of processes, and, in deriving the equation $MI^\nu = C$, we have analyzed the process of diffusion, which itself is one of expansion, into two components: one of these, I, corresponds to v, and the other, M, to p, in the equation pv^ν = const.

In conclusion, it may be stated that, upon applying the ideas involved in the conception of the ideal diffusion coefficient to the hydrodiffusion of electrolytes, and to the diffusion of gases into one another, the writer has succeeded in arriving at certain regularities; these, however, it is desired to further investigate, before publication. In connection with the diffusion of gases, an experimental investigation is also planned, since the right kind of data appear to be lacking in this case.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 98.]

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS. V. THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AND THE RELATIVE SPEED OF THE IONS IN THESE SOLUTIONS.[1]

BY CHARLES A. KRAUS.

Received March 11, 1914.

Introduction.

It was shown in the fourth paper of this series that the conduction process in solutions of the metals in ammonia is an ionic one. The positive carrier is identical with the positive ion of the salts of the same metal, while the negative carrier, which appears to be the same for different metals, can consist only of the negative electron e^-, either free or in association with ammonia. The characteristic properties of the metal solutions are due to the presence of the negative carrier.

With nonsoluble electrodes, such as platinum, the negative carrier passes into and out of the solution without observable material effects. That portion of the current which is carried through the solution by the negative carrier is, therefore, similar to the current in a metal, and in passing a current from a solution of one concentration to a solution of another concentration the only work involved is that of transferring the positive carrier.[2]

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[1] Previous papers of this series have appeared as follows: "I," THIS JOURNAL, 29, 1557 (1907); "II," *Ibid.*, 30, 653 (1908); "III," *Ibid.*, 30, 1197 (1908); "IV," *Ibid.*, 30, 1323 (1908). The sentence beginning on line 25, p. 1332 of the fourth paper should read: "According to this hypothesis, the negative carrier should move more *slowly* in dilute than in concentrated solutions, ..."

[2] This is true for very dilute and very concentrated solutions. At intermediate concentrations the influence of the solvent envelope must be taken into account, as will be described below.

In the metal solutions, Faraday's laws do not hold true in their ordinary sense; for the passage of one equivalent of electricity is not accompanied by a transformation or transfer of one equivalent of matter. Under given conditions, the material change accompanying the current is a definite fraction of that predicted by Faraday's law. To be applicable to the metal solutions, Faraday's laws must be extended to include not only ordinary matter, but also such forms of matter as we find in the negative electron. Under this generalization, Faraday's law would merely state that, in a medium carrying a current, the amount of electricity passing a given cross-section is equal to the number of carriers crossing the section multiplied by the number of charges on one carrier and the value of the unit charge. This view is that commonly accepted in the present-day theories of metallic conduction.

In dilute solutions of the metals in ammonia we thus have what is equivalent to a mixture of metallic and electrolytic conduction. Of course, in these solutions, the negative electron is in all probability surrounded with an envelope of solvent molecules; however, the work involved in carrying solvent from a solution of one concentration to that of another, approaches zero as a limit as the dilution increases indefinitely.

It is the purpose of this paper to adduce further evidence as to the nature of the negative carriers in the metal solutions. If the hypothesis that the negative carrier is associated with ammonia in dilute solutions is correct, we should expect the negative carrier to possess a speed comparable with that of ordinary ions in ammonia. Moreover, we should expect that at higher concentrations the size of the envelope would decrease or even disappear entirely. Consequently its speed should increase at higher concentrations.

As was shown in the fourth paper of this series, the positive ions in the solution of a metal are identical with the positive ions of the salts of the same metal. As has been shown by the work of Franklin and Cady,[1] the speed of ordinary ions in ammonia does not change greatly with concentration. We may, therefore, determine the variation of the speed of the negative carrier as a function of concentration by comparison with the speed of the positive carrier.

The ratios of the mean speeds of two carriers present in a solution are usually determined by means of the moving boundary or of the Hittorf method. Unfortunately, such measurements in the metal solutions are extremely difficult. It was therefore determined to employ the method of measuring the electromotive force of concentration cells, which likewise involves the transference numbers of the ions. In the case of the solutions of the metals in ammonia, this method has much to recommend it; for not only does the electromotive force method make it possible to

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[1] THIS JOURNAL, 26, 499 (1904).

work with very small quantities of material over large ranges of concentration, but both anode and cathode constitute reversible electrodes which are peculiarly free from disturbances.

