

π -bonding in the platinum complexes may result from the much higher energy of the P_3 orbital on platinum. Apparently, the p_z orbital on palladium and the p orbital of the ligand atom are closely similar in energy.

Study of the thermal decomposition of $[\text{Pd}(\text{en})(\text{en-H})]\text{I}$ has shown that the major products are Pd and $[\text{Pd}(\text{en})_2]\text{I}_2$ in a 3:1 mole ratio, ethylenediamine, ethylenediammonium iodide and unidentified minor products that presumably arise from secondary reactions of the (en-H) ligand. The decomposition of $[\text{Pd}(\text{en-H})_2]$ is similarly complicated; palladium and ethylenediamine are produced

in a 5:3 mole ratio, together with apparently a mixture of products of reactions of (en-H). Similar data are not available for the corresponding platinum compounds (other than that they are stable at room temperature); hence a direct comparison cannot be made at this time.

Finally, it should be noted that the reactions of $[\text{Pd}(\text{en})_2]\text{I}_2$ and $[\text{Pd}(\text{en})(\text{en-H})]\text{I}$ with potassium in ammonia involve direct reduction to elemental palladium without the intermediation of isolatable lower oxidation species of the type previously described^{2,3} as products of the reduction of the analogous platinum compounds.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA]

Solutions of Metals in Amine Solvents. IV. The Effect of Temperature on the Conductance of Lithium in Methylamine^{1,2}

BY ARMAND J. PANSON³ AND E. CHARLES EVERS

RECEIVED FEBRUARY 15, 1960

The conductance of moderately dilute solutions of lithium in methylamine has been studied in the temperature range from -78 to 20° . Maxima are observed in the conductance-temperature curves for the more dilute solutions; the maximum proceeds to higher temperatures with increasing metal concentration. Phenomenologically these results are similar to those observed for solutions of normal electrolytes. It is concluded that these data provide direct evidence for the existence of mass action equilibria in metal-amine solutions.

In the case of dilute solutions of metals in ammonia,^{2b,4} as well as in methylamine,^{2c} it has been suggested that mass action equilibria, involving several species, are responsible for the rapid decrease in conductance and in the magnetic susceptibility with increasing concentration. Further support of this thesis is furnished by nuclear magnetic resonance measurements.⁵

Although conductance and magnetic data appear interpretable in terms of mass action equilibria, it would be of value to have other, more direct evidence for the existence of these equilibria. In seeking such data we have studied the effect of temperature on the conductance of moderately dilute solutions of lithium in methylamine. It has been found that dilute solutions of lithium behave phenomenologically very much like solutions of normal electrolytes. This would seem to bear out the mass action hypothesis; ion association is well established in the case of electrolytes dissolved in a solvent such as methylamine.^{2c}

Experimental

Procedures employed in purifying and handling solvent and in preparing solutions of lithium were described previously.^{2a,c} Conductance cells of approximately 300 cc. capacity were used. They were provided with bright plat-

inum electrodes 1.5 mm. in diameter and approximately 2 mm. apart. Methods of fabricating metal-through-glass seals and of calibrating cells also have been described.^{2a}

The conductance cells were provided with a thermocouple well, sealed through a cap prepared from a 24-40 standard tapered ground glass joint. The well was drawn to a thin walled tip at the bottom, which was filled with a drop of alcohol to improve heat transfer. The cap was cemented on the cell with Apiezon wax in order to withstand super-atmospheric pressure when the temperature exceeded the boiling point of the solvent. Metal was introduced through a tube carried by the cap; the tube was then sealed. All glass blowing was done using a current of dry helium or argon gas.

Resistance measurements were made with a Leeds and Northrup Co., Jones-type, a.c. conductance bridge, in conjunction with an audio oscillator and amplifier; an oscilloscope was employed as the null point detector. Resistance measurements were recorded as a function of time on solutions which were either warming or cooling. Temperatures were measured with a Leeds and Northrup Co. adjustable range (0 to 40 m.v.) and adjustable zero recording potentiometer. Immediately after measuring the resistance of a solution, the temperature and time were recorded by marking the thermocouple potential-time curve. This was done by short circuiting the thermocouple signal momentarily, which caused a "pip" to be recorded on the temperature-time chart.

