

the jelly solidified, but the product was colored brown by oxidation products and was too impure to be analyzed.

Summary

Six new double fluorides of zirconium with the organic bases, aniline, brucine, cinchonine, quinine, quinidine and strychnine, have been prepared, their probable formulas proposed, and some of their properties noted.

No definite solubility determinations were made and, therefore, the idea of a new procedure for the separation of zirconium and titanium could not be fully investigated.

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THE CONDUCTANCE OF SOLUTIONS OF ALKALI METALS IN LIQUID AMMONIA AND IN METHYLAMINE

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The absorption spectra of the blue solutions of the alkali metals have been investigated by Gibson and Argo.¹ They showed that their observations could be accounted for by the following hypotheses.

The color of the solution is due in all cases to electrons combined with the solvent. In ammonia the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvated electrons. In other words, the solvation of the electrons is nearly complete. In methylamine, on the other hand, the concentration of un-ionized metal is no longer negligible and is responsible for the increased absorption at the shorter wave lengths. The solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased.

In order to throw further light on these questions, the conductances and the temperature coefficient of conductance of the blue solutions were investigated and form the subject of the present paper.

Since liquid ammonia was more available than methylamine, it was used as solvent in all earlier experiments, and later, when the manipulation was well established, solutions in methylamine were studied. While the investigation was in progress, the comprehensive study by Kraus² of conductances in liquid ammonia was published, and his results are confirmed at many points by our own.

Apparatus and Manipulation

The apparatus shown diagrammatically in Fig. 1 is constructed entirely of Pyrex glass.

¹ Gibson and Argo, *THIS JOURNAL*, **40**, 1327 (1918).

² Kraus, *ibid.*, **43**, 749 (1921).

Two small platinum ball electrodes E are sealed into the upper part of the conductivity bulb B which opens into A through a constriction C. The valve³ V, actuated from above by use of the taut rubber connection R', separates A from the waste reservoir W. There are calibrations at C and at D; D widens above into Z, which carries the side tube J through which the metal is to be introduced. The stirrer N is a very slender glass rod, well centered in the conductivity bulb, terminating above in the glass-covered iron core U, which is supported, when at rest, on the ledge M. During an operation a solenoid (not shown in Fig. 1) equipped with an interrupter lifts and drops the stirrer at the rate of about two hundred times a minute. The side tube J has at the top a ground glass cap K.

S is a reservoir for storing the pure dry solvent, and is surrounded at all times by a well-silvered Dewar vessel containing ammonia. Q is an auxiliary reservoir which contains sodium or potassium for the preliminary drying of the solvent when it is first introduced into the system and for subsequent drying, should it be necessary. S and Q are made independent of each other and of the rest of the system by the vacuum stopcocks T, R and P. Stopcock H connects the waste reservoir W and all of the system behind the valve V with the mercury pump, while G connects to the pump all of the conductivity cell proper up to the stopcock T.

With the stirrer in its position of rest, the volumes of A and B are accurately determined by calibration with mercury and the capacity factor of the cell is determined in the usual manner with 0.01 *N* potassium chloride solution.

An operation is now described.

Dry solvent is distilled through P' and P into Q and allowed to remain there on the metal until thoroughly dry. It is then distilled into S through R. With P, R and T closed, G and H are opened to the mercury pump and the conductivity bulb is heated strongly with a flame to remove adsorbed moisture, until a high vacuum is obtained.⁴ G and H are then closed, the cap K is removed and capillary of the metal to be studied, with its tip freshly broken off, is lowered quickly by a wire into the tube J to a point above the shoulder F. The cap K is replaced and the vessel evacuated as before. The metal is then melted out of the capillary by gently heating J and rests as a bright globule in F, whence by further heating it is distilled, in whole or in part as desired,

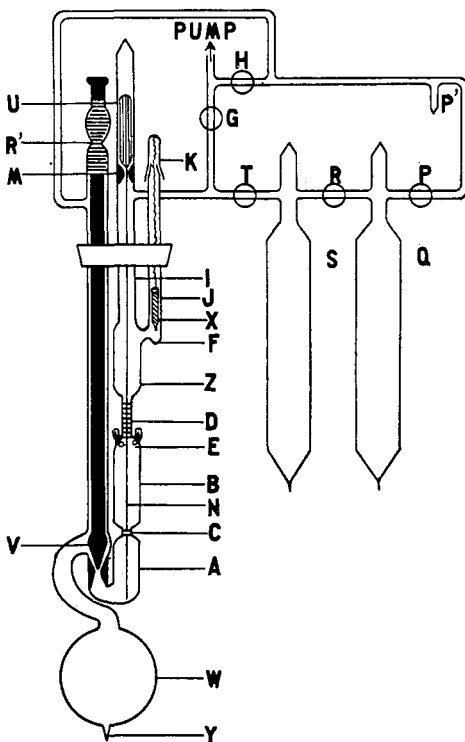


Fig. 1.—Diagram of Apparatus.

³ A similar valve is described by Kraus, *THIS JOURNAL*, 36, 866 (1914).

