$(C_{10}H_6NO_2)_3Co$ is not (or only slightly) attacked, the presence of *small* quantities of cobalt may escape detection (due to the fact that there is present a dark residue derived from the precipitated nitroso-naphthol) unless a confirmatory test by means of the borax bead is made. The use of nitroso-R-salt in the same conditions does not require an additional bead test. In the regular course of qualitative analysis the test with nitroso-R-salt can be applied to the residue of dry chlorides, or after separating the nickel, as a confirmatory test for cobalt.[1] The compound is rather expensive,[2] but considering the large number of determinations that can be made with a small quantity of material it is more economical to use than other reagents which are in use for the qualitative determination of cobalt.

TROY, N. Y.

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS. VI. THE CONDUCTANCE OF THE ALKALI METALS IN LIQUID AMMONIA.[3]

BY CHARLES A. KRAUS.

I. Introduction.

In the fifth paper of this series it was shown that, for a given concentration interval, the electromotive force of a concentration cell, in which sodium is employed as electrolyte in liquid ammonia between platinum electrodes, decreases rapidly at higher concentrations and apparently approaches a value of zero in very concentrated solutions. From the results of the fourth paper of this series it follows that, in solutions of sodium in ammonia, we have present normal sodium ions and a negative ion which appears to be characteristic of solutions of all metals in ammonia. If the electrode processes in the case of these concentration cells are reversible, and many facts indicate that this is the case, then the relative speeds of the positive and negative carriers may be calculated approximately, assuming the laws of dilute solutions to hold true. While these laws do not hold precisely, it may, nevertheless, be expected that the results of calculations based upon this assumption will be correct as to the order of magnitude.

The results indicate that, as the concentration of the sodium solution increases, the relative speed of the negative carrier increases. This increase is at first relatively slow, but, at the higher concentrations, the

[1] Noyes, "Qualitative Chemical Analysis," Procedures 68 and 70.

[2] Obtainable from Eimer and Amend.

[3] Previous papers of this series have appeared as follows: I, THIS JOURNAL, **29,** 1557 (1907); II, *ibid.,* **30,** 653 (1908); III, *ibid.,* **30,** 1157 (1908); IV, *ibid.,* **30,** 1323 (1908); V, *ibid.,* **36,** 864 (1914); *Trans. Am. Electrochem. Soc.,* **21,** 119 (1912).

rate of increase with increasing concentration is greatly accelerated. If it be assumed that the positive carrier is in fact the sodium ion and that the speed of this ion does not vary greatly with the concentration, then it follows that the speed of the negative carrier increases with increasing concentration, this increase being the greater the greater the concentration.

If the above conclusion is correct, it follows that the conductance of a solution of sodium in liquid ammonia should increase with the concentration at higher concentrations and that this increase should be the greater, the greater the concentration of the solution. On the other hand, in dilute solutions the speed of the negative carrier is approximately independent of concentration and, since sodium dissociates according to a binary process of ionization, the conductance should increase with increasing dilution and should approach a limiting value in very dilute solutions corresponding to complete ionization.

The only measurements heretofore recorded on the conductance of solutions of the metals in liquid ammonia are due to Cady,[1] who found that solutions of sodium in liquid ammonia are excellent conductors, the conductance being considerably greater than that of typical salts in the same solvent. It is the purpose of the present investigation to supply data relating to the conductance of metal solutions in ammonia as a function of their concentration. At the same time preliminary observations are given on the temperature coefficients of these solutions and on their photo-electric activity.

The chief difficulty met with in measuring the conductance of such solutions is due to the reaction of the metal with ammonia to form the metal amide. Traces of impurities serve to catalyze this reaction to a measurable extent, particularly in dilute solution. By excluding all impurities, particularly oxygen, from the apparatus it is possible to overcome this difficulty in a very large measure. In the case of conductance measurements, however, it is necessary to introduce electrodes which serve to catalyze the reaction; it was not found possible to overcome this difficulty entirely. Various metals, such as gold, were employed in place of platinum as electrodes but no appreciable advantage resulted from such substitution. The only solution of the difficulty lay in reducing the surface of the electrodes to a minimum and in stirring the solutions during the course of the measurements.

II. Apparatus and Manipulation.

The apparatus employed in carrying out the measurements on the conductance of the metals in liquid ammonia at its boiling point is shown diagrammatically in Fig. 1.

The conductivity cell A was provided with a pair of platinum electrodes, B, con-

[1] Cady, *J. Phys. Chem.*, **1**, 707 (1897).

sisting of 2 platinum wires having a diameter of 0.7 mm. and projecting into the cell a distance of about 4 mm.; the axes of the wires were separated by a distance of about 1.5 mm. These electrodes were connected externally with the tubes CC into which mercury was introduced. The cell was provided with a third electrode, D, which was intended for the purpose of measuring the conductance of solutions of higher specific conductance. In this case the resistance of the solution was measured between the pair of electrodes B and the electrode D, through the tube E, which had a diameter of approximately 5 mm. It was possible to measure the conductance of solutions up to concentrations as high as 2 N. The electrodes were not platinized, since the presence of platinum black greatly accelerates the reaction between metal and solvent, and since, owing to the reversibility of the metal electrodes in these solutions, a perfect minimum is obtained with unplatinized electrodes even at the highest dilutions. One difficulty, however, arises in the case of the more dilute solutions; reaction between the solvent and the dissolved metal takes place immediately in the neighborhood of the electrode surfaces. This results in a diminution of the measured conductance of the solution, even though the effect on the concentration of the solution as a whole is negligible. It was found possible to overcome this difficulty by means of the stirrer F which was suspended by means of a platinum-iridium spring G. A soft iron core H, enclosed in glass, was attached to the lower end of the spring. The tube I, within which the stirrer system was suspended, was provided externally with
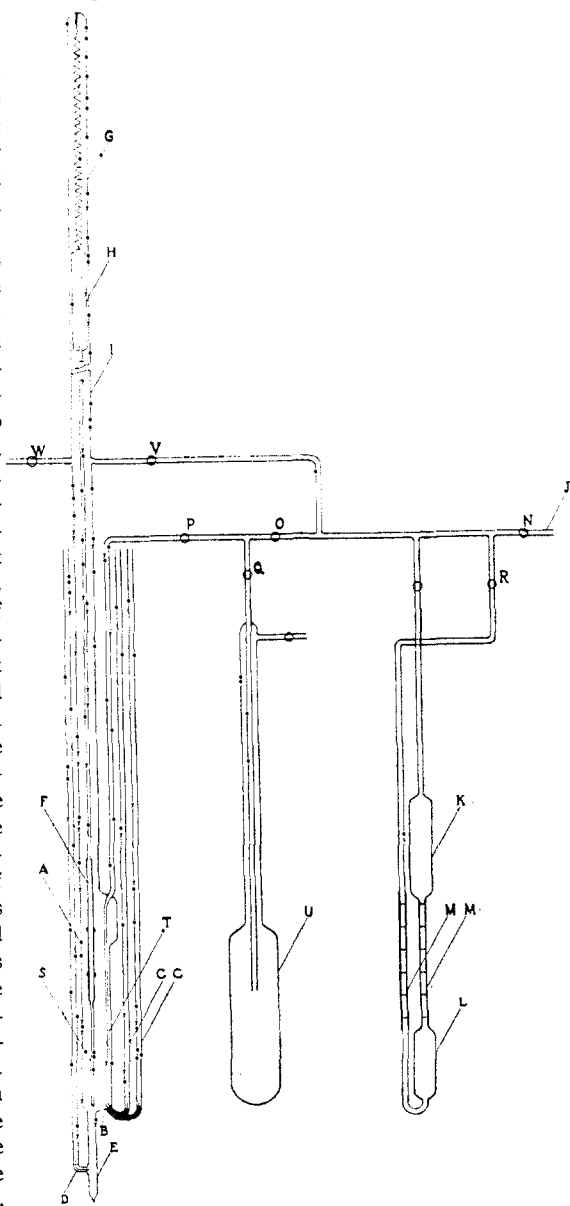

