THE PROPERTIES OF SOLUTIONS OF METALS IN LIQUID AMMONIA

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Liquid ammonia is an excellent solvent for a large number of different types of substances (1). Although it does not surpass water as a solvent for most inorganic substances, it appears to excel as a medium for organic compounds; in this it resembles alcohol. It exhibits a distinct advantage over water in that it dissolves the alkali and alkaline earth metals without appreciable reaction with them. The fact that reaction does not proceed is undoubtedly due to the extremely low concentration of the amide ions present in liquid ammonia. This condition is substantiated by the low conductivity of pure ammonia and also by the small tendency for ammonolytic reactions to proceed as compared to hydrolytic reactions in water. Substances which are readily hydrolyzed in water are, as a rule, not ammonolyzed in liquid ammonia. Thus it is possible to study the chemical and physical properties of the strongly electropositive elements in a comparatively inert medium possessing a high dielectric constant. In the present discussion we shall confine ourselves to the physical properties of these solutions and shall attempt to give a critical account of the results of the numerous investigations.

SOLUBILITY RELATIONS

Solutions of the alkali metals in liquid ammonia were first investigated by Weyl in 1864 (2). He observed that sodium and potassium were soluble in this medium, producing highly colored solutions. At the time of his studies the radical theory domi-

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nated chemistry. Naturally Weyl regarded these solutions in the light of the theories then prevailing, and concluded that the metals were joined to the nitrogen of ammonia, forming substituted ammonium groups, with the metal taking the place of one of the hydrogen atoms. He did not present any quantitative data to support his conclusions.

A few years later, Seely reported his observations on the solution of alkali metals in liquid ammonia. These results were published during the two years following his report (3, 4, 5). He contended that the metals are in solution in ammonia as such and that they are not united to nitrogen in the form of an ammonium radical. Although he presented no quantitative data to support his views, he described his observations clearly as follows:

> Now, the key to the whole subject is the fact that liquid anhydrous ammonia is a solvent, without definite chemical action on the alkali metals. I mean that these metals dissolve in the ammonia as salt dissolves in water—the solid disappears in the liquid, and on evaporating the liquid, the solid reappears in its original form and character. There is no definite atomic action in any such cases; the components of the solution are not changed in their chemical relations to other substances." He describes his apparatus and then continues: "When sodium is subjected in this apparatus to the condensing ammonia, before any ammonia is visibly condensed to the liquid state, it gradually loses its lustre, becomes of a dark hue, and increases in bulk. The solid then appears to become pasty, and at last we have only a homogeneous mobile liquid. During the liquefaction and for a little time after, the mass is of a lustrous, copper-red hue; the condensation of the ammonia and its mingling with the liquid steadily goes on, the liquid is progressively diluted, and passing through a variety of tints by reflected light at last it becomes plainly transparent and of a lively blue by reflected as well as by transmitted light; the liquid now closely resembles a solution of aniline blue or other pure blue dye-stuff. On reversing the process by cooling the ammonia generator, the ammonia gradually evaporates out of the liquid, and the changes observed during the condensation reappear in the reverse order, till at last the sodium is restored to its original bright metallic state. If the evaporation be conducted slowly and quietly, the sodium is left in crystals of the form seen in snow. The formation of the transparent blue liquid, and the restoration of the sodium are stead-

ily progressive; and the repeated and closest scrutiny of the process has failed to reveal the slightest irregularity in its continuity. The inevitable conclusion from such facts is that the blue liquid is a simple solution of sodium in ammonia, not at all complicated or modified by any definite chemical action.

Seely carried out similar experiments with potassium, lithium and rubidium, and arrived at conclusions analogous to those obtained in the case of sodium solutions. He also observed that lithium appears to be less soluble in ammonia than are the other alkali metals. He evidently did not have any of the alkaline earth metals at his disposal, for, if he had, he would undoubtedly have observed their peculiarities. On the other hand he noticed that aluminium, magnesium, thallium, indium, mercury and copper were not soluble in liquid ammonia.

With the exception of some facts on solubilities given by Gore (6, 7) immediately following the work of Seely, no experiments were reported for several years. The subject was finally revived by Moissan and Joannis who carried out many investigations over a period of years. Moissan (8, 8a) and Guntz (9) finally added cesium, calcium, barium and strontium to the list of soluble metals. Cottrell (10), at a much later date, found magnesium to be slightly soluble in ammonia, contrary to the observations of Seely. That the alkaline earth metals present a situation somewhat different from that of the alkali metals was observed by several investigators. This part of the discussion will be considered later in reference to the possibilities of the existence of combinations between the soluble metals and ammonia.

Although most of the earlier workers recognized that these metals are highly soluble in ammonia, relatively few attempts were made to determine the solubilities quantitatively. Ruff and Geisel (11) determined the solubility of lithium, sodium and potassium in liquid ammonia by a unique method, one which was subject to errors of considerable magnitude, but which, nevertheless, through careful and skillful manipulation, gave them fairly consistent and accurate results.

They allowed an amount of ammonia, insufficient to dissolve all the metal, to be added to lithium, sodium and potassium in small tubes. Some cotton wadding was placed above the mixtures and the upper end of each tube was sealed. The tubes were then agitated for three hours to insure saturation. After this period they were inverted to allow the solution to filter through the wadding. When an amount sufficient for analysis had filtered, the tubes were immediately placed in a Dewar flask containing liquid air, in order to freeze the entire contents. Then the bottom part of each tube was broken off immediately above the saturated solution without allowing the contents to melt. The solution was finally analyzed according to the usual procedures.

They found that the solubility of metallic lithium in ammonia does not appear to change over a temperature range from −80° to 0°, while that of potassium increases with increasing temperature from −100° to 0°. Over the same temperature range the solubility of sodium was found to decrease with increasing temperature. Although the changes in solubility with the temperature are relatively small in all three cases, it is difficult to understand the lack of change in the case of lithium. Since Ruff and Giesel took the average of two series of determinations, the values of which were decidedly at variance with each other, it seems probable that the accuracy of the method would not allow for the detection of small changes in solubility. Their values for these three metals are given in table 1.