⁴ The spark produced by a high-frequency 110v. coil was entirely extinguished. When a similar condition prevailed in other Pyrex vacuum lines, McLeod gages indicated a pressure of less than 0.000,01 mm.

into the wider tube Z where it appears as a bright mirror on the walls of the glass. Potassium and cesium distil very rapidly and even sodium distils quite readily in a very high vacuum. The slight amount of oxide which accompanied the introduction of the capillary remains in F throughout the run and solvent is never condensed upon it.

G and H are then closed, and the conductivity cell is surrounded by a bath of boiling liquid ammonia with its level at Z. Dry solvent is then distilled through T from the reservoir S and the metal is washed down completely into A and B until the blue solution fills the vessel from the valve up to a point in D. Stirring is continued until the conductivity reaches a constant value, when the volume is read with the stirrer at rest.

To make a dilution, the bath is lowered for a moment until the level is at C, and the valve is slightly unseated by upward tension at R' until the level of the blue solution has fallen to C. With a well-ground valve this regulation is very accurate. The bath is then replaced and fresh solvent distilled in as before, with the stirrer operating all the time. At the end of a run, which rarely required more than two hours, the stopcocks H, P and R are opened and the solvent is returned by distillation from the blue solution in W to S, leaving in W all of the metal which was originally present in the first solution studied. With the solvent isolated in S, the last traces of solvent are removed from the metal by evacuation and by slight warming of W. The tip Y is then broken and the metal is oxidized by a stream of moist air admitted at P'. W is then washed out thoroughly, the solution is evaporated to a small volume to remove ammonia and titrated with 0.1 *N* hydrochloric acid, with methyl orange as an indicator.⁵ All necessary data are now at hand for the calculation of volume-normal concentrations and specific and molecular conductivities.

To prepare the vessel for another experiment, the empty capillary X is withdrawn and the vessel filled through J down as far as the valve with cleaning mixture, which is then heated and allowed to stand in the vessel for several minutes. It is forced out by way of V through Y and followed by many changes of distilled water, which is removed in the same way. Finally, with the valve clamped open, the vessel is dried by a stream of warm air coming from P' and from K. The tips Y and P' are sealed off and the evacuation proceeds as before.

The filling of capillaries with metal is as follows: tubing of small bore is constricted further and bent at an angle of about 60° at the middle of the constriction. One end of the tube is sealed off at a suitable distance from the bend and the other end is attached to a vacuum line. After being evacuated, the tube is sealed off at a point which leaves a symmetrical V-shape. The point of the "V" is put below the surface of a globule of the molten metal and broken; this gives two tubes filled with bright, clean metal. To prevent oxidation of the metal at the tips, the capillaries are kept under oil.

The two temperatures employed in most of the experiments were the boiling point of liquid ammonia and a temperature about 15° lower (−48.5°), obtained by bubbling dried air at a controlled rate through the bath. By hand regulation the temperature was kept constant within 0.1° or 0.2°. Chloroform, frozen by means of solid carbon dioxide, was used as a bath in two or three of the experiments, but its temperature was found to be quite inconstant and because of the difficulty of making a satisfactory constant-temperature bath to operate in the neighborhood of −70°, work at the lower temperature was abandoned, although on account of the slower fading⁶ it seemed desirable to work at that temperature.

⁵ Alcohol was not used for dissolving the metal on account of the uncertainty of the end-point when it was present.

⁶ By "fading" is meant the reaction of the metal with the solvent to form the metal amide.

Conductance of Sodium in Liquid Ammonia

The results of the measurements with sodium are given in Table I. The specific conductance in $\text{ohm}^{-1}\text{cm.}^{-1}$ is designated by κ , the dilution in liters per mole by V and the molecular conductivity (κV) by Λ . The columns are self-explanatory.

Curves I, II and III of Fig. 2 show the logarithm of the specific conductance, $\log \kappa$, as a function of the logarithm of the "dilution," V and Curves I', II' and III' show the molecular conductivity, $\Lambda = \kappa V$, as a

TABLE I
CONDUCTANCE OF SODIUM IN LIQUID AMMONIA
-33.5°

SERIES I				SERIES II			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	3.198	0.111	2038	1	1.978	0.793	591
2	2.490	0.406	787	2	1.431	1.237	466
3	2.074	0.696	587	3	1.019	1.680	501
4	1.710	0.985	495	4	0.662	2.125	613
5	1.387	1.277	461	5	0.301	2.569	742
6	1.116	1.561	475	6	̄1.882	3.013	786
7	1.877	1.844	526				
8	0.657	2.125	605				
9	0.422	2.419	693				
10	0.172	2.708	759				
11	̄1.907	2.996	799				
12	̄1.633	3.283	825				
13	̄1.354	3.576	852				
SERIES III				SERIES IV			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	1.896	0.849	556	1	1.585	1.087	470
2	1.382	1.295	476	2	1.138	1.530	466
3	1.975	1.739	518	3	0.772	1.973	556
4	0.625	2.182	642	4	0.418	2.416	683
5	0.260	2.625	769	5	0.025	2.859	766
6	̄1.834	3.068	798	6	̄1.592	3.302	780
7	̄1.329	3.511	692	7	̄1.084	3.745	675
SERIES V				SERIES VI			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	2.062	0.641	505	1	2.200	0.536	545
2	1.500	1.086	386	2	1.616	0.981	396
3	1.023	1.531	358	3	1.120	1.423	349
4	1.630	1.984	412	4	1.715	1.873	388
5	0.282	2.427	512	5	0.359	2.322	480
6	̄1.910	2.870	603	6	̄1.975	2.765	550
7	̄1.472	3.320	620				
SERIES VII							
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	1.850	0.804	451	4	0.508	2.139	444
2	1.310	1.248	361	5	0.156	2.584	550
3	1.872	1.694	368	6	̄1.728	3.028	570

