acid, described in the literature, the 2-4-6-tribrom acid[1], is given as 170.5°

As it was found so difficult to obtain sharply melting products by this process of bromination, the work was suspended. It may be possible to obtain bromsubstitution products free of isomers by the method of bromination, so successfully used by Bogert and Hand[2] in their work on the ortho compound, and the matter will be further investigated.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, December, 1903.

ON THE VELOCITIES OF THE IONS IN LIQUID AMMONIA SOLUTIONS.

BY EDWARD C. FRANKLIN AND HAMILTON P. CADY.

Received February 23, 1904.

OBJECT OF THE RESEARCH.

INVESTIGATIONS on the electrical conductivity of liquid ammonia solutions, interpreted in accordance with the theory of electrolytic dissociation, have led to the conclusion that while salts at ordinary dilutions are dissociated to a much greater extent in water than in ammonia, the ions, nevertheless, in the latter solvent, travel with much the greater speed. It was to measure directly the speeds of the ions in liquid ammonia and compare the results thus obtained with the ionic velocities calculated by the method of Kohlrausch from conductivity measurements that this research was undertaken.

HISTORICAL.

Investigations on Liquid Ammonia.—In 1897, Cady[3] made the important discovery that liquid ammonia solutions of certain salts are excellent conductors of electricity, and in explanation of this fact he assumed that ammonia must approximate, or probably even surpass, water in its power to effect electrolytic dissociation.

The same opinion was expressed by Goodwin and Thompson[4] in a paper on the dielectric constant and electrical conductivity of

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[1] *Ber. d. chem. Ges.*, **10**, 1708.

[2] This Journal, **25**, 935.

[3] *Jour. Phys. Chem.*, **1**, 707 (1897).

[4] *Phys. Rev.*, **8**, 48 (1899).

liquid ammonia, notwithstanding the fact that they found the dielectric constant of the liquid to be about 22 units,[1] a value which, assuming the approximate validity of the Nerst-Thompson rule places liquid ammonia among the alcohols and far below water in its dissociating power.

It was suggested by Franklin and Kraus, as a result of their investigations on the ebullioscopic behavior of liquid ammonia solutions,[2] that, in all probability, the dissociating power of ammonia is much below that of water, and that the high conductivity of ammonia solutions is rather to be ascribed to the high speed with which the ions travel in this solvent.

In a research on the electrical conductivity of liquid ammonia solutions,[3] the same authors succeeded in establishing a maximum molecular conductivity for a number of salts in liquid ammonia solution, at dilutions very much higher than that required to produce practically complete dissociation in aqueous solutions. It was shown in this investigation, for example, that, whereas in water at 18° the molecular conductivities of the binary alkali metal salts approximate their maximum value of 100 to 130 Kohlrausch units at dilutions of 1,000 to 5,000 liters per molecule, ammonia solutions of the same salts, on the other hand, do not reach their much higher maximum values of 280 to 340 units until the dilution reaches 40,000 to 80,000 liters per gram-molecule. These are facts which, interpreted in accordance with the theory of electrolytic dissociation, lead to the conclusion that the dissociating power of liquid ammonia is comparatively low while the speed with which the ions travel in this solvent is exceptionally high.[4]

It may be worth while to point out here that in further agreement with this conclusion is the fact, frequently observed in this laboratory, that ammonia at —33° is a liquid of much less viscosity than is water at the ordinary temperature.

Measurements of Absolute Ionic Velocities in Aqueous Solutions.—We are indebted to Sir Oliver Lodge[5] for the ingenious conception of actually watching the advance of the ions through

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[1] Goodwin and Thompson's measurements were made at —34°. Coolidge (*Wied. Ann.*, **69**, 140 (1899)) obtained 16 as the value of the dielectric constant at 14°.

[2] *Am. Chem. J.*, **20**, 852 (1898), and **21**, 14 (1899).

[3] *Ibid.*, **23**, 297 (1900).

[4] Jones (*Am. Chem. J.*, **25**, 234 (1901)) also points out that it is necessary to assume a high velocity for the ions in liquid ammonia.

[5] British Association Reports, 1886, p. 389.

solutions carrying the electric current. In his experiments on the speed of the hydrogen ions, a glass tube was filled with a jelly made up from agar-agar and a dilute solution of sodium chloride containing a little phenolphthaleïn, and just enough sodium hydroxide to bring out the red color of the dye. The ends of the tube were then inserted in dilute sulphuric acid and a current of electricity was sent from dilute acid to dilute acid through the tube. As the current passed, the progress of the hydrogen ions along the tube was marked by the destruction of the red color of the indicator. His measurements on the speed of the hydrogen ions gave results in fair accordance with the velocity as calculated by the method of Kohlrausch. Similar experiments, however, for obtaining the speeds of other ions gave results differing widely from Kohlrausch's calculated speeds.

W. C. D. Whetham[1] pointed out some of the causes for the discrepancies in Lodge's determinations, improved the method, and obtained values for the speed of a number of ions in water and alcohol solutions which, in some of his measurements, are in good accord with the calculated velocities. The method used will be clear from the following quotation from Whetham's first paper.[2] "Consider the boundary of two solutions of slightly different density, which have one ion in common, but are of different colours. Let us denote the salts by *AC* and *BC*. When the 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 cation *A* or *B*, the boundary will move with the current, and the velocity will indicate that of the ion causing the change in colour." Whetham emphasized the necessity of knowing the electrical potential acting upon the moving ions, and showed how to make a fairly close approximation to a regular fall of potential along the velocity tube, by choosing solutions of nearly equal specific conductivity. He also showed that it is possible to dispense with the jelly in the velocity tube.

Nernst[3] has described a lecture experiment for demonstrating the movement of the permanganate ion against the current in a

[1] *Phil. Trans.*, **184**, 337 (1893), and **186**, 507 (1895).

[2] *Loc. cit.*

[3] *Ztschr. Elektrochem.*, **3**, 308 (1896-1897).

solution of potassium permanganate, and at the same time suggests that his method might easily be modified to permit of its use in measuring specific ionic velocities.

Professor Orme Masson[1] has made use of the method of Lodge for the direct measurement of Hittorf's transport numbers. The modifications introduced will be sufficiently obvious from a short description of one of Masson's experiments. Two electrode vessels, containing respectively solutions of copper chloride and potassium chromate, were connected by means of a tube filled with a solution of potassium chloride of known concentration in agar-agar jelly. As the current passes the tube, the yellow and blue boundaries travel to meet each other, and the ratio of the distances traveled in a given time is taken as the ratio of the speeds of the chlorine and potassium ions respectively. Masson showed both experimentally and theoretically that the motion of the boundary, provided the colored ion be chosen specifically slower than the colorless ion, is in reality a measure of the velocity of the latter ion and not that of the colored ion. He showed that under these conditions, the meniscus remains sharp, that there is no mixing of the solutions, and that the concentration of the colorless solution, and with it the slope of potential along this portion of the tube, remains constant independently of the extent of the encroachment of the colored zones.

Since the completion of the work described in this paper, Steele,[2] and Abegg and Gaus[3] have published the results of their important investigations on the velocities of the ions in aqueous solutions.

EXPERIMENTAL.

With the object in view of applying the method worked out by Masson to the measurement of the velocities of the ions in liquid ammonia, we have undertaken the construction of a form of apparatus adapted for use with this volatile liquid. After many changes, including the entire reconstruction of all the essential parts, the apparatus used finally took on the form herewith described.

The Constant Temperature Bath.—The measuring apparatus

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[1] *Phil. Trans.*, **192**, 331 (1899).

[2] *Ztschr. phys. Chem.*, **40**, 689 (1902); *J. Chem. Soc.* (London), **79**, 414 (1901); and *Phil. Trans.*, **198**, 105 (1902).

[3] *Ztschr. phys. Chem.*, **40**, 737 (1902).

proper, which includes the test-tube-shaped receptacle *A* (Fig. 2), together with its contents, is kept at a constant temperature by a bath of liquid ammonia contained in the vacuum-jacketed tube *B*.

