The calculated values are listed in Table II; values for trimethylamine and monoethylamine are also included.

Summary

1. The need for heat capacity data for the amines and the absence of such data in the literature are pointed out.

2. Experimental values for heat capacities are presented tabularly and the heat capacity–temperature relations for the mono- and dimethylamines are presented for a temperature range from 0 to 50°. The accuracy of the measurements is given.

3. Experimental values for the heat capacity ratio, γ, are presented for the methylamines and for monoethylamine.

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The Conductance of Bases in Liquid Ammonia

BY WILLIAM W. HAWES[1]

I. Introduction

It is well known that a molecular species which consists principally of an element of the second period differs markedly in its physical and chemical properties generally when compared with its analogs of the succeeding periods. That the same trend would be shown if the species under consideration were ionic seems likely and we would expect the electrolytic conductance of solutions of a compound of this type to show an abrupt change from the behavior of the commoner types of electrolytic solutions. The evidence in support of this hypothesis is meager but examination of the available data does show discontinuities that are probably characteristic of the second period elements. However, the specific effect is usually involved and is, therefore, difficult of generalization.

Perhaps the approach to the problem most likely of success is a comparative study of dissociation of electrolytes consisting of the simplest ions of second period elements. This would necessarily have to be carried out in a solvent of dielectric constant sufficiently low that its solutions of ordinary electrolytes would be measurably undissociated. Unfortunately, this field of investigation is very restricted because such compounds are ordinarily insoluble in suitable media. The only systems that are readily available are the alkali metal amides in solution in liquid ammonia. Ammonia is well suited to this purpose since no electrolyte as far as is known at present is completely dissociated in this solvent and also, the conductance values of a large variety of electrolytes are available for comparison.

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The conductance of solutions of sodium and potassium amides in liquid ammonia was measured by Franklin and Kraus[2] and by Franklin. Two significant facts are shown by these data; first, both electrolytes are exceptionally weak and, second, the order of their relative strength is reversed, that is, whereas sodium salts generally are more highly dissociated than potassium salts, the dissociation of sodium amide is much less than that of potassium amide. It has been shown by Kraus and Hawes[3] that the dissociation of an electrolyte is primarily determined by the size and configuration of its ions. The amide ion is undoubtedly small and therefore these amides would be weak. While this characteristic is thus, qualitatively, accounted for there is no ready explanation of the great difference in the dissociation of the two nor of the relative order of their constants. In addition, the unusual properties of these amides are clearly demonstrated by their reactivity. The most striking example is, perhaps, the formation of compounds, stable even in solution, between these amides and between them and amides of the other strongly electropositive first group elements.[4] In view, then, of the known properties of the amides it seemed likely that more precise data might yield additional knowledge concerning the behavior of second-period elements. In the present paper are reported new determinations of the conductance of these solutions in which the concentration range is extended and the values somewhat revised. Also, evidence is presented of additional anomalous behavior that cannot be accounted for on the basis of existing theory.

II. Apparatus and Materials

The apparatus employed, exclusive of electrical equipment, and the general procedure adopted in this investigation were the same as was developed by Kraus and Hawes[3] in the measurement of the conductance of ammonia solutions of substituted alkali metal amides. Electrical apparatus comprising an alternating current bridge assembly was constructed according to current notions of design, following largely the recommendations of Shedlovsky[5] but incorporating some of the suggestions of Jones and Josephs.[6]

Apparatus.—The bridge assembly consisted of a bridge proper, two resistance boxes, a vacuum tube oscillator and a detector. The bridge was an equal ratio arm instrument consisting in the main of coaxially mounted woven coils of 1000 ohms each and fine adjustments of 14K white gold wire on both the ratio arm branch and the resistance-cell branch. Coarse and fine adjustment variable air condensers were provided for continuous variation of capacity from 500 $\mu\mu$f in parallel with the unknown to the same capacity in parallel with the reference resistances. Grounding was accomplished by means of a Wagner ground. The resistance boxes had a combined resistance of 60,000 ohms variable in steps of 0.1 ohm. Coils up to 100 ohms were bifilar wound while those of 1000 and 10,000 ohms were of the woven type. All coils were so spaced that sensible interaction between them was eliminated. Also, the 10,000-

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[2] Franklin and Kraus, *Am. Chem. J.*, **23**, 292 (1900); Franklin, *Z. physik. Chem.*, **69**, 290 (1909).