The thermocouple and recording potentiometer were calibrated as follows. The 0° reference junction and measuring junction were both immersed in an ice-bath. The zero potential reading was then set at a convenient point on the potentiometer scale. The measuring junction was next removed and placed in a cooling bath of powdered Dry Ice and isopropyl alcohol. Meanwhile the latter had been covered and aged in a Dewar flask for about 2 hr. to assure equilibrium conditions. The potentiometer reading was then set to full scale. The temperatures of several Dry Ice-baths prepared in the same way were measured with a N.B.S. calibrated, platinum resistance, thermometer. The temperatures of these baths were found to be $-78.33 \pm 0.01^\circ$; the corresponding potential for the copper constantan thermocouple is -2.71 mv. This represented full scale deflection on the potentiometer. Temperatures between -78.3 and 0° were obtained by linear interpolation. The linearity of the recorder scale and thermocouple potential were checked by measuring the temperature of various

(1) Taken in part from a thesis by A. J. Panson, presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.

(2) Previous papers in this series are: (a) E. C. Evers, A. E. Young, II, and A. J. Panson, *THIS JOURNAL*, **79**, 5118 (1957); (b) E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, **30**, 61 (1959); (c) D. S. Berns, E. C. Evers and P. W. Frank, Jr., *THIS JOURNAL*, **82**, 310 (1960).

(3) E. I. du Pont de Nemours Fellow in Chemistry, 1955-1956.

(4) (a) E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956); (b) M. F. Deigen and Yu A. Tsvirko, *Ukrain Fiz. Zhur.*, **1**, 245 (1956). References to previous work may be found here.

(5) (a) H. McConnell and C. Holm, *J. Chem. Phys.*, **26**, 1517 (1957).

(b) W. Blumberg and T. Das, *ibid.*, **30**, 251 (1959).

melting point baths: carbon tetrachloride, -22.9° , chlorobenzene, -45.2° and chloroform, -63.5° .⁶ The values obtained here were within $\pm 0.2^\circ$ of the reported temperatures and were within the precision of our measuring system. Fluctuations in bath temperatures could not be detected with our equipment during the course of any one experiment.

After introducing metal and solvent into the cell, according to procedures described previously,^{2a,c} the solution was stirred at -78° until a constant resistance measurement was obtained, indicating complete dissolution of metal. The cooling bath then was lowered, and resistance and temperature measurements were made as described above. The solutions were stirred throughout the course of an experiment. The heating rate was controlled by the depth of immersion of the cell in the cooling bath. Cooling curves were obtained in the same manner. In general, both a heating and cooling curve could be obtained during the course of an hour.

After a conductance-temperature curve was obtained for a solution, sections of the curve were repeated in order to determine whether reaction of metal with solvent had been significant. When reaction was excessive the data were discarded. Occasionally check points were made by measuring the conductance at the temperature of the calibration baths referred to above.

At concentrations above about 0.05 *N* the curves obtained on heating and cooling were reproducible to within 0.3%, provided the upper temperature did not exceed approximately -10° . More difficulty was experienced at lower metal concentrations. However, these data were as reliable as those obtained at higher metal concentrations if the temperature did not exceed about -20° .