A convenient and accurate method for a determination of the solubility of a metal in liquid ammonia is to measure the vapor pressure of the solutions as a function of the concentration of dissolved metal. When ammonia is added to the metal, the resulting solution shows a constant vapor pressure, that of the saturated solution, as long as any undissolved metal remains. The change in the vapor pressure in passing from the saturated solution to those less concentrated in metal is very abrupt (see figure 1). It is possible to obtain several values of the pressure in this region by careful manipulation in the experimental procedure. When this curve is extrapolated to intersect the horizontal line representing the vapor pressure of the saturated solution, a point is obtained corresponding to the composition of the saturated solution.

Joannis (12) applied this procedure to solutions of sodium and also of potassium at many different temperatures. The results obtained by Joannis are not in accord with those of Ruff and Geisel and of later workers. In some temperature intervals, even the sign is opposite. It would appear that Joannis experienced difficulty in establishing equilibrium conditions and in maintaining constant temperature during the course of a series of determinations. It is quite doubtful that the temperatures were accurately known, since the boiling point of liquid ammonia was in error by at least 5°. The changes in vapor pressure of these solutions are very sensitive to small temperature changes.

TABLE 1

Composition of saturated solutions of alkali metals in liquid ammonia at different temperatures

A. Lithium

TEMPERATURE	0°	25°	−39.4°	−50°	−80°
Kraus and Johnson			3.61		
Ruff and Geisel	3.93	3.93	3.93	3.93	3.93

B. Sodium

TEMPERATURE	0°	−33.8°	−50°	−70°	−105°
Kraus, Carney and Johnson		5.48			
Ruff and Geisel	5.87	5.48	5.39	5.20	4.98
Kraus and Lucasse		5.37			
Johnson and Meyer	5.79				

C. Potassium

TEMPERATURE	0°	−33.5°	−50°		−100°
Kraus and Lucasse		4.87			
Ruff and Geisel	4.74		4.79		4.82
Johnson and Meyer	4.68	4.95	5.05		

Applying this procedure under conditions of equilibrium and controlled temperature, Kraus and Johnson (13), Kraus, Carney and Johnson (14), and Johnson and Meyer (15, 16) have determined the composition of saturated solutions of lithium, sodium and potassium at several temperatures. These results are given in table 1, and are expressed in terms of gram-molecules of ammonia per gram-atom of metal.

The values obtained by Kraus and Lucasse (17) are the result of resistance measurements. They noticed a decided change in the resistance of these solutions in passing from a saturated solution to those more dilute in metal. The point at which such a break occurs is identical with the composition of the saturated solution. Ruff and Zedner (18) give additional solubility data at temperatures ranging from −115° to +20°.

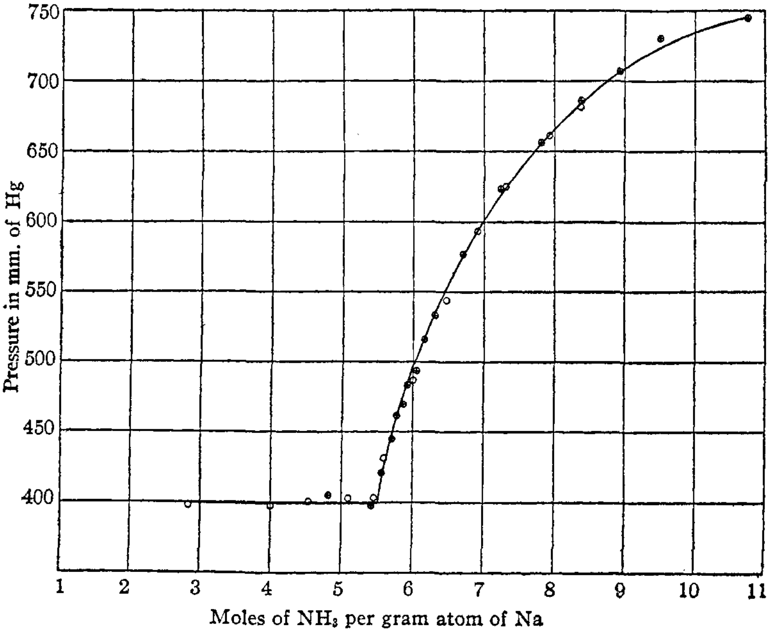

Fig. 1. The Vapor Pressure of Solutions of Sodium in Liquid Ammonia at −33°

Kraus (19) has taken the values for sodium secured from conductivity measurements and those of Ruff and Geisel to give the general form of the solubility curves over a considerable range of temperature. He also presents evidence to show that at low temperatures the sodium solutions separate into two liquid phases. Ruff and Zedner (18) determined the composition of these liquid phases in equilibrium with each other and with vapor, by noting the temperature at which the two-phase system disappeared. According to their results, this temperature lies at about −45° and at a composition of approximately two atom per cent of sodium. This value is not in accord with the vapor pressure curves of Kraus (20) which, at higher temperatures, show an inflection point at about 3.5 atom per cent of sodium. Later, Kraus and Lucasse (21) determined the composition of these two liquid phases at low temperatures. They found that when the temperature reaches that of the three-phase system the electrical resistance of the solution undergoes an abrupt change as the second liquid phase appears. This would necessarily be the case since the compositions of the two phases differ appreciably from that of the single liquid phase. The critical solution temperature was found to be −41.6° with a composition of 4.15 atom per cent of sodium. As the temperature is lowered one phase becomes richer in sodium while the other liquid phase decreases in sodium content. It is remarkable, however, that the critical phase appears at such a low concentration of dissolved sodium. Even at −60°, the compositions of the two liquid phases are only 1.7 and 8.3 atom per cent of sodium respectively.