TABLE I (Concluded)

-70.0°

SERIES VIII				SERIES IX			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	1.836	0.654	309	1	2.295	0.310	403
2	1.436	0.971	256	2	1.679	0.778	287
3	1.056	1.302	228	3	1.121	1.238	229
4	0.723	1.636	229	4	1.657	1.700	228
5	0.448	1.963	257	5	0.289	2.162	283
6	0.168	2.294	290	6	1.933	2.625	362
7	1.896	2.615	324	7	1.547	3.092	436
8	1.611	2.935	351				
9	1.321	3.256	360				

function of $\log V$. The agreement among the different runs is good as far as 0.001 N , but beyond that concentration fading⁶ is appreciable and erratic. At -33.5° the highest value for $\log \kappa$ at $\log V = 4.0$ (0.0001 N) corresponding to a molecular conductivity of 970 for sodium, which is lower than the best value of Kraus²—about 1000 at this dilution.

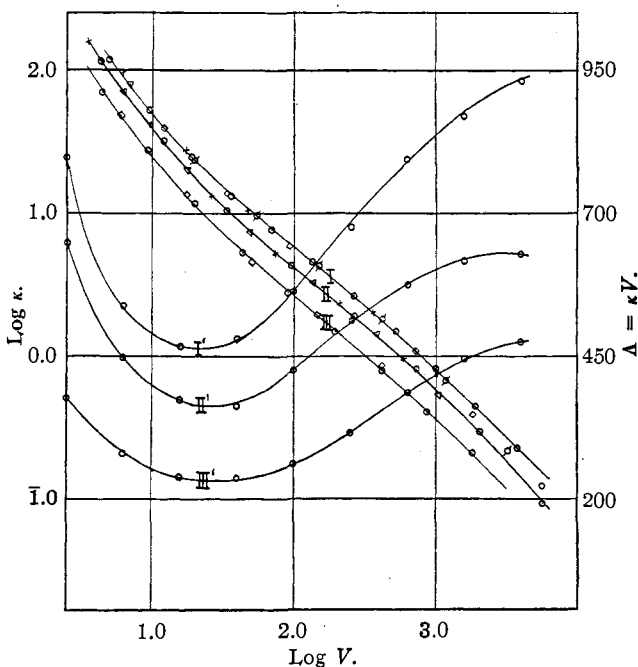


Fig. 2.—Sodium in liquid ammonia: I, -33.5° ; II, -48.5° ; III, -70.0° .

Since the concentrations dealt with here are volume-normal, whereas Kraus's concentrations were weight-normal, a direct comparison of the two would involve a knowledge of the densities; or assuming the accuracy

of the two sets of data, the densities could be calculated. Unfortunately, our measurements do not extend into the most concentrated blue solutions, where the densities are most abnormal. A careful comparison of two representative series obtained by the two methods showed that within the limits of experimental error, weight-normal and volume-normal data coincide between concentrations of 0.4 and 0.005 *N*. Divergences in solutions more dilute than 0.005 *N* were doubtless not density but fading effects.

The position of the minimum at all three temperatures is at a concen-

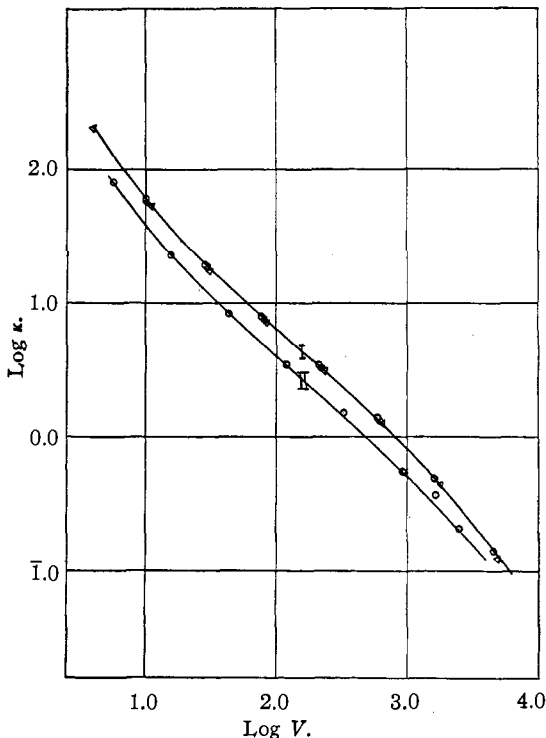


Fig. 3.—Potassium in liquid ammonia: I, -33.5° ;
II, -48.5° .

tration of about 0.04 *N*. The values at the minimum for the three temperatures, -33.5 , -48.5° and -70.0° were, respectively, 460, 360 and 235.