A particularly significant feature of this study, which will be considered in some detail below, concerns the appearance of maxima in curves of specific conductance *versus* temperature at low concentrations of metal. Unfortunately, these maxima occur at temperatures above -20° where reaction between metal and solvent makes quantitative studies difficult. It may be argued that the appearances of maxima in the heating curves could be due to reaction which becomes increasingly rapid with increasing temperature. However, it is significant that maxima also were obtained in the conductance on cooling, although the heating and cooling curves obtained under these conditions were not particularly reproducible. The effect itself, however, is reproducible; accordingly we feel justified in stating that the appearance of a maximum is peculiar to the behavior of the system itself and is not to be attributed solely to loss of metal by reaction. Maxima were obtained in a number of cases both where the concentration of metal was not known and in three cases where the metal concentrations were 0.004722, 0.01678 and 0.021810 *N*, respectively (Fig. 1). It would also appear that a maximum might be obtained for a solution which was 0.1066 *N* in metal but at a higher temperature than was obtainable here. However, it must be reemphasized that the metal concentrations and temperatures of the maxima are somewhat in doubt due to decomposition.

Curves of specific conductance *k* as a function of concentration were determined at seven metal concentrations ranging from 0.004722 to 0.6727 g. atoms/l. of solvent at temperatures between -78.3 and 20° . The results are shown in Fig. 1. The data recorded in Table I (taken from the curves in Fig. 1) cover the temperature range from -78.3 to -22.8° and were obtained during the heating cycle on freshly prepared solutions. These results are more precise than those obtained at higher temperatures; the precision may be judged by comparison with data obtained in previous investigations.^{2a,c} Concentration, *C*, is expressed in g. atoms metal per liter of solvent. In calculating concentrations and equivalent conductances at various temperatures, corrections were applied for the change in solvent density using the data of Felsing and Thomas.⁷ Included in the table are values for the solvent viscosity, η , in poise.^{2c}

Discussion

In the case of completely dissociated electrolytes the conductance change parallels the change in the

(6) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 56.

(7) W. A. Felsing and A. R. Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

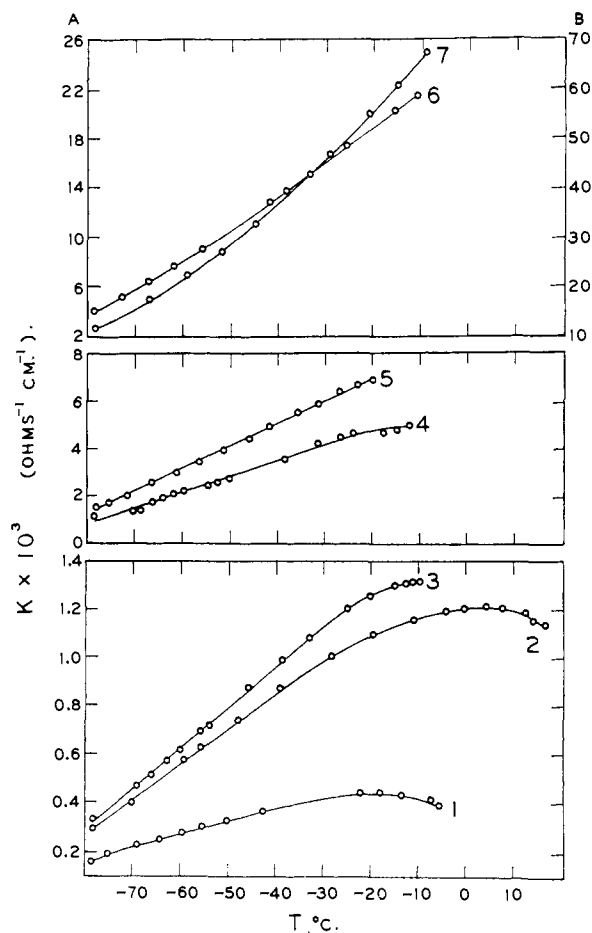


Fig. 1.—Lithium in methylamine, specific conductance, *K*, *versus* temperature: curve 1, 4.355×10^{-3} ; 2, 1.548×10^{-2} ; 3, 1.992×10^{-2} ; 4, 9.832×10^{-2} ; 5, 0.1370; 6, 0.2967; and 7, ordinate B, 0.6204 *N*. Concentrations are calculated for -78.3° .

fluidity of the solvent medium, *i.e.*, the conductance increases with increasing temperature. At higher concentrations the temperature coefficient of conductance is high but decreases with increasing temperature. In the case of all solvents, regardless of the dielectric constant, aqueous or non-aqueous, if the temperature is raised sufficiently high, it is found that the conductance reaches a maximum value, then decreases.⁸ A decrease in conductance with increasing temperature is direct evidence of the removal of conducting species through ion association as a result, undoubtedly, of a decrease in the dielectric constant of the solvent medium. This is a necessary conclusion since the fluidity of the solvent is decreasing steadily.

