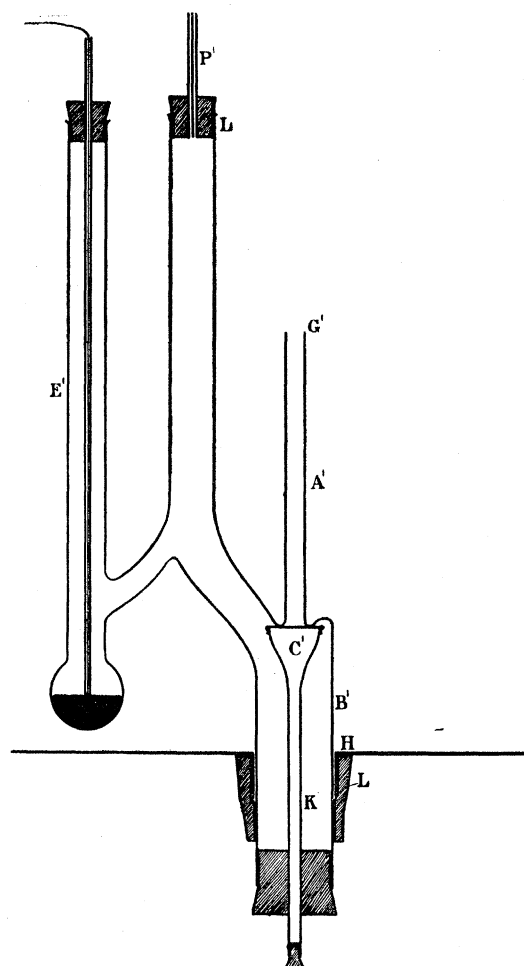


Fig. 2.

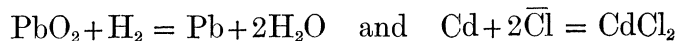
joined together at G or G'. If both indicators are lighter than the solution to be measured, the apparatus is made up of two halves of the form shown in fig. 1. If both are heavier, then both halves are of the form shown in fig. 2. If one indicator



is lighter and the other heavier than the solution to be measured, one-half of the form of fig. 1 and one-half like fig. 2 are used in constructing the apparatus.

In fig. 2 a hole with a collar is shown in the bottom of the thermostat H. The apparatus can be passed through this hole and held in position by a rubber ring, L. This was found to be the best way of supporting this half of the apparatus. Both forms of the apparatus consist essentially of three tubes, an electrode vessel, E or E', a vessel, B or B', containing the indicator solution, and the tubes A or A' in which the boundaries move. The tubes A and A' are made from carefully selected glass quill-tubing of about 4 to 5 millims. diameter, and are accurately calibrated. They are sealed into the wider tubes B or B' in such a manner that they form a shoulder projecting inwards. The lower extremity of the capillary tube K is expanded into a cone, C, around which a piece of parchment paper can be tightly stretched. This parchment paper fits over the projecting shoulder, so that when pressed upon it there is no mixing of the liquid poured into the apparatus through the tube K with the liquid previously placed in A. The tubes K and K' slide easily through holes in rubber corks, so that after an electrolytic margin has appeared in the tubes A or A' the membrane can be withdrawn from the shoulder, and a free passage is allowed for the current. The cones C are provided with holes to allow the passage of the liquid into B and also to permit the free flow of the electric current when the membrane is resting on the projecting shoulder.

The choice of electrodes and electrode solutions needs careful consideration if accurate results are to be obtained. It is obvious that no gas evolution at the electrodes must occur if a good margin is to be maintained. The indicator solutions most frequently employed were lithium chloride and sodium acetate, and in all our experiments the cathode consisted of lead wire dipping into and completely covered by a paste of lead peroxide, which completely prevented any evolution of hydrogen. The anode consisted of a copper wire dipping into cadmium amalgam, thus constituting a completely unpolarisable electrode. A rough calculation showed that the total volume change at the electrodes corresponding to the changes



was negligible. To prevent the hydroxyl ions formed at the cathode from finding their way back into the middle electrolyte, the cathode was surrounded with a solution containing acetic acid.

