N69-29708

FINAL REPORT COVERING PERIOD
FROM 8-21-64 THROUGH 7-31-67

Prepared for
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

Under
CONTRACTS NAS7-326 AND NAS7-437

GASEOUS ELECTROLYTES FOR BATTERIES AND FUEL CELLS

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C97-55806

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ABSTRACT

This program was undertaken to investigate the properties of dense gaseous electrolytes in relation to their application to energy conversion. Ammonia was used as the principal solvent due to its favorable critical properties. It was established that electrolytes using gaseous ammonia solvents are well behaved under equilibrium conditions. A typical dynamic process, the plating of silver from a silver nitrate ammonia-solution, was used to study the differences in liquid electrolyte-electrode and dense gaseous electrolyte-electrode interactions. Measurements were also made of the conductivity of dense gaseous silver nitrate-ammonia solutions. These measurements were carried out in conjunction with theoretical studies of the nature of dense gaseous electrolytes. The solvation of Cs^+ and the ionization of the salt cesium chloride in ammonia were subjected to a detailed theoretical examination.

INTRODUCTION

As early as 1878 to 1880, Hannay and Hogarth(1) showed that salts in gaseous methyl alcohol are solvated at temperatures as much as 100° above the critical point of the solution (240°C). The temperature was limited by the apparatus; there was no evidence of cessation of solvation at the highest temperatures attainable. Hence, solvation of ions by solvent molecules is not a critical phenomenon, but one that extends indefinitely into the dense-gas region. It was subsequently shown that other solvents, including water, exhibited ionizing power in the dense gas state(2).

Recently, Sourirajan and Kennedy(3) have shown that the solubility of sodium chloride in gaseous water increases with temperature and pressure, and that the limitation on attaining even higher solubilities than they obtained at 700°C (26.4% by weight) was due to limitations of their apparatus. They conclude that the solubilities would increase continuously at still higher temperatures and pressures until one obtains a one hundred per cent gaseous sodium chloride phase.

Fogo, et al(4) have measured the conductivities of NaCl in supercritical steam. The measurements covered a rather restricted range of experimental conditions, but the results are suggestive of exceptionally good electrical conductivity at temperatures and electrolyte concentrations somewhat beyond the range of their investigations. Mobilities, degrees of dissociation, and solubilities all increase with increasing temperatures in the liquid state until the liquid densities decrease too much so that the dielectic constant falls off.

Although gaseous electrolytic solutions have been studied for 85 years(1), they have not been discussed in text books, and are therefore not generally well known. Nontheless, one practical industrial production process(5), uses dense gaseous aqueous solutions in manufacturing quartz crystals by hydrothermal synthesis at about 400°C. This process is practical industrially because the solubility of SiO_2 in gaseous water is sufficiently high so that the rate of crystal growth is rapid enough to be useful. A few dozen other refractory minerals have also been synthesized in the laboratory by this technique.

This program of study was undertaken to extend the knowledge of dense gaseous electrolytes and provide information upon which to base practical applications. Of particular interest are power conversion applications where gaseous electrolytes can provide higher operating temperatures, lower electrolyte resistance and gravity independence. Also of interest are some diffusion limited applications such as special deposition processes.

The results of this program have, for the most part, been prepared as publications and submitted to various journals. This report consists of published papers, submitted papers and papers prepared for submission along with supporting material.

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THE BEHAVIOR OF AMALGAM CONCENTRATION CELLS USING A DENSE GASEOUS AMMONIA ELECTROLYTE*

by

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Solutions of salts and metals in dense gaseous solvents such as water and ammonia often exhibit liquid-like properties. Thus, gaseous water can be an excellent solvent for sodium chloride(1) and produces solutions which are electrolytic(2). Similarly dense gaseous sodium-ammonia solutions exhibit conductivities and colors similar to those of liquid solutions(3). On the other hand, some properties of these solutions, such as the absence of surface tension and the pvt relations, are gas-like. The present experiments were undertaken to see whether electrochemical reduction and oxidation processes at electrode-dense gaseous solution interfaces are well behaved as in the liquid state or whether they exhibit gaseous properties. The characterization was carried out by measuring the emfs of cells over an appreciable range of temperature with electrolyte in the liquid and dense gaseous states.

The cell couples for these studies had to use a common electrolyte to avoid gaseous junctions** since it would be difficult to maintain two half cells under different pressures with an adequate electrolytic conducting path between them. Of such junction-free cells, amalgam concentration cells were chosen since, if all of the

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* This work was supported by NASA under Contract NAS7-326.

** The gaseous equivalent to liquid junctions.

processes occurring in a cell are reversible, the state of the electrolyte should not affect the emf; that is,

$$Na(x_2' \text{ in Hg}) = Na(x_2'' \text{ in Hg}) \qquad (1)$$

and

$$-ENF = nRT \ln(a''/a') \qquad (2)$$

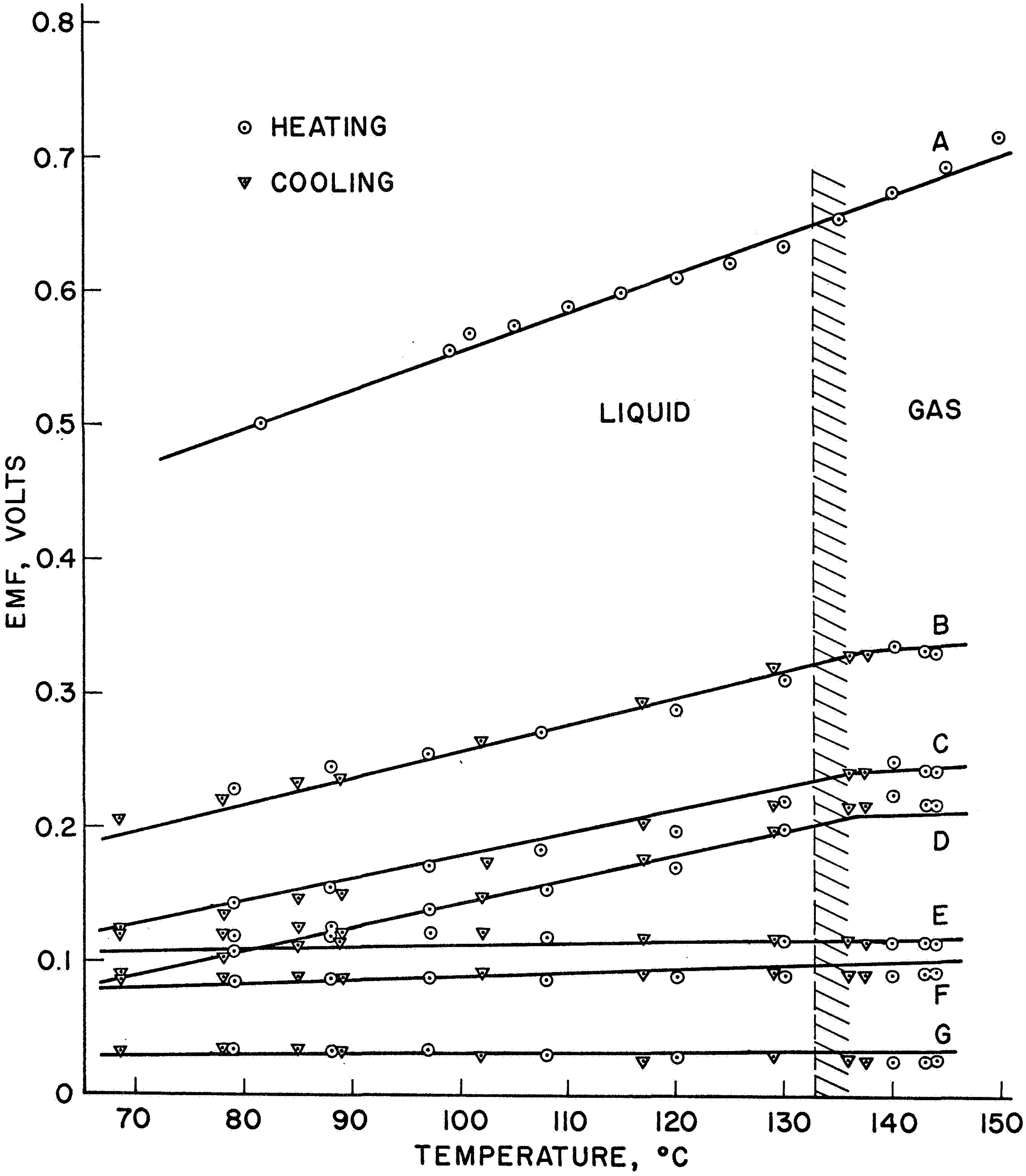
where a'' is the activity of Na in amalgam A''.

The chemicals used in these cells were specially prepared to remove contamination, which increases the tendency to bubble when NH_3 is used in the liquid state with no foreign atmosphere. Sodium (99.95%) was purified by multiple distillation and ammonia (99.99%) by passing it through an activated charcoal trap, then allowing it to stand as a liquid over sodium metal for 14 hours. Mercury was added to the individual electrode compartments using a hypodermic syringe before the cells were sealed onto the bakeable glass vacuum system for filling. Above each cell was located a sodium capsule and an ammonia condenser. The system was subjected to a mild vacuum bakeout so that only a little mercury was evaporated. After cooling, the breakseal to the sodium capsule was smashed and the sodium distilled into a cup below the condenser. Prepurified ammonia was then condensed onto the sodium and the solution allowed to flow into the cell at -78°C.

After seal-off, the cell was stored at low temperature for about a day. This allowed the sodium to be leached out of the ammonia by the mercury, forming amalgams, and to react with the ammonia , forming slightly soluble sodium amide, leaving a colorless solution. The cells were maintained under excess pressure in a temperature controlled steel high pressure vessel during runs to minimize breakage. The temperatures were measured using a copper constantan thermocouple and a K3 potentiometer, and the emfs were measured using a Calibration Standards DC110B electronic potentiometer.