Experimental.

Description of the Apparatus.—The apparatus employed in these experiments is outlined in Fig. 1. The solutions whose electromotive force was to be determined were prepared in the tubes *B* and *I*. These two tubes were connected by a tube, *M*, and the valve *L*. This valve was made by grinding a glass rod, *H*, into a conical seat in the glass tube at the bottom of *K*. The valve was polished with rouge and was quite impervious to liquids. A lubricant could not be employed. The plunger of this valve was sealed to a tube, *F*, of larger diameter, which was joined to the cell-arm *I* by means of a rubber tube, *G*. The greater portion of the rubber tube was covered with an impervious cement. No serious leakage was observed due to this connection. The valve was opened by raising the plunger *H* slightly. A clamp was provided to hold the plunger when desired. Normally, the valve was closed. The tube *B* was provided with a branch capillary, *N*, through which the metal was introduced in the manner described in previous papers.[1] The upper portion of the cell-arm *KI* consisted of a graduated tube which was calibrated with the plunger in position. The other cell-arm was provided with a narrower graduated tube, *A*, likewise calibrated. The volumes of the two cell-arms, up to fixed points on the graduated tubes, were determined. The lower portions of

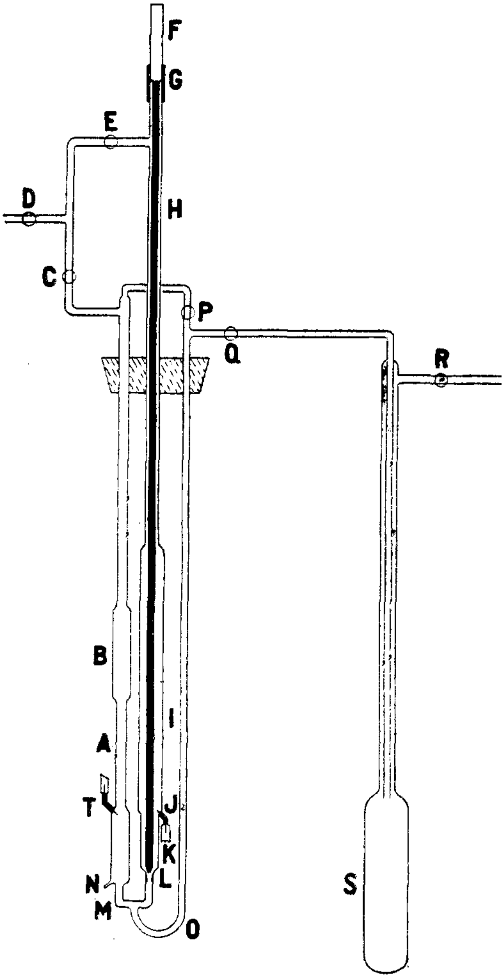

Fig. 1.

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[1] For a description of this operation, see THIS JOURNAL, 30, 1206 (1908).

the two cells each had a volume of about 4 cc. The tube *O*, which was joined to the bottom of the connecting tube *M*, was employed in changing the volume of the solution in the tubes *BI*. The electrode connections are shown at *JT*.

The procedure in manipulating the cell was somewhat as follows: After introducing the sodium, the cell was surrounded by boiling ammonia, connection was made through *DCE* with the source of ammonia, and liquid was condensed until its level reached the bottom of the smaller graduated tube *A*. The valve *L* was open in order that the liquid should be at the same level in both arms. The contents of the cell were thoroughly mixed. This was done by removing the bath, closing the cock *E*, and warming either of the tubes *BI* with the hand. The solution was thus driven into the other arm, and so back and forth until homogeneous. After replacing the bath, the volumes were read off on the graduated tubes when equilibrium had been established. Ammonia was now condensed into both tubes until the volume in the tube *KI* had been approximately doubled, the liquid levels being kept the same in the two arms. After mixing the solutions separately, the volumes were again read. Knowing the original volumes and the added volumes, it was possible to determine the relative concentrations of the solutions in the two tubes. The experiment was so carried out that the volumes were approximately in the ratio 1 : 2.