The cadmium chloride formed at the anode is to some extent hydrolysed, and the hydrogen ions thus formed travel towards the cathode across the cation margin and decrease the resistance of the solution there, and so also the fall of potential and the velocity of the margin. To prevent this, a little sodium or lithium hydroxide was added to the solution surrounding the cadmium electrode. If these precautions were neglected, slightly false values for the transport numbers were obtained.

The whole apparatus was held in position by means of a hinged wooden arm, and

placed in a bath with plate-glass sides. The framework of the bath was of copper and provided with flanged edges, on which the plate-glass sides were clamped. Rubber tubing was placed between the copper flanges and the glass, and in this way a perfectly water-tight junction was made and the use of putty rendered unnecessary, a considerable advantage if the bath is to be heated. The base of the bath was provided with two holes for the insertion and support of the apparatus shown in fig. 2.

In putting together the apparatus for an experiment, the electrode vessels E are first filled and the electrodes placed in position, care being taken that none of the electrode liquid passes over into B or A.\* The two halves of the apparatus are then connected by rubber tubing and the tubes A are filled just to the shoulder with the solution to be measured. The rubber cork carrying the tube K and the membrane is then placed in position† and pressed on the shoulder, care being taken not to imprison any air-bubbles below the membrane. The electrical connections having been made, the current is started by pouring the indicator through F (fig. 1) or L (fig. 2), after which the plugs P and P' are inserted. The appearance of the margins in the tubes generally occupies only a few minutes, and as soon as they have advanced about 1 centim. into the tubes the membranes are removed by lifting K or lowering K'. In this manner electric endosmose is entirely prevented. The velocities of the two margins are measured by observing the distance moved in stated intervals of time, the observations being made by means of a telescope with cross wires and a glass scale placed immediately behind the tubes A and A'.

One other point requires notice. The tubes K in apparatus fig. 1 and P' in apparatus fig. 2 must not have a greater diameter than about 1 millim. The reason for this is as follows:—Suppose that we are measuring the transport number of sodium chloride with lithium chloride and sodium acetate as indicators, both solutions being lighter than that of sodium chloride. In one measuring tube we have the solutions lithium chloride over sodium chloride, and in the other sodium acetate over sodium chloride, and the relative length of the columns of lithium chloride and sodium acetate depends on the position of the margins. Now the sodium ion travels more slowly than the chlorine ion, with the result that a longer column of sodium acetate than of lithium chloride is formed. These solutions have different densities, and so there is a difference of hydrostatic pressure tending to move the whole column of liquid up one measuring tube and down the other, and the level in the tubes K and P becomes slightly altered during the progress of the experiment. This change of level accelerates one margin and retards the other, and false values for the velocities and transport number are obtained. In order to reduce the effect of the change of level, the diameters of K and of P are made as small as possible, and hence, since the total change of level amounts to only a fraction of a millimetre, the

\* In the final form of apparatus the two halves were sealed together.

† In the case of the apparatus (fig. 2) used for heavy indicators, the tube K is placed in position before putting the solution into the tube A.

movement of the margin in the measuring tubes A due to this cause is infinitesimal and can be neglected. In our earlier experiments, in which the apparatus was tested with potassium chloride, the wide tubes B were open to the atmosphere, but as the potassium and chlorine ions have practically the same velocity, the effect described above did not manifest itself. But with  $n/10$  sodium chloride the introduction of the capillary tubes K changed the transport number for chlorine from 0.589 to its correct value, 0.614.

The electrical connections and the method of illuminating the boundary are the same as those described in previous papers.\*

#### *Testing the Method.*

The only difficulty in the present method has been found to lie in the choice of suitable indicators. The transport number of any ion in a given salt should be the same at the same concentration, provided that the indicator used fulfils certain conditions, which are briefly as follows:—

(1) The specific velocity of the indicator ion must be less than that of the ion whose progress it indicates.

(2) It must not react with any of the ions of the salt being measured, nor must it be hydrolysed or give rise to any other ion moving in the same direction as the indicator ion.

(3) The resistance of the indicator solution must not be too great, *i.e.*, the concentration of ions in the indicator must not be too small, nor must there be too great a difference between the specific ionic velocity of the indicator ion and that of the ion whose velocity is being measured.

The method was first tested by measuring the transport numbers of potassium and sodium chlorides with different indicators, and the following results (Table I.) were obtained:—

TABLE I.