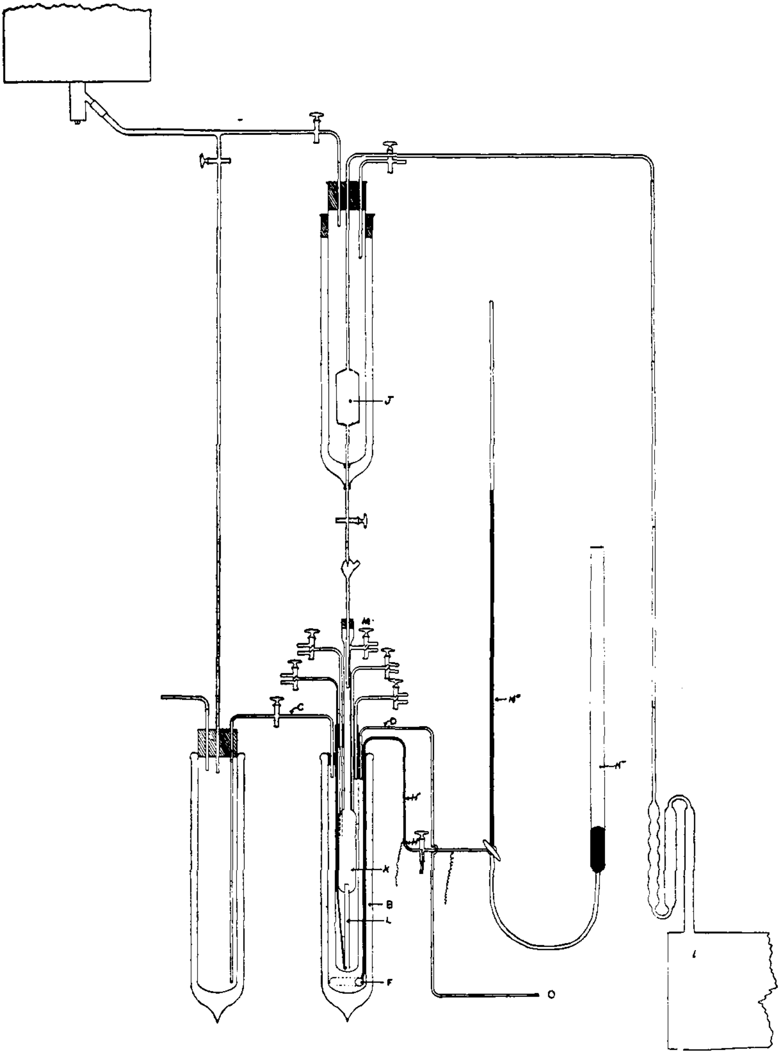

Fig. 1. One-tenth natural size.

Liquid ammonia is supplied to this bath through the tube *C*, while the ammonia gas escapes by way of tube *D*. The temperature of

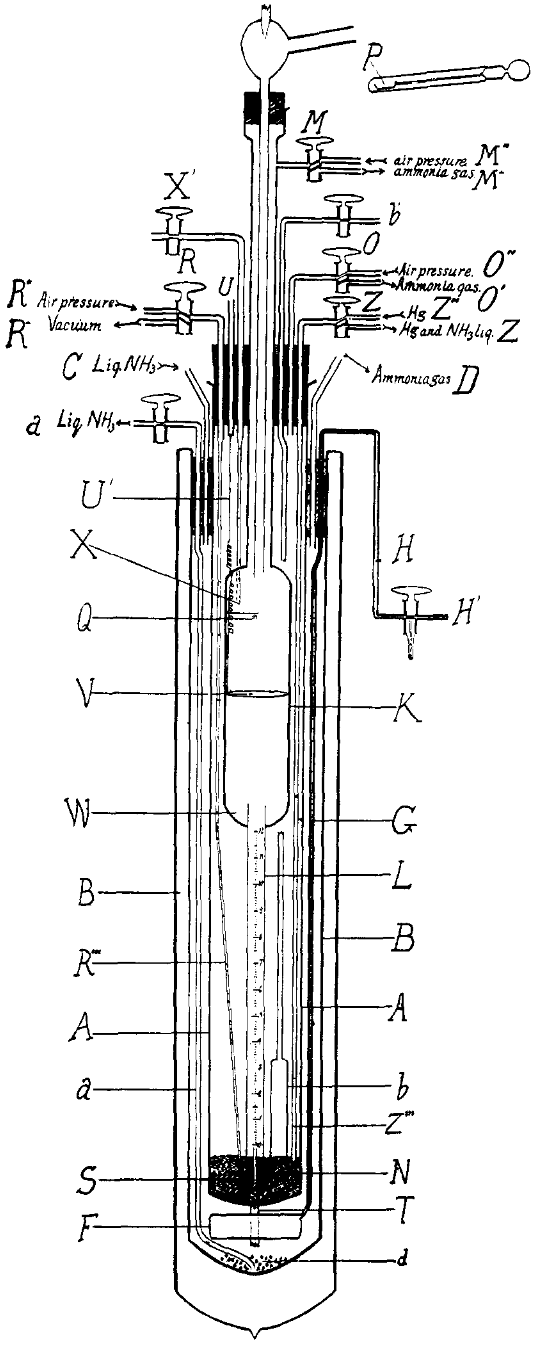

Fig. 2. One-third natural size.

the bath is regulated by an adaptation of Ostwald's constant temperature device. In the figures, *F* and *G H* are the bulb and stem respectively of an air thermometer which is set to maintain the temperature at any constant point by raising or lowering the mercury receptacle *H''*, connected with the stem *H'*, and a barometer tube, *H'''* (Fig. 1). If, after setting the receptacle to correspond to the temperature desired, the temperature of the bath is above that chosen, then the mercury in the thermometer stem fails to make contact at the platinum point *H*, and the passage from *D*, through the proper vessels for protection and capacity, to an ordinary Bunsen vacuum pump, remains unobstructed, with the result that the diminution of pressure on the surface of the liquid brought about by the action of the pump, causes the liquid to boil, and the temperature to fall rapidly. The cooling of the air in the thermometer bulb *F*, soon brings the mercury into contact with the point *H*, thereby completing an electric circuit which includes an ordinary telegraphic relay. This relay in its turn operates a telegraph sounder which is arranged to close down on a piece of rubber tubing inserted in the exit train from *D*, thereby putting the pump out of action. The liquid in the bath then warms up until the contact at *H* is again broken, and the liquid is again set to boiling. This cycle of operations repeats itself every twenty to sixty seconds and maintains the temperature of the bath constant to within 0.2°. To prevent bumping and to insure regular boiling of the ammonia contained in the constant temperature bath a quantity of platinum tetrahedra[1] is placed in the vacuum-jacketed tube at *d*.

The Measuring Cell.—After the constant temperature bath is in operation, ammonia is distilled from the steel cylinder *I* into the receptacle *J* (Fig 1), whence, with the stop-cock *M* (Fig. 2) set to carry off the ammonia gas through *M'*, it is drawn down into the cell *K L*, shown in detail in Fig. 2. Compressed air is then turned on to the surface of the liquid in *K* through the stop-cock *M'' M*. This forces the liquid from the cell *K L*, through the mercury *S*, into the outside compartment *A*, the stop-cock *O* having been previously set to carry off the ammonia gas. These operations are repeated several times until the cell *K L* is thoroughly washed, and the liquid in *A* stands well up on the out-

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[1] **Beckmann**: *Ztschr. phys. Chem.*, **21**, 248 (1896).

side of *K*. Stop-cock *M* is then set to open through *M'* and stop-cock *O* is turned to admit air pressure to the surface of the liquid in *A*. This raises a column of mercury in the graduated tube *L*, and insures against any transfer of material from *K* to *A* while the solution is being made up. A weighed quantity of solute is then introduced by means of the platinum spoon at *P*, and ammonia is run into the cell *K L* in the manner described above until the fine glass pointer *Q* is covered. Stop-cock *O* is then turned to shut off the air pressure and to open through *O'*. This brings the mercury to the same level inside and outside of the tube *L*. Air pressure is now turned on through *R''R'''* for the purpose of thoroughly mixing the contents of the cell *K L*. After the salt is dissolved and the contents of the cell are homogeneous, *R* is closed, and air pressure is gradually turned on at stop-cock *O*. This raises the mercury in the graduated tube *L*, and the point to which it rises on the scale is read just as the surface of the ammonia in *K* comes into contact with the pointer *Q*. This observation, together with the weight of solute introduced, gives the data necessary for calculating the concentration of the solution. With sufficient air pressure through *O* to maintain a short column of mercury in *L*, stop-cock *R* is turned to connect vacuum with the capillary stirring tube *R'''*. This fills the capillary tube with mercury and thereby precludes any possibility of the solution in *L* being disturbed by the chance escape of a bubble of air after the meniscus has started up the tube. With stop-cock *R* closed, and *O* opened through *O'*, the mercury in the graduated tube *L* sinks to a level with that outside, while *M'* and *O'* opening through short wide tubes into a common receptacle insure against any changes in the level of the mercury at the foot of *L* during the course of the measurement. The quantity of mercury at *S* has been previously so fixed as to just cover the end of the capillary tube *R'''* when the pressure inside and outside the cell *K L* is equalized.

Everything is now ready for beginning the observations on the movement of the meniscus. With the mercury *S* at the foot of the velocity tube constituting one electrode and the platinum ring *V* or a ring of mercury in the cup-shaped space *W* the other, a current of electricity, including in its circuit a rheostat and milliammeter, is turned through the solution in the cell. Connection is made with the upper electrode through the mercury cup *U* and the platinum wire *U'*, while the connection from the lower one is through a platinum wire, *T*, sealed into the bottom of the receptacle *A*, and thence through mercury contained in a tube sealed over the platinum wire *T* and reaching the exterior with the other tubes at the mouth of the constant temperature bath. This connection is not shown in the figure. The platinum ring *V* is used as cathode for the measurement of the ammonium ion, and as anode when observations on the speed of anions are being made. When the speeds of potassium, sodium and silver ions are being measured, the ring of mercury resting in the space *W* and connected with the ring *V* is made cathode.