The cocks *CEP* being open, the valve *L* was opened cautiously, and the electromotive force was measured. In general, the level in *A* was originally kept a little below that in *I*, so that on opening *L*, solution from *I* ran into the connecting tube, and the contact between the two solutions was made at a point where mixing was a minimum.

After determining the electromotive force, the valve *L* was closed, as were also the cocks *EP*. The tube *S*, which had previously been exhausted, was surrounded with ammonia boiling under reduced pressure. When the temperature was well below the normal boiling point of ammonia, the cock *Q* was opened and the solution in *B* was forced out through the tube *O* by the pressure of its own vapor. When the solution had been transferred, the cock *Q* was closed and the cocks *PE* and valve *L* were opened. Half the solution in *I* now ran into *B*, after which *L* was closed and the volumes were read. The cocks *CDE* were opened and fresh ammonia was distilled into the cell as before. The ammonia in *S* was meanwhile evaporated through *R*, the sodium being left behind. After determining the liquid volumes, the valve was again opened and the electromotive force was determined as before. In this way the more concentrated solution always occupied the arm *B*, and the dilute solution of one experiment formed the concentrated solution of the next succeeding one.

A correction, of course, had to be applied for the volume of the small graduated tube A.

When the dilution had been carried sufficiently far, the entire contents of the cell were run into S and evaporated. The apparatus was exhausted, the tube S disconnected, and the metal was dissolved in alcohol. This solution was then washed out and titrated to determine the sodium. Thus all the data were obtained for determining the concentrations of the different solutions. After a series of experiments, the entire apparatus was taken down, washed, and dried. It was then set up again and operations carried out as before.

The electromotive force was determined by comparing with a standard cell, a sensitive galvanometer of 3000 ohms resistance serving as null instrument. The sensitiveness, of course, decreased in very dilute solutions where the resistance of the cell became comparable with that of the galvanometer. In the more concentrated solutions a change of 0.1 millivolt caused a deflection of about 6.0 scale divisions, while in the most dilute solutions it produced a change of only about 1.0 division. The percentage accuracy in the dilute solutions did not decrease in this proportion for the reason that the total electromotive force measured was greater in these solutions.

Although the electrodes employed were very small, the constancy of the electromotive force was remarkable. Within the limits of sensitiveness of the galvanometer, no fluctuations could be observed except in the most dilute solutions, where electrode effects appeared.

Calculations.—We have seen that, when a current passes through a metal solution, the metal is carried from anode to cathode. On the other hand, the anion apparently consists merely of a negative electron or of an electron associated with ammonia.

In the solution we have the equilibrium

$$M^{+} + e^{-} \rightleftarrows Me$$

where M^{+} is the positive ion, e^{-} the negative ion (consisting of the negative electron) and Me represents the neutral metal atom. According to the results of a previous paper, work is involved only in the transfer of the positive metal ions from one solution to another. Equating the osmotic and electrical work and solving for the electromotive force, we have

$$E_1 = \frac{2nRT}{F} \log_e \frac{(M^{+})_1}{(M^{+})_2}, \qquad \text{I}$$

where E_1 is the electromotive force of the cell due to the transfer of solute, F is the electrochemical equivalent, n is the fraction of the current carried by the positive carriers, R is the gas-constant, T the absolute temperature, and $(M^{+})_1$ and $(M^{+})_2$ are the activities of the positive ions in the two solutions, respectively.