Salt and concentration.	Indicator ions.	Anion transport number = $p$ .	HITTORF'S value †
$\frac{n}{1}$ KCl	Li and acetate	0.508	} 0.514
	„ formate	0.513	
$\frac{n}{1}$ NaCl	„ acetate	0.614	} 0.637
	„ formate	0.621	
$\frac{n}{10}$ KCl	„ acetate	0.508	} 0.508
	„ formate	0.508	
$\frac{n}{10}$ NaCl	„ acetate	0.617	} 0.617
	„ formate	0.618	

\* STEELE, *loc. cit.*; DENISON, *loc. cit.*

† From KOHLRAUSCH and HOLBORN'S 'Leitvermögen der Electrolyte,' p. 201.



These results show that the method is capable of great accuracy. There is, indeed, a slight difference between the values of the transport numbers for the normal solutions according as acetate or formate is used as anion indicator, the percentage difference being about the same with potassium chloride as with sodium chloride. Although there is only a small difference between HITTORF's value for these solutions and that found by us with sodium acetate, it is too large to be attributed to errors of experiment. We have measured these solutions repeatedly, and with the utmost precautions, and invariably obtain results which lie between 0.508 and 0.510 for potassium chloride and between 0.613 and 0.615 for sodium chloride. It is, therefore, necessary to recognise the presence of some unknown disturbing factor in these experiments. Whatever this factor is, its effect has disappeared in the more dilute solutions, and for these accordingly we have continued to use sodium acetate as anion indicator. For stronger solutions, however, it is advisable to use sodium formate.

Sodium benzenesulphonate has been successfully employed by us as anion indicator in some experiments, but when it is used for stronger solutions than  $n/10$ , irregularities occur, the cause of which we have not yet succeeded in tracing.

#### *Experimental Results.*

We have measured the transport number and ionic velocities of those salts only which give rise to strong ions, that is, salts which undergo little or no hydrolysis in aqueous solution.

The necessity of paying attention to the possibility of hydrolysis in all electrolytic experiments cannot be too strongly emphasised. Thus, it is of no value to determine the velocity of the ions of a salt which, when dissolved, gives rise to a complicated ionic system. We cannot assume, *à priori*, that the transport number of any ion as determined by the present method will give us the true fraction of the total current which is carried by that ion in the presence of other ions of the same sign. In HITTORF's analytical method the actually measured transport number gives us the fraction of the total current carried by the ion in question, whether complex ions are present or not, if we assume that the current is wholly carried by the simple ions. Whether the direct method, and the method of HITTORF, will give the same transport number for a given ion in more complex ionic systems, or whether the presence of complex ions in solutions will affect the results obtained by the two methods to a different extent, are subjects for future experimental and mathematical investigation.

By means of the present method we have been enabled to obtain for the first time an experimental determination of the transport number for such salts as potassium chlorate, bromate and perchlorate, which present considerable difficulty in the determination by the analytical method.

In the following Table II., which contains the results of our transport-number determinations, the values given in the last column are taken from KOHLRAUSCH and HOLBORN's 'Leitvermögen der Electrolyte.' The salts used were obtained from KAHLBAUM and were not submitted to any further purification.

TABLE II.