COMBINATIONS BETWEEN METALS AND AMMONIA

Weyl (2) looked upon the solutions of metals in ammonia as being true compounds, in which the metal is directly connected to nitrogen as hydrogen is in the ammonium group. The term "metal ammonium" was used to represent such a combination. Seely deduced from his observations that the metals are actually in solution as individuals without combination with the solvent. Neither investigator presented evidence of a quantitative nature to support his view. Joannis (22, 23), at a later date, revived the ammonium theory and carried out a large number of experiments to determine the vapor pressures of the solutions and the molecular weights of the dissolved metals (24, 25, 26, 27). He believed his work showed that the molecules in solution contain two atoms of sodium or two of potassium. Among others, Moissan (8, 28, 29, 30, 31, 32) applied the method of Joannis with similar results. Thus the term "metal ammonium" was used for several years by a number of workers in the field and has without justification found some following even to the present day. After the careful experiments of Ruff and Geisel (11) and Kraus (33) had appeared, experiments which showed that, from the standpoint of the phase rule, no solid constituent containing ammonia could exist, the term "metal ammonium" has been to a large extent discarded.

The argument to show the non-existence of alkali metal-ammonia combinations appears simple when one examines carefully the form of the vapor pressure curves for these solutions. In figure 1, the horizontal line represents the pressure of saturated solutions of sodium in liquid ammonia at −33.5°. This value is about 400 mm. of mercury. The composition of the saturated solution is indicated at the point of intersection of the horizontal line with the vertical line representing pressures for the more dilute solutions. As the solutions become more dilute in metal the vapor pressure increases very rapidly and assumes a fairly constant value after having traversed a comparatively short range of concentration. Joannis argued that the decomposition pressure of sodium ammonium is the same as the vapor pressure of its saturated solution. In such a case a new solid phase would appear in the equilibrium, and, according to the phase rule, the condition could be realized only at one definite temperature since the system would be non-variant. Roozeboom (34) pointed out that Joannis must have carried out his experiments at the temperature of the non-variant equilibrium. However, measurements at other temperatures give the same type of curve to show that the solid phase separating from solution is identical with the phase of sodium metal. Measurements at very low temperatures, about −70°, show no change in the form of the vapor pressure curve. At these temperatures the ammonia may be easily removed from saturated solutions leaving metal only.

More recently Benoit (35) has published the results of an investigation of the phase relations in the system lithium-ammonia.

Working at −38.5° he found three regions within which the vapor pressure of the solutions appears to be independent of the composition of the system. He concluded from this that a lithium ammonium is present with the composition corresponding to the formula $[Li(NH_3)_4]_2$. Repetition of this work shows (13) the nonexistence of a region of constant pressure other than that for saturated solutions. It appears that Benoit did not establish true equilibrium conditions. It is impossible to obtain consistent results for the vapor pressure of these solutions unless they are strongly agitated throughout the series of measurements. It is also necessary to approach the equilibria from both sides to be certain of the conditions. Benoit gives no description of the method he employed for maintaining equilibrium. According to the data existing for the vapor pressure of pure ammonia, Benoit evidently worked at a temperature that was somewhat higher than he records.

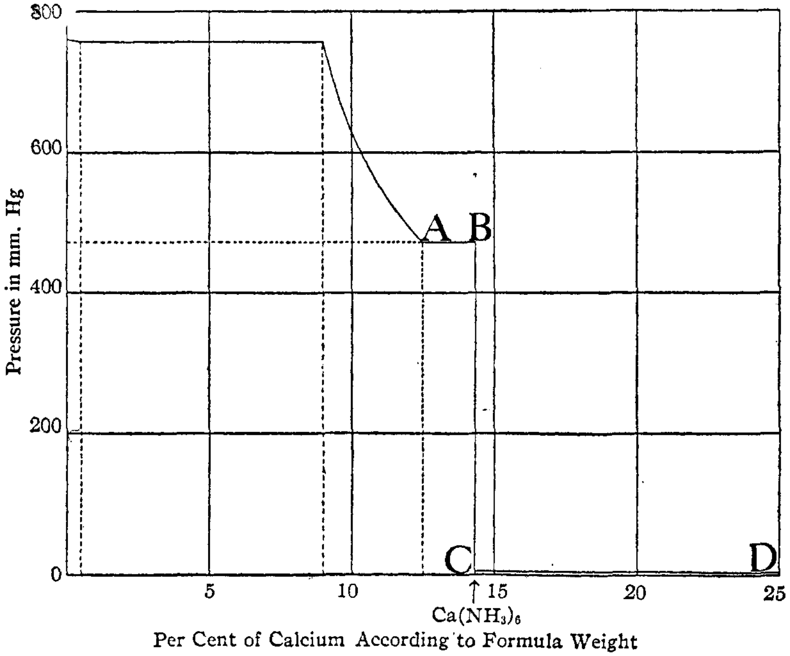

FIG. 2. THE SYSTEM CALCIUM-AMMONIA AT −32.5°

Thus all attempts to show the existence of combinations between the alkali metals and ammonia have failed completely. Even though there were no evidence to show this, it would be exceedingly difficult to conceive of a highly electropositive element taking the place of a hydrogen atom in the ammonium group.

An examination of solutions of the alkaline earth metals in liquid ammonia presents a somewhat different situation. A break in the vapor pressure curves is found in which the pressure is independent of the composition of the solution throughout a definite range of concentration. Kraus (33), (see figure 2), has shown that calcium forms a solid phase in which six molecules of ammonia are associated with an atom of the metal (8a). This compound, however, is to be regarded as an ammoniate, analogous to the ammoniated salts such as $CaCl_2 \cdot 6NH_3$, etc., rather than as a metal ammonium. It possesses the appearance of a metal and appears to have all the characteristic properties of metals. Mentrel (36) and Roederer (37) have established the existence of hexammoniates of barium and strontium. No similar combination has been noted for magnesium. The alkaline earth metal ammoniates have also been prepared and studied by Biltz and Huttig (54).