Fig. 1.—Conductance apparatus.

a solenoid (not shown in the figure), by means of which it was possible to actuate the stirrer. A slight motion of the stirrer served to equalize the concentration of the metal in the neighborhood of the electrodes and made it possible to obtain consistent measurements.

The metal was introduced at the bottom of the tube E by a method which has been described in a previous paper.[1] The stopcock W made connection with a vacuum pump. The ammonia supply was contained in a metal cylinder in which it was treated with metallic sodium; this stock cylinder was attached to the tube J. Since it was necessary to determine the concentration of the solutions, the ammonia introduced into the cell was measured before introduction. In order to do this, it was first condensed in the measuring cell K, which consisted of the chamber L and 2 graduated Tubes MM. These tubes were about 10 cm. in length and had a total capacity of 1 cc., graduated to 0.01 cc.; the cell having been calibrated, the volume of the ammonia could be determined within a few thousandths of one cc. The measuring cell was immersed in boiling ammonia during the process of condensation. When the desired amount of ammonia had been condensed in the measuring cell, the stopcocks N, R were closed and the stopcocks O, P and V were opened. It should be stated that, prior to these operations, the entire apparatus was exhausted to a pressure at least as low as 0.001 mm. of mercury. The measuring cell was provided with the enlarged chamber K in order to facilitate the boiling of the ammonia in the cell during the course of its transfer to the conductivity cell A. The solution was stirred while ammonia was being introduced into the cell, the stirrer F being provided with a smaller extension S reaching to the bottom of the tube E.

When the desired amount of ammonia had been measured and introduced into the conductivity cell. conductance measurements were made by means of a bridge and telephone. In the case of the more concentrated solutions, it was possible to employ a direct current in conjunction with a galvanometer, since polarization effects appear to be wanting in these solutions. It was found more convenient, however, to employ a telephone, inasmuch as this instrument had to be employed in the more dilute solutions in any case. The measuring cell had a volume of approximately 5 cc. and the conductivity cell was so designed that its volume up to the end of the small capillary Tube T was also approximately 5 cc. While carrying out the measurements on the conductance of the solution in the conductivity cell, a fresh supply of ammonia was condensed in the measuring cell. After having completed the conductance measurement, this ammonia was transferred to the conductivity cell, as has already been described. The volume added in each case was approximately the same, namely, 5 cc., and thus the concentration of the solution was reduced by one-half on each addition of fresh solvent. After completing the measurements on the conductance of the new solution, it was necessary to remove a known fraction, about $1/2$, of the solution, in order to be able to introduce new solvent; this was done by withdrawing a portion of the solution through the tube T. In order to do this, there was provided an auxiliary Tube U, immersed in liquid ammonia boiling below normal pressure; this tube, like the other parts of the apparatus, had been previously exhausted. When it was desired to transfer the solution from the conductivity cell to the tube U, the stopcock O was closed and the stopcocks P and Q were opened. On opening these stopcocks, the solution was forced under its own vapor pressure through the capillary T and the stopcocks P and Q into the cell U. Since the ammonia surrounding this cell was boiling under reduced pressure, sufficient pressure difference was maintained between cell A and the tube U to provide for the transfer of the ammonia from A to U. When the level of the solution in A reached the bottom of the capillary T, the transfer of solution ceased. In this way there was left

[1] THIS JOURNAL, 30, 1206 (1908).

in the cell A a quantity of solution approximately equal in volume to that originally present, and at a concentration approximately $^1/_2$ that of the original concentration. Into this solution a fresh quantity of ammonia was condensed and the conductance of the resulting solution measured. These operations were repeated until the concentration had been carried to as low a value as desired.

It was, of course, necessary to determine exactly the amount of ammonia left behind in the cell T after each operation. This was done by measuring the amount of solution transferred from the conductivity cell to the tube U. For this purpose, the bath surrounding the tube U was removed, and the ammonia evaporated rapidly and absorbed in a weighed flask of water. When the ammonia in U had been completely absorbed in water, the flask was again weighed and the amount of ammonia which had been carried to the cell U was thus determined. The amount of solution left in the cell was then found by subtracting the weight of the solution transferred from that originally present in the cell. In calculating the weight of ammonia in the measuring cell KL, the density of the liquid was assumed to be 0.674 at the boiling point of liquid ammonia.

When the conductivity measurements were completed, the ammonia remaining in the cell A was evaporated and absorbed in water. The amount of ammonia introduced into the cell, as measured in the measuring cell, could thus be checked by the total of the amounts absorbed in water. In the course of a run, practically all the metal was transferred from the conductivity cell A to the tube U. On the completion of the conductance measurements, a small amount of alcohol was introduced into U, thus converting the metal to an alcoholate. Water was then added, and the contents of the tube were washed out into a beaker and titrated against standard acid. In this way the amount of sodium present in the inital solution was determined. It should be noted in this connection that, prior to these operations, any residual ammonia in the apparatus was pumped out in order to insure the accuracy of the titrations.

The conductance cell was calibrated with respect to standard solutions of potassium chloride. Owing to the small area of the electrode surfaces and their unplatinized condition, it was not possible to determine the cell constant directly. This difficulty was overcome by comparing the constant of this cell with that of an auxiliary cell whose constant had been determined by means of standard potassium chloride solutions. For the purpose of this comparison, a solution of potassium iodide, nearly saturated with iodine, was employed. The electrodes in the case of potassium iodide-iodine solutions do not polarize, and minima can be obtained even with very small electrode surfaces. The relative constants of the pair of electrodes B and of the electrode D, with one of these electrodes, could be obtained in the course of any given series of measurements by measuring the resistance of a given solution across these 2 pairs of electrodes. The constants of the cell were changed slightly from time to time owing to minor alterations which were made in the cell. In the Series 16 to 19 the constants of the 2 pairs of electrodes were 39.51 and 0.9102. In the other series, however, the constants differed somewhat from these values.