Salt.	Concentration.	Indicator.		Anion transport number. $V/(U + V)$ .	KOHLEBAUSCH.
		Cation.	Anion.		
KCl	—	Lithium	Formate	0·513	0·514
	0·1 <i>n</i>	„	Acetate	0·508	0·508
	0·02 <i>n</i>	„	„	0·507	0·507
	0·02 <i>n</i>	„	Benzenesulphonate	0·507	0·507
NaCl	—	„	Formate	0·621	0·637
	0·1 <i>n</i>	„	Acetate	0·618	0·617
	0·05 <i>n</i>	„	„	0·614	0·614
	0·04 <i>n</i>	„	„	0·612	—
BaCl <sub>2</sub>	0·7 <i>n</i>	„	„	0·624	—
	0·1 <i>n</i>	„	„	0·580	0·585
	0·02 <i>n</i>	„	„	0·565	0·565
SrCl <sub>2</sub>	0·1 <i>n</i>	„	„	0·601	—
	0·02 <i>n</i>	„	„	0·589	—
CaCl <sub>2</sub>	0·1 <i>n</i>	„	„	0·602	0·64
	0·02 <i>n</i>	„	„	0·588	0·59
KNO <sub>3</sub>	0·1 <i>n</i>	„	„	0·498	0·497
	0·02 <i>n</i>	„	„	0·498	—
K <sub>2</sub> SO <sub>4</sub>	0·1 <i>n</i>	„	„	0·515	—
	0·02 <i>n</i>	„	„	0·512	—
KClO <sub>3</sub>	0·1 <i>n</i>	„	„	0·464	—
	0·02 <i>n</i>	„	„	0·466	—
KBrO <sub>3</sub>	0·1 <i>n</i>	„	„	0·430	—
	0·02 <i>n</i>	„	„	0·433	—
KClO <sub>4</sub>	0·1 <i>n</i>	„	„	0·477	—
KBr	0·1 <i>n</i>	„	„	0·519	0·507
	0·02 <i>n</i>	„	„	0·518	0·507
KI	0·1 <i>n</i>	„	„	0·514	0·507
	0·02 <i>n</i>	„	„	0·513	0·507
KOH	1·0 <i>n</i>	„	Bromide	0·738	0·735
	0·1 <i>n</i>	„	„	0·743	—
NaOH	1·0 <i>n</i>	„	„	0·839	0·82
	0·1 <i>n</i>	„	„	0·842	0·81
HCl	0·1 <i>n</i>	Potassium	Iodate	0·165	0·172
	0·02 <i>n</i>	„	„	0·165	—
HNO <sub>3</sub>	0·1 <i>n</i>	„	„	0·145	—
	0·02 <i>n</i>	„	„	0·154	—
H <sub>2</sub> SO <sub>4</sub>	0·1 <i>n</i>	„	„	0·172	0·191
	0·02 <i>n</i>	„	„	0·167	—

It will be seen from the table that our results agree excellently with those obtained by HITTORF'S method, the difference in most cases being only a few units in the third decimal place. One of the most marked exceptions is  $n/1$  sodium chloride, for which we find 0.621 instead of 0.637. We have repeated this experiment a number of times and always with the same result. Possibly the older value requires confirmation.

KOHLRAUSCH and HOLBORN give the same value, 0.508, for the anion transport number of potassium chloride, bromide, and iodide. On the other hand, we have found the following values :—

$$\begin{aligned} \text{Potassium chloride, } p &= 0.508. & \text{Potassium bromide, } p &= 0.518. \\ \text{Potassium iodide, } p &= 0.513. \end{aligned}$$

As these results were so different from what we expected, we have measured the last two salts several times and invariably with the same result, so that we were at last convinced that our numbers were correct. We have since found a paper by KOHLRAUSCH ('Zeit. für Electrochemie,' 1902, VIII., p. 630) which had escaped our notice. In this paper KOHLRAUSCH describes experiments showing that the velocities of the ions Cl', Br', and I', as determined from conductivity measurements, are as follows :—

$$\text{Cl} = 65.44. \quad \text{Br} = 67.63. \quad \text{I} = 60.40.$$

These figures give for the transport number of the three salts the following numbers :—

$$\begin{aligned} \text{Potassium chloride} &= 0.502, & \text{Potassium bromide} &= 0.511, & \text{and} \\ \text{Potassium iodide} &= 0.501, \end{aligned}$$

which is practically the same ratio as that found by us. The difference between the actual values is due to KOHLRAUSCH'S figures being for infinite dilution, whereas ours are for  $n/50$  solutions.

Further confirmation of the correctness of our results is afforded by the fact, which will be referred to again later, that the potassium ion has the same velocity in equimolecular solutions of the above three salts if our values for the transport numbers are correct, but its velocity is different if the ordinary values are correct.

#### *Measurement of the Ionic Velocities.*

The term "ionic velocity" appears to have been used by different writers in different senses, and as a consequence there is some confusion as to its exact significance. In what follows we shall speak of :—

- (1) The *actual measured velocity* of the ion or ionic margin, which is its velocity under the potential gradient of the experiment.
- (2) The *actual mobility* (U or V) or the velocity of the ion in a given solution under a potential gradient of 1 volt per centimetre.