As stated in the preceding section, the negative carrier consists of the negative electron, either free or associated with the solvent. The electrons themselves contribute nothing to the work of the cell. If, however, they are associated with the solvent, the solvent will be carried from a solution of higher to a solution of lower vapor-pressure. In concentrated solutions, we must, therefore, take this factor into account.[1] If m molecules of ammonia are associated with one electron, then for every equivalent of electricity, $m(1 - n)$ mols of ammonia will be carried from the dilute solution of concentration c_2 and vapor-pressure p_2 to the concentrated solution of concentration c_1 and vapor-pressure p_1, the factor $1 - n$ being the fraction of the current carried by the negative carrier. Since the negative carrier moves from the dilute to the concentrated solution, the solvent moves from higher to lower vapor-pressures, osmotic work is done, and the electromotive force due to the transfer of solvent will be in the same direction as that due to the transfer of metal. The solvent carried by the negative carrier will, therefore, contribute the electromotive force

$$E_2 = \frac{m(1 - n)RT}{F} \log_e \frac{p_2}{p_1}. \qquad \text{II}$$

We are assuming here that the amount of ammonia associated with the carriers in the two solutions is constant, an assumption which must be very nearly true, since the concentrations differ only in the ratio of 1 : 2. The ammoniation of the metallic ions does not enter into the osmotic work, since the metal does not lose its solvent at the electrode; for the metal in any case remains in solution. The only factor introduced here is due to change in the ammoniation of the positive ion, which may be neglected. Moreover, it will be shown that, even if this were very large, it would not produce an appreciable result in the electromotive force of the cell.

We have, therefore, for the electromotive force E of the cell in the direction from solution 1 to solution 2,

$$E = E_1 + E_2 = \frac{2nRT}{F} \log_e \frac{(M^+)_1}{(M^+)_2} + m(1 - n)\frac{RT}{F} \log_e \frac{p_2}{p_1}. \qquad \text{III}$$

If the concentrations are made sufficiently small the activities $(M^+)_1$ and $(M^+)_2$ become equal to the concentrations M_1^+ and M_2^+, respectively, and the second term vanishes, since p_2 and p_1 approach equality.

We have then

$$E = \frac{2nRT}{F} \log_e \frac{M_1^+}{M_2^+}, \qquad \text{IV}$$

from which n, the transference number of the metal, may be calculated.

It has been shown in a preceding paper[2] that Raoult's law does not

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[1] Lewis, This Journal, **30**, 1355 (1908).

[2] *Ibid.*, **30**, 1197 (1908).

hold for solutions of sodium in ammonia at moderate concentrations. At these concentrations, therefore, Equation IV does not apply strictly. Nevertheless, it may reasonably be assumed that the equation will yield results of a correct order of magnitude. In dilute solutions, however, as will be shown in the next paper, the mass-action law applied to solutions of metals in ammonia. For these solutions, therefore, Equation IV is exact and the resulting value of n yields a precise measure of the transference number of the metal ion.

As we shall see presently, the transference numbers of the carriers in the more concentrated solutions change rapidly with concentration. This factor also has been neglected in the preceding equation. It does not seem worth while to introduce a correction term for this factor, since so many other uncertainties underlie the application of the equation to concentrated solutions. The values obtained for n may be looked upon as mean values between the concentrations in question. Throughout the experiments the concentration ratio of approximately 1 : 2 was maintained between the solutions measured. Over this concentration-interval the ionization does not change greatly, so that the ratio of total salt concentrations may be employed in place of the ratio of ion concentrations. When the conditions of experiment warrant a greater precision, a correction will later be made.

It has also been assumed that the equilibrium existing in the solution is that of a binary electrolyte. The correctness of this assumption will be shown in another paper.

Experimental Results.—The results obtained in three independent series of experiments are embodied in the following table. The first column gives the number of the observation; the second and third columns give the concentration of the solutions in the cell, while the fourth column gives the logarithm (to the base 10) of the ratio of these concentrations. Under c_a is given the mean concentration of the two solutions and under $E \times 10^3$ the observed electromotive force in millivolts. Finally, in the seventh column, are given the values of the ratio $(1 - n)/n$, where n is the transference-number of the sodium ion Na^+, calculated from Equation IV, the absolute temperature being 240°.

Discussion.

The fraction of the current carried by the positive carrier Na^+ is n. That carried by the negative carrier is $1 - n$ and the ratio $(1 - n)/n$ is the ratio of the amount of the current carried by the negative carrier to that carried by the positive carrier. It is to be noted that in the case of the negative carrier this ratio does not necessarily represent the speed of any one negative carrier relative to that of the positive carrier, for the speed of all the negative carriers is not necessarily of the same order of magnitude. The ratio, therefore, involves the average value for all

TABLE I.—RELATION BETWEEN ELECTROMOTIVE FORCE AND CONCENTRATION.