III. Conductance of Sodium, Potassium, Lithium, and Mixtures of Sodium and Potassium at the Boiling Point of Ammonia.

The results of the measurements on the conductance of sodium in liquid ammonia are given in Table I. At the head of the table is given the series of the experiment. In the first column is given the number of the experiment, in the second column the dilution, V, in liters per gram atom of sodium, and, in the third, the equivalent conductance H in the customary

TABLE I.—CONDUCTANCE OF SODIUM IN AMMONIA.

	Series III.					Series X.	
No.	$V.$	$H.$	$l.$	No.	$V.$	$H.$	
1	0.5047	82490	163.5	1	0.8478	10050.0	
2	0.6005	44100	73.43	2	1.694	1118.0	
3	0.6941	23350	33.63	3	3.525	679.5	
4	0.7861	12350	15.71	4	7.023	542.1	
5	0.8778	7224	8.230	5	13.86	481.5	
6	0.9570	4700	4.872	6	27.50	476.7	
7	1.038	3228	3.082	7	55.35	524.3	
				8	109.0	613.2	
				9	203.3	688.7	
				10	417.8	778.4	
				11	847.2	844.8	
				12	1750.0	879.2	
				13	3621.0	906.6	
				14	7302.0	916.0	
				15	14980.0	916.2	

	Series XV.			Series XVI.	
No.	$V.$	$H.$	No.	$V.$	$H.$
1	0.7165	20280.0	1	0.7101	18000.0
2	1.438	1429.0	2	1.460	1308.0
3	3.411	690.8	3	3.007	712.9
4	7.485	535.3	4	6.845	538.3
5	16.08	477.5	5	14.98	473.6
6	37.04	491.7	6	33.25	483.9
7	80.65	565.2	7	73.99	555.1
8	174.3	676.6	8	162.9	668.8
9	389.1	800.4	9	360.8	790.3
10	865.8	888.8	10	796.2	886.8
11	1945.0	938.7	11	1763.0	944.3
12	4369.0	957.9	12	3873.0	969.9
13	9750.0	957.2	13	8352.0	981.5
14	21990.0	961.8	14	19050.0	960.7
15	51340.0	155.2	15	33230.0	1020.0

	Series XVII.			Series XIX.	
No.	$V.$	$H.$	No.	$V.$	$H.$
1	0.7332	20430.0	1	0.6107	46340.0
2	1.519	1292.0	2	1.239	2017.0
3	3.589	670.1	3	2.798	749.4
4	7.697	519.5	4	6.305	554.7
5	16.42	473.9	5	13.86	478.3
6	35.70	488.5	6	30.40	478.5
7	78.54	562.0	7	65.60	540.3
8	172.1	676.9	8	146.0	650.3
9	377.3	801.5	9	318.6	773.4
10	850.0	898.2	10	690.1	869.4
11	1887.0	954.1	11	1551.0	956.6
12	4075.0	977.9	12	3479.0	988.6
13	8954.0	988.8	13	7651.0	1009.0
14	19550.0	1000.0	14	17260.0	1016.0
15	44260.0	1020.0	15	37880	1034.0

Kohlrausch units.   In Series III the specific conductance l of the solution in reciprocal ohms is given in the last column.   In calculating the dilutions, V, corrections were not made for the densities of the solutions. All values given are based on the value 0.674 for the density of pure ammonia.   A saturated solution of sodium in liquid ammonia has a density only a little greater than 0.5.   Consequently the true dilutions in the more concentrated solutions are appreciably greater than those given in the table.

Each series of experiments was carried out as rapidly as possible and required from 3 to 5 hours for completion.   The results of some of the series carried out were discarded owing to accidents or obvious errors in the course of the experiments and other series have not been included as they add nothing material to the results here given.   A number of the earlier series of experiments have not been included owing to the fact that the results in the more dilute solutions are obviously in error.

In the earlier experiments the equivalent conductance in the more dilute solutions passed through a maximum value.   This result is unquestionably due to reaction between the metal and the solvent.   The sodium amide formed is relatively only a poor conductor and as a consequence the conductance of the solution falls.   As the experimental methods were refined, this difficulty was in a large measure overcome.   This is illustrated, for example, in Fig. 2, where the points in dilute solutions for each succeeding run from 15 to 19 lie one above the other.   In the more concentrated solutions, there was no indication of a change of the conductance with time, but in the most dilute solutions such a change was appreciable.   The change, however, in the later series of experiments was not large and it is believed that the error introduced, owing to this effect, is comparatively small, probably not exceeding a few per cent., if as great as this.

TABLE II.—CONDUCTANCE OF POTASSIUM IN AMMONIA.

	Series IV.			Series III.	
No.	V.	H.	No.	V.	H.
1	1.695	1414.0	1	2.635	848.6
2	3.459	751.9	2	5.384	652.5
3	7.560	596.1	3	11.30	554.2
4	15.87	532.1	4	23.80	526.0
5	34.14	534.8	5	49.56	582.4
6	70.94	594.6	6	105.2	646.0
7	150.6	686.6	7	226.2	752.6
8	324.4	787.2	8	483.5	844.5
9	680.6	860.0	9	1056.0	908.0
10	1434.0	894.3	10	2226.0	933.3
11	2990.0	884.1	11	4695.0	936.5
			12	9759.0	945.0

In Table II are given the results of two series of measurements with

potassium. It is evident from the form of the curve, as may be seen by referring to Fig. III, that the solutions of potassium were much less stable than those of sodium. In Series IV the curve exhibits a maximum in dilute solution and in Series III the conductance values are obviously low.

In Table III are given values for the conductance of lithium in ammonia. These measurements were not extended to the more dilute solutions owing to the fact that in these solutions the metal reacted with the solvent to a greater extent than either sodium or potassium.

TABLE III.—CONDUCTANCE OF LITHIUM IN AMMONIA.

No.	V.	H.
1	0.4229	25600.0
2	0.8323	9642.0
3	1.990	879.4
4	4.250	619.7
5	8.817	501.2
6	18.13	454.6
7	40.17	502.2
8	85.94	569.9
9	181.6	654.4

Finally, in Table IV are given the results of measurements on a mixture of sodium and potassium. The amounts of sodium and potassium present in the mixtures were determined approximately by weighing as chlorides which give the values of 59.4 atomic per cent. of sodium and 40.6 atomic per cent. of potassium present in the mixture.