The emfs for several electrode pairs are shown in Figure 1 for sodium mole fractions ranging from 10^{-7} to over 0.18. The compositions of the two-phase amalgam are based on the phase diagram of Hg-Na(4). The compositions of the one-phase amalgams were determined from the emfs with two-phase amalgam electrode half-cells using equation (2). The experimental data closely follow the analytical curves for amalgam concentration cells calculated using correlations of Iverson and Recht(5) for activity coefficients. In the absence of deviations of the data from the analytical curve, it is concluded that dense gaseous $NaNH_2$-NH_3 electrolytes are well behaved.

LIST OF FIGURES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Reprinted from Journal of The Electrochemical Society

Vol. 115, No. 9, September 1968

Conductivity Cell for Use with Dense Gaseous Electrolytes

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The principal problem in the measurement of conductivities of supercritical electrolytes is that of containing the electrolyte at the high temperatures and pressures involved. One approach is to use a cell with sufficient strength to withstand these conditions. This generally involves a massive steel cell having electrical insulators and a chemically inert lining to avoid reaction with the electrolyte (1). In our studies of supercritical electrolytes having ammonia (NH_3) as the solvent, we have used a glass conductivity cell and avoided rupture of the cell by matching the internal pressure of the electrolyte with an external pressure. The critical properties of ammonia (132.9°C, 112 atm) are convenient for this method, while the use of glass simplifies the handling of ammonia and leads to a cleaner system than could be easily obtained with a metal cell.

In order to apply the required external pressure the cell must be placed in a high-pressure vessel and hence must be compatible with the interior dimensions of this vessel. In the present case the high-pressure chamber was 38 mm in diameter. The spatial restrictions made the use of a d-c conductivity measurement attractive, as difficulties due to high interelectrode capacitance would then be avoided. D-C measurements are best carried out using the four probe method (2) in which two electrodes produce a current through the electrolyte while two additional electrodes, positioned between the current carrying electrodes, are used to measure the voltage gradient set up in the electrolyte. The voltage measuring electrodes should be reversible in the electrolyte being investigated and no current should be drawn through them when the voltage is measured.

The cell is shown in Fig. 1. It is divided into four electrode compartments joined by the central cylindrical section, hereafter called the conductivity tube. The two extreme electrodes (1 and 4) are used to carry the current, which flows through the conductivity tube. The intermediate electrodes (2 and 3) measure the voltage across the middle section of the conductivity tube. This potential difference is measured through a pair of narrow slit apertures perpendicular to and encompassing the whole circumference of the conductivity tube.

The end portions of the conductivity tube serve to reduce end effects and to allow the current density to become constant and uniform through the middle section. The use of slits rather than holes for the measuring electrode serves to average out any nonuniformities still existing, as well as being much narrower for the same area. The cell constant is therefore geometically well defined and can be taken as equal to $K = 4L/(\pi d^2)$ where L is the separation of the measuring slits and d is the internal diameter of the tube.

Key words: Conductivity cell, dense gaseous electrolytes, supercritical electrolytes, ammonia.

The electrode leads are brought into the cell through tungsten-uranium glass seals. The electrode compartments are suitable for containing amalgam electrodes of the sort sometimes used in ammonia (3), in which case the tip of the tungsten feedthrough is left bare and completely immersed in the amalgam. If solid metal electrodes are to be used, platinum wire is fused to the tungsten. All of the tungsten and part of the platinum are covered with glass. The exposed platinum is then welded to the electrode material.

The freeze cup was used in the sealing-off operation after filling the cell with ammonia. The ammonia was condensed in the cell and held there with the cell at –78°C in a dry ice, alcohol bath. Liquid nitrogen was poured into the freeze cup causing a plug of solid ammonia to form in the capillary. The system above this plug was then pumped to a high vacuum and the cell sealed off by fusion of the capillary above the freeze cup. This procedure allows the seal off to be made under high vacuum, reducing the impurities trapped in the cell. Its usefulness depends on the properties of the solvent being used.

The main problem in fabrication was making the conductivity tube, which must be sealed through the walls separating the electrode compartments without changing its internal dimensions. This was accomplished by collapsing a piece of ordinary glass tubing over a drill rod of the desired diameter by heating the tubing while maintaining a partial vacuum inside it. With the tube hot and the drill rod still inside, glass flanges were built up on the tube at the desired locations. These flanges were then sealed to the outer tubing and became the walls between the electrode

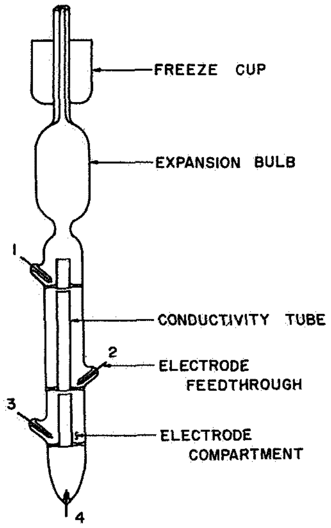

Fig. 1. Conductivity cell. Axis of cell is vertical in use

Table I. Effect of slit width on cell constant

Cell	d, cm	L, cm	W, cm	K, mhos/cm	K_{Hg}, mhos/cm	K_{KCl}, mhos/cm
A	0.4727	4.720	0.416	26.90	27.69	27.35
B	0.4747	4.774	0.041	26.98	26.94	25.56
C	0.4762	4.761	0.012	26.73	26.66	26.03

compartments. The different sections of the conductivity tube were held in alignment during cell fabrication by a carbon rod. When made in this way, the conductivity tube had a constant diameter over its whole length and could be made with very narrow voltage measuring slits.

The choice of slit widths is governed by the desired accuracy of the cell constant, the maximum allowable resistance between the measuring electrodes, and the requirement that good diffusion exist between the various parts of the cell. In order to examine the effect of slit width on the cell constant, three cells with different slit widths, W were built and the cell constants determined both geometrically and by measuring the cell resistance with known materials, namely, mercury and $1N$ KCl solution. Results are shown in Table I.

It is apparent that the slits in cell A, which are of about the same width as the diameter of the conductivity tube, are too wide for the geometrical cell constant to be meaningful. With cells B and C, however, the agreement between calculated and observed cell constants is good, particularly in the case of mercury. It should be noted that no special precautions were taken in the preparation of the KCl solution, ordinary reagent grade KCl and commercially bottled distilled water being the ingredients used. The conductivity of mercury is much less sensitive to the precautions taken than KCl solutions, and the values of the cell constant with mercury are therefore considered much more accurate. The tests indicate that for conductivity tubes whose length is much greater than their diameter, the use of voltage measuring slits of width 10% of the conductivity tube diameter or less will give a cell constant which can be easily calculated to better than ½%.

The cell has been used for conductivity measurements of solutions of $AgNO_3$ in NH_3 at temperatures well above the critical point of NH_3. Figure 2 shows the voltage drop measured across the conductivity tube as a function of the cell current obtained with a supercritical $AgNO_3$-NH_3 solution and using electrodes of high purity silver wire throughout. The linearity of the graph indicates that the cell is well behaved. The small emf (~ 1 mv) between the voltage probes may be due to surface impurities on the electrodes or to a small difference in the compositions of the electrolytes in the two electrode compartments. The cell used had 0.1 cm slits and a cell constant of 24 cm^{-1}. Conductivity cells suitable for d-c measurements with dense gaseous electrolytes can thus be fabricated with the desired, geometrically defined cell constant.

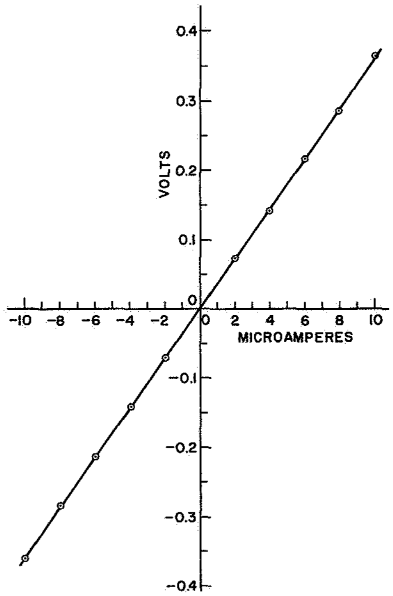

Fig. 2. Voltage drop across conductivity tube vs. cell current. Electrolyte is $AgNO_3$ at 0.02 moles/liter in dense gaseous NH_3 at 22 moles/liter and 151°C. Positive current flows upward.

Acknowledgment

This work was sponsored by National Aeronautics and Space Administration under Contracts NAS 7-437 and NAS 7-326.

Manuscript received Feb. 15, 1968.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1969 JOURNAL.

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ELECTRODEPOSITION OF SILVER FROM DENSE GASEOUS SOLUTIONS OF SILVER NITRATE IN AMMONIA*

by

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ABSTRACT

Silver was electrodeposited on platinum electrodes from solutions of $AgNO_3$ in NH_3 at temperatures from -70°C to 140°C. The solutions were 0.036 molar in $AgNO_3$ at -78°C. In the dense gaseous region, the concentrations of $AgNO_3$ and NH_3 were 0.018 and 22 moles/liter respectively.

The deposit was observed to become more and more crystalline in appearance as the temperature approached the critical temperature of NH_3(133°C). All electrodeposits at temperatures above 133°C were characterized by either dendritic or needle-like growths on sharp edges and corners. These were not observed at lower temperatures. Both three and four sided symmetries were observed, suggesting that the deposits were growing in the [111] and [100] directions, respectively.

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*Work supported by NASA under contract NAS 7437.