No.	C_1.	C_2.	log c_1/c_2.	c_a.	$E \times 10^2$.	$(1 - n)/n$.
			Experiment I.			
1	0.4560	0.1928	0.3741	0.325	0.85	41.0
2	0.1770	0.0863	0.3123	0.131	0.96	39.0
3	0.0805	0.0460	0.2434	0.063	1.00	21.4
4	0.0420	0.0148	0.3274	0.031	1.40	20.6
5	0.0177	0.0065	0.4373	0.012	2.55	15.0
			Experiment II.			
2	0.7628	0.3390	0.3522	0.551	0.609	54.0
3	0.3020	0.1892	0.2029	0.295	0.491	38.2
4	0.1625	0.0897	0.2580	0.126	0.790	32.0
5	0.0837	0.0490	0.2322	0.066	0.867	24.4
6	0.0447	0.0222	0.3046	0.033	1.355	20.4
7	0.0205	0.0121	0.2307	0.016	1.300	15.4
			Experiment III.			
1	1.014	0.6266	0.2344	0.870	0.080	277.6
2	0.9738	0.4693	0.3160	0.732	0.328	90.6
3	0.4571	0.3181	0.1525	0.387	0.336	42.2
4	0.4339	0.2310	0.2739	0.335	0.620	41.2
5	0.2224	0.1600	0.1437	0.191	0.384	34.6
6	0.2135	0.1153	0.2674	0.164	0.72	33.4
7	0.1109	0.0770	0.1580	0.094	0.50	29.2
8	0.1064	0.0570	0.2690	0.081	0.86	28.8
9	0.0548	0.0376	0.1639	0.046	0.65	23.2
10	0.0526	0.0274	0.2934	0.040	1.07	25.0
11	0.0263	0.0186	0.1510	0.023	0.78	17.4
12	0.0253	0.0140	0.2576	0.020	1.38	16.4
13	0.0135	0.0091	0.1582	0.011	0.92	11.4
14	0.0130	0.0070	0.2658	0.010	1.80	13.2
15	0.0065	0.0034	0.2779	0.0050	2.60	9.2
16	0.0031	0.0016	0.2883	0.0024	3.40	7.0

the negative carriers present. In the case of the sodium ion we may safely assume that all the ions move with the same mean speed, and that the speed is independent of concentration. Any variation of the ratio, therefore, represents the change in mean speed of the negative carriers.

In Fig. 2, the values of the ratio $(1 - n)/n$ are plotted as ordinates against those of the logarithms of the mean dilution (log $1/c_a$) as abscissae. The different points are in excellent agreement, both for points of the same and of different series. This shows that the results obtained are reproducible and represent equilibrium conditions. Such variations as appear are due partly to experimental error and partly to the approximations underlying the calculations.

It will be seen on inspection that in dilute solutions the negative carrier carries about seven times as much current as the positive carrier. The fraction of the current carried by the negative carrier increases with concentration, particularly as normal concentration is approached. In the most concentrated solutions (mean concentration 0.87 normal) the negative carrier carries approximately 280 times as much current as the positive carrier. In other words, the relative amount of current carried by the negative carrier at this concentration is 40 times as great as that at high dilutions.