The mixtures of sodium and potassium were made up by melting these metals together in the course of their introduction into the cell according to the method described in an earlier paper. If ammonia is employed for the purpose of driving the metal over into the conductivity cell, care must be exercised not to allow ammonia vapor to remain in contact with the metal for an appreciable period of time, since this vapor is soluble in the liquid alloy. Reaction takes place between the ammonia and the alloy, resulting in the formation of solid amide. That ammonia is soluble in the liquid metal, is shown by the fact that, when left in contact with the metal, there is a diminution of pressure. At the same time the surface of the metal becomes tarnished and minute gas bubbles are formed within the body of the metal due to an evolution of hydrogen within the metal. In the course of time the liquid becomes spongy, resembling in many respects the product obtained by the action of sodium amalgam on an ammonium salt. Ultimately the pressure again rises, due to the evolution of hydrogen. From these facts it appears that ammonia has a considerable solubility in the liquid metal and that reaction takes place between the ammonia and the metal within the body of the liquid metal phase. If the temperature of the alloy is raised, the amides fuse. The point of fusion depends upon the concentration of the amide, and, under proper conditions, the point of fusion may be brought down below 100°. The alloy is somewhat soluble in the mixtures of fused amides, as is indicated by a blue color which appears to be in every way identical with the color due to the metals dissolved in liquid ammonia[1]. This color, moreover, resembles that obtained when ammonia acts upon metallic sodium at elevated temperatures. Ordinarily the process of reaction consists in an initial solution of the metal in the fused amide and a reaction between the am-

[1] McGee, THIS JOURNAL, 43, 500 (1921).

monia and the metal in this phase.   The solutions of the alkali metals in the fusion of mixed amides appear to be entirely stable.

TABLE IV.—CONDUCTANCE OF MIXTURES OF SODIUM AND POTASSIUM IN AMMONIA.

No.	V.	H.
1	1.158	2493.0
2	2.292	885.1
3	4.983	633.3
4	10.53	526.6
5	21.44	495.0
6	44.78	524.2
7	93.56	604.5
8	193.8	712.0
9	407.5	828.1
10	846.1	917.3
11	1765.0	984.5
12	3645.0	1018.0
13	7556.0	1040.0
14	15250.0	1064.0

Preliminary measurements were also carried out on very concentrated solutions of sodium.   For this purpose a special cell was designed in which the conductance of the solution was compared directly with that of mercury.   As these measurements are only preliminary, it will be unnecessary to describe the cell in detail.   It may be stated, however, that the resistance element consisted of a glass tube having a length of approximately one meter and having a diameter somewhat smaller than one millimeter. The resistance of this cell, when filled with mercury at $0°$ was 2.65 ohms; and when filled with a saturated solution of sodium in liquid ammonia at the boiling point of liquid ammonia, was 5.49 ohms.   The specific conductance of the saturated solutions of sodium in liquid ammonia is 0.479 that of mercury, or 0.51×10^4 reciprocal ohms.

IV. Temperature Coefficient of the Conductance of Sodium in Ammonia.

The temperature coefficients of solutions of sodium in liquid ammonia were likewise measured for several solutions whose concentrations, however, were not determined.   The method employed was similar to that employed by Franklin and Kraus.[1]   The results are given in Tables V, A and V, B.   In Table V, A the temperature is given in the first column and the resistance in the second column, the reciprocal of the resistance in the third column, and in the last column the mean temperature coefficient of the conductance in terms of the conductance at $-33°$.   This series of measurements was carried out with a fairly dilute solution.   The results of the series of measurements with a much more concentrated solution are given in Table V, B, in which the temperature is given in the first column and the resistance in the second column.

[1] Franklin and Kraus, *Am. Chem. J.*, **24,** 83 (1900).

TABLE V.—TEMPERATURE COEFFICIENT OF THE CONDUCTANCE OF SODIUM AMMONIA.

A. Dilute solution.				Concentrated solution.	
t, ° C.	R.	$1/R \times 10^3$.	$\dfrac{\Delta(1/R)}{\Delta t(1/R)_{33}} \times 100$.	t, °C.	R.
—33	124.3	8.04	....	+18	0.70
—13	85.7	1.17	2.25	—33	2.10
+17	43.4	23.9	4.69	+16	0.71
+48	28.2	35.0	5.34	+50	0.47
+85	15.6	64.0	9.00	+24	0.65
+23	47.7	....	....	—33	2.70

It is apparent from these results that at the higher temperatures the rate of reaction between the metal and the solvent is greatly accelerated. This was quite evident during the course of the experiment, since, when the temperature was maintained constant, the resistance of the solution increased. After having raised the temperature of the cell above that of the room, on bringing it back to room temperature, it was invariably found that the resistance of the solution had increased. This will be seen from a comparison of the results at 17° and 23° in Table V, A, and further from the results of the two measurements at —33° in Table V, B. In the latter case, the resistance was increased from 2.1 to 2.7 ohms, after heating up to 50°. It is obvious that the conductance as measured at the higher temperatures is considerably below the true values, owing to this interaction between solvent and solute.

For the purpose of comparing the temperature coefficient of the metal solutions with those of other substances dissolved in ammonia, the following tables are included. In Table VI are given the results of measurements on the conductance of solutions of a compound of sodium and lead $NaPb_x$[1] at a series of temperatures, and in Table VII are given the results of measurements on the conductance of solutions of potassium amide.

TABLE V.		TABLE VII.	
Temperature coefficient of $NaPb_x$.		Temperature coefficient of potassium amide.	
t, ° C.	R.	t, ° C.	R.
—33	134	—33	69.9
— 9	150	— 6	71.8
+ 6	156	+20	63.4
+25	155	+38	50.5
+38	150		

V. Photo-Electric Properties.

One of the characteristic properties of the alkali metals is their photo-electric activity under the action of visible radiations. This property is found not alone in the case of the elementary metals, but also in the case of their alloys. A preliminary experiment was carried out to determine whether or not the solutions of the metals in ammonia exhibited photo-electric activity. For this purpose 0.25 g. of lithium was introduced

[1] Smyth. THIS JOURNAL, 39, 1299 (1900).

into a tube having a diameter of approximately 3 cm. and a length of 35 cm. A platinum wire was sealed in the bottom of the tube making contact with the metal solution, and an aluminum wire was fixed about 3.5 cm. above the surface of the metal and connected with an electrometer. When ammonia gas was introduced, photo-electric activity was observed as soon as the metal began to go into solution. With an illumination in the room due to one or two 16-candle power lamps, the charge was still observable at the end of 5 minutes. With a 16-candle power lamp held about a foot from the metal, the electroscope was discharged in the course of 5 seconds. It should be noted, however, that the discharge took place with negative, as well as positive charge of the electrometer system. This action was doubtless due to the fact that, owing to the presence of the platinum lead wire in the solution, decomposition took place rapidly and particles of the solution were projected on the aluminum wire with which the electrometer was connected. It is obvious that the photo-electric action was not due to the presence of free metal, since the vapor pressure of the saturated solution of lithium in liquid ammonia is very low. As the pressure due to ammonia in the apparatus was much above the saturation pressure of the solution, it is obvious that free metal could not have existed. It follows, therefore, that, in a solution of an alkali metal in liquid ammonia, the metal is photo-electrically active just as it is in the case of the free element or of an alloy.