INTRODUCTION

The process of electrodeposition out of a dense gaseous electrolyte is expected to have characteristics intermediate between comparable deposition processes out of the gaseous and liquid phases. This expectation is based on the continuous transformation of many properties, as gas densities are increased, from gaseous to liquid-like. Thus the dielectric constant of dense gaseous water exhibits a rapid increase with increasing density(1). The solubility of NaCl in dense gaseous water at 750°C increases with increasing solvent density until it exceeds the solubility in liquid water at room temperature(2). However, ionic mobilities of dense gaseous electrolytes are expected to be higher than those of liquids. In addition, the dense gaseous medium is effectively without surface tension.*

Because of the absence of surface tension, hydrogen produced during electrolysis in a gaseous electrolyte, when desorbed, is expected to diffuse away from the cathode surface rather than being trapped there as bubbles. Such bubbles may interfere with the continuous growth of crystalline metallic deposits from a liquid electrolyte. In general, foreign material appears to inhibit continuity of crystalline growth out of both liquid and gaseous states. Traces of impurities have been shown to play an important role in determining relative growth rate in aqueous solutions(4). The use of a solvent which reacts with metal may produce a chemisorbed surface which may interfere with continuous crystal growth. For

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*However, Knapp and Sabersky has shown that, under large temperatures differentials, bubble-like flow can be produced in dense gaseous CO_2(3).

the present experiments ammonia was chosen as the solvent not only because of its convenient critical constants (132.9°C, 112 atm), but because of its chemical inertness toward metals (e.g. Na at 190°C in the absence of catalysts). Silver nitrate was chosen as the salt because of its solubility in liquid ammonia as well as the insolubility of the electrodeposited metal in ammonia.

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*Data to 165°C have been reported(5), more recent unpublished data in this laboratory show the same inertness to 190°C.

EXPERIMENTAL

The cells (Figure 1) were made from 30 mm (O.D.) borosilicate glass tubing and were about 8 cm long, exclusive of the freeze valve. The internal volumes of the cells ranged between 35 cc and 40 cc. Three of the four electrodes were used as cathodes while the remaining one was used as the anode.

The anode was a platinum wire of either 0.4 or 0.5 mm dia. fused to a 0.75 mm diam. tungsten wire. The tungsten wire was brought into the cell through a uranium glass seal and the glass extended along the wire to completely cover the tungsten and part of the platinum wire. The glass-covered part extended 1 to 2 cm into the cell while the exposed platinum wire extended another 4 to 5 cm.

Several types of cathodes were tried but only two proved to be useful. The first of these was a platinum wire identical to the anode. The second was made by cutting the platinum wire flush with the feedthrough glass covering the tungsten and the lower portion of the platinum wire. The wire cutters used left the end of the wire in a wedge shape. Thus the exposed part of the cut off type cathode was wedge shaped, as was the end of the long wire type cathode.

Each cell was prepared as follows. Reagent grade silver nitrate was introduced into the cell which was then sealed onto the vacuum system. The system was then baked out under vacuo at 100°C for an hour. Pumping continued while the ammonia was being prepared. Tank ammonia (Matheson, 99.99%) was passed through an activated charcoal trap and stored overnight as a liquid over metallic sodium.

The ammonia was then condensed in the cell, which was maintained at -78°C with a dry ice-alcohol bath. When the liquid level rose to a calibrated mark on the cell, the introduction of ammonia was discontinued. The fiducial mark was located at 50% of the sealed-off cell volume. At -78°C, the filled cell contained 0.036 N $AgNO_3(NH_3)$. When heated into the dense gaseous state, the solution would be 0.018 molar in $AgNO_3$ and 22 molar in NH_3, assuming that all of the $AgNO_3$ remained in solution.*

The solution in the cell was maintained at -78°C and liquid nitrogen poured into the freeze cup above the cell. In this way the electrodes were not subjected to thermal shock and strain. A solid ammonia plug formed in the capillary in the freeze valve. The plug was pumped to high vacuum and the cell sealed off.

The wires on the filled cell were soldered onto leads going through a head in a high pressure vessel and the cell placed therein. External nitrogen pressure inside the pressure vessel was used to keep the glass under compression thereby preventing the ammonia pressure within the cell from rupturing the glass cell. The external pressure was kept about 30 atm above the predicted internal pressure(6) during heating of the cell and electrodeposition.

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*It is probable that all or at least most of the $AgNO_3$ remained in solution in the dense gaseous phase. The overall conductance of the cell with the gaseous electrolyte was comparable to that of the liquid at room temperature. The situation is slightly complex because with increasing temperature the amount of the electrode exposed to the solution increases as the solution expands.

RESULTS

The initial runs were done using the long cathodes at current densities of 1 to 2 ma/cm^2 for from 600 to 800 sec. Deposits made from the liquid showed increasingly crystalline appearance as the critical temperature was approached. At -70°C the deposit appeared black, fluffy and non-metallic. At 15°C the deposit was smooth and "silvery", giving spectral reflection. At 103°C the deposit was "silvery" or metallic in appearance but somewhat sparkly, suggesting some crystallinity in the deposit.

At temperatures above the critical point of ammonia, the deposits were much more crystalline in character, as can be seen from Fig. 2. This shows the wedge shaped tip and some of the cylindrical body of a wire type cathode. Electrodeposition was carried out for 690 sec. at a current density of 1.6 ma/cm^2 and a voltage of 0.5 V. The deposit on the body appears to be made up of tiny crystals while at the tip are several projections which are presumably single crystals of silver. These are in the form of four sided square cylinders with uniform cross section over most of their length but starting from a narrower base and ending in a pyramidal point.

Figures 3 and 4 show photographs of much larger needles and dendrites grown on cut off type cathodes. Because only the sharp, wedge shaped tip is exposed in these cathodes, the dendrites tend to cover the entire cathode and to rapidly increase the effective cathode size as they grow. Thus it was possible to grow much larger dendrites in a shorter time. In this case the electrodeposition was done at constant voltage rather than constant current, the current being allowed to increase as the deposit, and hence the effective electrode area, grew. The voltages used were 1.05 v and 0.85 v, respectively, while the total charges passed were 2.2 and 2.4 coulombs, respectively.

In Fig. 3 the needle like growths are up to 6 mm in length. Examination of the longest growth with a low power microscope reveals that it consists of a three-sided central stem coming to a sharp point at one end and having the sides covered with short, stubby growths. These growths show both rectangular and hexagonal symmetries while there are also some longer, pointed branches, having three sides like the central stem. The dendrite shown in Fig. 4 is 7 mm long and has the central stem completely covered with branches growing perpendicular to the stem in two perpendicular planes. Although the branches tend to obscure the central stem, examination under a low power microscope suggests that it is four sided with three-sided fern-like branches growing from the edges.

It should be noted that dendrites of the type shown in Fig. 4 occurred only in one run while the needle like growths of Fig. 3 were obtained in several runs. The difference is believed to be due to the presence of impurities giving rise to the dendrites.

DISCUSSION

The results indicate that there is a strong tendency for crystalline needles or dendrites to grow from sharp corners on the cathode in gaseous $AgNO_3$-NH_3 solution. The tendency for dendrites to grow on sharp corners was also found and explained by Arouete and Blurton in their studies of the electrodeposition of zinc in silver-zinc batteries(7). A detailed account of the electrocyrstallization process has been given by Bockris and Damjanovic(8).

The observation of triangular and square symmetries suggests that the central stem and branches of the dendrites were growing by the propagation of screw dislocations in the [111] and [100] planes, respectively. Silver dendrites have been grown out of aqueous solution at room temperature by Wrangler(9) who observed only a flat form of dendrite which he deduced to be growing perpendicular to the [110] plane with the branches in the [111] plane. With other metals (e.g. zinc) he also observed [100] dendrites of a similar form to that shown in Fig. 4. In these experiments a supporting electrolyte (e.g. NH_4NO_3) was added to the metal salt ($AgNO_3$), and the current density was found to be an important factor in dendritic growth. In the present experiments, no supporting electrolyte or precautions regarding current density were necessary, but needles or dendrites were obtained on sharp corners whenever electrodeposition was performed in the supercritical region of ammonia.

The tendency for continuous crystal growth is probably strongly inhibited in the liquid, partially due to hydrogen bubble formation interrupting the growth on a single crystal face. It may also be that the mobility of adsorbed ions over the crystal surface is greater when the electrolyte is gaseous, thus allowing the ions to reach the sites of lowest activation energy so that the crystal structure is preserved as the deposit grows. It should be noted that as the critical region is approached the differences between liquid and gaseous fluids become small so that it is not surprising that as low as 100°C the surface becomes sparkly due to small crystals.

The results are somewhat similar to those of vapor deposition in that with increasing temperature, vapor deposits tend to become more crystalline.

Finally, the ease with which fairly large crystalline electrodeposits are obtained in the supercritical region suggests that electrodeposition from dense gaseous ammonia might prove to be a useful process for growing whiskers or other desirable crystalline forms.