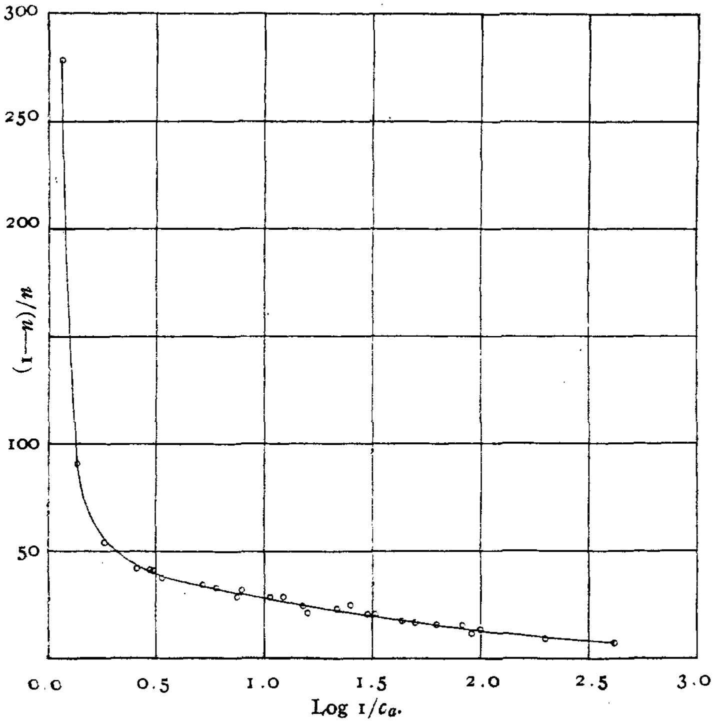

Fig. 2.—Showing change of $(1 - n)/n$ with the concentration.

The values of $(1 - n)/n$ are, of course, affected to some extent by the approximations made in the calculations. The ionization is changing with concentration, so that, even at the highest dilutions, the concentration ratio c_1/c_2 is somewhat greater than the ratio $c_1\gamma_1/c_2\gamma_2$ of the ion-concentrations. The error due to this source is negligible in comparison with the observed change in the ratio $(1 - n)/n$. At higher concentrations the ionization of electrolytes does not follow the mass-action law. This error also is small in comparison with the change observed in this ratio. As to order of magnitude, therefore, the values of $(1 - n)/n$ are doubtless correct.

It follows, then, that the fraction of the current carried by the negative carrier increases enormously with increasing concentration. This shows that the mean speed of this carrier increases greatly with increasing concentration.

In dilute solutions the value of $(1 - n)/n$ appears to be approaching a definite limit which is probably not far from 7, the lowest value measured. The ionic conductance due to the sodium ion as deduced from conductance and transference measurements is 130.[1] The conductance of the negative carrier in a sodium solution is, therefore, $7 \times 130 = 910$, and therefore the molecular conductance of sodium at zero concentration is 1040. As will be shown in another paper, this is in excellent agreement with the directly measured value.

Since, in dilute solutions, the speed of the negative carrier is of the same order of magnitude as that of the sodium ion, it follows that the negative carrier must be associated with solvent molecules. In concentrated solutions, where the vapor-pressure lowering due to the solute becomes appreciable, the solvent associated with the negative carrier has an appreciable influence on the electromotive force, and a maximum value of the number of solvent molecules (m) associated with one negative carrier can be calculated. It can thus be shown that a portion of the current is carried by carriers not associated with the solvent. Namely, by placing n equal to zero in Equation III we may calculate a maximum value of m from the measured electromotive force (0.080 volt) of the pair of solutions used in Expt. III, No. 1, where the two concentrations are 1.014 and 0.627 normal, and where the ratio of the two vapor-pressures is 1 : 1.006.[2] The value so calculated is 0.67. The assumption that n is zero implies, of course, that there is *no* transference of the positive ion, and, therefore, that the whole electromotive force corresponds to the work done in the transference of ammonia. Since this assumption, even in the more concentrated solutions, is not strictly true, the value of m is doubtless considerably less than 0.67, but it can not be greater than this. This fact shows that at least one-third of the current is carried by electrons which are not associated with solvent, since those that are so associated must carry at least one molecule of ammonia.

Moreover, it is evident from the table that, at higher concentrations, the electromotive force approaches zero, or at least a very small value, as a limit. If one molecule of ammonia were associated with a single electron, a very considerable electromotive force would necessarily result, since the vapor-pressure of the solution changes rapidly with concentration.[2] The greater portion of the current is, therefore, carried by negative carriers which are wholly unassociated with ordinary matter. Doubtless, except in the case of very concentrated solutions, the larger proportion of the negative electrons is associated with ammonia; but their

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[1] Kraus and Bray, THIS JOURNAL, **35**, 1368 (1913).

[2] *Ibid.*, **30**, 1210 (1908).

speed under a given potential gradient is relatively so small that they contribute but little to the conducting power of the solution.