VI. Discussion of Results.

The results of the conductance measurements with the sodium solutions at the boiling point of ammonia are shown graphically in Fig. 2, where the equivalent conductances are plotted as ordinates and the logarithms of the dilutions as abscissas. Curve A relates to the more dilute solutions, up to a concentration of about 1 N. In Curve B are plotted
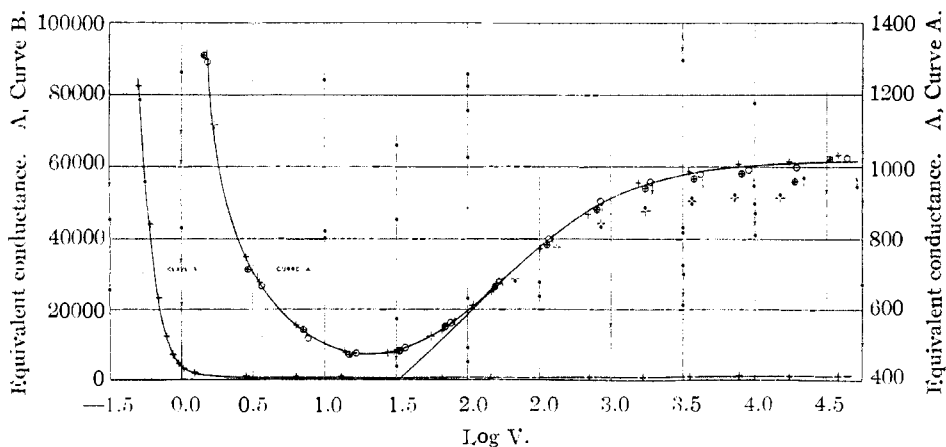

Fig. 2.—Showing conductance of sodium as a function of dilution.

the results up to a concentration of approximately 2 N. In order to represent the results at these higher concentrations, the scale of ordinates has been diminished in the ratio of 100 to 1. The scale for the more dilute solutions appears on the right-hand margin of the figure, and that for the more concentrated on the left. On Curve A, values due to Series 19 are represented by crosses, Series 17 by circles, Series 16 by combined crosses and circles, Series 15 by a broken vertical line, and Series 10 by an open cross. The points for the more concentrated solutions on Curve B are taken from Series 3. The remainder are taken from Series 19.

Considering first the more dilute solutions, it is apparent that as the dilution increases the equivalent conductance increases and approaches a limiting value. The form of the curve in general appears to be very similar to that of ordinary electrolytes dissolved in liquid ammonia. In the dilute solutions the curve appears to conform to the mass-action law. In Fig. 2, the curve as drawn in the more dilute solutions corresponds to the mass-action constant 77.27×10^{-4}, assuming the value of $\Lambda_0 = 1016$. As may be seen from the figure, the points lie upon this calculated curve within the limits of error up to a concentration of approximately 0.01 N, after which the experimental curve begins to diverge very rapidly from the calculated one, which is here continued as a line sloping downward. It is doubtful, however, whether the mass-action law applies up to this concentration in reality. In dilute solutions the chief source of error is due to the formation of amide which tends to reduce the observed value of the conductance of the solution. It is possible, therefore, that the curves in dilute solutions are somewhat flattened out owing to this effect. This might readily lead to an apparent agreement with the mass-action law, which does not exist in fact. In this connection it is to be noted that, as the manipulations were refined, the values observed in the dilute solutions rose continuously as shown in Fig. 2. Furthermore, it will be noted that, in Fig. 3, the curve for a mixture of sodium and potassium rises continuously and apparently considerably more steeply in dilute solutions than does the curve for sodium. Since the sources of error are in a direction to yield too low a value of the conductance, it appears not improbable that the highest values observed in the case of the sodium solutions are lower limits and that the true values should be somewhat higher than these. If this is the case, then the mass-action law does not hold at the higher concentrations; and the value of the mass-action constant would be materially decreased, if it be assumed that the mass-action law applies in the more dilute solutions as it does in the case of typical salts.

In any case, it is evident that the general form of the curve is similar to that of the salts in liquid ammonia solutions. It is remarkable, however, that the limiting value which is approached in the case of the am-

monia solutions is very much higher than it is in the case of typical salts. The highest value so far observed in the case of salts is in the neighborhood of 340, which is only about $1/_3$ that of the metal solutions.

The most striking result obtained, however, is that in the more concentrated solutions. After passing through a minimum at a concentration of about 0.05 N, the curve of the equivalent conductance begins to rise rapidly with increasing concentration. The general type of the curve corresponds somewhat to an exponential relation between the conductance and the concentration. For a concentration of approximately normal, the equivalent conductance rises to a value of approximately 3000, and in doubling the concentration the equivalent conductance reaches a value of approximately 80,000. For example, the equivalent conductance of a solution of sodium having a dilution of 0.5047 liter per gram atom is 82490, which corresponds to a specific conductance of 0.01635 × 10^4. The order of the conductance at this concentration is evidently approaching that of a metal; thus, the specific conductance of mercury is 1.063 × 10^4 or about 6 times that of the solution in question.

The results for potassium and lithium and for mixtures of sodium and potassium are shown in Fig. 3. Here the uppermost curve is that of potassium, the intermediate one that of a mixture of sodium and potas-
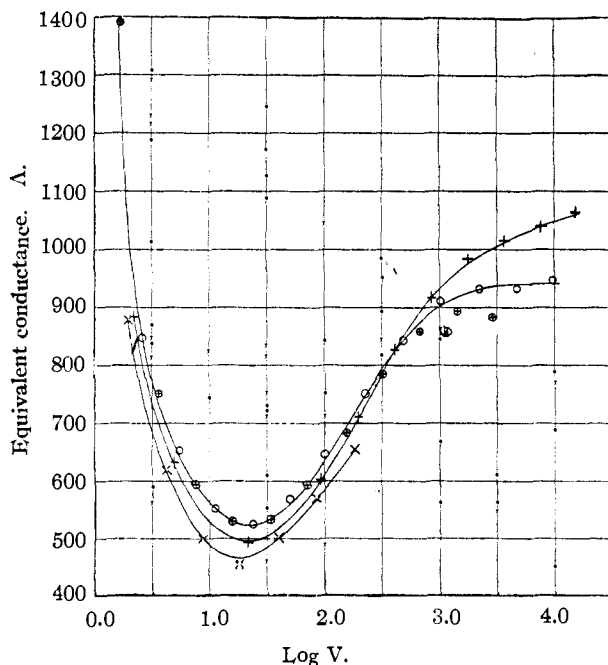

Fig. 3.—Showing conductances of potassium, lithium and mixtures of sodium and potassium as functions of the dilution.