The Cation Boundary.—As the current passes up the tube, mercury ions are formed at the anode, thus giving rise to a solution of mercury salt denser than the solution above it, and serving most excellently the purpose of a cation indicator. With a current of proper strength passing through the tube, the meniscus soon comes out as a very distinct line separating the mercury solution from the superimposed solution. The meniscus is most distinct when observed against a sky background. The position of the meniscus on the scale is read every ten minutes and at the same time a measurement is taken of the current. After the desired number of readings has been made, the contents of the cell *K L* are forced out into the compartment *A*, and the cell is washed with ammonia after the manner described above, when the cell is ready for beginning another measurement. As the compartment *A* is filled up past the level *X*, the excess of ammonia is removed by forcing it out through *X'*, for which purpose the air pressure must be turned on simultaneously through *M''M* and *O''O* to avoid disturbing the level of the mercury at the foot of the velocity tube. At the end of a series of measurements the entire contents of *A* and *K L* are removed through *Z Z'*, and the constant temperature bath is emptied through *a*, air pressure being turned on through *M''M* and *D* for this purpose.

The Anion Boundary.—To measure the speed of the anion, an indicator must be introduced into the foot of the velocity tube *L*, and the direction of the current reversed. Before assembling the apparatus, a quantity of the indicator, compressed into tablets, is packed into the enlarged portion of the tube *b*, care being taken to leave a channel for the free passage of air and liquid up the tube. The apparatus is then put together, and mercury is run into the compartment *A*, through *Z″Z*, until the lower ends of both *L* and *b* are well covered. The process of filling the compartment *A* with ammonia, and the cell *K L* with solution, is then carried out as described above. The level of the liquid in *A* is adjusted to be somewhat above that of the solution in *K*, in order that the indicator solution may flow into the foot of the velocity tube as described below. A quantity of lead peroxide is now introduced through the tubulure *P*, sufficient to cover the surface of the mercury in the bottom of the velocity tube. The lead peroxide is used to prevent the evolution of hydrogen at the cathode and the consequent disturbance to the meniscus by rising bubbles of gas. Mercury is now gradually drawn out of *S* through the tube *Z‴* and the stop-cock *Z′* until the lower end of *b* is uncovered and ammonia begins to enter the indicator receptacle *b*. As soon as sufficient solvent has run in upon the indicator to dissolve it, mercury is again run into *S* to close the mouth of the receptacle *b* until the indicator is dissolved. The solution of the solid is accompanied by the evolution of heat. To prevent the consequent forcing out of the liquid and the escape of bubbles of air and ammonia gas up through the liquid in compartment *A*, the stop-cock *b′* is opened while the indicator is dissolving. The stop-cock *b′* is now closed, and the mercury in *S* is again lowered until the dense indicator solution runs out and spreads over the surface of the mercury in the form of a sharply defined layer. The mercury at *S* is then further carefully lowered until the minute hole *N*, in the lower end of the graduated tube, is just exposed. The indicator solution flows in quietly and forms a stratum beneath the solution in the velocity tube. As soon as sufficient indicator has entered the tube, mercury is again run into *S* until the pin-hole *N* is well covered, when the current is immediately turned on and the observations on the moving meniscus are begun and carried on as described above for the cations. If the operations attendant upon the introduction of the indicator solutions are sucessfully carried out, there is little mixing of the solutions, and the meniscus comes out sharply soon after starting the current. If, however, the solutions are allowed to mix to any considerable extent, a thing which is prevented only by the exercise of the greatest care in manipulation, more time elapses before the meniscus comes out, or it may even fail altogether to appear.

CONDITIONS NECESSARY FOR THE DEVELOPMENT OF A MENISCUS.

From the experimental and theoretical work described in the papers by Whetham,[1] Weber,[2] Kohlrausch,[3] Masson,[4] and Abegg[5] it appears that the conditions affecting the movement of a boundary between two solutions carrying a current are as follows:

(1) *The indicator ion must be specifically slower than the ion whose speed is to be measured.* We have had abundant occasion to confirm this requirement in its application to ammonia solutions. In every case, when a well-formed meniscus is traveling up the velocity tube, separating a faster preceding ion from a specifically slower pursuing one, the reversal of the current soon brings destruction to the meniscus.

Attempts were made to show that the velocity of the meniscus is independent of the indicator ion so long as this fulfils the condition of being specifically slower than the pursued ion. Amalgams of aluminum, lead, bismuth and copper were substituted for pure mercury as anode in a number of experiments. With aluminum no meniscus could be obtained. Bismuth and lead both gave good boundaries, but because of "hydrolysis"[6] of the salts of these metals the results obtained were low. Experiments in which copper and mercury were used to indicate the progress of potassium and ammonium ions show that the speed of the meniscus is, in fact, the same whichever indicator is used.

(2) *If, as in the experiments described in this paper, the meniscus dividing the two solutions travels up the tube, then the indicator solution must be specifically heavier than the superimposed solution.* We learn from the work cited above that the concentration of the indicator solution adjusts itself to that of the solution above in such a way that the concentrations of the two solutions are to each other as the transport numbers of the pursuing and pursued ions. That is, $n/n' = p/p'$, in which n' and p' are the concentration and transference number respectively of the pursuing ion in the indicator solution, and n and p the corre-

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[1] *Phil. Trans.*, **184**, 337 (1893), and **186**, 507 (1895).

[2] *Sitzungsber. Akad. Wiss.*, Berlin, 1897, p. 936.

[3] *Wied. Ann.*, **62**, 209 (1897).

[4] *Phil. Trans.*, **192**, 331 (1899).

[5] *Ztschr. Electrochem.*, **7**, 618 (1900-1901).

[6] *Vide.*, p. 512.

sponding values for the upper solution. The result of this relation is that the indicator solution will always be the more dilute, a fact which must be taken into consideration in selecting an indicator.

(3) *The current through the tube must not be strong enough to produce a heating effect sufficient to bring about a mixing of the indicator solution into the solution above.* The fact that the specific resistance is greater in the indicator solution determines a greater heating effect in the latter solution. If the difference in the temperature of the two solutions is allowed to become too great, an inevitable mixing of the solutions results. We have frequently observed the destruction of the meniscus from this cause in our experiments. The first indication of danger is the bulging up of the center of the meniscus, to be followed soon by a thin streamer of the indicator solution making its way up through the center of the tube.

A similar relation exists between the resistances of the solution in the velocity tube and in the upper wider portion of the cell. The effect of the greater heating in the narrow tube is to cause a circulation of the solution, which, however, would not be objectionable were it not for the diluting of the solution in the upper portion of the cell by the action of the current at the cathode. The effect of diluting the solution above the meniscus is to produce a sharper fall of potential along the velocity tube and a consequent increase in the speed of the meniscus. This may explain the gradual increase in the velocity of the meniscus observed in the experiments on the potassium, sodium and ammonium ions.

On the other hand, no such acceleration of the motion of the meniscus was observed in the experiments on the speed of the anions. A plausible explanation of this fact is again the action at the upper electrode, which, in these experiments, is made the anode. As is shown (under 4) below, the action of the current at the anode is to increase, or in any event, not to diminish the concentration. A retarding effect, which might be expected as the result of an increase in the concentration of the solution in the velocity tube has, however, not been observed.

(4) *The fall of potential along the tube must be great enough to bring out a sharp meniscus.* In several of our experiments

the difference in density of the solutions used was obviously too slight to permit the realization of this condition. When the attempt was made to use picric acid as indicator for the iodine ion in ammonium iodide and potassium iodide the current could not be made sufficiently strong to bring out a meniscus without at the same time causing much mixing of the solutions. Even with iodoeosine, which seemed to work better than picric acid, mixing still took place to some extent when the current was made sufficiently strong to bring out a good meniscus.

(5) *The action at the electrodes must not be such as to introduce new ions which are faster than the ions traversing the tube.* It is plain that faster ions from either direction entering the velocity tube would alter the potential slope here by an unknown amount and thus render the calculation of the ionic velocities impossible.

That the action at the electrodes produced no disturbing effects in our experiments the following considerations will show. In all measurements on the velocities of the cations the action at the anode consists simply in the formation of the mercury ion, while at the cathode the action depends on the cation undergoing measurement. When this is sodium or potassium, the possible formation of a metalic amide is avoided by using a mercury cathode in which the metal dissolves; when it is ammonium, the action consists in the formation of ammonia and the evolution of hydrogen. When the speed of the anions is being measured, the upper electrode becomes the anode, and, in case the anion is the nitrate ion, the action here consists in the evolution of nitrogen and the formation of ammonium nitrate. This, to be sure, when the salt in the tube is not already ammonium nitrate, introduces a new ion, but in the experiments in which sodium and potassium nitrates are the salts used to furnish the nitrate ions the new ion is not faster than the cation already present. When the halogens are being measured, the action at the anode might be expected to give rise to the formation of halogen substitution products of ammonia, or to the evolution of nitrogen and the formation of ammonium halide, or, as a third possibility, the free halogen itself might be liberated. In our experiments the anode space developed a color as the electrolysis proceeded, which suggested the presence of the free halogen.[1] At the cathode, on the other hand, while the considerations advanced above show that there is no formation of a new faster ion, there is, especially with ammonium salts, evolution of hydrogen gas which passes up the tube and disturbs the meniscus. This difficulty was overcome by the introduction of a layer of lead peroxide upon the surface of the cathode as depolarizer. The action of the depolarizer in all probability gives rise to the formation of water and a lead salt, or possibly metallic lead, none of which, however, can have any influence upon the motion of the meniscus.