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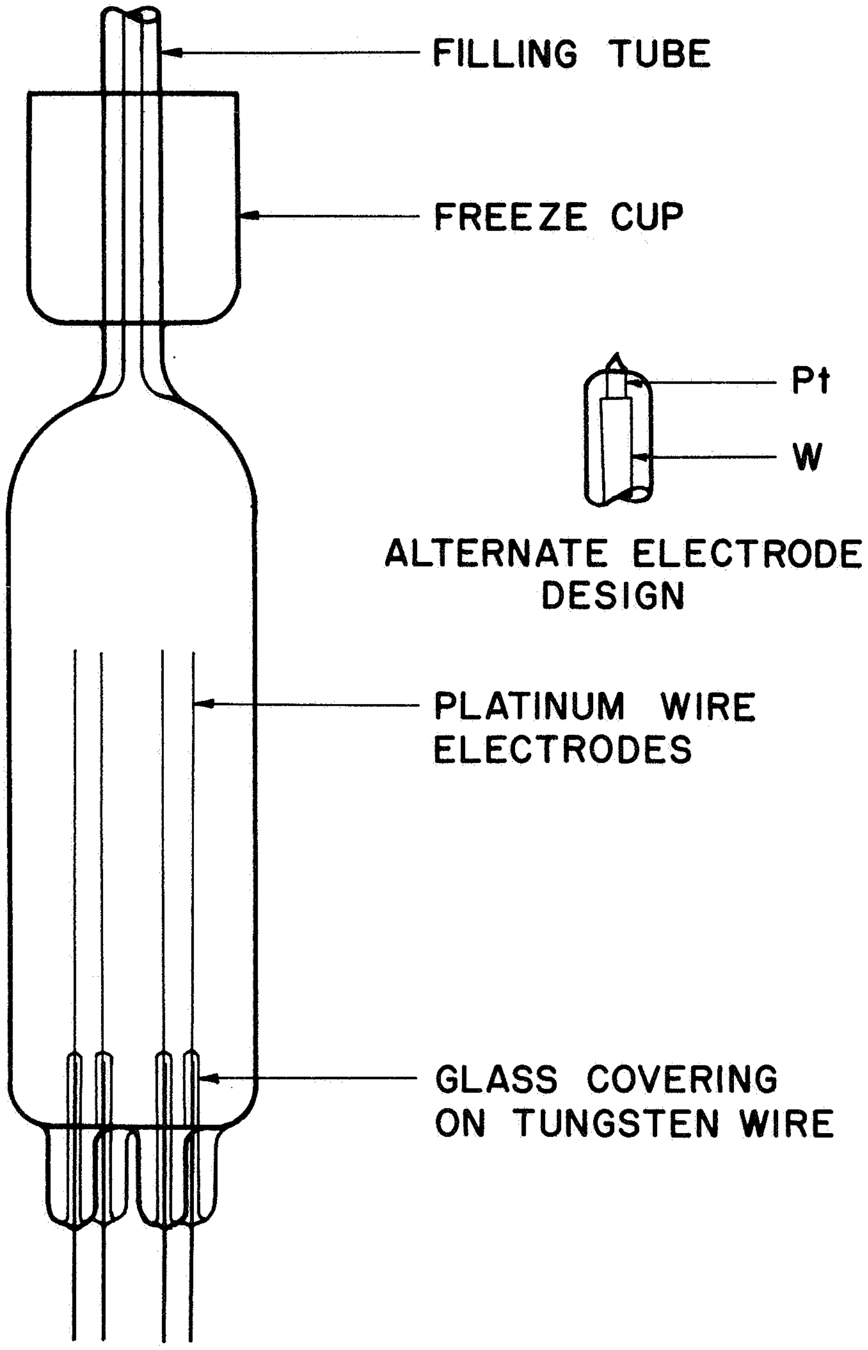
FIGURE TITLES

Figure 1. Cell for Electrodeposition from Dense Gaseous Ammonia Solutions.

Figure 2. Photograph of Electrodeposit made at 140°C on Long Wire Type Cathode.

Figure 3. Needles Deposited at 140°C on Cut-Off Type Cathode. Longest needle appears to have grown in [111] direction.

Figure 4. Dendrite Obtained at 141°C on Cut-Off Type Cathode, Central Stem appears to have grown in [100] directions.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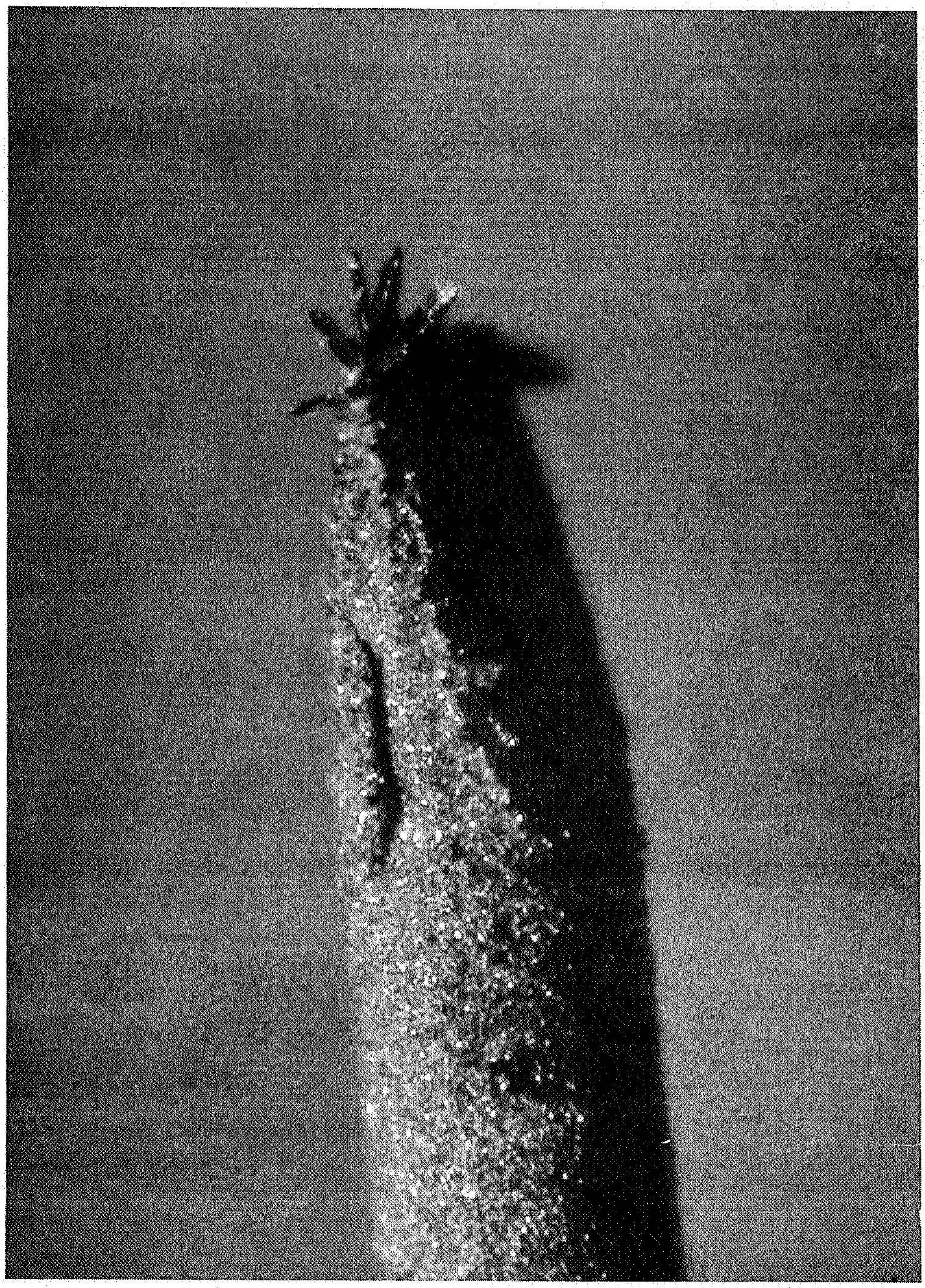

Figure 2. Photograph of the Whiskers Deposited on End of Pt Cathode in Cell E8 From $AgNO_3/NH_3$ Solution at 140°C.

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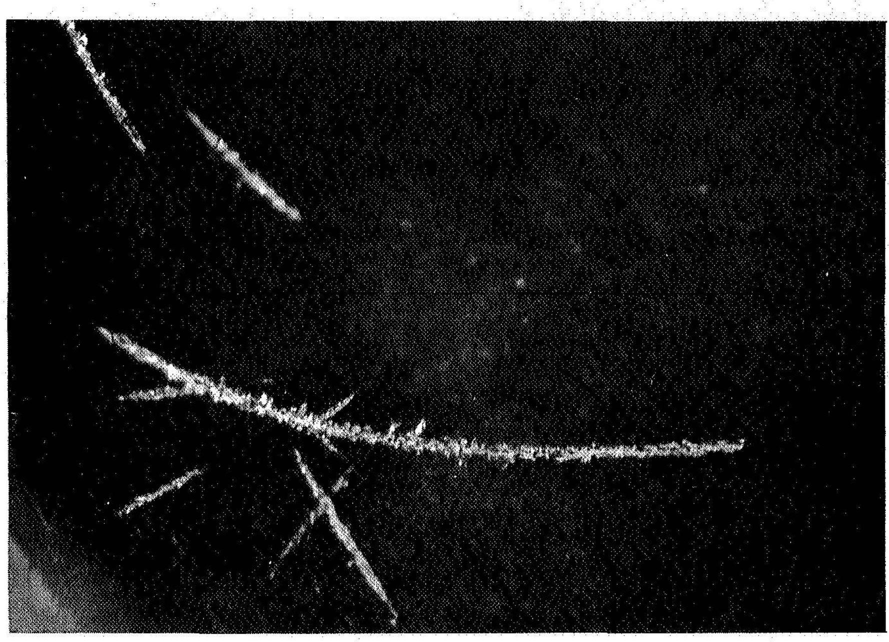

Figure 3. Photograph of Whiskers Deposited in Cell E13 from $AgNO_3/NH_3$ Solution at 140°C. Length of longest whisker is about 5 mm.

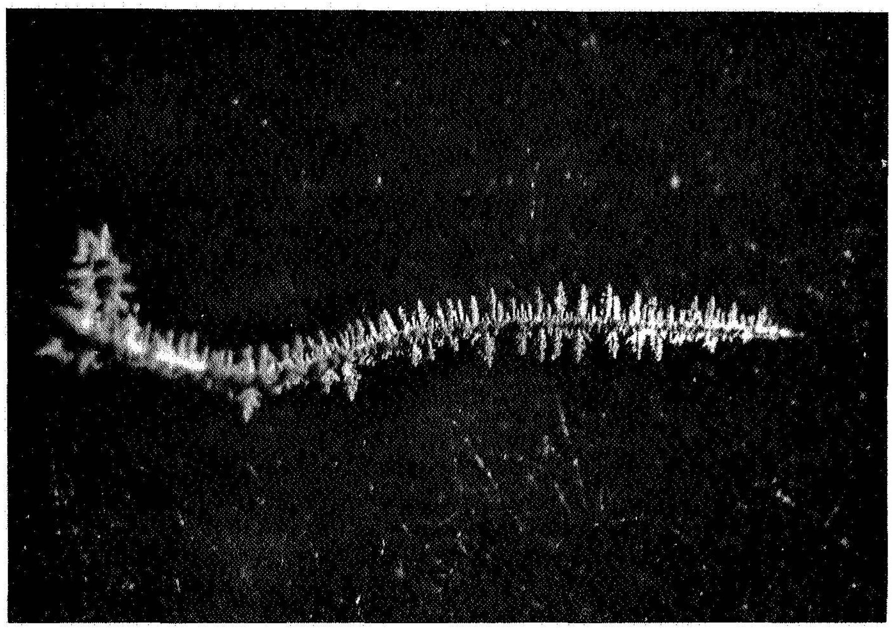

Figure 4. Photograph of a Tree Grown From Gaseous $AgNO_3/NH_3$ Solution at 141°C in Cell E14. The length of the tree is about 6.5 mm.