sium, and the lowest one that of lithium. The curves in all cases have
approximately the same form. In the more dilute solutions the curve
for potassium falls below that of sodium. There can be no question but
that this result is due to the formation of amide in reaction between
potassium and the solvent; this reaction apparently takes place much
more readily in the case of potassium than in the case of sodium. It is
safe to assume, therefore, that the actual curve for potassium lies every-
where above that for sodium in the more dilute, as well as in the more
concentrated solutions. The curve for lithium lies somewhat below that
of sodium, although not so much as might be expected. Since only one
run was made with lithium, it is possible that the position of this curve
is somewhat in error owing to possible errors in determining the concen-
tration. In all three cases the minimum point of the curve occurs at
approximately the same concentration. The forms of the curves in the
more concentrated solutions are similar in the cases of the three metals.
The same holds true for the mixture of sodium and potassium. This mix-
ture of sodium and potassium appears to have been exceptionally stable
and a comparison of this curve with that of pure sodium affords perhaps
a better means for determining the relative conductance of sodium and
potassium than do the solutions of pure potassium. If the negative
carrier is the same for the three metals, then it follows that in the more
dilute solutions, the difference in the conducting power of two metals should
correspond to the difference in the conducting power of their positive
ions. Roughly, this is borne out by the results as shown in the curves
for sodium and potassium and in those for the mixture of sodium and
potassium, although the results so far are not sufficiently precise to make
an exact comparison possible. These results indicate, also, that if an
equilibrium exists between the positive and negative ions, this equi-
librium is approximately the same for a solution of a mixture of sodium and
potassium as it is for solutions of these elements alone. This is what
we should expect if the solutions of the metals themselves behaved in a
manner similar to that of the salts, or if the solutions of the metals had
dissociation functions of approximately the same value.

The solutions of the metals differ markedly from solutions of ordinary
electrolytes as regards their temperature coefficients. In general, the
temperature coefficients of salts are positive in the neighborhood of the
boiling point of ammonia where they have a value of approximately two
per cent. per degree. As the temperature rises, the coefficient decreases,
passes through zero, and thereafter becomes negative. This behavior is
exemplified in the case of the examples given for solutions of potassium
amide and $NaPb_x$. In the case of the alkali metal solutions in liquid
ammonia, the temperature coefficient in the neighborhood of the boiling
point of ammonia is slightly higher than that of typical electrolytes, and,

as the temperature increases, the value of the temperature coefficient increases rapidly. For the temperature interval between —33° and —13°, the coefficient has a value of 2.25%, while between 48° and 85° the coefficient has a value of 9.0%. These values, it is to be borne in mind, are lower limits, since the conductance as measured at the higher temperatures is materially reduced, owing to the formation of amide. It will be observed also that the coefficient for the more concentrated solutions differs but little from that of the more dilute. Between —33° and +17° the resistance decreases in the ratio of 124.3 : 43.4, or approximately 3 : 1. For the temperature interval —33° to +16°, the resistance of the more concentrated solution decreases in the ratio of 2.10 : 0.71, a value almost identical with that of the more concentrated solution. Similar relations hold for the higher temperature intervals.

In order to determine the value of Λ_o, the limiting value which the equivalent conductance approaches as the concentration decreases, it is necessary to assume or determine the form of the conductance function. As has already been stated, the results up to 0.01 N are in agreement with the law of mass action assuming 1016 for the value of Λ_o. This value is a lower limit since the sources of error tend to give too low a value of the conductance. It seems unlikely that the upper limit can be higher than 1050 if the experimental values in dilute solutions are anywhere near correct. The lower limit 1016 may be assumed as correct for the purpose of this discussion.

If we assume 1016 as the limiting value of the equivalent conductance for a sodium solution in liquid ammonia, and if we assume for the equivalent conductance of the sodium ion the value 130, we obtain for the equivalent conductance of the negative carrier in dilute metal solutions the value 886. This result may be compared with that obtained in the preceding paper of this series. It was there shown that the speed of the negative carrier approaches in dilute solution a value approximately seven times that of the positive carrier. The ratio of the conductance of the negative carrier in a sodium solution to that of the sodium ion, on the basis of the values given above, yields the value 6.8 for the ratio of the speeds of the two ions. This value is, therefore, in excellent agreement with the results of the electromotive force measurements in dilute solutions of sodium in liquid ammonia.

If the carrier in these solutions is the negative electron, it must be assumed to be associated with ammonia molecules in order to account for the low value of its equivalent conductance. It is interesting to compare the speed of the negative electron in ammonia with the speed of the negative electron in other solvents. Jaffe[1] has measured the speed of the negative electron produced by radiations in hexane. He found the

[1] Jaffe, *Ann. Physik.*, **32**, 148 (1910).

value 4.17 $\times$ 10^{-4} cm. per volt-second. On the basis of the above value for the conductance of the negative electron in liquid ammonia solutions, we calculate for the speed of this ion the value 91.7 $\times$ 10^{-4} cm. per second. We thus see that in liquid ammonia the speed of the negative carrier is approximately 20 times as great as that of the negative electron in hexane. The fluidity of ammonia at its boiling point is 376 and that of hexane is 312. It has been found that the speeds of ions of a given type are roughly proportional to the fluidities of the solvents in which they are dissolved—at any rate, this is very nearly true in the case of the larger ions. It may be inferred, therefore, that the negative electron in ammonia is associated with a much smaller number of solvent molecules than it is in hexane, as is to be expected since the dielectric constant of ammonia is 22 and that of hexane is 1.85. It is not possible to say what the exact nature of the combination between the electron and the ammonia molecule is. That the combination is indeed a very loose one is fairly certain from the behavior of the more concentrated solutions. Such a combination is not to be looked upon as a chemical compound in the ordinary sense of the word; such as we have, for example, in the case of the chlorine ion. In the latter case the combination between the negative electron and the chlorine atom is a fixed one, and the formation of such an ion is unquestionably associated with the evolution of considerable energy. This is not the case with the association formed between the negative electrons and the ammonia molecule.

As was shown in the fifth paper of this series, at higher concentrations, the relative speed of the negative carrier increases enormously. If the speed of the positive carrier remains fixed, or approximately fixed, it follows that at higher concentrations the speed of the negative carrier increases rapidly with increasing concentration. As a result, it follows that, unless the number of carriers at higher concentrations decreases very greatly, the conductance of these solutions should increase largely at the higher concentrations. Such is indeed found to be the case.