[3] Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

[4] Franklin, *J. Phys. Chem.*, **23**, 36 (1919).

[5] Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

[6] Jones and Josephs, *ibid.*, **50**, 1049 (1928).

ohm coils were arranged so that they were completely disconnected when not in actual use. They were oil immersed and thermostated. The absolute values of the resistances were determined by comparison with Bureau.of Standards calibrated coils using direct current. The oscillator was of the type described by Shedlovsky and was designed to give frequencies from about 1000 cycles per second upward in convenient steps throughout the audible range. The data given below were obtained using a single frequency of 1000 cycles per second but higher frequencies were used as well in checking possible frequency dependence in the resistance measurements. The oscillator was coupled to the bridge circuit through a variable air transformer. The detector consisted of a single high resistance telephone used in conjunction with a two-stage, transformer coupled, vacuum tube amplifier. The characteristics of the amplifier were such that a peak amplification was given in the neighborhood of 1000 cycles with considerable attenuation of lower frequencies. Attenuation of the higher frequencies was less pronounced so that bridge settings of the required accuracy could be made up to 5000 cycles. Each of the units of the assembly was shielded electrostatically as completely as possible except the oscillator, of which the output coil only was shielded. The shielding was well removed from current-carrying parts of the assembly. All external electrical connections were made through shielded single conductor copper wire, insulated by an extra heavy rubber covering of very low dielectric constant.

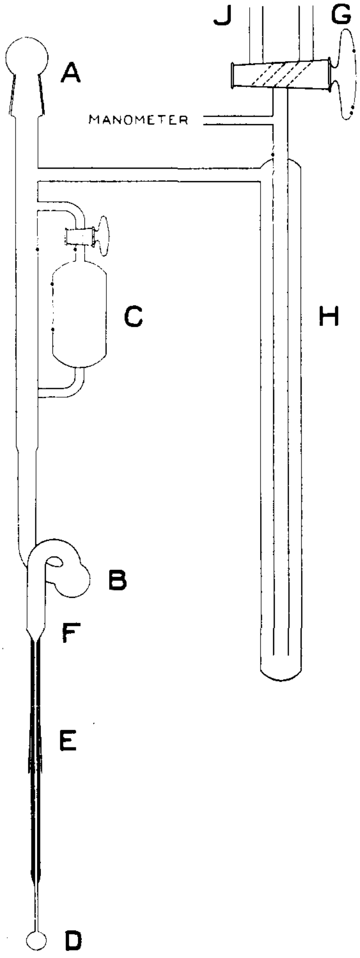

Fig. 1.

Materials.—The metal amides were prepared in the conductivity cell by the interaction of ammonia and a known quantity of the metal in the presence of oxidized iron. The cell having been washed repeatedly with pure ammonia until its specific resistance was sufficiently high, a fragile glass bulb containing the metal was crushed and the reaction allowed to proceed to completion. In the case of potassium this required only a few minutes but a much longer time was required for sodium, the time ranging from two or three days to a week. After the reaction was complete the solvent was evaporated without boiling, a stoppered Dewar tube being kept around the cell. This procedure was necessary to ensure complete retention of the amide. Hydrogen resulting from the reaction was removed by evacuation.