THE CONDUCTIVITY OF $AgNO_3$ IN LIQUID AND DENSE GASEOUS NH_3 AS A FUNCTION OF TEMPERATURE*

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The main work on dense gaseous electrolytes had been done with water as the solvent. The practical application of such electrolytes is limited due to the high critical temperature and pressure of water (374°C, 217.7 Atm). Ammonia, on the other hand, while not as strongly ionizing a solvent as water, has more convenient critical constants (133°C, 112 Atm) and is, in addition, less reactive toward metals than is water. Consequently, it is of interest as a dense gaseous solvent and the properties of dense gaseous ammonia electrolytes are in need of investigation. Silver nitrate was chosen for the present experiment because of its good solubility in NH_3 and because of the high reversibility of silver electrodes in silver nitrate. The following reports a measurement of the conductivity of a solution of silver nitrate in ammonia over a range of temperatures including the liquid and dense gaseous region.

The principal problem in supercritical experiments is containment of the dense gaseous solution. With ammonia, the critical temperature and pressure are sufficiently low that the solution may be contained in a glass cell under external pressurization. This procedure takes advantage of the ease of fabrication, chemical inertness, and good electrical insulating properties of glass. The

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*This work was sponsored by National Aeronautics and Space Administration under Contract NAS 7-437.

size and configuration of the cell, however, are limited by the internal dimensions and configuration of the high pressure system required. In the present case, the special restrictions were such that the problem of interelectrode capacitance made the use of a DC method attractive.

It was decided to use the four-probe method(1), in which two electrodes are used to produce a current through the cell while two others are used to measure the voltage drop across a known portion of the conducting electrolyte. The current electrodes may be allowed to polarize while the voltage probes should be reversible. The cell used for the measurements had a geometrically determinable cell constant and has been described in some detail elsewhere(2). The electrodes were of 0.4 mm diameter high purity silver wire about 3 cm long coiled inside the cell. Silver nitrate was weighed and introduced into the cell through the filling capillary and the cell sealed to a vacuum system and evacuated. Ammonia was condensed over sodium and allowed to stand as a sodium-ammonia solution for a few hours before being condensed into the cell.

When a liquid, such as ammonia, is held in equilibrium with its vapor in a closed volume and heated to its critical point, the density of the liquid decreases while that of the vapor increases until they become equal at the critical point of the solution, or until either all the liquid evaporates or the liquid expands to fill the cell before the critical point is reached. For the present experiment, the cell had a volume of 30.2 cc and was loaded with 15.2 cc of NH_3 at -78°C. In this case, the liquid fills the cell below the critical temperature. The predicted pressure and liquid volume as a function of temperature(3) are shown in Fig. 1. During the experiment, the cell was kept under an external nitrogen pressure 30 atm in excess of the predicted internal pressure.

Conductivity measurements were made at intervals of 10°C from room temperature to 150°C and back to room temperature. Each measurement involved determining the current-voltage relationship across the geometrically defined portion of the conductivity tube. This was done in each case for currents from 0 to 10 μa in steps of 2 μa. At each current, measurements were made with the current flow in one direction and then reversed. This procedure allows any static emf between the voltage probes to be averaged out. The static emf was found to be small (0 to 20 mv) and was independent of current, changing only as the temperature was changed. It is believed that this emf was caused by differences in electrolyte concentrations between the voltage electrode compartments. In some cases, measurements were also made at 80 μa and 800 μa. It was always found that the current-voltage relationship remained linear throughout the whole range of currents used, indicating that the cell was always well behaved.

The measured equivalent conductivity is shown as a function of temperature on Fig. 2. The ascending temperature points between 98° and 127°C were abnormally low and are not shown. This is believed to be due to formation of a bubble in the conductivity tube. Such bubbles form very easily at temperatures slightly below the critical temperature. The equivalent conductivity behaves in a manner similar to that observed (Franklin and Kraus(4)) for other salts in ammonia. The decrease in Λ with increasing temperature reflects the decrease in dissociation due to decreasing dielectric constant as the solution expands. Above the temperature where the cell fills and the density of the solution becomes constant the conductivity is seen to decrease much less rapidly with increasing temperature.

The equilibrium constant for the ionic dissociation of silver nitrate in ammonia can be calculated from the equivalent conductivity on the basis of the following assumptions. If the concentration of ions in the solution is sufficiently low that interionic forces can be neglected, then the equivalent conductivity, Λ, is related to the ionization constant, K, and the concentration, C, by the expression

$$K = \frac{C\Lambda^2}{\Lambda_o(\Lambda_o - \Lambda)} \tag{1}$$

where Λ_o is the equivalent conductivity at infinite dilution. The concentration C was found from the calculated liquid volumes (See Fig. 1). In the absence of additional conductivity measurements, Λ_o was found from the known value at -33^oC(5) and the known values for the viscosity of ammonia. Assuming that the solvation states of the ions are essentially independent of temperature, Λ_o is then given by

$$\Lambda_o(T) = \frac{7.32\times10^5}{n(T)} \tag{2}$$

where n(T) is the viscosity of NH_3 in micropoise. The viscosity was found by interpolation between the measured values of Akhumov and Ezerova.(6) The K curve shown on Fig. 2 was then calculated from the curve drawn through the measured values of Λ.

Neglecting vibrational and electronic excitation, the dissociation constant may be expressed theoretically in the form(7)

$$K \equiv \frac{C_{Ag^+} \cdot C_{NO_3^-}}{C_{AgNO_3}} = AT^{n/2}e^{-X/kT}. \qquad (3)$$

The value of n is equal to the total number of degrees of translational and rotational freedom for Ag^+ and NO_3^- less the number of degrees of translational and rotational freedom for $AgNO_3$. Assuming that the Ag^+ is solvated, each species has 3 degrees of rotational freedom in addition to 3 degrees of translational freedom so that $n = 6$. The dissociation energy X, in the presence of the solvent is assumed to be of the form

$$X = E_o/D + x$$

where E_o is the coulombic part of the dissociation energy in the absence of the solvent, D is the dielectric constant of the solvent, and x is the non-coulombic or electron exchange part of the dissociation energy. The non-coulombic energy is smaller than the covalent bond energy, since the latter is partially ionic.

The dielectric constant of NH_3 is known from -77.7°C to 35°C(8) and K for dilute solutions of $AgNO_3$ in NH_3 has been measured at -33°C(9). Using this value ($K = 2.8 \times 10^{-3}$ moles/liter) plus our value at 25°C, values of A and x were obtained for assumed lower and upper limits of 4 ev and 7 ev for E_o. This lead to values of $x = 0.18$ ev and $x = 0.23$ ev, respectively, indicating that the binding is more than 95% coulombic. The corresponding values for A were 8.25×10^{-3} and 50.5. Using these values in equation 3, the dielectric constants corresponding to the K curve on Fig. 2 were calculated and are shown on Fig. 3 along with the measured values of Grubb, et al.(8)

It is seen that the dielectric constant is not very sensitive to the assumed value of E_o. Furthermore, the points of Grubb, et al are in best agreement with the curve for $E_o = 7$ e.v. and suggest that an even larger value of E_o should be assumed. It should also be noted that in the constant density region, D continues to fall with increasing temperature, presumably due to further breaking of hydrogen bonds. Also, there is no apparent discontinuity at the critical temperature of NH_3, indicating that the transition from the liquid to the dense gaseous state is continuous. Finally, the measurements of Keyes, et al(10) on ammonia gas at densities of 1 to 4 moles/liter in the 100° to 175°C temperature range yielded values of D between 1.3 and 1.6. In the present case, the NH_3 concentration in the constant density region is 22 moles/liter so that the values of 6 to 9 obtained for D appear reasonable.