Conductance of Potassium in Liquid Ammonia

The results of the measurements with potassium are given in Table II and plotted in Fig. 3. The columns are as before.

As noted by Kraus,² the fading is very rapid in potassium solutions and the results are doubtless several per cent. low even at 0.001 *N*. At the lower temperature the fading was less, but still much more rapid than with sodium at the higher temperature.

TABLE II
CONDUCTANCE OF POTASSIUM IN LIQUID AMMONIA

SERIES I				-33.5°	SERIES II			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ	
1	1.766	1.015	604	1	1.774	1.015	615	
2	1.283	1.460	554	2	1.292	1.458	563	
3	0.889	1.903	620	3	0.897	1.901	628	
4	0.526	2.346	746	4	0.542	2.344	769	
5	0.135	2.790	842	5	0.154	2.786	871	
6	$\bar{1}.579$	3.234	651	6	$\bar{1}.698$	3.228	844	
7	$\bar{2}.862$	3.677	346	7	$\bar{1}.168$	3.673	694	
SERIES III				SERIES IV (-48.5°)				
1	2.315	0.595	813	1	1.914	0.752	464	
2	1.731	1.045	598	2	1.374	1.197	373	
3	1.245	1.489	542	3	0.929	1.640	371	
4	0.860	1.932	620	4	0.552	2.082	431	
5	0.500	2.374	749	5	0.185	2.524	512	
6	0.100	2.815	823	6	$\bar{1}.749$	2.967	521	
7	$\bar{1}.647$	3.258	805	7	$\bar{1}.329$	3.410	549	
8	$\bar{1}.103$	3.703	640					

Conductance of Potassium, Cesium and Cesium Iodide in Methylamine

Sodium is very slightly soluble in methylamine and lithium also forms only a very dilute blue solution. The most concentrated cesium solution studied was about 0.3 *N*. In the case of potassium, two layers form at -33.5°, and the most concentrated blue layer obtainable is near 0.01 *N*. Since the presence of the bronze layer makes a correct analysis of the blue layer impossible, only small quantities of potassium were introduced into the cell, and the most concentrated potassium solution determined was less than 0.01 *N*. On this account the analyses were subject to large percentage errors. Potassium solutions were much more stable than cesium solutions in methylamine. The fading of cesium solutions was quite marked even at intermediate concentrations.

In Tables III and IV the results with cesium, cesium iodide and potassium are given. The columns are as before.

TABLE III
CONDUCTANCE OF CESIUM AND OF CESIUM IODIDE IN METHYLAMINE

SERIES I (-33.5°)				SERIES II (-33.5°)			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	0.556	1.145	50.3	1	1.302	0.527	67.5
2	0.160	1.591	56.4	2	0.707	0.985	49.9
3	$\bar{1}.839$	2.035	74.9	3	0.273	1.453	53.3
4	$\bar{1}.529$	2.476	101.2	4	$\bar{1}.926$	1.911	68.8
SERIES III (-33.5°)				SERIES IV (-48.5°)			
1	0.048	1.728	59.7	1	0.850	0.708	36.1
2	$\bar{1}.740$	2.171	81.5	2	0.362	1.163	33.5

TABLE III (Concluded)

No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
3	$\bar{1}.418$	2.620	109.2	3	0.005	1.606	40.9
4	$\bar{1}.087$	3.061	140.7	4	$\bar{1}.695$	2.049	55.5
5	$\bar{2}.703$	3.503	159.6	5	$\bar{1}.386$	2.492	75.5
SERIES V (-48.5°)				SERIES VI (-48.5°)			
1	0.691	0.880	37.3	1	$\bar{1}.588$	2.233	66.3
2	0.233	1.325	36.2	2	$\bar{1}.302$	2.678	95.5
3	$\bar{1}.897$	1.768	46.3	3	$\bar{2}.972$	3.125	125.1
4	$\bar{1}.577$	2.212	61.6	4	$\bar{2}.612$	3.569	151.8
5	$\bar{1}.257$	2.653	81.3	5	$\bar{2}.187$	4.011	157.8
SERIES VII (CESIUM IODIDE)							
-33.5°				-48.5°			
1	$\bar{1}.797$	1.296	12.4	1	$\bar{1}.747$	1.288	10.8
2	$\bar{1}.370$	1.744	13.0	2	$\bar{1}.326$	1.736	11.5
3	$\bar{1}.022$	2.193	16.4	3	$\bar{1}.978$	2.185	14.6
4	$\bar{1}.708$	2.642	22.4	4	$\bar{1}.670$	2.634	20.1
5	$\bar{2}.430$	3.091	33.2	5	$\bar{2}.384$	3.083	29.3