We are now able to form a very good picture of the process by which conduction takes place in the solutions of metals in ammonia. As we have seen, the metal dissociates in solution according to the equation

$$Me = M^+ + e^-,$$

where Me represents the neutral atom of metal which is to be looked upon as a combination between the positive metal ion M^+ and the negative electron e^-. For the alkali metals both ions M^+ and e^- are univalent as will be shown in a later paper. The process of ionic dissociation obeys the mass-action law, so that

$$\frac{(M^+)(e^-)}{(Me)} = K,$$

where the symbols in parentheses represent the activities of the different molecular species, which may be replaced by the concentrations themselves in dilute solutions. It is probable that both the metal ions M^+ and the neutral metal molecules Me are ammoniated to a greater or less extent. That the electrons e^- are associated with ammonia in dilute solutions can not be doubted, for the ratio of the mobilities of the two ions Na^+ and e^- approaches a limiting value lying in the neighborhood of 7.[1]

Since the viscosity of the solution does not change materially with the concentration, the change in speed of the negative electron can not be due to viscosity change. But if the electrons are associated with ammonia, then, as soon as the activity of the solvent becomes sensibly constant, the ammoniation of the electron becomes sensibly constant, and the speed being determined by the friction of the ionic envelope with the solvent molecules, the mobility remains constant.

As the concentration increases, the size of the ionic envelope must diminish and since the frictional resistance diminishes with the size of the envelope the mobility of the negative carrier increases. But this is not a complete description of the processes involved as the concentration of the solution increases. The speed of an electron associated with only one molecule would not be greatly different from that of an electron associated with a larger number of molecules. Since the current carried by the negative carrier increases at least 40 times, when the concentration changes from about 0.001 normal to normal, a mere change in the size of the envelope will not suffice to account for the increased carrying capacity of the negative ions. What takes place as the concentration becomes greater is that a portion of the electrons are completely freed from ammonia for a fraction of the time. No individual electron is free for any considerable length of time, but the free electrons, the solvent, and the solvated elec-

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[1] Compare Kraus, THIS JOURNAL, 36, 35 *et seq.* (1914).

trons are in kinetic equilibrium. In concentrated solutions we have, in fact, three carriers present, namely: Na^+, $e^-(NH_3)_x$, and e^-. When free from ammonia, the electrons possess a mobility comparable with that of the electrons in a metal. A very small number of free electrons will, therefore, suffice to produce an enormous increase in the carrying capacity of the negative carriers in solution. The great increase in the proportion of current carried by the negative carrier is thus due to the presence of a small number of free negative electrons.

The free electrons on reaching the electrodes pass into it freely and produce no material change in state in this process. The process of conduction from the solution to the electrode is thus like that in the metal itself in that it consists entirely in a motion of the electrons.

On the basis of these considerations, we are able to predict what will be the properties of very concentrated solutions of the metals in ammonia. The number of electrons, which at any instant possess no envelope of ammonia in a solution of metal at normal concentration, is very small and they possess a mobility many hundred times greater than that of the metal ion. As the solution becomes more concentrated, the number of electrons free from ammonia will finally be comparable with the number of sodium ions present. As a result, such solutions must possess a conducting power many hundred times greater than that of a normal solution of sodium in ammonia. If such is the case, these solutions should begin to approach the metals in conducting power. If the properties of metals are due to the presence of free electrons, it follows that, since concentrated solutions of the metals contain these electrons, these solutions should exhibit those properties which are characteristic of metals. In another paper I shall show that this is the case.

The negative carrier present in dilute solutions of the metals in ammonia possesses considerable interest. The fact that this carrier possesses a speed approximately seven times that of the sodium ion indicates that the solvent envelope surrounding the negative electron is relatively small. It is interesting to note that the speed of the negative electron in ammonia is many times greater than that of the negative ion produced by radiations in hexane.[1] The dielectric constant of ammonia is much greater than that of hexane and it is not unlikely that the greater speed in ammonia is a consequence of this circumstance, for the higher the dielectric constant of the medium, the smaller will be the field of force due to the electric charge.