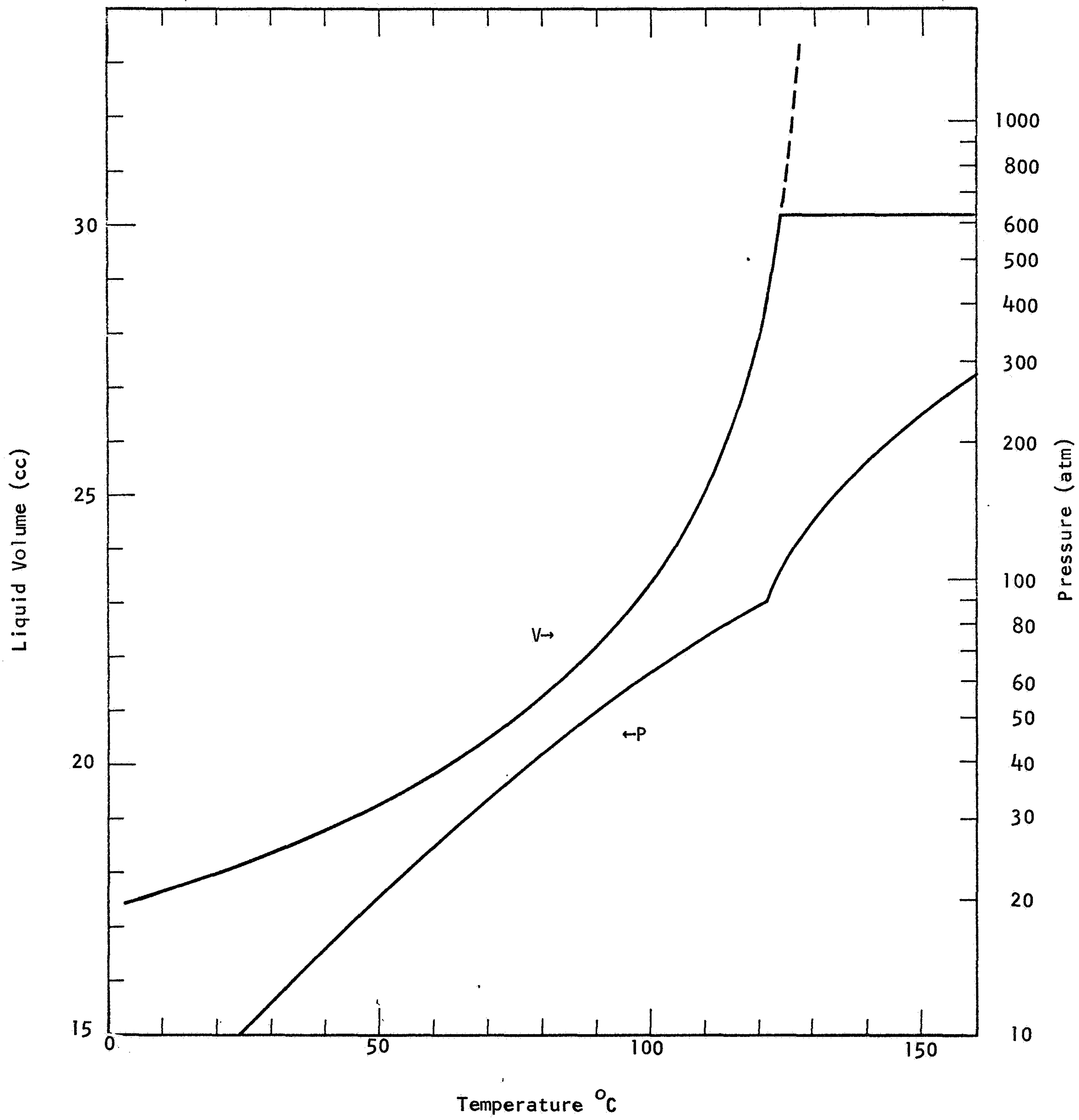

Figure 1. Calculated Pressure and Liquid Volume of NH_3 Inside Conductivity Cell.

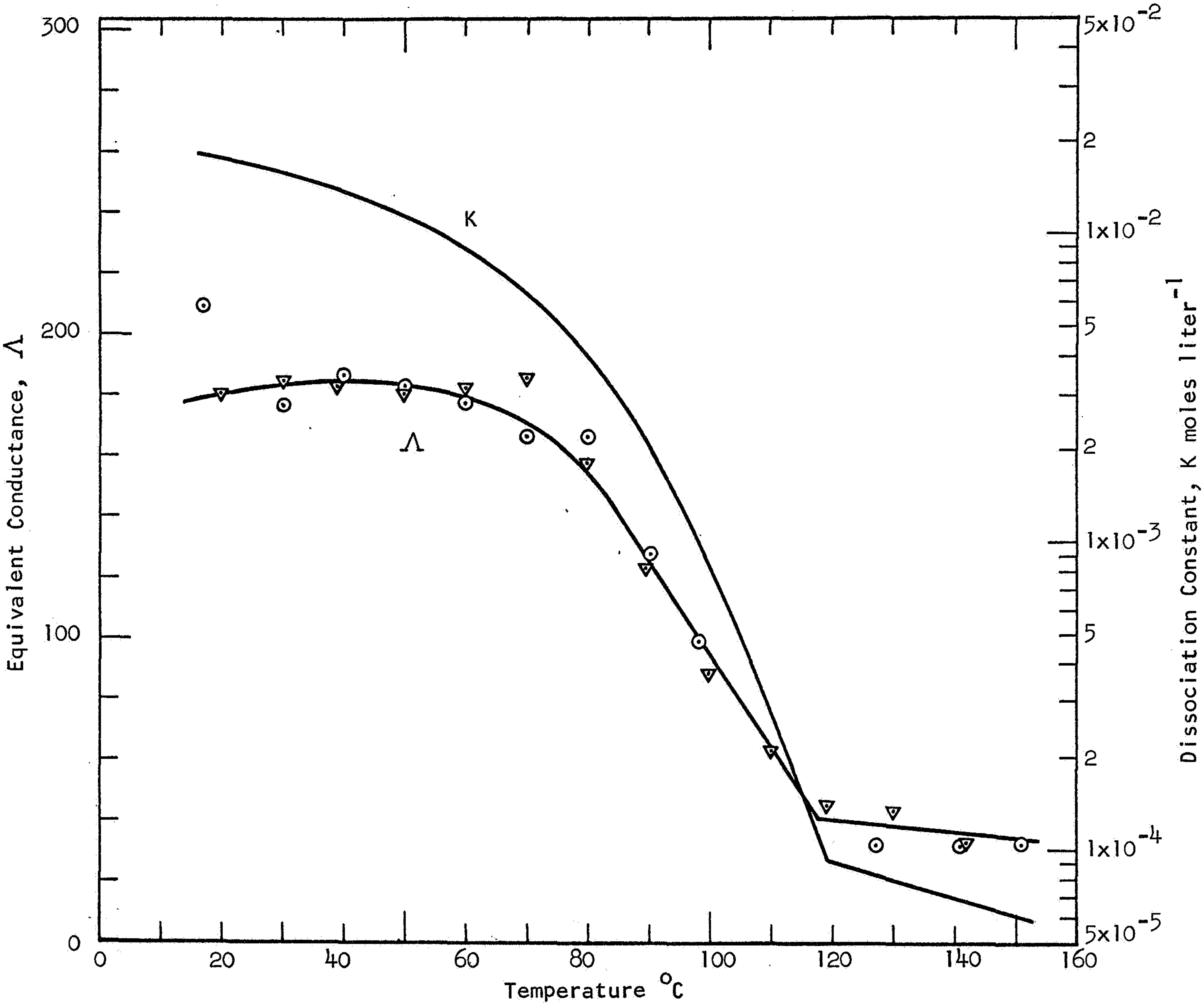

Figure 2. Temperature Dependence of Equivalent Conductivity and Estimated Dissociation Constant for $AgNO_3$ in NH_3

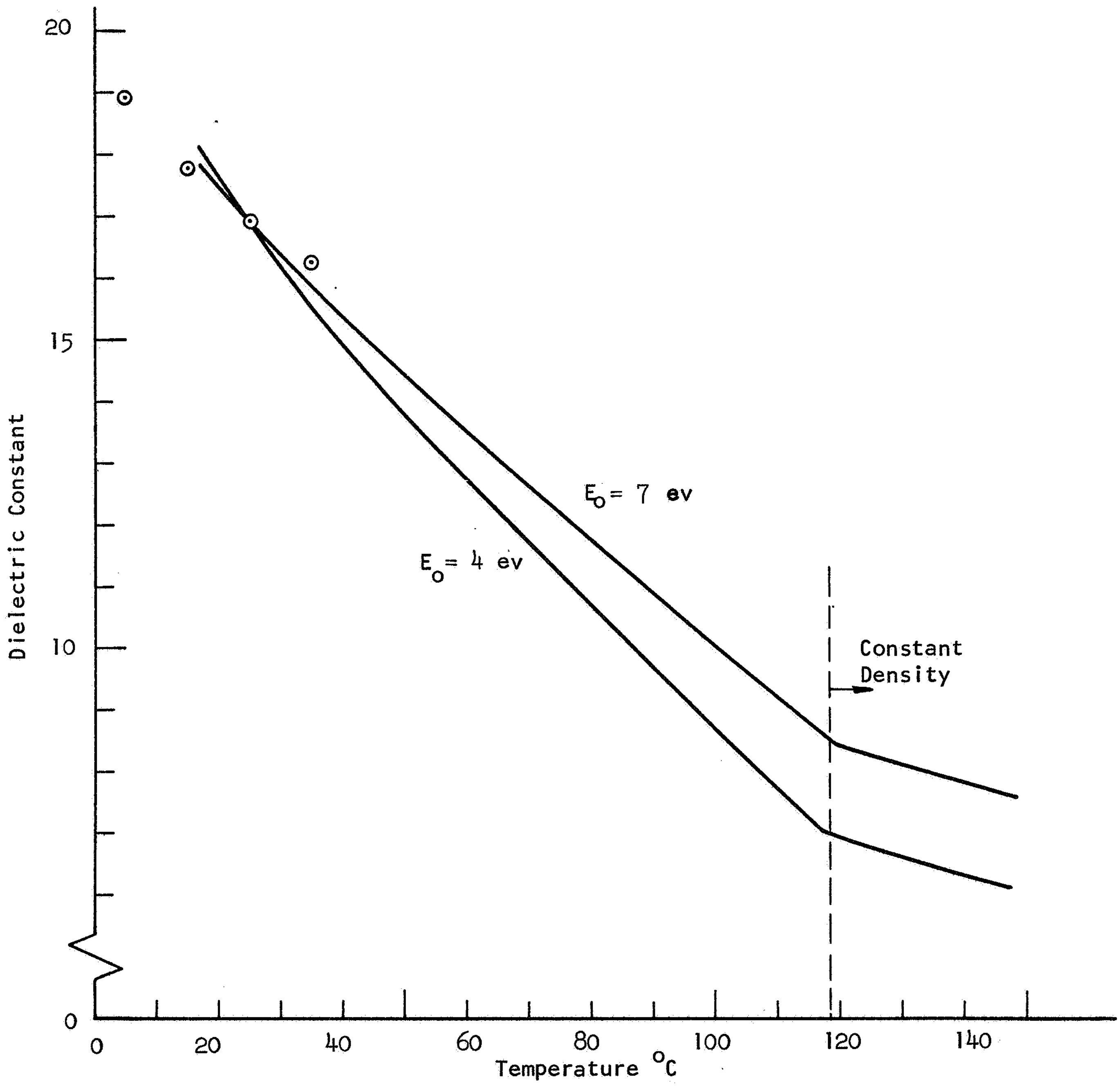

Figure 3. Estimated Dielectric Constants for Liquid and Dense Gaseous NH_3

Circled points are measurements of Grubb, et al.(8)

POLAROGRAPHY EXPERIMENT

INTRODUCTION

For each ionic species present, including different solvation states of the same ion, there is a characteristic potential above which (in the absolute sense) it will be oxidized or reduced, as the case may be, and below which it will not. It is thus possible to identify the species present in a solution, including different solvation states of the same ion. From a measurement of diffusion limited current for a particular species it is possible to obtain the diffusion constant for that species if the concentration is known; or the concentration if the diffusion constant is known.