(6) *The salt used for furnishing the indicator ion must be one which does not undergo hydrolysis.*[2]

We have demonstrated in our experiments that this requirement applies also to ammonia solutions. When the attempt was made to use bismuth amalgam for furnishing the indicator ion for an ammonium nitrate solution, it was found that a bulky, white precipitate separated from the bismuth solution and settled on the surface of the bismuth-mercury anode. Lead behaved in a similar manner, but hydrolysis in this case was by no means so marked. Even with mercury, when the iodine ion was present in the standard solution, there was evidence of hydrolytic action. With bromine ions in sodium bromide solution the mercury in-

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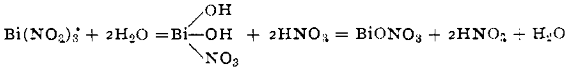
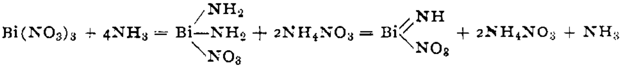
[1] Moissan (*Compt. Rend.*, **133**, 713 (1901)) states that free chlorine is evolved at the anode when a solution of ammonium chloride in liquid ammonia is electrolyzed at —35°.

[2] NOTE.—When the many points of similarity between water and liquid ammonia are recalled, it is not surprising to find that certain salts react with ammonia in a manner entirely analogous to hydrolytic action in aqueous solutions. For example, a reaction parallel to that which takes place when bismuth nitrate is treated with water might be expected to follow the introduction of this salt into liquid ammonia. Bismuth nitrate reacts with water to form basic bismuth nitrate and free nitric acid :



$$Bi(NO_2)_3 + 2H_2O = Bi\begin{cases}OH\\OH\\NO_3\end{cases} + 2HNO_3 = BiONO_3 + 2HNO_3 + H_2O$$

In an analogous manner bismuth nitrate might be expected to react with liquid ammonia to give a compound bearing a relation to ammonia similar to the relation borne by basic bismuth nitrate to water, together with ammonium nitrate, a compound related to ammonia as is nitric acid to water (*Am. Chem. J.*, **23**, 305 (1900)):



$$Bi(NO_3)_3 + 4NH_3 = Bi\begin{cases}NH_2\\NH_2\\NO_3\end{cases} + 2NH_4NO_3 = Bi\begin{cases}=NH\\NO_3\end{cases} + 2NH_4NO_3 + NH_3$$

That some such action as the one indicated takes place is rendered very probable by the formation of a white mass, soluble in ammonium nitrate, when bismuth nitrate is treated with liquid ammonia, and by the behavior of bismuth and lead solutions described in the paragraph below.

Although it is a rather violent procedure etymologically to use the term hydrolysis in connection with a solvent other than water, we shall nevertheless use the word in this paper with the meaning explained above.

dicator gave an abundant precipitate in the velocity tube; whether, however, the precipitate was the result of hydrolysis or was rather due to the limited solubility of mercury bromide has not been determined. With solutions of nitrates, neither mercury nor copper gave the slightest evidence of hydrolytic action.

Since one of the products of the hydrolysis of salts in ammonia is the formation of ammonium ions, it follows that the indicator solution will contain these faster ions, and that these must interfere with the motion of the meniscus, first, in the case that ammonium ions are in the solution above, by retarding its motion and second, when the pursued ions are potassium or sodium, by destroying the difference of density necessary for the maintenance of a good boundary.

(7) *The fall of potential along that portion of the tube containing the ion whose speed is to be measured must be known.*

Masson has suggested that this may be accomplished either by measuring the resistance of the upper solution by the method of Kohlrausch, or by direct measurements of the potential slope by means of wires sealed through the walls of the tube. Both methods were tried by us, the latter, in some preliminary experiments on aqueous solutions, without satisfactory results, the former in a modified form of the cell *K L*, with electrodes sealed in for the purpose. Since, however, measurements at the beginning of an experiment, by means of electrodes placed in the upper portion of the cell, could give no certain guarantee that the concentration of the solution in the narrow tube below does not change as it moves up the tube, this device was abandoned, and dependence placed in the theoretical and experimental work referred to above as demonstrating that the concentration of the solution in front of the meniscus and consequently the slope of potential through the tube does not change during the progress of an experiment. The fall of potential along the tube is calculated from the known current and the known constants of the tube and solution in a manner given in detail below.

(8) *The two solutions must contain one ion in common.* We have departed from the conditions laid down by previous investigators in that we have not in all cases used an indicator with one ion in common with the other salt. For example, we have used picric acid, which undoubtedly forms ammonium picrate when it

goes into solution, for indicating the movement of the nitrate ion in potassium nitrate, sodium nitrate and ammonium nitrate, and the concordant results obtained seem to justify the procedure.

A reconsideration of the theory of the moving boundary, moreover, leads to the conclusion that the movement of the boundary must be independent of the nature of both the cation and anion of the indicator so long as the indicator ion itself is specifically slower than the pursued ion.

Consider Figure 3. A solution of sodium nitrate is superimposed upon a solution of ammonium picrate. As the current passes down the tube the sodium and ammonium ions travel in the direction of the current, while the nitrate ions move in the opposite direction, followed by the picrate ions. After a short time the condition shown in Fig. 4 is produced; that is, there are now three zones instead of two. Above is the sodium nitrate zone, below which and above the ammonium picrate solution is a layer containing both sodium picrate and ammonium picrate. Since the ammonium ions travel down the tube, none of these can be mixed with the sodium ions at the meniscus and we have thus automatically produced the requirement of Masson that the solutions on each side of the meniscus must contain one ion in common. Even in the case that the upper solution contains the faster potassium ion, the solutions on the two sides of the meniscus will still contain a common ion without any admixture of ammonium ions, for the motion of the latter will always be away from the

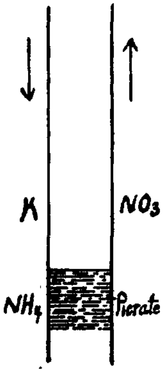


Fig. 3.

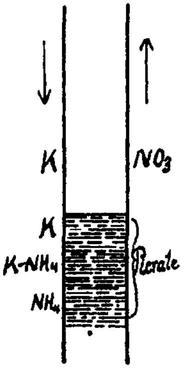


Fig. 4.

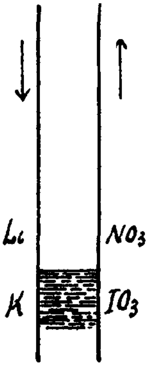


Fig. 5.

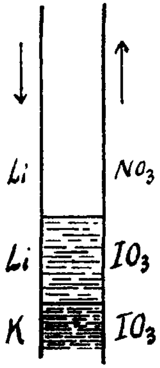


Fig. 6.

meniscus. When the potassium ion follows the ammonium ion down the tube there will be a mixing of the potassium and ammonium picrates in the space below the meniscus. In the case, however, that the cation above is specifically slower than the one below, then a meniscus separating them ought to show itself traveling down the tube. Such a meniscus was observed in the following described experiment. The lower end of the velocity tube was filled with a tenth-normal solution of potassium iodate in 2 per cent. aqueous agar agar jelly upon which an equivalent aqueous solution of lithium nitrate was introduced, as shown in Fig. 5. On passing the current down the tube a very distinct meniscus traveled up the tube from the upper surface of the jelly, marking the progress of the nitrate ions, while at the same time a sharp, but less distinct, meniscus was observed moving from the same starting point down the tube, as shown in Fig. 6.

(9) *Either the indicator or pursued ion must be colored.* We have found that it is not necessary that either solution contain a colored ion for the purpose of making the boundary between the two solutions visible; a slight difference in the refractive index of the two solutions is all that is required.[1]

Following the example of Whetham and of Masson, we considered it necessary in our earlier experiments to introduce a solution of copper into the foot of the graduated tube to form a visible meniscus. This proving itself to be a very troublesome operation, the plan was tried of substituting copper amalgam with bits of amalgamated copper floating on its surface, in place of pure mercury as anode. It was expected that the copper, because of its lower electrolytic solution tension, would go into solution and thus supply the desired colored indicator. However, experiments showed the indicator solution to be a mixture of mercury and copper, the relative quantities of the two metals present depending upon the density of the current. Copper is but slightly soluble in mercury; consequently, when copper amalgam is used as anode the surface layer of the amalgam in contact with the solution is soon so far exhausted of its copper that the potential rises to that required for the solution of the mercury. The result is an indicator solution containing copper and mercury, in some cases, very little copper and much mercury. If the current

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[1] Steele (*Phil. Trans.*, **198**, 105 (1902), *J. Chem. Soc.* (London), **79**, 414 (1901), *Ztschr. phys. Chem.*, **40**, 689 (1902)) has antedated us in this discovery.

is weak, or if care is taken to have plenty of copper, better even if some of it is unamalgamated, in the foot of the velocity tube, then the strong blue color of a practically pure copper solution results. In those experiments in which the solution is but slightly colored the meniscus still showed very plainly, an observation which led us to abandon altogether the use of copper and to depend on the mercury alone for supplying the indicator ion.

THE INDICATORS.

The Cathion Indicator.—Mercury, lead, copper and bismuth have been used in the manner described above.