For solutions of KCl in water at concentrations between 0.1 and 3.0 *N* the maximum appears around 300° . At 0.002 *N* there is no maximum up to 306° .⁸ The lower the concentration, the higher the temperature of the maximum. This is to be expected since ion interactions become less signifi-

(8) (a) C. A. Kraus, "The Properties of Electrically Conducting Systems," *Am. Chem. Soc. Monograph No. 7*, Reinhold Publishing Corp., New York, N. Y., 1922, p. 114, 122, 145, 164. (b) I. M. Rodnyanskii and I. S. Golinker, *Doklady Akad. Nauk, S.S.S.R.*, **105**, 115 (1955).

TABLE I
CONDUCTANCE-CONCENTRATION DATA FOR SOLUTIONS OF
LITHIUM IN METHYLAMINE AT VARIOUS TEMPERATURES

$T = -22.8^\circ,$ $\eta = 3.57 \times 10^{-3}$			$T = -30^\circ,$ $\eta = 3.94 \times 10^{-3}$		
$C \times 10^2$	$k \times 10^2$	Λ	$C \times 10^2$	$k \times 10^2$	Λ
0.4355	0.439	100.5	0.4406	0.418	94.8
1.548	1.07	69.4	1.566	0.990	63.3
1.992	1.24	62.0	2.015	1.134	56.3
9.832	4.43	45.5	9.947	3.95	39.7
13.70	6.71	49.0	13.86	6.00	43.3
29.67	18.8	63.4	30.02	16.7	55.7
62.04	53.1	85.6	62.77	46.0	73.3
$T = -40^\circ,$ $\eta = 4.54 \times 10^{-3}$			$T = -50^\circ,$ $\eta = 5.31 \times 10^{-3}$		
0.4475	0.378	84.5	0.4551	0.334	73.6
1.590	0.861	54.2	1.614	0.718	44.5
2.047	0.973	47.5	2.077	0.797	38.4
10.10	3.33	33.0	10.25	2.70	26.4
14.07	5.03	35.7	14.28	4.07	28.5
30.48	13.6	44.6	30.94	10.7	34.6
63.75	37.1	58.6	64.69	28.7	44.3
$T = -60^\circ,$ $\eta = 6.31 \times 10^{-3}$			$T = -70^\circ,$ $\eta = 7.62 \times 10^{-3}$		
0.4607	0.276	59.9	0.4671	0.220	47.1
1.637	.572	35.0	1.660	.427	25.8
2.107	.617	29.3	2.137	.440	20.6
10.40	2.10	20.2	10.55	1.50	14.2
14.49	3.09	21.3	14.69	2.11	14.4
31.39	8.10	25.8	31.83	5.80	18.2
65.63	21.9	33.4	66.55	15.9	23.9
$T = -78.3^\circ,$ $\eta = 9.08 \times 10^{-3}$					
0.4722	0.1687	35.73			
1.678	0.2985	17.79			
2.160	0.3242	15.01			
10.66	1.093	10.25			
14.85	1.529	10.30			
32.17	4.032	12.53			
67.27	11.48	17.07			

cant at low electrolyte concentration and disappear at infinite dilution.