Between 0.5 and 1 N, the relative speed of the negative carrier begins to increase very rapidly, according to the electromotive force measurements, and over this concentration range the conductance of these solutions likewise begins to increase very rapidly. The fact that, at somewhat greater concentrations, the equivalent conductance reaches values of an entirely different order of magnitude from that in the more dilute solutions, shows clearly that this increase in the conductance cannot be due to an increase in the number of ions. It must, therefore, be due to an increase in the mean speed of the carriers. This may be accounted for on the assumption that at higher concentrations the carriers in part become free from their association with the surrounding ammonia molecules and therefore move with velocities comparable with that of the

negative electrons in metals. The current transported by such carriers fulfils the conditions for metallic conduction. It may be surmised, therefore, that conduction in metals is effected by the same carrier.

In dilute solutions, as has been shown above, the conductances of the alkali metals differ in the order of the conductance of their positive ions, and the difference in these conductances corresponds approximately with the difference in the conductances of these ions. It follows, therefore, that the negative carriers in solutions of the different alkali metals have the same conducting power, or in other words are identical.[1] Since the

[1] This is further borne out by the photometric investigation of these solutions by Gibson and Argo. (*Phys. Rev.*, **1**, 33 (1916); THIS JOURNAL, **40**, 1327 (1918)). They found that the absorption curves for the solutions of different metals in liquid ammonia are practically identical. Such a result can only be accounted for on the assumption that there is present in these solutions a charged particle which has the same optical properties in all of them. The solutions in question were comparatively dilute, in which case there were present no carriers which were not associated with ammonia. Apparently, therefore, the absorption spectrum is due to a complex between the negative electron and the solvent. Since it has been shown that it is only at much higher concentrations that the carriers become free, to an appreciable extent, from the ammonia molecules, it follows that evidence as to the presence of these free carriers by means of photometric observations can be gained only by a study of the more concentrated solutions. In the dilute solutions studied Beer's Law apparently holds. Since the ionization in these solutions is relatively high, it follows that this result cannot be interpreted as excluding the possibility that Beer's Law may fail in the more concentrated solutions; that is, the absorption spectrum, due to a negative electron combined with a metal atom, may differ from that of the negative electron combined with an ammonia molecule alone. In the case of ordinary electrolytes the absorption due to the un-ionized fraction appears to be identical with that due to the ions. In order to harmonize this result with our conceptions of the ionization of electrolytes, it is necessary to assume that the optical properties of the ions are not materially affected by the union of the ions to form a molecule. Such an hypothesis seems quite permissible in the case of ordinary electrolytes. In the case of the metal solutions, however, it is scarcely to be assumed that the motion of an electron associated with a metal atom will be identical with the motion of an electron associated with an ammonia molecule. It would appear, therefore, that at higher concentrations deviations from Beer's Law should be found. Should this not prove to be the case, it would be necessary to assume that the neutral molecule consists not merely of the metal atom, but of the metal atom in association with ammonia; and, moreover, it would have to be assumed that the combination of the negative carrier with ammonia is not materially affected by the presence of the metal atom. In view of the fact that at higher concentration the negative carrier is dissociated from the ammonia molecule, it seems improbable that this is the case. It would seem, therefore, that a photometric study of the more concentrated solutions should afford means for establishing the existence of neutral molecules in the solutions of the metals. In this connection it may be noted that the absorption curves for the metals in methyl amine, as observed by Gibson and Argo, are much more complex than they are in the case of ammonia. In this case, Beer's Law does not hold. Although conductance data are not available, it appears probable that the ionization of the metals in methyl amine is much lower than it is in ammonia. The ionization of the metals in ammonia is of the same order of magnitude as that of the salts in this solvent. If, similarly, the

conductance in the more concentrated solutions appears in every way similar to that in ordinary metals, it appears highly probable that all metals owe their power to conduct the current to the presence of this carrier.

These solutions, therefore, constitute a connecting link between metallic and electrolytic conductors. In dilute solutions the process is, at least in part, electrolytic. A portion of the current is carried by the positive carriers which differ in no respect from the positive carriers as they appear in solutions of the common salts. The negative carrier is chemically uncombined, but is associated with one or more molecules of the solvent. These carriers are identical for solutions of all metals, and, when discharge occurs at the anode, the only material process which takes place is that a portion of the solvent is left behind in the immediate neighborhood of this electrode. As the concentration of the solutions increases, the nature of the phenomenon changes only insofar as the combination of the negative carrier with ammonia is affected. At the higher concentrations, the negative carriers are free from association with the ammonia molecules to a greater and greater extent. And, since under these conditions, the negative carrier is associated with no matter of atomic dimensions, it follows that all material effects cease so far as these carriers are concerned. It is not to be understood that a given carrier is free from association with the solvent molecules for any considerable period of time. Obviously, an equilibrium must exist between the free carriers and the combined carriers and ammonia, which results in a constant interchange between the free and the bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in the metals. As the concentration is further increased, the number of these free carriers constantly increases. It is evident that their number in the more dilute solution, for example in the neighborhood of normal, must be relatively small, since at higher concentrations the equivalent conductance reaches values some one hundred times as great as that at normal concentration. It is not possible to determine the actual number of carriers in the more concentrated solutions. In the more dilute solutions, however, it appears that the number of carriers decreases with increasing concentration, just as it does in the case of normal electrolytes in liquid ammonia.

VII. General Summary.

The purpose of the present investigation, the results of which have been given in the preceding series of papers, was to determine the nature of

ionization of the metals in methyl amine were of the same order of magnitude as that of the salts in methyl amine, it follows that at the concentrations at which the photometric measurements were made, appreciable amounts of the un-ionized molecules are present.

the solutions of the metals in liquid ammonia and in particular to determine the nature of the conduction process in these solutions.

The alkali metals do not form compounds with ammonia, and, while it is possible or even probable that ammonia may be associated with the metals in solution, such an association must be a comparatively feeble one, since the energy change accompanying the process of solution is inconsiderable. Calcium forms a hexammoniate and in all likelihood barium and strontium likewise form ammoniates. The compound formed between calcium and ammonia possesses metallic properties. It is evident that the mechanism of the union between calcium and ammonia is very different from that of compounds of calcium in which this metal appears combined with a strongly electronegative element, or group of elements.

From measurements of the vapor pressure of dilute solutions of sodium in liquid ammonia, it has been possible to reach certain conclusions with regard to the molecular state of these solutions. The apparent molecular weight of sodium in liquid ammonia, as calculated on the assumption of the laws of dilute solutions, decreases with decreasing concentration and apparently approaches a value less than the normal atomic weight of sodium. While it has been shown that the solutions of the metals in liquid ammonia are very exceptional in their osmotic behavior, so that the laws of dilute solutions do not appear in general to be applicable, nevertheless, from the general trend of the molecular weight as a function of the concentration, it may be concluded that the true molecular weight of sodium at low concentrations is less than 23. It appears, therefore, that, in solutions of sodium in liquid ammonia, there is present a molecular species other than the sodium atom. Since these solutions are conductors of the electric current, it may be concluded that the low value of the molecular weight is due to the presence of the negative carrier in these solutions.