The Anion Indicator.—Since no known material, capable of forming anions under the action of the current, can be used as an electrode after the manner described above for mercury, it is necessary to choose as indicator a salt whose equivalent solution is specifically lighter than the solution to be measured and to introduce it at the top of the graduated tube, or to select one giving an equivalent solution of greater density and place it in the foot of the tube over the mercury cathode. Altogether nine substances were investigated with respect to their behavior as anion indicators, *viz.*, potassium permanganate, ammonium acetate, potassium nitroprusside, potassium argentocyanide, sodium bromate, trinitraniline, picric acid, potassium picrate and iodoeosine. With the exception of sodium bromate, each of these indicators gave a meniscus which could be followed when the current was turned on. Experiments showed that, in all probability, the permanganate ion is faster than the nitrate ion, for the meniscus developed only when the current passed from permanganate to nitrate solution, and faded away when it was reversed. Potassium argentocyanide gave a good meniscus which, however, traveled with, instead of against, the current, as it was expected to do. Among the rest of the indicators picric acid gave the best results in the preliminary test; it was consequently chosen for making most of the measurements given in this paper.

THE MOVING BOUNDARY AND THE ABSOLUTE VELOCITY OF THE IONS.

The experimental and theoretical work cited above[1] show that when a solution containing a salt, *A B*, is placed in contact with a solution of a second salt, *B C*, and an electric current is sent

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[1] *Vide*, p. 509.

from the one solution to the other, while at the same time the conditions outlined above for the maintenance of a sharp meniscus are realized, then the velocity of the meniscus is identical with the working velocity of the ions *A* and *C*, under the potential gradient realized in the experiment. Consequently

$$U = U_0 \frac{dV}{dl},$$

in which U is the observed velocity of the meniscus, U_0 is the working velocity of the ions under unit potential slope, and dV/dl is the potential slope acting on the ions. No convenient method for measuring dV/dl[1] during the course of an experiment is known, but it may be easily calculated for the solution in front of the meniscus from the known specific resistance of this solution and the cross section of the tube containing the solutions.

From Ohm's law

$$\frac{dV}{dl} = I \frac{dR}{dl}.$$

The work above referred to shows that dV/dl maintains a constant value at the meniscus, therefore

$$U = U_0 I \frac{R_0}{A} \text{ or } U_0 = \frac{UA}{R_0 I},$$

in which I is the current, R_0 is the specific resistance of the solution and A is the cross section of the tube.

But

$$R_0 = \frac{1}{\kappa} = \frac{V}{\Lambda_v}$$

from which it follows that

$$U_0 = U \frac{A\Lambda_v}{IV} \qquad (1)$$

in which κ is the specific conductivity, V is the dilution, and Λ_v is the molecular conductivity of the solution.

This formula permits the calculation of the working velocity of the ion from observations on the speed of the meniscus, U, the cross section of the tube A, the current I, and the values for Λ_v and V from the measurements of Franklin and Kraus.[2]

If the salt is not completely dissociated, and furthermore, if the

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[1] *Vide*, p. 513.

[2] *Am. Chem. J.*, **23**, 288 (1900).

assumption is made that the concentration of the solution has no effect on the absolute speeds U_0 of the ions, then

$$U_0 = \frac{U_0}{\alpha} = U\,\frac{A\Lambda_v\,\Lambda_\infty}{IV\Lambda_v}$$

or

$$U_0 = \frac{UA\Lambda_\infty}{IV} \qquad (2)$$

CALIBRATION OF THE CELL *K L*.

The tube *L* (Fig. 2) was graduated by the usual method with mercury before it was sealed into the upper portion of the cell. As the mean of four concordant series of measurements it was found that the cross section along the tube is as follows: From 0 to 3 cm., 0.288 sq. cm.; from 3 cm. to 6 cm., 0.287 sq. cm.; from 6 cm. to 9 cm., 0.286 sq. cm.; from 9 cm. to 12 cm., 0.284 sq. cm. The total volume of the cell was determined by weighing the cell empty, and then filling with water from zero on the scale to the glass pointer *Q*, and weighing again. During these operations the lower end of the velocity tube was closed by means of a plug of paraffin. As the mean of four concordant determinations the cell was found to hold 24.49 grams of water at 18°. In calculating the results given in this paper the volume of the cell at the boiling-point of ammonia was assumed to be 24.49 cc. The error thereby introduced is of no significance.

RECORD OF OBSERVATIONS AND CALCULATIONS OF RESULTS.

To show the method of recording the observations and calculating the final results therefrom, a series of measurements on the ammonium ion in a solution of ammonium nitrate, taken from the laboratory note-book, is given in detail.

139.40 milligrams of pure, dry ammonium nitrate, weighed in the platinum spoon *J*, were introduced into the cell *K L* (Fig. 2). After stirring the solution and adjusting the mercury in the velocity tube as described above, the mercury stood at 0.10 cm. on the scale. The volume of the solution was consequently $24.49 - (0.288 \times 0.10) = 24.46$ cc., and the dilution of the solution v was $80 \times 24.46/139.40 = 14.06$. 80 is the molecular weight of ammonium nitrate.

Below is a transcription of the note-book record in which v is the dilution of the solution, Λ_∞ is the maximum molecular conductivity of ammonium nitrate in Kohlrausch units, taken from the work of Franklin and Kraus, T is the time of making the observations, i is the current in milliamperes measured at time T, I is the mean current for the ten-minute period, S is the position of the meniscus on the graduated tube at time T, $600\,u$ is the disance in centimeters traveled by the meniscus during the ten-minute period, U_0 is the velocity of the ion in centimeters per second per volt calculated by means of the formula (2) above and t is the temperature of the bath.

VELOCITY OF THE CATION IN A SOLUTION OF AMMONIUM NITRATE.

Date: $v = 14.06$. $\Lambda_\infty = 300$. Mercury indicator.

No.	T.	i.	I.	S.	$600\,u$.	U_0.	t.
1	4:15	5.06		1.85			
			4.99		0.65	0.00133	—34.0
2	4:25	4.91		2.50			
			4.83		0.60	0.00127	—34.0
3	4:35	4.75		3.10			
			4.67		0.62	0.00136	—34.2
4	4:45	4.59		3.72			
			4.53		0.59	0.00133	—34.2
5	4:55	4.46		4.31			
			4.40		0.59	0.00137	—34.0
6	5:05	4.33		4.90			
	Current increased.						
7	5:10	5.22		5.20			
			5.12		0.69	0.00136	—34.1
8	5:20	5.02		5.89			
			4.95		0.62	0.00128	—34.2
9	5:30	4.87		6.51			
					Mean:	0.00133	

EXPERIMENTAL RESULTS.

In the following tables the symbols Λ_∞, v, I, $600\,u$, and U_0 have the significance described above. S' is the point on the velocity tube at which the last reading on the meniscus was taken. Excepting where otherwise indicated, mercury and picric acid were used for cathion and anion indicators respectively. The spaces in the vertical columns indicate points in the progress of the experiments at which the strength of the current was changed.

THE AMMONIUM ION IN A SOLUTION OF AMMONIUM NITRATE.

Λ_∞ FOR $NH_4NO_3 = 300$.

1.

$v = 6.28$

I.	600 u.	U_0.
8.10	0.41	0.00116
7.91	0.45	0.00130
7.72	0.43	0.00127
7.56	0.44	0.00133
9.48	0.57	0.00138
9.22	0.50	0.00124
9.00	0.53	0.00134
8.77	0.51	0.00133
8.56	0.46	0.00122
8.38	0.52	0.00142
8.20	0.50	0.00139
9.60	0.58	0.00138
9.35	0.54	0.00132
9.14	0.56	0.00140
8.95	0.52	0.00133
8.76	0.53	0.00138
8.56	0.52	0.00149
8.38	0.53	0.00144

$S' = 11.38$ Mean : 0.00133

2.

$v = 14.06$

I.	600 u.	U_0.
4.99	0.65	0.00134
4.83	0.60	0.00128
4.67	0.62	0.00136
4.53	0.59	0.00133
4.40	0.59	0.00137
5.12	0.68	0.00136
4.95	0.62	0.00128

$S' = 6.50$ Mean : 0.00133

3.

$v = 58.7$

I.	600 u.	U_0.
2.28	1.26	0.00135
2.14	1.14	0.00131
2.04	1.10	0.00132
1.94	1.06	0.00133
1.84	1.00	0.00133
1.76	0.99	0.00138
1.70	0.95	0.00137
1.64	0.93	0.00139

$S' = 10.63$ Mean : 0.00135

THE AMMONIUM ION IN A SOLUTION OF AMMONIUM IODIDE.

Λ_∞ FOR $NH_4I = 304$.[1]

4.[2]

$v = 29.8$

I.	600 u.	U_0.
4.20	1.10	0.00128
3.75	0.95	0.00124
3.41	0.90	0.00129
3.16	0.80	0.00124

$S' = 5.30$ Mean : 0.00126

5.[3]

$v = 31.05$

I.	600 u.	U_0.
2.51	0.70	0.00131
2.375	0.63	0.00125
2.255	0.62	0.00129
3.19	0.89	0.00131
2.99	0.82	0.00128
2.825	0.79	0.00131
2.685	0.73	0.00127
2.56	0.72	0.00132
2.455	0.70	0.00134
2.37	0.68	0.00134
2.29	0.62	0.00127

$S' = 10.35$ Mean : 0.00130

3.41[4]	1.17	0.00161

---

[1] Assumed to be the same as ammonium chloride.