The metals were purified by distillation in the apparatus shown in Fig. 1. A commercial metal was introduced through the top A into the bulb B. The reservoir C was filled with nitrogen and closed off by the stopcock. The nitrogen was a commercial grade from which oxygen had been removed by passage over hot reduced copper and which had been stored over phosphorus pentoxide long enough to ensure complete drying. The weighed fragile bulb D was attached to the distilling apparatus through the capillary ground joint E, sealed internally with de Khotinsky cement on the outer end only. A tubular electric resistance furnace was placed in such a position around the distilling apparatus that a part of the metal was distilled from the bulb B to the top of the capillary F. The system (with the exception of the nitrogen reservoir) was evacuated continually during distillation by means of a diffusion pump connected at G, being protected from back diffusion of mercury by the trap H which was surrounded with liquid air. After the desired amount was collected at F the stopcock I was closed, the furnace removed and an oil-bath placed so as to immerse the fragile bulb and connecting tube to a height somewhat above the distilled metal. Maintaining the temperature of the bath slightly above the melting point of the metal, nitrogen was introduced from the reservoir C forcing the molten metal through the capillary into the bulb D. Sufficient additional nitrogen was then introduced from a storage flask attached at J to bring the pressure to within a few millimeters of atmospheric pressure. Removing the bath and allowing time for thermal equilibrium, the pressure and temperature of nitrogen were observed, after which the fragile bulb was sealed off. The lower half of the ground joint E was removed and weighed together with the bulb. After taking into account necessary corrections, the weight of metal was given by difference. The apparatus was constructed of soda lime glass, this glass being less readily attacked by the vapors of sodium and potassium than other common glasses.

A micro balance sensitive to 0.001 mg. was employed to weigh the samples of metal. Platinum weights intercompared by the Richards method[7] and checked at intervals throughout the range of the set against Bureau of Standards calibrated Class "A" weights were used. The principal correction to the observed weight was made necessary by the volume of air displaced by metal and nitrogen. This was determined by weighing the bulb under water on an analytical balance. All corrections significant to 0.001 mg. were taken into account. The weights of metal recorded below may be relied upon probably to 0.005 mg.

The ammonia was a synthetic product dried by sodium and stored in a metal cylinder from which it was distilled as needed. The vapor was passed through a filter of washed and ignited asbestos. The specific conductance of the ammonia in the conductivity cell was found to be about 1×10^{-7} and the data here given are corrected by this amount.

III. Experimental Results

Below are tabulated the conductance values at various dilutions for sodium amide, $NaNH_2$, and potassium amide, KNH_2. At the head of each table are given the temperature at which the measurements were made and the weight of metal used. Other data in the case of potassium amide were obtained, especially over the more concentrated range, which are in good agreement with the data given here but which are omitted for economy of space. V is the dilution in liters per equivalent and Λ the equivalent conductance in the usual units.

TABLE I

CONDUCTANCE VALUES OF BASES IN AMMONIA

Temp., −33.04°. Sodium Amide. Na, 0.013681 g.

V	Λ	V	Λ	V	Λ
72.48	10.24	272.7	21.90	1024	41.35
140.7	15.28	528.8	30.47	1986	55.20

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(7) Richards, THIS JOURNAL, **22**, 144 (1900).

TABLE I (*Concluded*)

Temp., −33.01°. Na, 0.010195 g.

V	Λ	V	Λ	V	Λ
97.43	12.20	1351	47.64	18,760	137.8
189.7	17.81	2607	63.92	36,210	168.3
366.2	25.29	5022	84.57	...	...
703.6	35.00	9727	109.5	...	...
Temp., −33.01°. Potassium Amide. K, 0.063529 g.					
17.61	19.00	495.1	66.93	13,660	208.1
34.36	23.36	963.2	88.32	26,590	230.8
67.18	29.82	1871	113.3	51,720	253.4
130.7	38.82	3650	143.6	...	...
254.1	50.95	7087	176.2	...	...
Temp., −32.95°. K, 0.134012 g.					
8.37	16.12	230.7	49.25	6,374	173.5
16.25	18.61	447.5	64.66	12,400	204.2
31.56	22.73	868.1	84.79	24,130	228.3
61.01	28.84	1688	110.0	47,020	255.3
118.7	37.48	3283	140.1	...	...