TABLE IV
CONDUCTANCE OF POTASSIUM IN METHYLAMINE
 -48.5°

SERIES I				SERIES II			
No.	Log κ	Log V	Λ	No.	Log κ	Log V	Λ
1	$\bar{1}.394$	2.408	63.4	1	$\bar{1}.592$	2.088	47.9
2	$\bar{1}.049$	2.869	82.8	2	$\bar{1}.269$	2.534	63.6
3	$\bar{2}.721$	3.314	108.4	3	$\bar{2}.940$	2.977	82.6
4	$\bar{2}.366$	3.758	133.1	4	$\bar{2}.590$	3.425	103.6
5	$\bar{3}.891$	4.201	152.1	5	$\bar{2}.229$	3.868	125.1
-33.5°							
SERIES III				SERIES IV			
1	$\bar{1}.426$	2.542	92.9	1	$\bar{1}.679$	2.143	66.4
2	$\bar{1}.096$	2.984	117.5	2	$\bar{1}.357$	2.586	87.7
3	$\bar{2}.726$	3.427	142.3	3	$\bar{2}.009$	3.030	109.4
4	$\bar{2}.303$	3.870	149.1	4	$\bar{2}.640$	3.476	130.7
SERIES V							
1	$\bar{1}.514$	2.328	69.6				
2	$\bar{1}.250$	2.773	105.5				
3	$\bar{2}.884$	3.218	126.5				

Fig. 4 shows the results of several experiments with cesium in methylamine and Fig. 5 shows the results of five runs with potassium. Curves III and IV of Fig. 4 are constructed from Curves I and II of the same figure. The minimum in the molecular conductivity curves occurs at about 0.07 N (in more concentrated solution than is the case with sodium and potassium in liquid ammonia). At the minimum the values of Λ at -33.5° and -48.5° are, respectively, 51 and 33. For both cesium and

potassium, " Λ_0-k " plots,⁷ which assume the validity of the mass law, were constructed, and led to the following values:

Temp., °C.	Metal	Λ_0	k (mass law const.) $\times 10^4$
-33.5	K	159	21.4
-48.5	K	144	11.2
-33.5	Cs	188	19.4
-48.5	Cs	174	13.9

A single run was also made with cesium iodide⁸ in methylamine and the results of this experiment appear in Fig. 4 Curves V and VI. The posi-

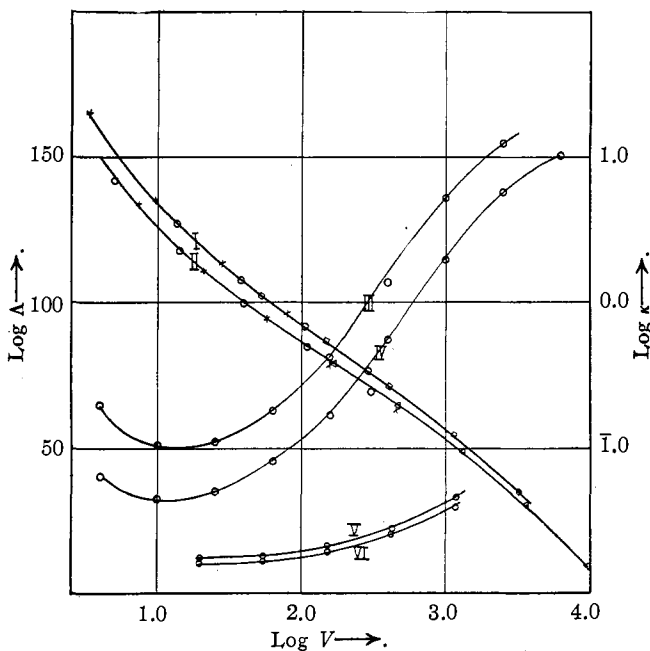


Fig. 4.—Cesium in methylamine: I and III, -33.5° ; II and IV, -48.5° . Cesium iodide in methylamine: V, -33.5° ; VI, -48.5° .

tion of these curves is substantially the same as that for potassium iodide in methylamine given by Franklin and Gibbs.⁹

" Λ_0-k " plots for cesium iodide led to the following values:

Temp., °C.	Λ_0	k (mass law const.) $\times 10^4$
-33.5	60.6	4.91
-48.5	56.2	4.64

Temperature Coefficients of Conductance in Ammonia and Methylamine

In Table V is a summary of temperature coefficients calculated from the $\log \kappa$ curves in the preceding figures. The values of $d(\log \kappa)/dt$ were

⁷ Nomenclature of Kraus and Bray, *THIS JOURNAL*, **35**, 1315 (1913).

⁸ Cesium chloride was found to be insoluble.

⁹ Franklin and Gibbs, *ibid.*, **29**, 1391 (1907).