[2] In this experiment a precipitate was formed in the indicator solution, probably the result of hydrolysis of the mercury iodide.

[3] Lead amalgam was used as anode in this experiment. The indicator solution here also showed some evidence of hydrolysis, not so marked, however, as in Experiment 4.

[4] The indicator solution was forced out of the velocity tube and the ammonium iodide solution was stirred before making this measurement. In calculating U_0 the dilution of the solution was assumed to remain unchanged.

THE POTASSIUM ION IN A SOLUTION OF POTASSIUM NITRATE.

Λ_∞ FOR $KNO_3 = 338$.

6.

$v = 8.02$

I.	600 u.	U_0.
8.89	0.70	0.00159
8.57	0.75	0.00177
8.30	0.67	0.00163
8.10	0.68	0.00170
7.88	0.70	0.00181
7.69	0.65	0.00171
7.53	0.65	0.00175
7.38	0.65	0.00178
7.21	0.60	0.00168
7.06	0.60	0.00172
6.91	0.65	0.00190
6.78	0.60	0.00179
6.64	0.55	0.00168

$S' = 10.00$ Mean: 0.00174

7.

$v = 9.61$

I.	600 u.	U_0.
7.53	0.78	0.00175
7.31	0.74	0.00171
7.09	0.75	0.00179
6.87	0.70	0.00173
6.67	0.72	0.00182
6.49	0.70	0.00182
6.32	0.68	0.00182
6.16	0.65	0.00178
6.02	0.65	0.00182
5.88	0.65	0.00189
5.74	0.65	0.00191

$S' = 9.70$ Mean: 0.00180

8.

$v = 9.62$

I.	600 u.	U_0.
8.52	0.85	0.00168
8.16	0.85	0.00178
7.87	0.82	0.00176
7.67	0.79	0.00174
7.44	0.78	0.00177
9.23	0.95	0.00174
8.86	0.95	0.00182
8.59	0.95	0.00187
8.35	0.93	0.00188
4.28	0.49	0.00194
4.21	0.48	0.00193

$S' = 10.70$ Mean: 0.00181

9.

$v = 23.52$

I.	600 u.	U_0.
5.18	1.28	0.00170
4.92	1.15	0.00163[1]
4.68	1.20	0.00177
4.43	1.27	0.00179[2]
4.24	0.98	0.00177[3]
4.07	1.10	0.00186
3.88	1.10	0.00195
3.73	1.00	0.00186

$S' = 11.40$ Mean: 0.00179

I.	600 u.	U_0.
7.10	2.25	0.00218[4]

10.

$v = 56.2$

I.	600 u.	U_0.
2.58	1.51	0.00170
2.43	1.48	0.00176
2.29	1.35	0.00171
2.16	1.35	0.00181
2.07	1.25	0.00175
2.00	1.25	0.00180

$S' = 10.35$ Mean: 0.00176

11.

$v = 187.5$

I.	600 u.	U_0.
1.205	1.15	0.00168
1.16	1.17	0.00178
1.115	1.06	0.00167
1.075	1.12	0.00182
1.025	1.05	0.00179
0.99	1.00	0.00177

$S' = 10.90$ Mean: 0.00176

---

[1] The current was accidentally interrupted for a short time.

[2] 11 minutes.

[3] 9 minutes.

[4] The liquid in the velocity tube was forced out and this measurement made on the dilute solution from the cathode space. It was assumed in making the calculation that the concentration was unchanged.

THE SODIUM ION IN A SOLUTION OF SODIUM NITRATE.

Λ_∞ FOR $NaNO_3$ = 298.[1]

12.[2]

v = 4.16

I.	600 u.	U_0.
9.70	0.37	0.00132
9.59	0.33	0.00120
9.52	0.37	0.00134
9.44	0.33	0.00121
9.36	0.35[3]	0.00124
9.17	0.32[4]	0.00127

S′ = 4.30 Mean : 0.00126

13[5].

v = 4.42

I.	600 u.	U_0.
17.44	0.69	0.00129
17.12	0.66	0.00126
16.76	0.64	0.00124
16.44	0.68	0.00134
16.22	0.60	0.00121

S′ = 5.10 Mean : 0.00127

14.

v = 9.53

I.	600 u.	U_0.
8.94	0.81	0.00136
8.60	0.74	0.00130
8.29	0.73	0.00133
8.01	0.65	0.00122
7.82	0.67	0.00129
7.61	0.65	0.00129
9.72	0.87	0.00134

S′ = 8.57 Mean : 0.00132

15.

v = 11.97

I.	600 u.	U_0.
5.85	0.65	0.00133
5.73	0.60	0.00126
5.60	0.61	0.00131
7.23	0.80	0.00133
6.98	0.75	0.00129
6.80	0.72	0.00127
6.61	0.68	0.00123
9.68	1.15	0.00142
9.33	1.03	0.00133
8.96	1.00	0.00134

S′ = 10.90 Mean : 0.00131

16.

v = 35.15

I.	600 u.	U_0.
2.65	0.85	0.00131
3.91	1.23	0.00129
3.72	1.23	0.00136
3.53	1.12	0.00130
3.33	1.10	0.00135
3.22	1.05	0.00134
3.07	1.05	0.00140
2.94	1.00	0.00139

S′ = 10.85 Mean : 0.00135

17.

v = 59.8

I.	600 u.	U_0.
2.505	1.33	0.00128
2.345	1.29	0.00133
2.205	1.44[6]	0.00132
2.62	1.51	0.00139
2.45	1.45	0.00143
2.30	1.47	0.00155

S′ = 10.90 Mean : 0.00138

18.

v = 62.3

I.	600 u.	U_0.
2.43	1.40	0.00134
2.28	1.32	0.00135
2.15	1.30	0.00144
2.065	1.23	0.00137
1.995	1.20	0.00139
1.91	1.15	0.00139
1.90	1.48[7]	0.00139

S′ = 10.28 Mean : 0.00138

---

[1] Assumed 4 units less than sodium bromide.

[2] This experiment was stopped when the meniscus reached 4.30 in the scale, because the current necessary for the production of a good meniscus exceeded the capacity of the milliammeter.

[3] 10.5 minutes.

[4] 9.5 minutes.

[5] A shunt was used in connection with the milliammeter in this experiment. Measurements were interrupted when the meniscus reached 5.10 on the scale by the dropping of crystals of sodium amalgam down the tube from the mercury cathode.

[6] 12 minutes.

[7] 13 minutes.

THE SODIUM ION IN A SOLUTION OF SODIUM BROMATE.

Λ_∞ FOR $NaBrO_3 = 276$.

19.

$v = 33.5$

I.	600 *u*.	U_0.
3.51	1.15	0.00129
3.30	1.02	0.00122
3.10	1.03	0.00131
2.92	0.96	0.00130
2.77	0.92	0.00132
2.64	0.90	0.00135
2.54	0.75[1]	0.00137

$S' = 10.08$ Mean : 0.00131

20.

$v = 85.7$

I.	600 *u*.	U_0.
1.26	1.06	0.00130
1.195	1.00	0.00129
1.135	0.95	0.00129
1.07	0.87	0.00126
1.015	0.85	0.00129
0.975	0.82	0.00130
0.935	0.80	0.00132
0.90	0.75	0.00128
0.875	0.76	0.00134

$S' = 9.58$ Mean : 0.00130

1.125	1.20	0.00165[2]
1.055	1.15	0.00169

21.

$v = 109.3$

1.30[3]	0.96[4]	0.00132
1.058	1.23	0.00137[5]
1.025	1.15	0.00135

$S' = 4.10$ Mean : 0.00135

THE SILVER ION IN A SOLUTION OF SILVER NITRATE.

Λ_∞ FOR $AgNO_3 = 295$.[6]

22.

$v = 24.2$

I.	600 *u*.	U_0.
3.59	0.68	0.00110
3.61	0.68	0.00109
3.50	0.67	0.00111
3.39	0.63	0.00107
3.32	0.64	0.00112
3.25	0.63	0.00113
3.19	0.62	0.00113
3.27	0.63	0.00112

$S' = 6.95$ Mean : 0.00111

THE NITRATE ION IN A SOLUTION OF AMMONIUM NITRATE.

Λ_∞ FOR $NH_4NO_3 = 300$.

23.

$v = 25.17$

I.	600 *u*.	U_0.
3.585	1.00	0.00159
3.535	1.17	0.00187
3.485	1.08	0.00176
3.445	1.09	0.00180
3.385	0.99	0.00167
3.335	1.04	0.00178
3.300	1.02	0.00176

$S' = 10.22$ Mean : 0.00175

---

[1] 8.5 minutes.

[2] The indicator solution was forced out and readings were begun anew.

[3] 1.30 milliamperes threatened and then destroyed the meniscus.

[4] 5.5 minutes.

[5] The indicator solution was forced out and readings were begun anew. Further measurements were not made for the reason that there was some uncertainty as to the concentration of the solution in the velocity tube.

Unpublished measurements.

THE NITRATE ION IN A SOLUTION OF POTASSIUM NITRATE.