It has been shown that, in dilute solutions of the alkali metals in liquid ammonia, the conduction process is an ionic one, and that the metallic ion is positively charged and moves toward the cathode in these solutions. It has also been shown that there is present in these solutions a negative carrier which is instrumental in carrying a portion of the current through the solution. When the negative carrier is discharged at the anode, there is no indication of a product at this electrode. If a solution of potassium in liquid ammonia is placed between two solutions of potassium amide in ammonia, then, under the action of an electromotive force, the characteristic blue color moves toward the anode. That portion of the solution from which the color disappears apparently contains nothing but potassium amide after the process has taken place. Since it has been shown that the metallic ion in these solutions moves toward the cathode, it follows that the metallic ion is apparently identical with the positive

ion of the amide of this metal. At the same time, it appears that the blue color of the solution, as well as the other properties which are characteristic of this solution, are due primarily, not to the metallic constituent, but to the negative carrier, either free or combined with the metal. It follows, also, that an equilibrium exists between the positive and negative carriers and the un-ionized metal, as well as between the positive ion, the amide ion and the neutral amide. The fundamental metallic constituent, or, in other words, that constituent to which the metals in common owe their characteristic metallic properties, is the negative carrier. So far as the results obtained with these solutions are concerned, there is no evidence indicating that any other ion or molecule is primarily concerned with the metallic properties of metals. In the more concentrated solutions the electrolytic properties diminish and ultimately become inappreciable. Apparently this is due to an increase in the speed of the negative carriers in the more concentrated solutions. as a result of which the fraction of the current carried by the cation gradually decreases with increasing concentration and ultimately becomes so small as not to be recognizable.

That this is the case, follows from the results of measurements on the electromotive force of concentration cells, as well as from measurements of the conductance of these solutions. From a study of the electromotive force of concentration cells, it has been found possible to determine the relative amounts of the current carried by the two ions. In dilute solutions the negative carrier has a carrying power approximately 7 times that of the sodium ion. The greater carrying power of the negative ion is doubtless due to its greater mean speed. As the concentration increases, the relative speed of the negative carrier increases slowly, at first, and then more rapidly. In the neighborhood of normal concentration the increase in the speed of the negative carrier becomes very great, so that, at this concentration, its speed is several hundred times that of the positive carrier. In order to account for the observed speed of the negative carrier in dilute solutions, it must be assumed that this carrier has dimensions of the same order of magnitude as that of the sodium ion. Since there are no other molecules present, save sodium and ammonia, and since the sodium atom is a constituent of the positive ion, it follows that the negative carrier must be associated with one or more molecules of ammonia. At higher concentrations, however, some of these carriers are freed from their combination with the ammonia molecules for a fraction of the time. If these carriers have sub-atomic dimensions, then, as their association with ammonia is lost, their speed should be very great under the action of a given potential gradient. In other words, the conducting power of a solution of a metal in ammonia should increase very greatly with the concentration at the higher concentrations.

In the case of concentrations in the neighborhood of normal, a portion of the negative carriers cannot be associated with the solvent. This follows from the fact that if ammonia is associated with a negative carrier, then, in a concentration cell, it will be carried from a solution having a higher vapor pressure to one having a lower vapor pressure, which process involves work. The vapor pressures of these solutions being known, it is possible to calculate the work and consequently the electromotive force of a cell, on the assumption that the only source of energy is due to this process. Or, rather, given the electromotive force of a cell, it is possible to calculate an upper limit to the mean solvation of the negative carrier. As a result of such a calculation, it was found that the electromotive force of a cell operating between concentrations of approximately 1 N and 0.5 N is such as to yield a value of 0.67 for the mean solvation of the negative carrier. The true value must necessarily be below this. It is not to be understood from this that one-third of the negative carriers are unassociated with the solvent under these conditions, but that at least one-third of the current is carried by carriers which are not associated with the solvent. Since the conductance of these solutions is not much greater than that of the more dilute solutions and since the conductance of the negative carrier is unquestionably very great, it follows that the actual number of negative carriers which are not associated with ammonia at a given instant of time is a very small one indeed. This number, however, increases very greatly at higher concentrations.

The chief results of the foregoing considerations are: first, that an ionic equilibrium exists in solutions of a metal in liquid ammonia; and second, that the negative carrier is identical for all metals and exhibits abnormal conducting power in the case of the more concentrated solutions. It follows as a consequence that the conductance curve for such solutions should exhibit a minimum. In the more dilute solutions the conductance curve should rise and approach a limiting value in virtue of the process of ionization. In dilute solutions, therefore, the conductance curve should correspond approximately with that of ordinary salts in liquid ammonia. In the more concentrated solutions the conductance curve should rise with increasing concentration owing to the increase in the speed of the negative carrier. It has been shown that such is in fact the case. The form of the conductance curve corresponds precisely with that required by these considerations. In dilute solutions the conductance approaches a limiting value according to a curve which is of the same general form as that of ordinary electrolytes. At a concentration of approximately 0.05 N, the equivalent conductance has a minimum value after which it begins to increase rapidly with increasing concentration. This increase is particularly pronounced in the neighborhood of 1 N, corresponding with the increase in the relative speed of the negative carrier as deduced from the

results of measurements of the electromotive force of concentration cells. At still higher concentrations, the conductance approaches that of metallic conductors. At approximately $2 N$ a solution of sodium in liquid ammonia has an equivalent conductance of approximately 83,000 and a specific conductance of 0.0164×10^4. A saturated solution of sodium in liquid ammonia has a specific conductance approximately half that of mercury at $0°$.

The conductance curves of sodium, lithium and potassium, as well as of mixtures of sodium and potassium, are similar in form but are displaced as regards the value of the conductance. The difference in the conductance of the more dilute solutions corresponds approximately to the difference in the conductance of the positive ions of these metals. This is in agreement with the conclusion reached above, that the negative carriers in the case of these three solutions are identical.

It appears that the solutions of the metals in liquid ammonia form the connecting link between electrolytic and metallic conductors. It has been definitely shown that the conduction process in the case of these solutions is an ionic one. There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radio-active and other phenomena.

WORCESTER, MASS.

THE HEATS OF DILUTION AND THE SPECIFIC HEATS OF DILUTE SOLUTIONS OF NITRIC ACID AND OF HYDROXIDES AND CHLORIDES AND NITRATES OF LITHIUM, SODIUM, POTASSIUM, AND CESIUM.

BY THEODORE W. RICHARDS AND ALLAN WINTER ROWE.

In a recent paper an indirect but accurate method of determining the specific heats of dilute solutions was described,[1] together with data and results concerning hydrochloric acid. The method depends upon the law of Kirchhoff, and bases the values for the more dilute solutions upon the change of heat capacity which occurs during dilution, as calculated from the temperature coefficient of the heat of dilution. The specific heats of the initial concentrated solutions must have been determined directly.

[1] Richards and Rowe, THIS JOURNAL, 42, 1621 (1920).