TABLE V
SUMMARY OF TEMPERATURE COEFFICIENTS

Log V	Temp. range, °C.	Solute	Solvent	$d(\ln \kappa)/dt, \times 10^3$	Av.
1.4	-33 to -48	Na	NH ₃	20.9	20.4
2.4	-33 to -48	Na	NH ₃	20.7	
1.4	-48 to -70	Na	NH ₃	18.6	
2.4	-48 to -70	Na	NH ₃	21.6	
1.4	-33 to -48	K	NH ₃	27.4	29.1
2.4	-33 to -48	K	NH ₃	30.7	
2.0	-33 to -48	K	CH ₃ NH ₂	20.6	19.8
3.0	-33 to -48	K	CH ₃ NH ₂	19.0	
1.0	-33 to -48	Cs	CH ₃ NH ₂	27.6	23.9
2.0	-33 to -48	Cs	CH ₃ NH ₂	20.3	
3.0	-33 to -48	Cs	CH ₃ NH ₂	9.2 (fading)	
1.3-3.0	-33 to -48	CsI	CH ₃ NH ₂	7.7	7.7

taken directly from the plots. In the last column of Table V appear the values of $d(\ln \kappa)/dt$ at one or more dilutions for each solute and also an average value of each solute.

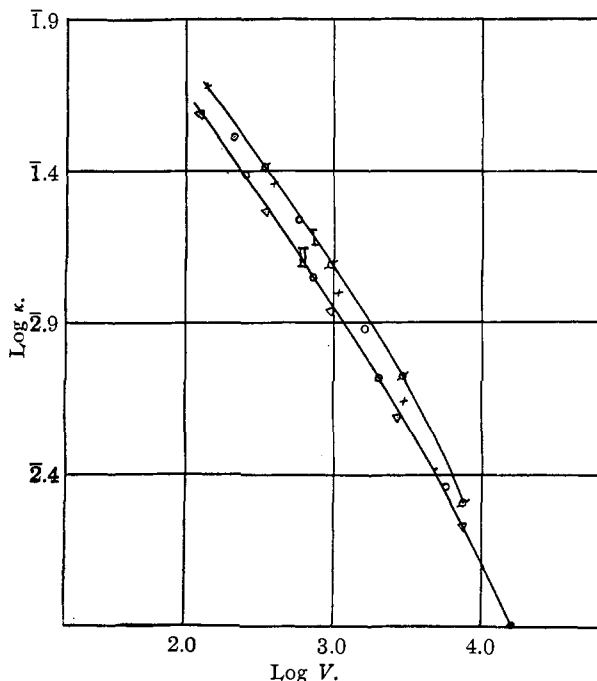


Fig. 5.—Potassium in methylamine: I, -33.5°; II, -48.5°.

The temperature coefficients are about the same in the two solvents. The apparent rapid decline in the temperature coefficient of cesium in methylamine is to be ascribed to fading. For a 0.001 N potassium solution, in which the fading was much slower, the temperature coefficient is

still 19×10^{-3} , whereas at the same dilution in a cesium solution the value has fallen to 9×10^{-3} , which is probably in error owing to fading.

In recent articles Kraus and Lucasse¹⁰ have given the temperature coefficients of conductivity for solutions of potassium and sodium in liquid ammonia. They define as the "resistance temperature" coefficient the quantity $\gamma = (1/R_{-33.5})(\Delta R/\Delta t) \times 100$ and find that γ diminishes as the temperature increases. The differential temperature coefficient $(1/R)(dR/dt)$ is, however, practically constant.

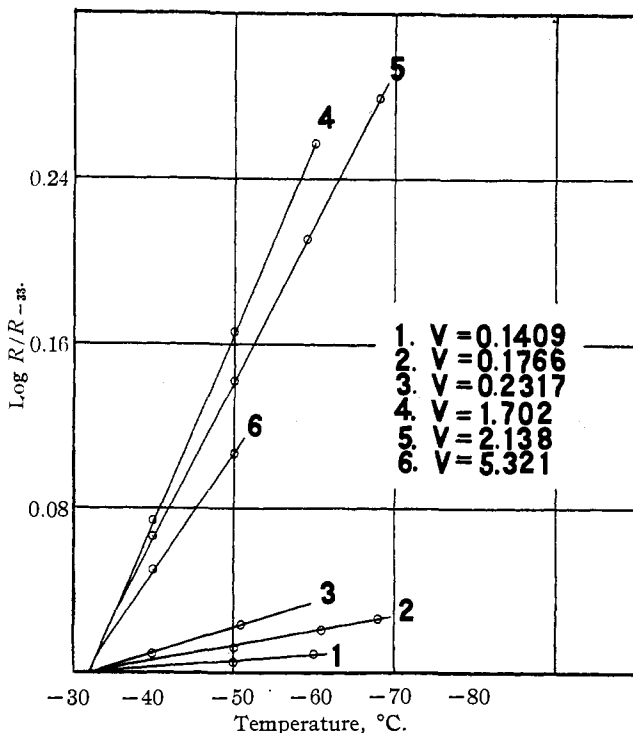


Fig. 6.—Variation of $\log R/R_{-33}$ as a function of temperature for sodium in liquid ammonia (Kraus and Lucasse).

The differential temperature coefficient may be calculated as follows. Kraus and Lucasse give a series of values of γ and the corresponding temperature intervals, but do not give the actual value of the resistance at any temperature. We have, however, for ratios of the actual resistance R to R_{-33} , $R/R_{-33} = 1 + (\Sigma \Delta R/R_{-33}) = 1 + \Sigma \gamma \Delta t$, Δt being the temperature interval corresponding to the increment of resistance ΔR .