MOLECULAR WEIGHTS

The first molecular weight determinations of the metals in liquid ammonia were carried out by Joannis (12, 27). Working with solutions of sodium and potassium, he determined the change in the vapor pressure of the solvent as a function of the composition of the solution. Then, by means of Raoult's law, he calculated the molecular weight from the data. Some of his results are undoubtedly in error due to the fact that he assumed an incorrect value for the boiling point of liquid ammonia. He observed the boiling point of the solutions under atmospheric pressure, employing a value of $-38.2°$ for the boiling point of pure ammonia. Several independent determinations have since shown the boiling point of ammonia to be about $-33.5°$. Joannis also applied the law of Raoult to solutions highly concentrated in metal; the most dilute solutions measured were about 3.70 N

with respect to sodium or potassium. It is evident that at such high concentrations the application of Raoult's law would have no meaning, particularly in systems of this type which appear to deviate from the law to a greater extent than do typical solutes. Thus one is not justified in using the results of molecular weight experiments in highly concentrated solutions to determine the state of the molecular species, whether it is postulated as a representation of solvent combination or of more simple species. This is one reason why similar arguments proposed by Joannis for the state of aggregation of the so-called metal ammoniums bear little weight. This fact was pointed out by Kraus and Ruff and Geisel (see preceding discussion).

TABLE 2

Apparent molecular weight of sodium in ammonia at different concentrations

CONCENTRATION	APPARENT MOLECULAR WEIGHT	CONCENTRATION	APPARENT MOLECULAR WEIGHT
2.903	32.23	0.3665	25.31
1.841	30.70	0.3587	25.27
1.220	29.06	0.2669	23.53
0.9910	28.80	0.2516	23.43
0.9038	28.46	0.2261	23.41
0.5614	26.39	0.1565	21.62
0.5558	26.47	0.1519	21.58
0.4104	25.36		

Franklin and Kraus (38) determined the molecular weight of sodium and also of lithium in liquid ammonia by the boiling point method. The concentration of the sodium solution ranged from 0.3 N to 1.3 N and the *apparent* molecular weight showed an increase from 36 to 59. Similar results were obtained with lithium. The boiling point method was recognized as not admitting of a high degree of accuracy owing to several factors. In dilute solutions, particularly at the temperature of boiling ammonia, the metals exhibit some tendency to react with the solvent to form the metal amides, which in turn act as catalysts for this reaction. Small amounts of impurities in the metals such as oxides, iron, etc. appear to have a similar effect.

With careful manipulation and exclusion of impurities Kraus (20) devised a method to determine pressure changes resulting in the addition of sodium to liquid ammonia. He was able to secure an accuracy of about 1 per cent when the total pressure change was as small as 10 mm. The measurements were carried out at 15° and the dilutions of the solutions varied from 1 to 13 liters per gram-atom of sodium. He demonstrated that Raoult's law could not be applied to solutions more concentrated in metal than 0.1 *N*. The results are exceedingly interesting in that in dilute solutions the apparent molecular weight is less than 23, while in the more concentrated solutions this value becomes markedly greater than 23. (See table 2.) A value of 23 was obtained at concentrations in the neighborhood of 0.1 *N*. An examination of the vapor pressure curves (figure 1) shows that in the more concentrated solutions the change in the vapor pressure is exceedingly large in relation to the change in composition. Deviations from Raoult's law would be expected to be very great in these regions. It would be desirable to have additional data in solutions more dilute in metal than have thus far been studied, but the difficulties in manipulation and control limit the methods applicable to such systems. Ruff and Zedner (18) also measured the change in the boiling point of solutions of sodium, potassium and lithium. Their results are in agreement with those of Kraus in that, in fairly dilute solutions, the apparent molecular weight is too small and in concentrated solutions it is too great. This corresponds to a deviation in the vapor pressure first on one side and then on the other side of the theoretical curve.

The fact that the molecular weight values obtained in the more dilute solutions are less than 23 is an indication of dissociation. It is known that these solutions are excellent conductors of the electric current and exhibit electrolytic properties in dilute solutions. Since the alkali metals behave as binary electrolytes in this medium, very dilute solutions should show a value of the molecular weight approaching one-half that of the atomic weight of sodium. It may be possible to demonstrate this at a later date.

ELECTRICAL PROPERTIES

A study of the nature of the conduction process in solutions of metals in liquid ammonia has occupied the attention of relatively few workers. On the other hand, the results available to date have attracted considerable interest, since these systems represent a metal dissolved in a non-metallic medium in which a continuous change of one type to the other is exemplified. These results bear an important relation to the metallic state of matter and the process of the passage of electricity in metals.

From the earlier studies it was observed that liquid ammonia is capable of dissolving considerable amounts of the alkali metals to form stable solutions. Studies with solutions of acids, bases and salts in ammonia showed in the pioneering work that the solutions possessed the ability to conduct the electric current. They also demonstrated ammonia to be an excellent dissociating medium. That solutions of the metals should conduct the current with great facility, even to a greater extent than do the typical electrolytes in this solvent, probably would have been beyond the highest expectations.

Cady (39) was the first to make any observations in this direction. He found solutions of sodium in ammonia to be excellent conductors, with the order of magnitude of the conductance being markedly greater than that of typical electrolytes in the same solvent. He also noticed that in concentrated solutions no material effects appear to accompany the passage of electricity, while in dilute solutions there is an increase in the concentration of metal at the cathode. The problem was later studied systematically and thoroughly by Kraus, whose results are reported in a series of papers appearing in the period of 1907–1921 (19, 20, 33, 40, 41, 42, 43). Gibson and Argo (44, 45) and Gibson and Phipps (46) added materially to the problem.

Shortly following, the work of Cady, Franklin and Kraus (47) confirmed the fact that ammonia solutions of the metals conduct electricity without polarization at the electrodes.