- (3) The *specific mobility* ( $u$  or  $v$ ) or the velocity which the ion would have under a potential gradient of 1 volt per centimetre if the salt were completely dissociated. These are related to the actual mobilities as follows :

$$U = \alpha u \quad \text{and} \quad V = \alpha v,$$

$\alpha$  being the degree of dissociation of the salt.

- (4) The “Ionen Beweglichkeit” ( $l_a$  or  $l_k$ ) of KOHLRAUSCH, which is given by the relation

$$\mu = \alpha (l_a + l_k),$$

$\mu$  being the molecular conductivity.

The use of the term “specific ionic velocity” for  $l_a$  and  $l_k$  is confusing, and we suggest instead the name “specific ionic conductivity.”

- (5) The “ionic conductivity” for a given strength of solution can then be conveniently represented by

$$L_a \text{ and } L_k, \quad \text{where} \quad L_a = \alpha l_a \quad \text{and} \quad L_k = \alpha l_k.$$

The actual mobilities  $U$  and  $V$  are obtained from the measured velocities by dividing the latter by the potential gradient in the measuring tube. This potential gradient,  $\Pi$ , is easily calculated as follows:—According to OHM’S law the current,  $C$ , flowing through the apparatus,  $C = \Pi/r$ .  $C$  is measured, and  $r$ , or the resistance of 1 centim. of the liquid, is obtained from its specific conductivity,  $\kappa$ , and the area of cross-section,  $A$ , of the tube,  $r = 1/\kappa A$  and hence  $\Pi = C/\kappa A$ .

The actual mobilities of the ions of a number of salts have been measured, and the results at  $18^\circ$  are contained in Columns 6 and 9 of Table III, and, for comparison with these, two sets of figures are given in Columns 7 and 10 and 8 and 11 respectively. These figures are calculated from KOHLRAUSCH’S conductivity data in the following manner:—

The molecular conductivity

$$\mu = \kappa/\eta = \alpha (l_a + l_k) = L_a + L_k,$$

whence

$$\kappa = (L_a + L_k) \eta,$$

$\eta$  being the concentration in gramme equivalents per cubic centimetre.

Now,  $\kappa$  is the specific conductivity, or the quantity of electricity carried in one second between two electrodes 1 centim. apart in a tube of 1 sq. centim. cross-section under a potential gradient of 1 volt per centimetre.

This obviously depends on ( $\alpha \times \eta$ ), or the number of ions present, on their specific mobility ( $u$  and  $v$ ), and on the quantity of electricity carried by one gramme ion, viz., 96540 coulombs. Hence

$$\kappa = \alpha \eta (u + v) 96540 = \eta (U + V) 96540,$$

TABLE III.