Finally, even when no ions are being oxidized or reduced at the DME, a small current flows. Because no ions are being oxidized or reduced on the DME, there is effectively an insulating layer between the mercury drop and the surrounding electrolyte. The voltage applied to the cell occurs across this layer which is called the electrical double layer. The mercury drop and surrounding electrolyte thus form the two plates of a capacitor. As the mercury drop grows, the capacitance increases, requiring a current to flow to maintain same voltage across it. This is the residual current. From a measurement of the residual current, the differential capacity of the electrical double layer can be obtained, which can be interpreted in terms of conditions at the surface of the DME. Thus a polarographic experiment can identify the ionic species present, including different solvation states of the same ion, give the diffusion constant or the concentration of each species, depending upon which is known, and give information about the electrical double layer at the electrode surface. Such information, if obtained with the electrolyte in the gaseous state, would be extremely interesting and pertinent to the present program.

BACKGROUND

Voltammetry is the branch of electrochemistry that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. The dropping mercury electrode consists of a very fine glass capillary with one end connected to a mercury reservoir while the other is immersed in the solution being investigated. Mercury flows through the capillary causing a drop to grow on the end of the capillary and then fall. As soon as one drop falls, another begins to form. Each drop exactly duplicates its predecessor so that the currents are reproducible from one drop to the next. Also, solid products cannot accumulate on the electrode surface which could change its properties. With a dropping electrode, a momentary shock or vibration will cause one drop to behave erratically whereas with a stationary electrode the whole measurement can be ruined by changing the structure of the diffusion layer which is slowly growing away from the electrode surface.

A polarographic cell contains the solution to be measured, the dropping mercury electrode (DME) and a reference electrode against which the potential of the DME is established. Because of the very large surface area of the reference electrode and the low currents involved, the reference electrode, which also serves as the counter electrode, does not polarize. To investigate a metal ion in the solution the potential of the DME is varied from zero towards negative values. If only one cation is present, the current will remain constant until the potential of the DME is sufficiently negative to reduce the cation. At this point the current increases rapidly as the DME becomes more negative until all of the cations which diffuse to the DME are reduced on its surface. From this point, as the DME is made still more negative, the current remains constant and is limited by the rate at which the cations can diffuse to the DME. Anions produce similar results when the DME is made positive.

EXPERIMENT

Cell Design

The basic cell design is shown in Fig. 4. The mercury runs from the reservoir, down the inner tube and through the very fine capillary. This capillary was formed by drawing down 1/2 mm capillary to give drop times of 4 to 6 seconds in air. It was hoped that the drop time in dense gaseous NH_3 would be similar to that in air. The working and reference electrodes are of Zn which should be reversible in NH_3 when used at low currents with a chloride electrolyte. A return path between the lower chamber and the mercury reservoir allows the mercury to be rerun through the cell after all the mercury from the reservoir has been used. This return tube also serves as a vent between the two chambers so that no pressure differences leading to erratic behaviour of the DME will occur.

Polarograph

A recording polarograph was used to vary the potential between the reference electrode and the DME at a constant rate between desired initial and final points while recording the current through the cell. A schematic of the electrical circuit for this device is shown in Fig. 6. In addition to the voltage sweep and current measuring and recording sections, it contains a circuit to compensate for voltage drops across the current sensing resistor and the internal resistance of the cell and an integrating circuit to provide a desired amount of damping of the current swings produced by the DME. As each drop falls, the current drops practically to zero and then increases to its maximum as the next drop grows. It is usually desirable to average these swings to some extent. The present device uses flashlight cells to obtain the necessary voltages while a clock motor drives the ganged voltage dividing voltage sweep and internal resistance compensator. The voltage across the current sensing resistor is recorded on a Baush and Lomb VOM 5 recorder, having a sensitivity of 10 mv full scale and an input resistance in excess of 10 megohms. The cell voltage can be swept through any desired amount between 0 and 4.5 V in a time of 8 minutes while the initial voltage can be set anywhere between ±1.5 V. Current can be measured over the range from 0.5 μa to 100 μa, and the integration time can be set at 0, 2, 4, 8 and 20 seconds.

Method

The mercury reservoir was half filled with mercury with the cell in a nearly horizontal position and the filling tube to the reservoir tipped off. The cell was then inverted and 0.1 gm of NH_4Cl added through the remaining filling tube. The cell was then sealed to a high vacuum system, evacuated, and filled with NH_3 at -78°C to 50% of the volume remaining after the addition of Hg. This was usually 20 to 25 cc of NH_3. The cell was then sealed off and stored in a refrigerator.

The cell was loaded in the bomb in a horizontal position with the return tube at the bottom and heated until the temperature reached 120°C to 140°C. The external pressure was kept somewhat above the predicted internal pressure. When the desired temperature was reached, the pressure vessel containing the cell was tilted to the vertical position, allowing Hg to flow down the inner tube and through the capillary. The voltage was scanned from 0 to -2 to 3 v between the DME and the working electrode while the current through the cell was recorded.

Results

The early attempts at running the polarography experiment failed due to cell breakage at low temperature (~40°C). It was soon realized that this was due to blockage of the inside of the high pressure vessel by the mercury resevoir, which was only slightly smaller in diameter. The cell was modified so that the mercury resevoir was much narrower and a thermocouple was taped to the cell below the mercury resevoir to monitor the NH_3 temperature in the cell. During the running of this cell, the external pressure was kept 30 atm above the predicted internal pressure. The cell failed at 70°C. The next cell was run at only 10 atm above the predicted internal pressure and a temperature of 120° C was successfully reached.

Attempts were made at 100°C and 110°C to obtain polarograph from this cell, since it was felt that at these temperatures, the properties of the liquid NH3 would not be very different from dense gaseous NH_3. No dropping mercury action could be observed, at these temperatures, however, and it was concluded that the capillary was blocked. At 120°C, however, the DME appeared to be functioning and a voltage scan was started. The resulting current was voltage recording is shown in Fig. 3. It is seen that the DME produced oscillation in the current until a voltage of ~0.85 v at which point they ceased. It is believed that the cell ruptured at this point. The results, therefore are incomplete and provide only an indication of the feasibility of DME polarography experiments in NH_3 at temperatures near the critical point.