The first experiments of Kraus were carried out for the purpose of determining whether or not the conduction process is ionic in nature. This was done by observing the migration phenomena in solutions containing only the metals and ammonia. Since the metals exhibit characteristic colors in solution (48), and in dilute solutions as small an amount as 1/40000 *N* of metal can be easily detected, it is possible to follow changes visually. Thus, a small amount of sodium was dissolved in liquid ammonia in a cell designed for the experiment. On the application of a potential of 110 volts, the color about the anode at once began to grow less intense, while the color in the neighborhood of the cathode deepened perceptibly. The color of the solution above the cathode did not change appreciably and thus served as a standard in determining the colors in other parts of the cell. At the end of half an hour, the cathode region became quite opaque while the anode electrode was visible. No evidence was found of an anode product. When the solution about the anode had become quite dilute, the current was reversed; the clear space at once became broadened in the form of a wedge with the apex at the bottom of the electrode. The blue solution was now in contact with the bottom of the cathode electrode. This effect appeared to be more pronounced in dilute than in concentrated solutions. When the current was measured as a function of the time, it was observed to decrease quite rapidly, and to follow the color changes taking place in the neighborhood of the electrodes.

Kraus (40) interpreted these results as indicative of an ionic conduction process, since a transfer of matter was found to take place with the electric current. The experiments showed sodium to be a constituent of the positive ion, while the negative ion was postulated as being identical with the negative electron which is in equilibrium with the positive sodium ion and sodium metal as follows:

$$\mathrm{Na} = \mathrm{Na}^+ + \mathrm{Y}^-$$

Kraus states:

> Aside from the important fact that the conduction process in metal solutions is an ionic one, which follows at once from the preceding experiments, it remains to examine more closely the phenomena taking place in the neighborhood of the electrodes. We will first consider the anode,

where the phenomenon is less complex. There can be no question that a gaseous product is not evolved here. The solution being transparent, the formation of minute bubbles of gas would readily be observed. At the same time the current is by no means inconsiderable, rising to as much as 0.05 ampere. A current of 10 milliamperes generates a cubic millimeter of hydrogen per second. A gas, therefore, is not evolved. Moreover, no electrolytic product results at the anode by interaction between the negative carrier and the solvent, or the electrode, for in that case we should always have left in the anode space a certain amount of ionic material. In these solutions, however, the resistance increases to something like a million ohms per centimeter in a comparatively short time. The only remaining possibility then, is that the negative ion reacts at the anode to form a soluble neutral molecule. As the electrodes are not attacked, such reaction could involve only the solvent itself.

It is difficult to imagine a reaction taking place between ammonia and the anion Y^- to form a soluble, non-electrolytic substance at the anode, unless ammonia itself constitutes the negative ion Y^-. In that case, of course, the ammonia would be discharged at the anode and simply add itself to the remaining solvent. We must not forget that the ion Y^- is formed by dissolved neutral metal atoms in neutral ammonia and that this solution permits of reversible separation of its components. If the metal forms the positive ion Na^+, as we have shown, then the negative charge only can be associated with ammonia. According to our present views of matter and electricity, negative electricity consists of discrete charges called electrons, whose mass is about 1/1000 that of the hydrogen ion. If we assume tentatively that the metal atoms lose electrons when they dissolve in ammonia, then the solvent may of course take up the negative electrons in some way.

Making use of these results, the above expression may be rewritten as follows:

$$Na = Na^+ + e^-$$

where Na^+ represents the normal sodium ion and e^- the electron. They also indicate that the electron cannot be free as such in ammonia, but that it is undoubtedly associated with the solvent molecules. Thus, the ammoniated electron is in equilibrium with ammonia and the free electron:

$$e^-(NH_3)_n = e^- + n\ NH_3$$

Kraus then carried out some migration experiments with solutions of potassium in potassium amide dissolved in liquid ammonia and was successful in showing that the positive ion obtained by dissolving metallic potassium in ammonia is identical with the positive ion resulting from the dissociation of potassium amide in the same medium.

Measurements of the electromotive force of concentration cells of solutions of sodium in ammonia were made by the same investigator at a later date (41). Transference numbers for several different concentrations were calculated from the results. The ratio of the fraction of the current carried by the two ions was found to approach a limiting value of approximately 7 in dilute solutions, and to increase to a value of 280 at a concentration of a little less than normal. (See table 3.) With a constant speed assumed for the positive sodium ion, the mean speed of the negative carrier increases in the neighborhood of 40 times between 0.001 and 1.0 *N* (53). Previous transference experiments with salt solutions give a value of 130 for the equivalent conductance of the sodium ion. On this basis, the value for the negative carrier is 910, and in dilute solutions of the metals the equivalent conductance should approach a value of 1040. This value is in good agreement with that obtained from conductivity data which were published several years later.

TABLE 3

E.M.F. of concentration cells and values of n and (1 – n)n for solutions of sodium in liquid ammonia

C_a	$E \times 10^3$	n	$(1 - n)/n$
0.870	0.080	0.00359	277.6
0.732	0.328	0.0109	90.6
0.335	0.620	0.0231	41.2
0.164	0.72	0.0291	33.4
0.081	0.86	0.0336	28.8
0.040	1.07	0.0385	25.0
0.020	1.38	0.0575	16.4
0.010	1.80	0.0704	13.2
0.005	2.60	0.0980	9.2
0.0024	3.40	0.125	7.0

Kraus interprets these results on the assumption that the ions Na^+ and e^- exist in solution with the negative carrier surrounded by an envelope of ammonia molecules. The extent of ammoniation of these carriers is postulated as the determining factor in their velocity. He explains his results at higher concentrations in that some of the electrons are freed from the ammonia envelope and consequently move with a speed comparable to that of electrons in metals. This accounts for the rapid increase of the transference number of the negative carrier at high concentrations. The number of free electrons was found to increase as the proportion of metal to ammonia increases, that is, on the basis of transference.

Studies of the conductance of metal solutions have shown that the process is essentially similar to that in aqueous solutions and that our familiar ideas of conduction and dissociation can be extended to ammonia solutions. On dilution, the molecular conductivity approaches a maximum value, just as does that of aqueous solutions, to show that at infinite dilution there is complete ionization. It is perhaps significant, however, that ammonia solutions of strong electrolytes conform more nearly to the law of mass action at low concentrations than do similar water solutions. A rather remarkable fact is that the ions travel faster in ammonia than in water. One cause of this may be the low viscosity of liquid ammonia. Because ammonia is less viscous and is a weaker dissociating agent than water, dilute ammonia solutions are better conductors than dilute aqueous solutions, while water solutions excel when concentrated.