1.	Salt and concentration.	2.	3.	4.		5.	6.			8.	9.	10.	11.
				Transport number, $V/(U+V)$ .			Anion velocity $V$ in centimetre/seconds.						
		Molecular conductivity found from $U+V$ .	Molecular conductivity given by KOHL-RAUSCH.	Found.	KOHL-RAUSCH.	Found.	Calculated from our transport number.	Calculated from KOHL-RAUSCH'S transport number.	Found.	Calculated from our transport number.	Calculated from KOHL-RAUSCH'S transport number.		
KCl	0.1 <i>n</i> 0.02 <i>n</i>	110.6 118.5	111.9 120.0	0.508 0.507	0.508 0.507	0.000582 0.000624	0.000588 0.000630	0.000588 0.000630	0.000563 0.000606	0.000568 0.000613	0.000568 0.000613		
KBr	0.1 <i>n</i> 0.02 <i>n</i>	112.8 119.7	114.0 119.5	0.519 0.518	0.508 0.507	0.000607 0.000642	0.000613 0.000641	0.000600 0.000629	0.000562 0.000598	0.000568 0.000598	0.000582 0.000611		
KI	0.105 <i>n</i> 0.021 <i>n</i>	113.0 119.0	113.8 121.2	0.514 0.513	0.508 0.507	0.000601 0.000632	0.000606 0.000645	0.000597 0.000637	0.000570 0.000600	0.000574 0.000611	0.000580 0.000619		
NaCl	0.1 <i>n</i>	92.5	92.5	0.617	0.617	0.000591	0.000591	0.000591	0.000367	0.000367	0.000367		
KNO <sub>3</sub>	0.1 <i>n</i> 0.02 <i>n</i>	103.1 112.6	104.3 115.2	0.498 0.498	0.497 —	0.000532 0.000581	0.000538 0.000594	0.000536 —	0.000536 0.000587	0.000543 0.000600	0.000544 —		
K <sub>2</sub> SO <sub>4</sub>	0.1 <i>n</i> 0.02 <i>n</i>	95.7 111.6	95.9 111.8	0.514 0.512	— —	0.000510 0.000593	0.000511 0.000595	— —	0.000482 0.000564	0.000482 0.000565	— —		
KClO <sub>3</sub>	0.1 <i>n</i>	98.8	99.1	0.464	—	0.000474	0.000476	—	0.000549	0.000550	—		
KBrO <sub>3</sub>	0.1 <i>n</i> 0.02 <i>n</i>	93.4 102.3	95.1 104.5	0.430 0.433	— —	0.000416 0.000460	0.000424 0.000468	— —	0.000551 0.000602	0.000561 0.000614	— —		
BaCl <sub>2</sub>	0.1 <i>n</i> 0.02 <i>n</i>	91.7 103.0	92.2 103.3	0.583 0.565	0.585 0.565	0.000554 0.000603	0.000556 0.000605	0.000559 0.000605	0.000396 0.000464	0.000398 0.000466	0.000396 0.000466		
SrCl <sub>2</sub>	0.1 <i>n</i> 0.02 <i>n</i>	89.6 99.4	90.2 101.0	0.600 0.588	— —	0.000557 0.000605	0.000560 0.000615	— —	0.000372 0.000424	0.000374 0.000431	— —		
CaCl <sub>2</sub>	0.105 <i>n</i> 0.021 <i>n</i>	87.4 97.6	87.8 99.1	0.602 0.586	0.64 0.59	0.000545 0.000594	0.000547 0.000602	0.000582 0.000605	0.000360 0.000419	0.000362 0.000425	0.000327 0.000421		
HCl	0.1 <i>n</i> 0.02 <i>n</i>	350 368	351 367	0.165 0.165	0.172 —	0.000600 0.000629	0.000601 0.000627	0.000626 —	0.00303 0.00318	0.00303 0.00318	0.00301 —		
HNO <sub>3</sub>	0.1 <i>n</i> 0.02 <i>n</i>	350 359	350 364	0.145 0.153	— —	0.000526 0.000569	0.000527 0.000578	— —	0.00310 0.00315	0.00310 0.00319	— —		
H <sub>2</sub> SO <sub>4</sub>	0.1 <i>n</i> 0.02 <i>n</i>	234 280	225 286	0.175 0.167	0.191 —	0.000424 0.000485	0.000408 0.000495	0.000446 —	0.00200 0.00242	0.00182 0.00247	0.00188 —		
KOH	0.1 <i>n</i>	218	214	0.740	0.735	0.00167	0.00164	0.00163	0.000588	0.000577	0.000589		



and from these two equations we obtain

$$U + V = (L_a + L_k) \times \frac{1}{96540}, \quad \text{and} \quad u + v = (l_a + l_k) \times \frac{1}{96540}.$$

We thus obtain the value of  $(U + V)$ , and by multiplying this by the anion transport number  $U/(U + V)$  we obtain  $U$  and, consequently,  $V$  also.

It will be noticed that the figures given in columns 7 and 10 agree on the whole much better with the directly observed mobilities than do those given in columns 8 and 11. In calculating the former our transport number has been used, those of KOHLRAUSCH having been used in calculating the latter. The two sets of transport numbers are given in columns 4 and 5.

The comparison can be made in the opposite manner,  $\mu$  being calculated from the actual mobilities from the relation

$$\mu = \alpha (l_a + l_k) = \alpha (u + v) \times 96540 = (U + V) \times 96540.$$

This calculation has also been made and the results are given in the second column of the table, KOHLRAUSCH'S values for  $\mu$  being given in the third column.

Table IV. contains a similar set of results to those given in Table III., the measurements having been made at  $25^\circ$  with  $10^{\text{th}}$  normal solutions. As conductivity

TABLE IV.