IV. Discussion

The results for sodium and potassium amide are shown graphically in Fig. 2, in which the equivalent conductance is plotted as a function of the logarithm of the dilution. Only one of the sets of data given is plotted in each case. The data not plotted fall on the curve shown practically as well as those which are plotted except, possibly, in the most dilute region where the experimental uncertainty becomes relatively larger and since the points of check determinations tend to cluster they are omitted to avoid confusion. It is apparent that in both cases the equivalent conductance varies but little with concentration in the concentrated region but rises rapidly in the moderately dilute range, indicating a high value of the limiting conductance. A minimum in the curve for potassium amide exists at a concentration slightly higher than the range of these measurements. There is no minimum in the sodium amide curve but it may be inferred that the effect which produces the minimum in the potassium amide curve is present here also. This minimum is accounted for in solvents of very low dielectric constant by the hypothesis of ion triples.[8] It may well be that the same situation obtains here but no method of analysis is available to separate the effect precisely. Even so, it is obvious that both these electrolytes are extremely weak.[9]

Errors are present in the data for sodium amide of both Franklin and Kraus[10] and Franklin.[11] Franklin reports the conductance up to concentra-

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(8) Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933).

(9) The primary effect of ion triples is to increase the conductance.

(10) Franklin and Kraus, *Am. Chem. J.*, **23**, 292 (1900).

(11) Franklin, *Z. physik. Chem.*, **69**, 290 (1909).

tions of 5.7 liters and Franklin and Kraus up to 27.5 liters, Moreover, these two sets of data do not agree over the range in which they overlap. In the concentration range that the present data cover, namely, down to 72.5 liters, the general shape of the curve is the same as that of Franklin and Kraus but it lies above by an amount corresponding to an error of around 7 or 8% assuming that the present data are substantially correct. The author has found it impossible to prepare solutions of sodium amide substantially more concentrated than those reported. No accurate determination was made of the limit of solubility but qualitative observations indicated that saturation would be attained at approximately 50 liters. The results of Franklin and Kraus could be explained on the assumption that undissolved salt was present in the first three solutions they report but that all of the salt was dissolved thereafter. Their first four points were determined without removal of solution so that any error due to this source would be limited to calculated concentrations greater than approximately 50 liters. From this point on their results would be correct except for an initial concentration error. The error that is found is in the direction that would be expected from the manner in which their salt was prepared. The present revision of these data is not large in absolute magnitude, the relatively high percentage error being due to the low value of the conductance in this concentration range. The results of Franklin are obviously in considerable

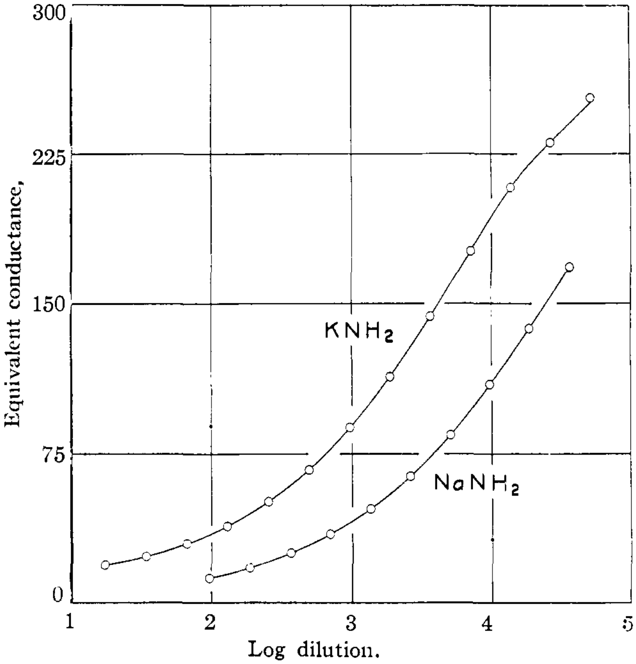

Fig. 2.