In non-aqueous media of intermediate dielectric constant, the maxima become accessible at lower temperatures and concentrations.^{8a} The temperature of the maximum shifts rapidly to lower values with decreasing dielectric constant of the solvent medium. For example, a 0.03 *N* solution of KI in ammonia shows a maximum at 10°; in methylamine this is found at -45°. However, with solvents like methylamine, where ion association is quite prevalent even in dilute solution, the relation between concentration and the temperature of the maxima becomes somewhat involved.^{8a,9} In solutions of KI at a concentration of 0.035 *N* the curve shows a maximum at -33°; at 0.03 *N*, this has moved to about -45°; at much lower concentrations the maximum proceeds to higher temperatures with decreasing concentration as with solutions in solvents of higher dielectric constant. Above about 0.035 *N* the maximum also proceeds rapidly to higher temperatures with increasing concentration. In the more concentrated region, ion aggregates al-

ready present at lower temperatures probably are undergoing increased degradation and ionization from the increased thermal energy of the system. A higher temperature is therefore required before the dielectric effects overcome thermal effects.

Conductance-temperature curves for dilute solutions of lithium in methylamine are shown in Fig. 1. These resemble very much those shown by solutions of KI. It is to be noted that the maximum moves to higher temperatures with increasing metal concentration. At 0.005 *N* the maximum comes at about -20°, at approximately 0.02 *N* the maximum has moved to about -5°; apparently this trend continues. On the basis of these facts we conclude that the underlying phenomena are much the same in both cases. We believe that conducting species are being removed through mass action effects as the temperature is raised. If conductance in dilute solutions occurs by a "quasi-electrolytic" transport mechanism, as appears to be the case, the appearance of a maximum can hardly be caused by drastic changes in ionic mobilities. Measurements of the relative transport numbers of the negative to the positive species, t^-/t^+ , for dilute solutions of lithium in methylamine have demonstrated no extraordinary effects. The transport ratio changes with temperature in the expected direction; namely, as the temperature is raised the faster moving species slows down relative to the slower moving species. Thus, for a solution of lithium containing approximately 0.013 g. atoms per liter of methylamine, t^-/t^+ changes from about 8.8 to 10.3, or about 14% over the temperature interval from -63.5 to -78.3°. A change of this magnitude is not overly abnormal, judging by the results for a 0.01 *N* solution of HCl in water. For example, in this case, the relative transport number, t^+/t^- , changes from 4.7 to 5.3 in the temperature interval from 25 to 10°, or about 11%.¹¹ Although these comparisons are being made at quite different temperatures, the relative transport number in either case is a fairly linear function of temperature. These observations would seem to strengthen our opinion regarding the more or less normal electrolytic behavior of dilute solutions of lithium in methylamine. At concentrations above about 0.10 *N* (Fig. 1) the specific conductance-temperature plots do not show a maximum in the temperature range accessible to study. As the concentration is increased there is an increasing tendency for the curves to become concave upward; this is particularly noticeable at a concentration of 0.67 g. atom per liter of solvent.

The functionality between conductance and temperature at various concentrations of lithium may be illustrated conveniently by reference to the results presented in Table II. Given here is the mean percentage temperature coefficient of specific conductance, $\alpha = \frac{1}{k_1} \frac{\Delta k \times 100}{\Delta t}$, over ten degree intervals ranging from -78.3 to 10°, where k_1 is the conductance at the lower temperature in the interval. Concentrations are those computed at -78.3°. Included in column 2 of the table for

(10) H. M. Klein, unpublished results, this Laboratory.

(11) H. S. Harned and E. C. Dreby, *THIS JOURNAL*, **61**, 3113 (1939).

(9) F. F. Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

TABLE II
THE PERCENTAGE TEMPERATURE COEFFICIENT OF CONDUCTANCE, α , AS A FUNCTION OF THE TEMPERATURE INTERVAL AND CONCENTRATION