1.	2.	3.	4.	5.	6.	7.	8.
Salt.	T = 25° C.		Transport number, $V/(U + V)$ .	Anion velocity, V.		Cation velocity, U.	
	Molecular conductivity, $\mu$ , from $U + V$ .	Molecular conductivity, $\mu$ , KOHLRAUSCH.		Found.	Calculated.	Found.	Calculated.
KCl	128.2	128.8	0.507	0.000674	0.000676	0.000654	0.000658
KBr	131.9	132.0	0.520	0.000710	0.000711	0.000656	0.000657
KI	130.0	130.9	0.517	0.000696	0.000701	0.000652	0.000655
KNO <sub>3</sub>	119.8	119.4	0.499	0.000619	0.000618	0.000621	0.000620
KBrO <sub>3</sub>	107.7	107.2	0.430	0.000480	0.000479	0.000636	0.000635
KClO <sub>3</sub>	113.2	113.2	0.463	0.000544	0.000544	0.000631	0.000631
K <sub>2</sub> SO <sub>4</sub>	108.9	109.0	0.521	0.000588	0.000588	0.000540	0.000540
CaCl <sub>2</sub>	101.0	101.4	0.604	0.000631	0.000635	0.000412	0.000416
BaCl <sub>2</sub>	105.2	105.2	0.584	0.000638	0.000638	0.000452	0.000452
SrCl <sub>2</sub>	101.2	101.2	0.596	0.000626	0.000626	0.000424	0.000424

determinations at this temperature were not available, the calculated mobilities given in columns 6 and 8 were obtained from our own conductivity measurements, which are given in column 3 for comparison with the molecular conductivities (column 2) as

calculated from our specific mobilities (columns 3 and 5), whilst the agreement between the found and calculated values is remarkably close in the majority of instances. A few cases, where the differences are larger, call for special comment. For example, the calculated and observed mobilities of the hydrogen ion in hydrochloric and nitric acid solutions agree very well indeed, whereas the agreement is by no means good for the velocities of the anions of these acids. This is explained by the fact that the velocity of the hydrogen ion is about five times as great as that of the chlorine ion (or nitrate ion), and as a consequence the latter only moves about 10 millims., whilst the former moves through the whole length of the tube. The result of this is that there is a very much larger percentage experimental error introduced in the measurement of the mobility of the anion than in that of the cation of an acid. The same applies, but in the opposite sense, to the measurement of the mobilities of the anion and cation of an alkali.

The observed values for  $n/10$  sulphuric acid are quite different from the calculated values. Whether this is due to the inaccuracy of the transport number, or to the occurrence of complexes in the system, it is not possible to say, but the cause of error seems to have completely disappeared in the  $n/50$  solutions.

Interesting results are obtained when we compare the velocities of the same ion in equimolecular solutions of different salts. KOHLRAUSCH'S law of the independent wandering of the ions depends on the assumption that, in solutions sufficiently dilute for any variation in "electric friction" to be neglected, the same ion has the same velocity in whatever solution it occurs. If this is so, and remembering that it is only the specific mobility,  $u$ , that is invariable, and that the actual mobility  $U = au$ , we see at once that it is only in solutions of salts that are equally ionised that we can expect to find the same actual mobility for the same ion, and, on the other hand, where we do find this, we have strong evidence that the salts in solution are equally ionised.

On comparing the velocities of the potassium ion in equimolecular solutions of all the potassium salts that we have measured (see Table V.), we find that this velocity is identical in solutions of potassium, chloride, bromide, and iodide, but is a little smaller in the other solutions. This identity of mobility is manifested not only in

TABLE V.—Velocity of K ion in various Salt Solutions.

Salt.	$n/10$ at $18^\circ$ .	$n/50$ at $18^\circ$ .	$n/10$ at $25^\circ$ .
KCl	0·000563	0·000606	0·000654
KBr	0·000562	0·000598	0·000656
KI	0·000564	0·000599	0·000652
KClO <sub>3</sub>	0·000549	—	0·000631
KBrO <sub>3</sub>	0·000551	0·000601	0·000636
KNO <sub>3</sub>	0·000536	0·000583	0·000621
K <sub>2</sub> SO <sub>4</sub>	0·000510	0·000593	0·000540

10<sup>th</sup> normal solutions at 18° and 25°, but also in 50<sup>th</sup> normal solutions at 18°. In the same way the mobilities of the chlorine ion in equimolecular solutions of different salts have been gathered together in Table VI. In this case, also, the same mobility

TABLE VI.—Velocity of Cl ion in various Salt Solutions.