Kraus (43) made an extensive study in which he measured the electrical conductances of solutions of sodium, potassium and lithium over a wide range of concentration. Using small platinum electrodes in his cells, so as to reduce the reaction between metal and ammonia to a minimum, and employing an electromagnetic stirrer to maintain the solutions in equilibrium, he was successful in securing reproducible results. In figure 3, the results of these measurements are plotted for the three alkali metals mentioned above. The equivalent conductance Λ is plotted against the logarithm of the dilution, V. (Since the densities of these solutions were not known at the time of the conductance measurements, the dilution is expressed in terms of 1000 cc. of ammonia). Due to the exceedingly high values for the conductivity at high concentrations, it is not possible to include them on a single graph with the values at low concentrations.

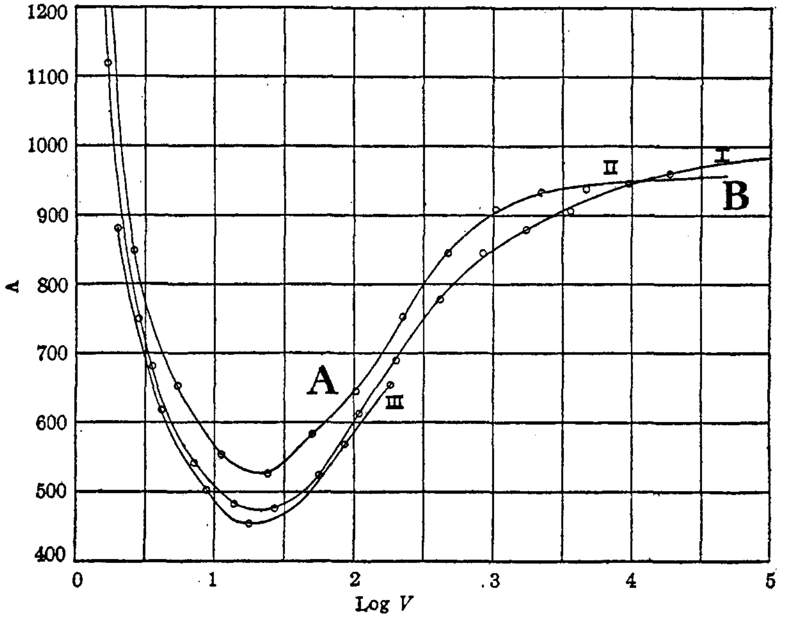

FIG. 3. THE CONDUCTIVITIES OF SOLUTIONS OF SODIUM (I), OF POTASSIUM (II), AND OF LITHIUM (III) IN LIQUID AMMONIA AT −33°

In the dilute regions it is at once noticed that as the dilution increases the equivalent conductance increases and approaches a constant value. The form of the curve in this region, from A to B, is similar to that of ordinary electrolytes dissolved in liquid ammonia. When C is plotted against $1/\Lambda$, where C represents the concentration ($C = 1/V$), a straight line is obtained for the values at low concentrations, which gives on extrapolation a value of 1016 for the equivalent conductance at infinite dilution. (See table 4.) Thus the value of the mass action constant is

77.27×10^{-4}. In the most dilute solutions, some of the points are somewhat irregular owing to the reaction of metal with ammonia. It is interesting to note, however, that the limiting value of the conductance which is approached at low concentrations is very much higher than it is in the case of typical salts dissolved in ammonia. Some salt solutions approach a value as high as 340, which is only about one-third of that reached in the metal solutions.

As the concentration of the metal in solution is increased, the conductivity is noticed to drop off considerably and pass through a minimum at a concentration of about 0.05 *N*. Further increased concentration of metal causes the conductance to rise rapidly to values of almost unimaginable dimensions. For a concentration of approximately normal, the equivalent conductance rises to a value of approximately 3000, while at 2 *N* a value of 80,000 is reached for sodium solutions. Kraus and Lucasse (17) have determined values for saturated solutions of sodium and potassium and have found the specific conductivities to be 0.5047×10^4 and 0.4569×10^4, respectively. The specific conductance of mercury is 1.063×10^4, which value is only a little more than twice that of a saturated solution of sodium in ammonia and only 6 times that of a solution 2 *N* in sodium. If a comparison is made

TABLE 4

The conductance of sodium in liquid ammonia at −33.5°

V	Λ	V	Λ
0.5047	82490.0	13.86	478.3
0.6005	44100.0	30.40	478.5
0.6941	23350.0	65.60	540.3
0.7861	12350.0	146.0	650.3
0.8778	7224.0	318.6	773.4
0.9570	4700.0	690.1	869.4
1.038	3228.0	1551.0	956.6
1.239	2017.0	3479.0	988.6
2.798	749.4	7651.0	1009.0
6.305	554.7	17260.0	1016.0
		37880.0	1034.0

on the basis of atomic conductances instead of specific conductances, a better correlation is noted. For example, the atomic conductance of iron is 0.8031×10^6, of strontium, 0.7194×10^6, and of mercury, 0.1564×10^6, while that of a saturated solution of sodium in liquid ammonia is 0.6720×10^6, if the assumption is made that the density of the solution is equal to that of the pure solvent. Since the density is now known to be considerably less than that of the pure solvent, the above value calculated for sodium is less than the true value. It is quite apparent that such large conductance values can not be attributed to electrolytic conduction.

If a value of 1016 is taken for the equivalent conductance at infinite dilution, and a value of 130 for the equivalent conductance of the sodium ion, the equivalent conductance of the negative carrier must be 886. This value is in good agreement with that obtained from the results of electromotive force measurements in dilute solutions. If the negative carrier at low concentrations is the electron, it immediately follows that it must be assumed to be associated with solvent molecules to account for its low conductivity. If it were free to move without any solvent disturbances or combinations, it would readily move much faster than is indicated by the results of conductivity measurements. Jaffe (49) has measured the speed of the electron produced by radiations in hexane and found a value of 4.17×10^{-4} centimeters per volt second. On the basis of the value of the conductance of the electron in ammonia solutions the speed of this negative carrier is 91.7×10^{-4} centimeters per second. So the electron appears to move much faster in ammonia than in hexane. Since the dielectric constant of ammonia is much higher than that of hexane, it would be expected that the electron would be less associated with solvent molecules in ammonia than in hexane. That the combination is not a very stable one is seen in the high conductance values at high concentrations, where a large part of the negative carriers must be free to move without the constraints of the solvent, much as the electron moves in metals. The ammoniated electron may be looked upon as possessing a stability of the order of magnitude found in the ammoniation or hydration of other ions.