Λ_∞ FOR KNO_3 = 338.

24.

$v = 35.6$

I.	600 u.	U_0.
1.05	0.40	0.00174
1.125	0.45	0.00183
1.125	0.45	0.00183
1.115	0.43	0.00176
1.105	0.42	0.00174
1.09	0.43	0.00180
1.315	0.50	0.00174
1.305	0.50	0.00175
1.30	0.52	0.00182
1.675	0.65	0.00178
1.655	0.63	0.00174

S′ = 8.73 Mean : 0.00178

25.

$v = 94.6$

I.	600 u.	U_0.
0.55	0.57	0.00178
0.55	0.60	0.00188
0.55	0.53	0.00166
0.61	0.62	0.00175
0.608	0.62	0.00176
0.603	0.63	0.00180
0.598	0.60	0.00173
0.645	0.65	0.00174
0.635	0.65	0.00176

S′ = 9.90 Mean : 0.00176

THE NITRATE ION IN A SOLUTION OF SODIUM NITRATE.

Λ_∞ FOR $NaNO_3$ = 298.[1]

26.

$v = 27.0$

I.	600 u.	U_0.
1.12	0.37	0.00177
1.105	0.36	0.00174
1.09	0.34	0.00167
1.69	0.57	0.00180
1.66	0.55	0.00177
1.625	0.53	0.00174
1.925	0.64	0.00178
1.885	0.65	0.00184
1.85	0.55	0.00159
1.78	0.65	0.00195
1.715	0.57	0.00177
1.70	0.53	0.00167
1.68	0.55	0.00175

S′ = 10.95 Mean : 0.00175

27.

$v = 28.8$

I.	600 u.	U_0.
1.31	0.45	0.00172
1.29	0.45	0.00174
1.55	0.55	0.00178
1.515	0.50	0.00165
1.49	0.53	0.00178
1.785	0.60	0.00169
1.75	0.63	0.00180
1.725	0.60	0.00175
1.70	0.57	0.00168
1.675[2]	0.60	0.00179

S′ = 8.80 Mean : 0.00174

28.[3]

$v = 35.6$

I.	600 u.	U_0.
2.12	0.83	0.00158
2.03	0.87	0.00174
1.95	0.80	0.00166
1.875	0.85	0.00184
1.80	0.70	0.00158
1.73	0.75	0.00180

S′ = 10.00 Mean : 0.00170

---

[1] Assumed 4 units less than sodium bromide.

[2] It was attempted at this point to increase the current. 2.3 milliamperes, however, destroyed the meniscus and ended the experiment.

[3] The indicator was considerably mixed with the sodium nitrate solution at the beginning of the experiment. Low results were expected.

THE CHLORINE ION IN A SOLUTION OF AMMONIUM CHLORIDE.

Λ_∞ FOR $NH_4Cl = 304$.

29.

$v = 4.98$

I.	600 *u*.	U_0.
5.02	0.55	0.00320
4.925	0.55	0.00326
4.925	0.53	0.00316
4.975	0.54	0.00318
5.00	0.46	0.00270
5.00	0.52	0.00302
9.00	1.00	0.00337

S′ = 7.45 Mean : 0.00309

30.

$v = 8.46$

I.	600 *u*.	U_0.
4.115	0.75	0.00312
4.205	0.70	0.00287
4.255	0.70	0.00284
4.305	0.70	0.00281
4.365	0.70	0.00277
4.425	0.67	0.00262
4.475	0.63	0.00243
4.535	0.70	0.00294

S′ = 10.30 Mean : 0.00280

31.

$v = 18.23$

I.	600 *u*.	U_0.
3.965	1.23	0.00249[1]
4.415	1.25	0.00227
4.385	1.25	0.00228
4.275	1.15	0.00215
4.09	1.10	0.00216
3.85	1.15	0.00239

S′ = 8.05 Mean : 0.00229

32.

$v = 40.7$

I.	600 *u*.	U_0.
1.67	1.05	0.00226
2.015	1.27	0.00226
2.085	1.28	0.00220
2.15	1.30	0.00218
2.63	1.55	0.00213
2.705	1.75	0.00231

S′ = 10.40 Mean : 0.00222

33.

$v = 52.75$

I.	600 *u*.	U_0.
1.38	1.13	0.00227
1.41	1.13	0.00223
1.435	1.14	0.00221
1.46	1.15	0.00218
1.485	1.15	0.00214
1.515	1.15	0.00210
1.54	1.15	0.00208

S′ = 10.50 Mean : 0.00217

THE CHLORINE ION IN A SOLUTION OF SODIUM CHLORIDE.

Λ_∞ FOR $NaCl = 302$.[2]

34.

$v = 29.45$

I.	600 *u*.	U_0.
2.15	0.73	0.00168
2.11	0.75	0.00176
2.07	0.75	0.00179
2.025	0.75	0.00183
1.98	0.75	0.00187
1.95	0.70	0.00177
1.92	0.70	0.00180
1.90	0.70	0.00182
1.88	0.70	0.00184
1.845	0.67	0.00180
1.82	0.67	0.00181

S′ = 9.14 Mean : 0.00180

35.

$v = 58.5$

I.	600 *u*.	U_0.
1.40	1.03	0.00183
1.385	0.95	0.00170
1.35	0.97	0.00182
1.315	0.97	0.00183
1.285	0.93	0.00178
1.26	0.93	0.00184
1.27	0.92	0.00181
1.28	0.90	0.00176
1.25	0.90	0.00179

S′ = 9.75 Mean : 0.00180

---

[1] Bubbles of gas began to appear rising through the velocity tube, the result of omitting inadvertently the lead peroxide. The solution was forced out of the tube, depolarizer was added, and a fresh start made.

NOTE: The anode space was colored yellow, slightly in the dilute solutions, more strongly in the more concentrated.

[2] Assumed same as sodium bromide.

NOTE.—The anode space in both experiments took on a yellow color. The color was stronger in the more concentrated solution.

The Bromine Ion in a Solution of Ammonium Bromide.

Λ_{∞} FOR $NH_4Br = 304$.[1]

36.

$v = 17.01$.

I.	600 u.	U_0.
4.00	0.90	0.00192
3.985	0.93	0.00199
3.975	0.92	0.00198
3.97	0.90	0.00194
3.965	0.92	0.00198
3.97	0.90	0.00194

S′ = 9.47 Mean : 0.00196

37.

$v = 19.1$

I.	600 u.	U_0.
1.97[2]	0.53	0.00205
1.75[2]	0.50	0.00218
1.72[2]	0.40	0.00177
1.72	0.40	0.00177
3.11	0.70	0.00172
3.10	0.80	0.00194
3.095	0.80	0.00197
2.945	0.67	0.00174
2.92	0.78	0.00204
3.75	0.95	0.00193
3.70	0.95	0.00195

S′ = 10.90 Mean : 0.00188

38.

$v = 41.75$

2.475[3]	1.27	0.00179
2.49	1.35	0.00189
2.495	1.35	0.00188
2.48	1.37	0.00191
2.46	1.32	0.00186
2.40	1.34	0.00194

S′ = 10.53 Mean : 0.00188

2.47[4]	0.62	0.00176

The Bromine Ion in a Solution of Sodium Bromide.

Λ_{∞} FOR $NaBr = 302$.

39.[5]

$v = 21.35$

I.	600 u.	U_0.
2.61	0.65	0.00170
2.135	0.53	0.00169
2.15	0.57	0.00185
2.175	0.55	0.00173
2.15	0.55	0.00174
2.11	0.54	0.00174
2.045	0.53	0.00176
2.00	0.52	0.00177
1.965	0.51	0.00177
1.935	0.52	0.00183

S′ = 8.15 Mean : 0.00176

40.[6]

$v = 45.7$

I.	600 u.	U_0.
1.50	0.82	0.00174
1.375	0.78	0.00185
1.345	0.67	0.00159
1.35	0.72	0.00169
1.295	0.68	0.00167
1.23	0.68	0.00176
1.23	0.62	0.00160
1.215	0.70	0.00183

S′ = 8.10 Mean : 0.00172

41.

$v = 59.75$

1.015	0.75	0.00179
0.99	0.69	0.00169
0.965	0.70	0.00176
0.935	0.68	0.00177
1.18	0.86	0.00177
1.145	0.84	0.00178
1.120	0.82	0.00178
1.075	0.80	0.00180
1.00	0.78	0.00188

S′ = 9.10 Mean : 0.00178

---

[1] Assumed same as ammonium chloride.

[2] These readings were made on the color front, the meniscus not being visible. The succeeding observations were made on the meniscus, which, however, presented a convex front indicative of too strong a current.

[3] This reading was on the color front; those following were made on a very sharp meniscus.

[4] For this measurement the current was reversed. The meniscus gradually faded out. U = 0.62 is for five-minute period.

NOTE.—In these experiments the anode space became colored.

[5] The first four readings were made on the color front, the succeeding ones on a good meniscus.

[6] These measurements were made on a very damp day. Some current leaked through moisture deposited on the stopper, as was proved by testing the apparatus with the cell empty.

NOTE.—The anode space became colored.

THE IODINE ION IN A SOLUTION OF AMMONIUM IODIDE.[1]

Λ_∞ FOR $NH_4I = 304$.[2]

42.