error. In his procedure the salt was made in an auxiliary cell and a solution siphoned to the measuring cell. The initial concentration would be far less than that reported so that subsequent concentrations and, of course, values of equivalent conductance, would be in error. The present data for potassium amide agree well with those of Franklin but are more consistent among themselves and also between separate series of measurements. Franklin's data fit the curve in Fig. 1 almost as well as any curve that might be drawn through them up to about 7500 liters. The present values of conductance are somewhat higher over this range of concentrations but the difference is within the experimental uncertainty of the earlier work.

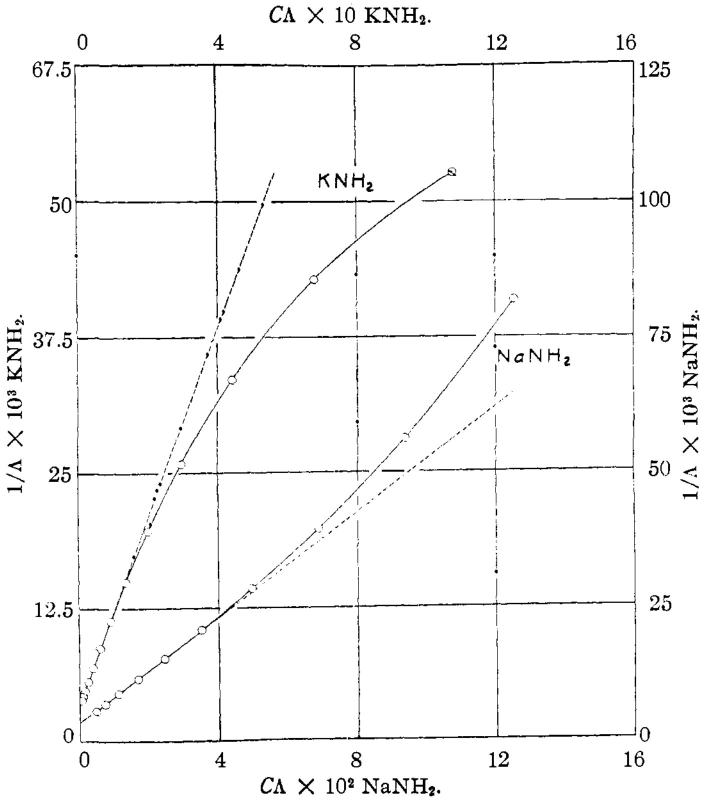

Fig. 3.

In Fig. 3 are plotted values of specific conductance (concentration times equivalent conductance) against the reciprocal of the equivalent conductance for a typical series each of measurements on sodium and potassium amide. It may be seen from these curves that both electrolytes apparently approach the law of mass action in the dilute region. The curve for potassium amide is normal and departs from linearity in the concentrated region in the manner that would be expected. Sodium amide, on the other hand, behaves quite differently. A pronounced curvature away from the axis of specific conductance is apparent. In other words, out to fairly dilute solutions sodium amide is a poorer conductor than is required by the law of mass action. This behavior is unique; no other salt as far as is known deviates in this manner.[12] The apparent agreement of the data with the Ostwald dilution law may be fictitious. Aside from the theoretical objection that no account is taken of the interaction of ions, the factors which are responsible for the abnormal curvature of the sodium amide curve might well compensate over a particular concentration range for the inaccuracies of the theory. The same effect may be entering with both electrolytes. Furthermore, extrapolation to zero concentration by this method yields values of Λ_0 almost identical for both the sodium and potassium amides.