Kraus has summed up the results of his studies of the conductivities of solutions of metals in liquid ammonia (43):

> These solutions, therefore, constitute a connecting link between metallic and electrolytic conductors. In dilute solution the process is, at least in part, electrolytic. A portion of the current is carried by 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 the 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 solution increases, the nature of the phenomenon changes only insofar as the combination of the negative carrier with ammonia is effected. At the higher concentrations, the negative carriers are free from association with 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 the 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 bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in metals. As the concentration is further increased, the number of free carriers 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 the 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 ammonia.
>
> 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 the 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 radioactive and other phenomena.

Gibson and Phipps (46) measured the conductance of solutions of sodium and also of potassium in liquid ammonia, and of cesium, cesium iodide and potassium in methylamine at several different temperatures. Their results in liquid ammonia correspond well with the measurements of Kraus. They used a constant volume method, and it was possible for them to express the concentration of the solutions in terms of volume normal. Since the densities of these solutions at high concentrations are exceedingly abnormal, deviations in the conductance as determined by the two methods are more marked; however, in the more dilute solutions, the agreement is good. Their results in methylamine solutions are very interesting. They found the metals to be less ionized in methylamine, with the minimum in the conductivity occurring at a higher concentration than in ammonia. The properties of the metals in solvents related to liquid ammonia constitute another subject which cannot be discussed here at length.

The resistance-temperature coefficient of dilute solutions of sodium in ammonia has been shown by Kraus (43) to be positive and, in the neighborhood of the boiling point of liquid ammonia, to have a value of about 2.5 per cent per degree in terms of the resistance at the boiling point of ammonia. In the more concentrated solutions, similar measurements were carried out by Kraus and Lucasse (21) from the saturation point to a dilution of 5.02 liters and at temperatures from $-33.5°$ to $-60°$. The temperature coefficient of a saturated solution was found to have a value of 0.066 per cent. With decreasing concentration, the coefficient increases markedly, passing through a maximum value of about 3.6 per cent at a dilution of 1.1 liters, and thereafter decreases to a value of about 1.55 at dilutions above 4.0 liters. In the case of potassium solutions (50) similar results were obtained. Gibson and Phipps measured the temperature coefficients of resistance for sodium and potassium solutions with corresponding results. They calculated the differential temperature coefficient, which was found to be independent of the temperature. In other words, the conductance is an exponential function of the temperature at all dilutions.

That the negative carrier is the same in all solutions of metals in ammonia has been well brought out by Gibson and Argo (44, 45) in their photometric measurements. They determined the absorption of lithium, sodium, potassium, magnesium and calcium solutions at low concentrations and obtained practically identical results. The absorption curves for all these metal solutions were found to be the same. This result must necessarily lead to the assumption that in these solutions there is present a particle that is common to all. Since the experiments were made in dilute solutions, in which there are no free electrons, it would appear that the color and the absorption is due to complexes being formed between the electron and solvent molecules. It would be highly interesting to investigate the absorption of these solutions at higher concentrations where there are present negative carriers that are not associated with molecules of ammonia.

DENSITIES

Seely (4) observed in his first qualitative experiments that an increase in volume results when ammonia is added to the alkali metals. Kraus and Lucasse (17, 21) noticed this abnormal change and made some calculations based on the volume of their conductivity cells. They calculated the density of a saturated solution of sodium in liquid ammonia to be 0.54, and that of a saturated potassium solution, 0.632. The density of pure liquid ammonia at −33.8° is 0.6824 (51). Kraus, Carney and Johnson have measured the density of sodium solutions over a fairly wide range of concentration at −33.8°. A value of 0.5782 was found for the density of the saturated solution. This means that if a saturated solution of sodium in ammonia is prepared, one in which for every gram-atom of sodium (23 grams) there is present approximately 93 grams (5.5 moles) of ammonia the volume of the mixture is markedly greater than the sum of the volumes of the two constituents. Twenty-three grams of sodium occupy about 23 cc. and 93 grams of liquid ammonia about 135 cc. at

−33°. If no change in volume were to take place when the sodium is dissolved, the total volume of the solution would be about 160 cc. However, calculations from the measured density as given above show that the total volume is slightly more than 200 cc., which represents a volume increase of 41 cc. or approximately 25 per cent. No other system shows a volume change of such magnitude.

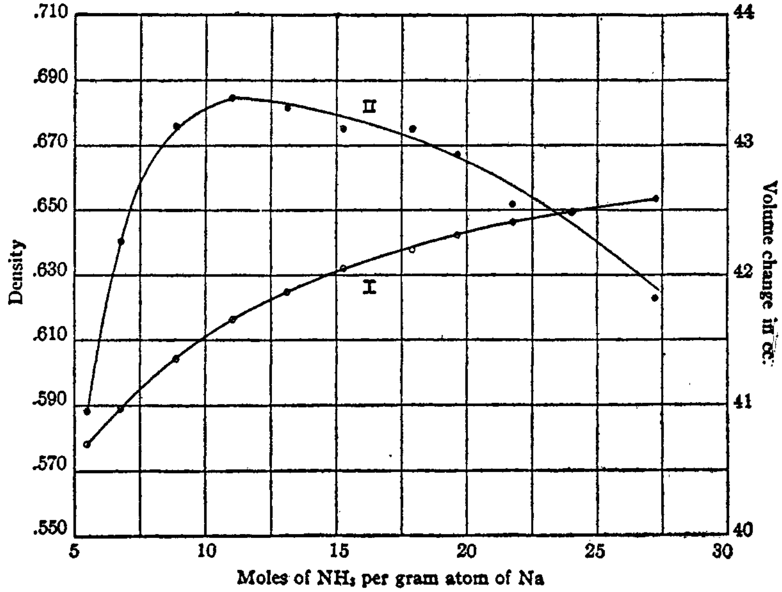

FIG. 4. THE DENSITY AND VOLUME CHANGE FOR SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT −33.8°