$v = 60.0$

I.	600 u.	U_0.
0.513	0.37	0.00174
0.495	0.38	0.00185
0.743	0.53	0.00172
0.708	0.51	0.00174
0.685	0.50	0.00176
1.195[3]	0.80	0.00161
1.165[3]	0.73	0.00152
0.625	0.45	0.00173

$S' = 5.90$ Mean : 0.00176

THE IODINE ION IN A SOLUTION OF POTASSIUM IODIDE.[4]

Λ_∞ FOR $KI = 341$.[5]

43.

$v = 57.6$

I.	600 u.	U_0.
0.523	0.27	0.00147
0.510	0.30	0.00166
0.500	0.30	0.00170
0.790	0.45	0.00162

$S' = 2.29$ Mean : 0.00161

44.

$v = 128.0$

I.	600 u.	U_0.
0.450	0.62	0.00176
0.433	0.58	0.00171
0.412	0.50	0.00159
0.725	0.95	0.00161
0.700	0.85	0.00154

$S' = 5.90$ Mean : 0.00164

SUMMARY OF ABSOLUTE VELOCITIES OF THE IONS.

In making up this summary the observations above 6 to 7 on the velocity tube, in the case of the cathions, have been omitted.

The Ammonium Ion

v.	U_0.
of NH_4NO_3.	
6.28	0.00131
14.06	0.00133
58.5	0.00133
of NH_4I.	
29.8	0.00126
31.05	0.00129

The Potassium Ion of KNO_3.

v.	U_0.
8.02	0.00172
9.61	0.00178
9.62	0.00177
23.27	0.00174
56.2	0.00175
185.7	0.00171

---

[1] Several attempts were made to follow the iodine ion in a solution of ammonium iodide by the picric acid ion. A meniscus appeared, but even with the weakest current, which was still strong enough to bring out the meniscus at all, the indicator solution persistently mixed up into the solution above. The difference in the density of the two solutions is probably not sufficiently great. Iodoeosine was used as indicator in this experiment. The dye dissolves readily and forms a solution which is strongly purple when concentrated and yellow when dilute. It gave a very sharp meniscus.

[2] Assumed the same as ammonium chloride.

[3] When the current was increased, the surface of the indicator solution was washed off badly and mixed with the solution above.

[4] Iodoeosine was used as indicator in both these experiments. The meniscus was very sharp, but had the appearance of being washed away from above with the result that the supernatant potassium iodide solution soon became colored. It seems that either the dye contains a faster anion as an impurity, or what is perhaps more likely, the greater heating effect in the dye solution is sufficient to cause the mixing of the slightly denser indicator solution with the solution above. In each experiment, when the current was increased, the meniscus was destroyed.

[5] Assumed the same as KBr.

The Sodium Ion
of $NaNO_3$.

v.	U_0.
4.16	0.00126
4.42	0.00127
9.53	0.00130
11.97	0.00130
35.15	0.00132
59.8	0.00131
62.3	0.00132

of $NaBrO_3$.

v.	U_0.
33.5	0.00129
87.5	0.00129
109.3	0.00135

The Silver Ion
of $AgNO_3$.

v.	U_0.
24.2	0.00111

The Nitrate Ion
of NH_4NO_3.

v.	U_0.
25.17	0.00175

of KNO_3.

v.	U_0.
35.6	0.00178
94.6	0.00176

of $NaNO_3$.

v.	U_0.
27.0	0.00175
28.8	0.00174
35.6	0.00170

The Chlorine Ion
of NH_4Cl.

v.	V_0.
4.98	0.00309
8.46	0.00280
18.23	0.00229
40.7	0.00222
52.75	0.00217

of NaCl.

v.	V_0.
29.45	0.00180
58.5	0.00180

The Bromine Ion
of NH_4Br.

v.	V_0.
17.01	0.00196
19.01	0.00188
41.75	0.00188

of NaBr.

v.	V_0.
21.35	0.00176
45.7	0.00172
59.75	0.00178

The Iodine Ion
of NH_4I.

v.	V_0.
60.0	0.00176

of KI.

v.	V_0.
57.6	0.00161
128.0	0.00164

The results summarized in this table show that the assumption that the speeds of the ions are independent of the degree of dilution is justified in the case of ammonium nitrate, potassium nitrate, sodium chloride and sodium bromide. In solutions of ammonium chloride and ammonium bromide there is obviously a rapid increase in the transport number of the anion with the concentration. Ammonium iodide shows a similar but much less marked behavior.

COMPARISON OF THE OBSERVED IONIC VELOCITIES WITH THE VELOCITIES CALCULATED BY THE METHOD OF KOHLRAUSCH.

Kohlrausch[1] has shown that, for a binary electrolyte, the sum of the speed of the cation and anion traveling under a potential slope 1 volt per centimeter, is

$$U_0+V_0=\frac{\Lambda_\infty}{96540}$$

centimeters per second. In the equation, U_0 and V_0 represent

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[1] *Wied. Ann.*, **6**, 196 (1879); Ostwald: "Lehrbuch Allgemeinen Chemie," 2te Aufl., Bd **2**, p. 718; Kohlrausch und Holborn: "Leitvermögen der Elektrolyte," p. 105.

the speeds of the cation and anion respectively, and Λ_∞ the maximum molecular conductivity of the salt in Kohlrausch units. By means of this formula, then, the sum of the velocities of the cation and anion of a salt in solution in liquid ammonia may be calculated from the conductivity measurements.

In the table below are given in column 2 the sums of the velocities of the salts indicated in column 1, calculated according to the method of Kohlrausch from the maximum molecular conductivity values of Franklin and Kraus.[1] In columns 3 and 4 are given the directly determined velocities of the cation and anion respectively, in column 5 the sums of these velocities, while in column 6 appears the ratio of Λ_∞ for ammonia solutions at —33° to Λ_∞ for aqueous solutions at +18°.

Salt.	$V_\infty/96540$.	U_0.	V_0.	$U_0 + V_0$.	
NH_4NO_3	0.00311	0.00133	0.00176	0.00309	2.4
KNO_3	0.00350	0.00175	0.00176	0.00351	2.7
$NaNO_3$	0.00309	0.00131	0.00176	0.00307	2.8
NaCl	0.00313	0.00131	0.00180	0.00311	2.7
NaBr	0.00313	0.00131	0.00176	0.00307	2.7
$AgNO_3$	0.00306	0.00111	0.00176	0.00287	2.5

TRANSFERENCE NUMBERS IN LIQUID AMMONIA.

The attempt was made to measure the anion transference number for ammonium nitrate and potassium nitrate by observing, after the manner of Masson,[2] the speed with which two boundaries approach each other in the velocity tube. Ammonium acetate was introduced, by a device not shown in the figure, into the space at the top of the tube as anion indicator while the mercury at the bottom of the tube supplied the cation indicator. While in several of the experiments a meniscus was obtained traveling down the tube to meet the boundary from below, in one experiment only, and that the first one upon ammonium nitrate, was the meniscus sufficiently distinct and regular in its motion to permit of readings. In this experiment the boundaries met at 5.90 cm. on the scale, the anion and cation boundaries having traveled respectively 6.00 cm. and 4.35 cm. in two hours. This gives for the ratio, $V/U = 6.00/4.35 = 1.38$, and for the transport number of the anion.

$$V/(U + V) = \frac{6.00}{4.35 + 6.00} = 0.58.$$

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[1] *Am. Chem. J.*, **23**, 277 (1900).

[2] *Phil. Trans.*, **192**, 331 (1899).

The values for the ratio, V_0/U_0, and the transport number, $V_0/(U_0 + V_0)$, for the salts measured calculated from the specific velocities of the ions, are given in the following table:

Salt.	U_0.	V_0.	$\frac{V_0}{U_0}$	$\frac{V_0}{U_0 + V_0}$	
NH_4NO_3	0.00133	0.00176	1.32	0.570	0.487
KNO_3	0.00175	0.00176	1.00	0.501	0.481
$NaNO_3$	0.00131	0.00176	1.34	0.574	0.577
NaCl	0.00131	0.00180	1.37	0.581	0.596
$AgNO_3$	0.00111	0.00176	1.58	0.614	0.522

In column 6 the transport number of the anion in aqueous solution is given.

The work embodied in this paper was completed in the summer of 1902.

SUMMARY OF RESULTS.

A form of apparatus has been constructed by means of which the absolute velocities of certain ions in liquid ammonia have been determined.

The velocities of a number of univalent ions in liquid ammonia at —33° are from 2.4 to 2.8 times as great as they are in aqueous solutions at 18°, and are in agreement with the velocities calculated from conductivity measurements by the method of Kohlrausch.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A RAPID AND CONVENIENT METHOD FOR THE QUANTITATIVE ELECTROLYTIC PRECIPITATION OF COPPER.

BY THEODORE W. RICHARDS AND HAROLD BISBEE.

Received February 23, 1904.

IN ORDER to precipitate copper in a coherent film, suitable for careful washing and accurate weighing, it is necessary that during the electrolytic deposition there should always be enough ionized copper immediately at the surface of the cathode to carry the current from the solution to the electrode. If there is not copper enough present, hydrogen, or some other convenient cation, begins to carry the current, and the film becomes spongy or impure. This case may be discussed as a typical one.