Let us now consider what takes place around an electrode when a current passes continuously through the solution of a metal in ammonia. At the cathode the concentration of metal is increased under the action

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[1] THIS JOURNAL, 36, 59 (1914).

of the current. As soon as such concentration increase reaches an appreciable value, a relatively smaller quantity of metal is carried up for a given current. Consider a number of equipotential surfaces in the neighborhood of the cathode at which the concentration of the metal increases as the cathode is approached. The amount of metal carried across these surfaces decreases in proportion to the decrease of the transference number of the metal ion as the electrode is approached. There is, thus, a distributed accumulation of the metal throughout the volume of the solution in the neighborhood of the electrode. In the end, if the current be sufficiently great, no further change will take place immediately at the electrode surface. At a distance from the electrode the concentration change will increase up to a certain point and then again decrease until the normal concentration of the solution is reached.

The metal, then, is not deposited at the electrode surface, but is distributed throughout the electrode volume. Of course, the phenomenon is modified by diffusion and, under certain conditions, by convection. It is also greatly influenced by concentration. At very high concentrations the phenomena are much less marked than at low concentrations. The phenomena described in the fourth paper of this series are completely accounted for by the above hypothesis.

At the anode, with a non-soluble electrode, the phenomenon differs greatly from that at the cathode, if the solution is not too concentrated. Assume an electrode surrounded by a dilute solution of given concentration. When an electromotive force is applied, the negative carriers move to the electrode while the positive carriers move away from it. Now, the negative carrier moves up to the anode and then enters the metal. The only physical change accompanying this process is that ammonia is left behind at the electrode surface. In a dilute solution the ammonia thus left behind is relatively so small that it has no material influence on the observed phenomena. At the electrode surface there is, therefore, no manner of mechanical disturbance and we are able to observe phenomena which in ordinary solutions would be obscured by secondary effects.

The withdrawal of positive metal ions from the immediate vicinity of the anode surface causes an almost instantaneous removal of all metal from this region. The speed of this process is accelerated owing to the fact that when the concentration change sets in, the potential gradient in this region rises and thus increases the speed of the carriers.

In the immediate neighborhood of the anode there will, therefore, result a region which contains no metal whatever and across which the current is carried entirely by the negative carriers moving freely under the action of the applied potential. The extent of this region will depend on the electromotive force applied, the concentration of the solution, the shape and size of the electrodes, and other specific factors. As was described in the fourth paper of this series, the boundary of the metal-free region is usually very clear and distinct. Up to this boundary the metal is maintained in position by processes of diffusion and convection, the latter factor being the most important if a considerable potential is applied.

It is thus seen that in the case of an anode in a dilute metal solution, where one of the carriers is removed from solution when it reaches the electrode surface, the current is carried entirely by one carrier over an appreciable distance. That a similar phenomenon obtains in solutions of ordinary electrolytes appears highly probable.

Summary.

The electromotive force of concentration cells of solutions of sodium in liquid ammonia has been measured over an extended concentration range.

From these measurements approximate values of the transference numbers have been calculated for different concentrations. The ratio $(1 - n)/n$ of the fraction of the current carried by the negative and positive ions approaches a limiting value of approximately 7 in dilute solutions, and increases to a value of 280 at a mean concentration somewhat less than normal.

Assuming the speed of the positive ion to remain constant, the mean speed of the negative ion increases 40 times between about 0.001 and 1.0 normal. Assuming the equivalent conductance of the positive ion to be 130 (that of the sodium ion), the equivalent conductance of the dilute metal solution is calculated to be 1040.

These results are accounted for on the assumption that the ions Na^+ and e^- exist in solution. At high dilutions the negative electron e^-, which serves as negative ion, is surrounded by an envelope of ammonia which determines its speed. At higher concentrations some of the negative electrons are free from the ammonia envelope for a fraction of the time. Under these conditions they move with a speed comparable with that of the negative electrons in metals. This accounts for the rapid increase of the transference number of the negative carrier at higher concentrations, for the number of free electrons increases as the proportion of metal to ammonia increases.

The electrode phenomena described in the fourth paper of this series are in accord with the above hypothesis.

On the basis of the osmotic work involved, it is shown that in the case of the most concentrated solutions a portion of the current is carried by carriers not associated with ordinary matter.

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