The results for sodium solutions are plotted in figure 4. Curve I represents the density as a function of the concentration expressed in terms of gram-molecules of ammonia per gram-atom of sodium. Curve II gives the volume change accompanying the formation of the solutions from their components. The density is seen to increase steadily with increasing dilution and to approach the value for pure ammonia at low concentrations. The volume change for a saturated solution is about 41 cc. per gram-atom of sodium. With decreasing concentration, the volume change first increases, reaching a maximum of 43.4 cc. per gram-atom of sodium at a concentration of 11.25 gram-molecules of ammonia per gram-atom of sodium. At still lower concentrations the value of the volume change decreases slowly.

Johnson and Meyer (16) have made some measurements of the densities of sodium and potassium solutions. In the case of the sodium solutions, the density was determined at a concentration as low as 64.14 gram-molecules of ammonia per gram-atom of sodium, and as high as that of the saturated solution. These values agree with those shown in the figure, while the values at low concentrations give a regular curve. When it is extrapolated to infinite dilution, a value for the density of pure ammonia is obtained which agrees with that given by Cragoe and Harper. The density of a saturated solution of potassium in liquid ammonia is somewhat higher than that for sodium. The value at $-33.2°$ is 0.6282. This is in good agreement with the value calculated by Kraus and Lucasse. The form of the density curve for potassium is the same as that for sodium. The volume change curve is also of the same type; a value of 27.34 cc. per gram-atom of potassium is found for the saturated solution. As the solution becomes more dilute in metal, the volume change increases to a maximum value of 29.50 at a concentration of about 13.0 gram-molecules of ammonia per gram-atom of potassium; then, in the more dilute regions, the volume change gradually decreases.

If one examines the densities of solutions of ordinary salts in liquid ammonia (16), no abnormalities are found. A solution of sodium bromide in ammonia has a density greater than that of pure ammonia, and as the solution is diluted the density decreases and approaches that of ammonia. Thus, the increase in volume noted in the case of the metal solutions can not be attributed to the metal ions; it must be due to the negative constituent, the electron associated with solvent molecules. The envelope of ammonia molecules associated with the electron must possess a considerable volume to account for these results. The partial molal volumes have been calculated (16) for sodium and potassium in liquid ammonia as well as for some of the salts in this medium. It is quite probable that when sufficient data of this nature have been collected, so that a comparison may be made of the metal solutions with the salt solutions at very low concentrations, more may be said about the nature of this negative constituent. It should be possible to obtain a relative value for the volume occupied by the ammoniated electron.

ACTIVITIES

An examination of the form of the vapor pressure curves (figure 1) for solutions of metals in liquid ammonia reveals a tremendous change in the vapor pressure with composition, particularly in the more concentrated regions. In order to apply the vapor pressure results for a comparison of the various thermodynamic functions for different metal solutions, the activities of metals in liquid ammonia have been calculated (16). For this purpose the Duhem equation is applied in the following form:

$$d \log a_2 = - N_1/N_2 \, d \log a_1$$

If the mole ratio N_1/N_2 is plotted as ordinates against $10 + \log a_1$ as abscissae, then, upon integrating between the limits a_s and a_m, where a_s is the activity of the saturated solution which, as a standard, may arbitrarily be set equal to unity, and a_m is the activity at any molality m, the following is obtained:

$$\log a_m/a_s = - \text{Area under the curve between } a_s \text{ and } a_m$$

In this calculation a_1, the activity of the solvent, is set equal to p_1/p_1^0, where p_1 is the vapor pressure of the solution at any given temperature, and p_1^0 is the vapor pressure of the pure solvent at the same temperature. Such calculations of a_2, the activity of the metal, have been carried out for lithium, sodium and potassium in liquid ammonia at different temperatures. With the value of a_2 taken as 1.0 for the saturated solution in each case, calculations show it to be greatly reduced as the concentration of dissolved metal decreases. The activity of potassium changes about 25,000 times at 0° as the concentration changes only 2.571 times, and for lithium the change is about 3×10^9 for a change in concentration of about 4.0 times (temperature of −39.4°). The large change here is due to the fact that the vapor pressure changes from 4 mm. to 500 mm. over a very small range of concentration. The activity change with concentration in the case of sodium is less than that found for potassium. Brönsted (52) gives values for sulfuric acid in which the change in activity is approximately 2500 times for a concentration change of 17 times.

When vapor pressure data are available for these solutions in the more dilute regions, it would be desirable to calculate the activities on the basis of a 1 N solution as the standard state; thus all calculations might be placed on a comparable basis. Then a comparison of the activities of the metals in ammonia could be made with those of salts in the same solvent under comparable conditions. Such a comparison would undoubtedly lead to interesting results.

PHOTOELECTRIC PROPERTIES

A preliminary experiment has been carried out by Kraus (43) to determine whether or not the solutions of metals in ammonia exhibit photoelectric activity. He introduced 0.25 gram of lithium into a tube with a platinum wire sealed in at the bottom to make contact with the metal solution. An aluminum wire was fixed about 3.5 centimeters above the surface of the metal and connected with an electrometer. When the metal dissolved in the ammonia, a photoelectric activity was immediately observed. With a 16-candle power lamp held about a foot from the metal, the electroscope was found to discharge in 5 seconds. It was also observed that the discharge took place with negative as well as positive charge of the electrometer system. This action is explained by the fact that, owing to the presence of the platinum wire in the solution, decomposition takes place rapidly and particles of the solution are projected on the aluminum wire. It was observed that the photoelectric effect is not due to free metal since, in the experiments, the vapor pressure of the solution was much above that required of a saturated solution. The effect is therefore due to the solution of lithium in ammonia.

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