Hence the differential temperature coefficient of resistance is given by $\partial \ln R/\partial t = \partial \ln(1 + \Sigma \gamma \Delta t)/\partial t$. In other words, if we plot the quantity

¹⁰ Kraus and Lucasse, *THIS JOURNAL*, **44**, 1941 (1922); **45**, 2551 (1923).

$\ln(1 + \Sigma\gamma\Delta t)$ against t , the slope of the curve gives the differential temperature coefficient of resistance.

Carrying out this calculation with the data of Kraus and Lucasse, the graphs in Figs. 6 and 7 were obtained. They are very nearly linear in all cases, so that the differential temperature coefficient is practically independent of temperature. There is a slight indication of curvature in the graphs of Fig. 7, but this may be due to experimental error since the effect is absent in the corresponding curves for sodium in Fig. 6.

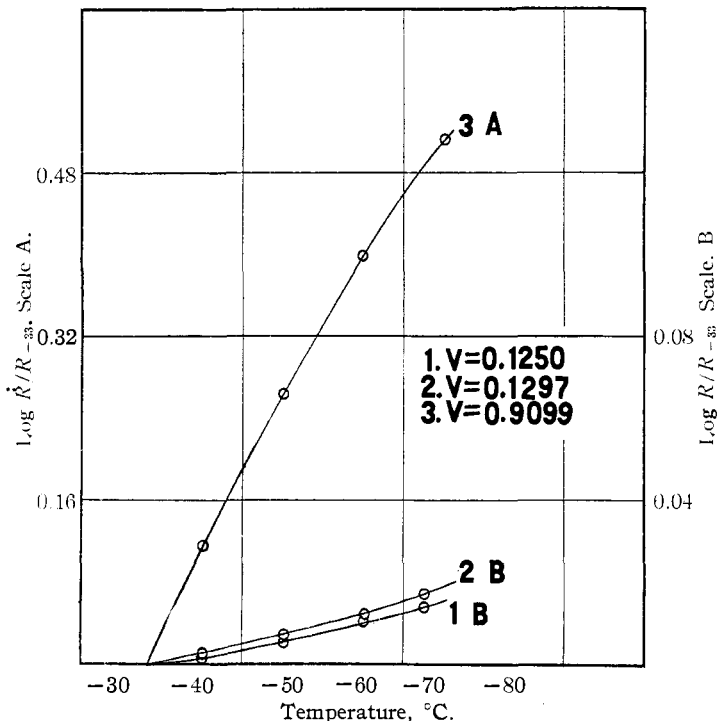


Fig. 7.—Variation of $\log R/R_{-33}$ as a function of temperature for potassium in liquid ammonia (Kraus and Lucasse).

The value of the temperature coefficient for sodium in ammonia found by us in much more dilute solutions ($V = 100$) differs only slightly from that found by Kraus and Lucasse at $V = 2.135$. There appears to be a minimum in the temperature coefficient somewhere between these two dilutions, beyond which, at the greater dilutions, the temperature coefficient becomes practically constant. Over the whole range of concentration the conductance is approximately an exponential function of temperature.

It has been pointed out by Kohlrausch¹¹ that the temperature coefficient

¹¹ Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," Teubner, Leipzig and Berlin, 1916, p. 127.

cient of conductivity and viscosity in aqueous solutions of most salts are approximately the same. Hydrogen and hydroxyl ions are exceptions to this rule, the temperature coefficients of conductivity being abnormally low. Johnston¹² studied the relationship between viscosity and conductivity over a wide range of temperature in water and in non-aqueous solvents, and showed that the equation, $\Lambda = k\gamma^m$, where γ is the fluidity, and m and k are constants, appears to be generally applicable. The value of m is usually very nearly unity. Hydrogen and hydroxyl ions are again exceptional. We may remark in passing that the low value of the temperature coefficient of conductivity of these ions might be accounted for if we assume the conductivity to be due in part to the liberation of a hydrogen or an hydroxyl ion at one end of a chain of water molecules and a simultaneous binding of a hydrogen or an hydroxyl ion at the other end of the chain, without actual migration of the ions through the solution, as has been suggested by various authors¹³ to account for the abnormally high conductance of these solutions. For, if we assume that such chains of water molecules become less stable at the higher temperatures, the diminution in this type of conduction would counteract the increase due to the diminishing viscosity of the solution and thus give an abnormally low temperature coefficient.

If we assume that the rule of Kohlrausch holds for methylamine, the temperature coefficient of the conductivity of all salts in this solvent should be approximately equal to that of cesium iodide. If this is true, the temperature coefficient of conductivity of the alkali metals in methylamine is abnormally high. This could be accounted for by a decreased solvation of the electrons with rise in temperature—as was assumed by Gibson and Argo¹ as a possible explanation of the diminution in the coefficient of absorption of these solutions with increasing temperature. It is evident that the abnormality cannot be attributed to chains of solvent molecules as was suggested in the case of hydrogen and hydroxyl ions in water, since the deviation of the temperature coefficient from the normal has the opposite sign in the metallic solutions.