An attempt to extrapolate these data for sodium amide by the method of Fuoss and Kraus[13] yielded no result. Their extrapolation requires that the plot of $f\sqrt{c}$ against $\gamma/\sqrt{1-\gamma}$ be a straight line passing through the origin. Here f is the activity, c the concentration and γ the degree of dissociation corrected for the interionic effect. This plot for sodium amide does not yield a straight line over any range of concentration and the direction of the deviation is again opposite to that found in every other case tried. It is not certain whether or not the data for potassium amide can be extrapolated by the method of Fuoss and Kraus. The curve shows a slight structure below 0.001 normal that is not readily explicable corresponding to conductance values progressively lower than predicted. It is not impossible that this is caused by a systematic experimental error. However, the deviations at the most dilute points are considerably greater than might be expected and are reproducible within much closer limits.

The only value of the dissociation constant of sodium amide that can be obtained at present is that given by the limiting slope of the curve shown in Fig. 3 assuming the simple mass action law (in the classical sense). The value so obtained; $K = 2.65 \times 10^{-5}$, is probably an upper limit for this constant. In the case of potassium amide, an extrapolation can be made by the Fuoss and Kraus method by disregarding the data below 4000 liters. The values so derived for the equivalent conductance at infinite dilution and the dissociation constant are $\Lambda_0 = 343$ and $K = 7.3 \times 10^{-5}$. Franklin's data extrapolate by this method to the values $\Lambda_0 = 351$ and $K = 7.0 \times 10^{-5}$. The simple mass action law gives $\Lambda_0 = 286$ and $K = 1.41 \times 10^{-4}$. The slope of the extrapolation curve in the Fuoss and Kraus

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(12) Kraus and Bray plotted this function for a large number of salts of widely differing dissociation constant some of which were of the same order of magnitude, and less than that of sodium amide, and in no case did they find a curve of this structure. Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913); Kraus, "The Properties of Electrically Conducting Systems," The Chemical Catalog Company, New York, 1922, pp. 55 ff.

(13) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

method which yields their determination of K seems to approach a much smaller limiting value than the simple mass action extrapolation in both cases.

In view of the failure of the theory to account for the conductance of sodium amide and the uncertainty of the treatment of potassium amide it would be useless to calculate ion sizes. If the underlying notions of the theory are at all justified it is certain, however, that the amide ion is exceedingly small. It may be that the unusual properties that have been found are specific for the amide ion but it seems more likely that they will prove rather to be characteristic of small ions in general.

V. Summary

The electrical conductance of sodium and potassium amide has been measured in liquid ammonia solution up to concentrations of 36,000 and 52,000 liters, respectively. The data for sodium amide deviate from the theory of Fuoss and Kraus as well as from the simple mass action theory. The agreement is better in the case of potassium amide but is not as good as might be desired. The results indicate that the specific properties of extremely small ions are important in the case of these electrolytes.

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The "Salting-out" and "Salting-in" of Weak Acids. I. The Activity Coefficients of the Molecules of Ortho, Meta and Para Chlorobenzoic Acids in Aqueous Salt Solutions[1]

BY ARTHUR OSOL AND MARTIN KILPATRICK

In general the solubility of a non-electrolyte is increased or decreased by the addition of an electrolyte, but the effect is not independent of the solvent salt. The results may be expressed by the equation

$$\log S_0/S = \log f \qquad (1)$$

where S_0 is the solubility at zero ion concentration, S the solubility in the salt solution and f the activity coefficient of the non-electrolyte. It has been found that the equation

$$\log f = kC \qquad (2)$$

C being the concentration of electrolyte in moles per liter and k a constant, holds over a wide range of concentration. The constant k is known as the "salting-out" constant. Provided a correction is made for the part

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[1] Abstracted from the dissertation of Arthur Osol presented April 1, 1933, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy Paper presented in part before the Washington meeting of the American Chemical Society, March, 1933.