Temp. range, °C.	β	α , For various concentrations, $C \times 10^2$						
		0.4722	1.678	2.160	10.66	14.85	32.17	67.27
1. Solutions of lithium in methylamine								
-78.3 to -70	2.2	3.38	4.83	5.41	5.53	6.40	5.28	4.65
-70 to -60	2.1	2.58	3.39	3.98	4.03	4.64	3.97	3.78
-60 to -50	1.9	2.06	2.53	2.84	2.88	3.17	3.22	3.12
-50 to -40	1.7	1.71	2.01	2.20	2.24	2.40	2.53	2.51
-40 to -30	1.5	1.06	1.50	1.80	1.82	1.93	2.21	2.39
-30 to -20	1.4	0.50	0.84	1.18	1.52	1.63	1.74	2.18
-20 to -10	1.3	-0.14	0.68	0.44	0.46	1.40	1.35	1.90
-10 to 0	1.2	0.34
0 to 10	1.1	-0.10
2. Solutions of sodium in ammonia (ref. 12)								
		18.8	46.7	58.4	71.2	83.5	101.6	431
-40 to -32.5	..	1.61	2.11	2.48	3.05	3.60	3.50	0.262

comparison is the temperature coefficient of solvent fluidity, $\beta = \frac{1}{\phi_1} \frac{\Delta\phi \times 100}{\Delta t}$, where ϕ_1 is the fluidity at the lower temperature. A number of values for solutions of sodium in ammonia in the temperature interval from -32.5 to -40° are also recorded.¹²

From the data in Table II it is apparent that there is very little correlation between the coefficients of fluidity and conductance. The latter is greater at the lower temperature and falls off more rapidly than the fluidity with increasing temperature. At $5 \times 10^{-3} N$ the two coefficients become equivalent in the temperature interval from -50 to -40° ; at higher concentrations the curves intersect at higher temperatures.

Of particular interest is the fact that in certain intervals of temperature the percentage temperature coefficient proceeds through a maximum. In the temperature interval from -78.3 to -70° this occurs in the neighborhood of $C = 0.15$. This concentration lies just to the right of the minimum in the $\Delta-C$ curve² and in the region where metallic properties are just commencing to show up. As the temperature is raised, the maximum shifts to higher concentrations and disappears completely in the temperature interval from -40 to -30° , within the concentration range covered in this study. For solutions of sodium in ammonia the maximum occurs in the neighborhood of $C = 0.9$ in the temperature interval from -32.5 to -40° ; solutions of potassium behave similarly.¹³ It is not unlikely that solutions of lithium in methylamine might also show a similar behavior at higher concentrations in the range from -4 to -30° , judging by the trend in the values of the coefficients.

The appearance of a maximum in the temperature coefficient-concentration curves appears to be related to the appearance of metallic-like proper-

ties. In ammonia at -34° , at a concentration of approximately $0.6 N$, the conductance-concentration curve commences to increase exponentially with increasing concentration. At the same time, the temperature coefficient has gone through a maximum and commences to decrease rapidly, reaching very small values toward saturation; in fact it would appear that the coefficient might even become negative, which is characteristic of the metallic state, if the concentration could be increased somewhat above the saturation value.^{12,13} Furthermore, as noted above, the relative transport number increases with decreasing temperature¹⁰; the electron therefore carries a proportionately larger share of the current. A shift in the maximum to lower metal concentrations with decreasing temperature, such as is shown by the data in methylamine, does not seem unreasonable.

The appearance of a minimum in the $\Delta-C$ curve, as well as a maximum in the $\alpha-C$ curve, evidently results from two competing processes. At low metal concentrations association removes conducting species, leading to a decrease in conductance with increasing metal concentration. Association effects are finally overcome at higher concentrations by the appearance of electrons free to move in the metallic sense. This might be achieved in the first instance by aggregation, *e.g.*, of dimers, which could provide a path for highly mobile electrons.⁴ On the other hand, at higher concentrations conduction by tunneling could conceivably occur quite readily, possibly as described by Farkas, who used a simple lattice model.¹⁴

Acknowledgments.—We wish to thank the Office of Naval Research and the Office of Ordnance Research, United States Army, for partial support of this research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(12) C. A. Kraus and W. W. Lucasse, *THIS JOURNAL*, **45**, 2551 (1923).

(13) C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1941 (1922).

(14) L. Farkas, *Z. physik. Chem.*, **A161**, 360 (1932).