In order to account for the deviation from Beer's law for the shorter wave lengths in solutions of the alkali metals in methylamine, Gibson and Argo assumed that the absorption at these wave lengths was partly due to un-ionized metal. Since the solutions in ammonia do not show this deviation from Beer's law, they assumed that the ionization in ammonia is more complete than in methylamine. The dissociation constant for the metals in ammonia is greater than that in methylamine, but the difference is hardly sufficient to account for the deviations which they observed. The deviation from Beer's law may, nevertheless, be due to

¹² Johnston, *THIS JOURNAL*, **31**, 1010 (1909).

¹³ Lewis, *ibid.*, **34**, 1642 (1912). Latimer and Rodebush, *ibid.*, **42**, 1432 (1920).

un-ionized metal, for the absorption due to un-ionized metal in ammonia may not be in the visible spectrum. This point cannot be decided without a knowledge of the absorption curve in ammonia at other wave lengths.

We have already mentioned that the conductivity curves of the metals in ammonia and in methylamine are of the same general type, the conductivity diminishing at first according to the mass law in dilute solutions, becoming greater than would be predicted from the mass law in more concentrated solutions, until a minimum in the conductivity is reached, after which the conductivity rises very rapidly as the concentration is further increased. The minimum is approximately the same for all the metals in any one solvent, but occurs at a somewhat lower concentration in ammonia than in methylamine. If we assume the increase in conductivity at the higher concentrations to be due to the influence of free ions in the solution, which cause a diminution in the forces which hold together the ions in the un-ionized molecule—for much the same reason that an increase in the dielectric constant would cause a diminution in these forces—we should expect a deviation from the mass law to occur at lower concentrations in a solution which is highly ionized than in one which is less so. We have shown that the metals are more highly ionized in ammonia than in methylamine; hence the solutions in ammonia, other things being equal, should show a minimum at lower concentrations than those in methylamine, as is actually observed. The extreme rapidity of the increase in conductivity at concentrations beyond the minimum, points to a rapid diminution in the solvation of the electrons as the concentration is increased. This would seem to indicate that the forces binding the electron to the solvent are diminished in concentrated solutions for the same reason that the ionization of the metal is increased, namely, owing to a diminution in these forces because of the presence of free ions in the solution.

Summary

The conductance of solutions of sodium and potassium in ammonia and of cesium, cesium iodide and potassium in methylamine have been determined at several temperatures. The results in ammonia are in agreement with the measurements by Kraus. The temperature coefficient of conductance, $d \ln R/dt$, is independent of temperature, that is, the conductance is an exponential function of temperature at all dilutions.

The metals are less ionized in methylamine than in ammonia. The minimum in the molecular conductivity occurs at a lower concentration in ammonia than in methylamine.

The theoretical bearing of these and other phenomena on the nature of the conduction in these solutions is discussed, and it is shown that they are in accord with the hypothesis that the negative carriers are elec-

trons largely combined with solvent molecules, the degree of solvation diminishing as the temperature is increased.

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THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN CONCENTRATED SOLUTIONS OF STRONG ELECTROLYTES

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In previous communications,¹ a few series of electromotive data were obtained from which the activity coefficient of hydrochloric acid could be computed in solutions of the alkaline and alkaline earth chlorides. With the intention of obtaining more complete and more reliable experimental data, this earlier work has been revised and extended.

Recently, a very interesting theory of concentrated solutions of strong electrolytes has been developed by Debye and Hückel,² and Hückel³, by means of which the thermodynamic properties of strong electrolytes and their mixtures are described. Although it is hard to believe that all the factors which influence these properties are included in this theory, it will be shown in the following discussion that there are no outstanding contradictions to be inferred from the numerous series of results on chloride solutions which we shall consider.

Experimental Part

The experimental technique of cells of the types $H_2 | HCl(m_1), MCl_x(m_2) | HgCl | Hg$ and $H_2 | HCl(m_1), MCl_x(m_2) | AgCl | Ag$, has been frequently described elsewhere.⁴ No great difficulty has been found in obtaining reliable results in solutions which contained acid of a strength greater than 0.01 M and salts at concentrations below approximately 1 M as long as the ordinary precautions regarding the electrodes were observed. A critical survey of the earlier results brought to light two sources of experimental error. When, in the earlier work,^{1b} the temperature coefficient of the cell with calomel electrodes was measured, the cell was introduced into the thermostat on the day before the measurements were made and then measured at different temperatures during a period of from four to six days. Although the temperature coefficients of the cells containing solutions of concentrations greater than 1 M remained the same,

¹ (a) Harned, *THIS JOURNAL*, **38**, 1986 (1916); (b) **42**, 1808 (1920). (c) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922).

² Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

³ Hückel, *ibid.*, **26**, 93 (1925).

⁴ Ref. 1 a. Loomis, Essex and Meacham, *THIS JOURNAL*, **39**, 1133 (1917). Ming Chow, *ibid.*, **42**, 497 (1920).