Salt.	$n/10$ at 18°.	$n/50$ at 18°.	$n/10$ at 25°.
KCl	0·000582	0·000622	0·000674
NaCl	0·000585	—	—
BaCl <sub>2</sub>	0·000554	0·000603	0·000638
SrCl <sub>2</sub>	0·000559	0·000604	0·000626
CaCl <sub>2</sub>	0·000542	0·000596	0·000631

occurs in solutions of potassium and sodium chlorides, and similarly for the hydrogen mobilities which are given in Table VII.

These results indicate that the direct measurement of the actual ionic mobility gives us a means of comparing the degree of ionic dissociation of equimolecular

TABLE VII.—Velocity of H ion in various Acids.

Salt.	$n/10$ at 18°.	$n/50$ at 18°.	$n/10$ at 25°.
HCl	0·00304	0·00317	—
HNO <sub>3</sub>	0·00311	0·00315	—
H <sub>2</sub> SO <sub>4</sub>	0·00201	0·00242	—

solutions of salts containing a common ion. If we assume that in dilute solutions  $v$ , or the specific mobility of a given ion, is invariable in different salt solutions, then, since  $U = \alpha v$ ,  $\alpha$  is proportional to  $U$ . Table VIII. contains a comparison on this basis of the degrees of dissociation of all the salts containing one ion in common that have been measured by us. The figures are given as the ratio of the degree of dissociation of the salt to that of potassium chloride, which has been taken as standard, and the same ratio has been calculated from the conductivity data, and the results are given for comparison in the third and fifth columns of the table.

From the very satisfactory agreement of the results obtained by the present method with the corresponding numbers given by KOHLRAUSCH, it is evident that a considerable degree of accuracy in the direct measurement of ionic velocities has been attained. It is interesting to look over HITTORF's early transport numbers, amongst which deviations of 5 and 10 per cent. are frequently met with.

The numbers subsequently obtained were much more concordant, but the method, as already stated, is difficult and laborious, and only rarely can an experiment be

completed in a day. The direct method, in its present form, gives results at least as accurate as the indirect one, and with much less trouble. In dilute solution the determination is generally complete in about half an hour, as the high voltage, which is necessary in such solutions, imparts a considerable velocity to the ions. After

TABLE VIII.—Degrees of Dissociation.

Salt.	$n/10.$		$n/50.$	
	Found.	Calculated.	Found.	Calculated.
KBr	1.00	1.00	0.98	—
KI	1.00	1.01	0.98	1.01
KNO <sub>3</sub>	0.95	0.97	0.96	1.00
K <sub>2</sub> SO <sub>4</sub>	0.85	0.83	0.93	0.91
KClO <sub>3</sub>	0.98	—	0.91	—
KBrO <sub>3</sub>	0.98	—	0.90	—
NaCl	1.01	0.99	—	—
BaCl <sub>2</sub>	0.95	0.88	0.97	0.93
SrCl <sub>2</sub>	0.96	0.88	0.97	0.93
CaCl <sub>2</sub>	0.94	0.87	0.96	0.91
HCl	1.01	1.07	1.02	1.04
HNO <sub>3</sub>	1.02	1.01	1.01	1.00

becoming accustomed to the method, it is easy to perform five or six experiments in a day. In general the total amount of motion for anion and cation was about 6 centims., with a probable error in reading of about 0.01 centim. for each boundary, *i.e.*, a total error of about 0.3 per cent. The error in measuring the conductivity might be 0.5 per cent., and the error in measuring the small amount of current flowing through the apparatus also about 0.5 per cent. The error in the calibration of the tube is negligible, and, therefore, in a good experiment the transport number should be correct to about 1 part in 300, and the ionic velocities to at least 1 part in 100. As a matter of fact, this degree of accuracy is easily attainable for the transport number. In the case of the separate ionic velocities the accuracy obtainable is not quite so great owing to the accumulation of errors from the various measurements involved.