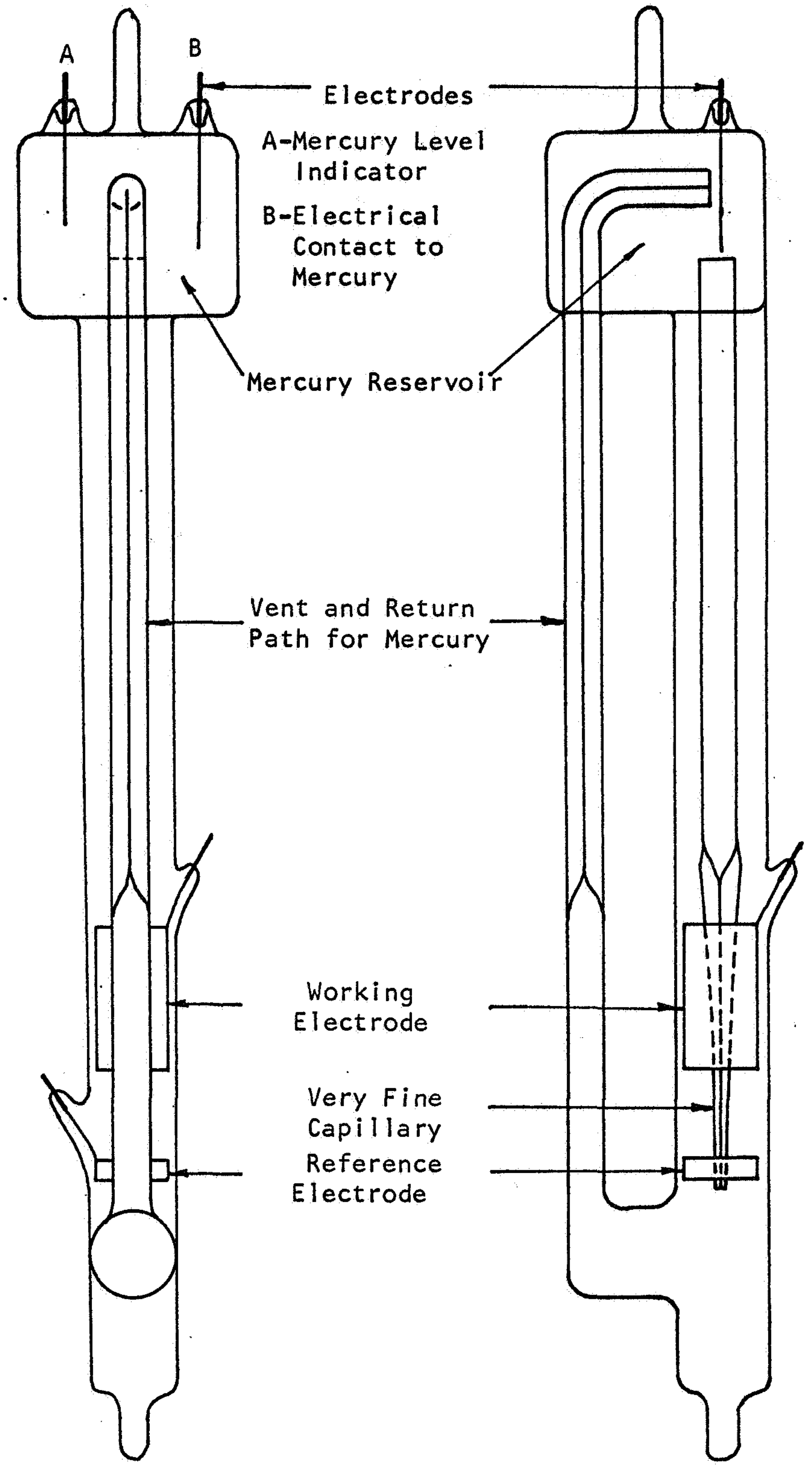

Figure 1. Cell for DME Polarography in Dense Gaseous Electrolytes

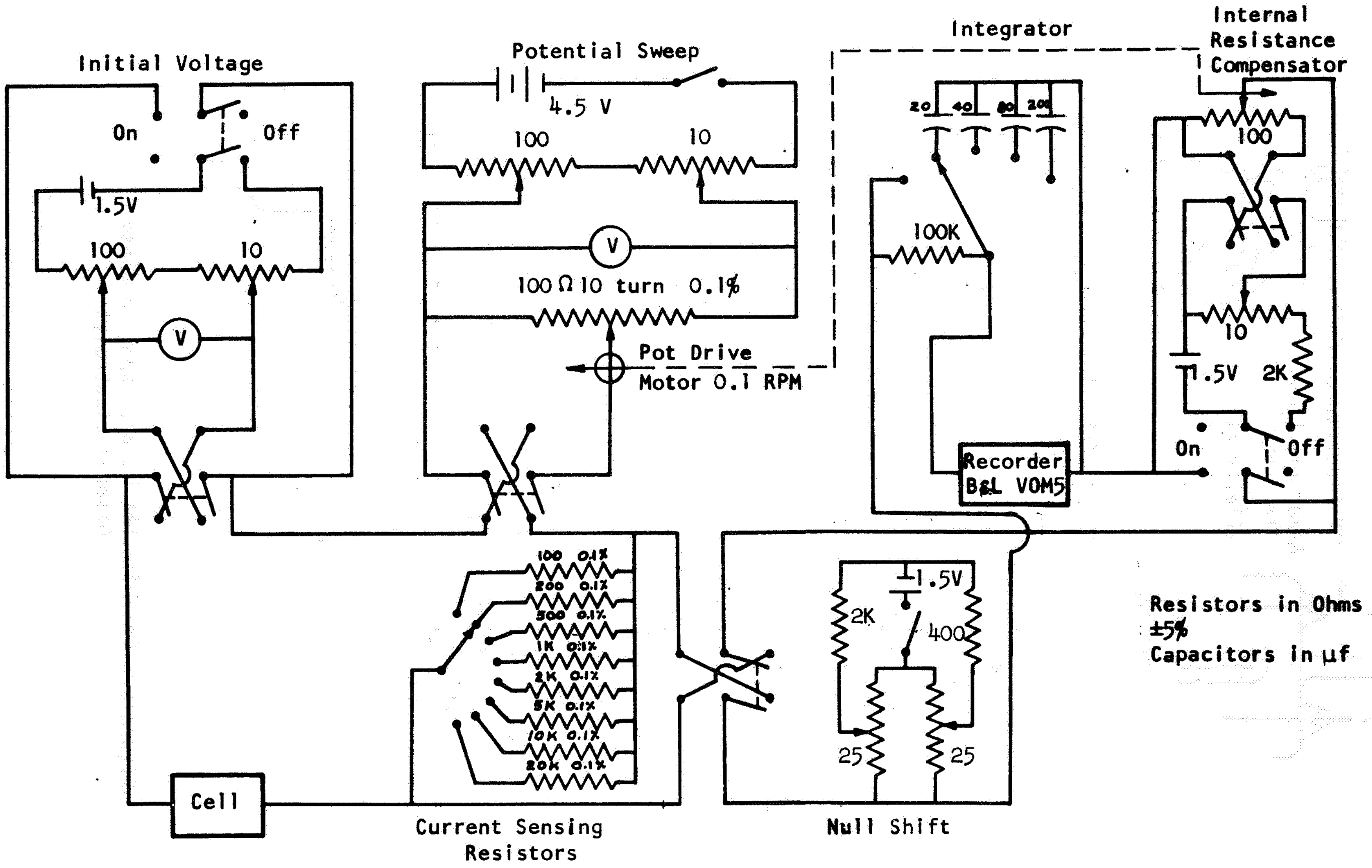

Figure 2. Polarograph Circuit

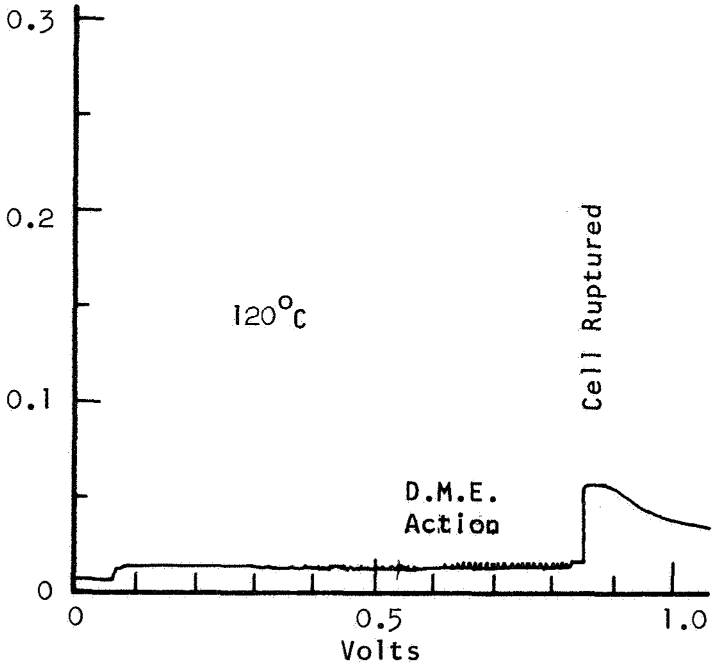

Figure 3. Polarogram

THERMODYNAMIC PROPERTIES OF GASEOUS $CsNH_3^+$

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ABSTRACT

Thermodynamic properties of gaseous $CsNH_3^+$ are calculated using statistical thermodynamics, a previously measured value of the dissociation energy of $CsNH_3^+$, and estimates of the length and fundamental frequency of the Cs-N bond. With all species at 1 atmosphere and $298.15^\circ C$, the results are; for $CsNH_3^+$, $S^\circ = 61.8 \pm 1$ cal mole^{-1} $^\circ K^{-1}$; for $CsNH_3^+ + e^-$, $\Delta H_f^\circ = 94.0 \pm 0.9$ kcal/mole and $\Delta G_f^\circ = 102.4 \pm 0.9$ kcal/mole; for $CsNH_3^+ + NH_3$, $\Delta E^\circ = 4.4 \pm 0.9$ kcal/mole, $\Delta G^\circ = -2.4 \pm 0.9$ kcal/mole and $K = 55 \times 10^{\pm 0.7}$ atm.

Work supported by Office of Saline Water Contract OSW 14-01-0001-424 and National Aeronautics and Space Administration Contract NAS 7-437.

INTRODUCTION

The presence of the gaseous species $NaNH_3^+$ has been discussed by Loeb in his review of ionic mobility measurements(1). Recently, in this laboratory, the energy of attachment of an NH_3 to a Cs^+ in the gas phase has been measured using photoionization techniques(2). These data are now subjected to a detailed analysis to provide the thermodynamic properties of gaseous $CsNH_3^+$ in its standard state as a perfect gas at 1 atmosphere, 298.15°K. Then, the behavior of Cs^+ in a carrier gas is examined briefly.

DISSOCIATION ENERGY OF $CsNH_3^+$ at 0^oK

The energy of attachment of an NH_3 to a Cs^+ in the gas phase (6.57 ± 0.9 kcal/mole) has been measured in this laboratory using a photoionization technique. A mixture of cesium and ammonia gases at 173^oC is subjected to monochromatic radiation and the photoionization spectrum is measured. At photon energies below 3.89 ev all of the discrete ion spectra occur only at the absorption lines of cesium so that the ionization mechanism is

$$Cs + h\nu = Cs^*; \quad \Delta E_1' = h\nu' \qquad (1)$$

where the primes denote data at 446^oK. This is followed by

$$Cs^* + NH_3 = CsNH_3^*; \quad \Delta E_2' = 0 \qquad (2)$$

If the sum of the radiation and binding energies is sufficiently great, ionization can occur.

$$CsNH_3^* = CsNH_3^+ + e^-; \quad \Delta E_3' = -Q_c' \qquad (3)$$

When ammonia is introduced into Cs vapor it is found that there is a critical wavelength above which all ion currents are attenuated and below which all are amplified. It is assumed that this critical radiation energy ($h\nu_c$) corresponds to the minimum radiation energy required for the process in equation (3) to take place so that at $Q_c' = 0$, the translation energy of the $CsNH_3^+$ corresponds to the temperature of the system, and the rotational and vibrational modes are in the ground state and the translational energy of the electron is zero.

The overall change in state at $0^{o}K$ is then,

$$Cs + h\nu' + NH_3 = CsNH_3^+ + e^-;$$

$$(\Delta E_o^{\,o})_4 = h\nu_c' + E'(NH_3) - E_o^{\,o}(NH_3) \qquad (4)$$

where the subscript "o" denotes data at $0^{o}K$.

In order to determine the dissociation energy of $Cs—NH_3^+$, $(\Delta E_o^{\,o})_4$ is equated to the increase in internal energy of an alternate path for the same change of state. In this second path, cesium at $0^{o}K$ is subjected to radiation with energy just equal to its ionization potential.

$$Cs + h\nu_{ip} = Cs^+ + e^-; \quad \Delta E_5 = h\nu_{ip} \qquad (5)$$

Then an ammonia molecule at $0^{o}K$ in the gas phase attaches itself to the cesium ion at constant temperature:

$$Cs^+ + NH_3 = CsNH_3^+; \quad \Delta E_6 = -E_{Do}^{+o} \qquad (6)$$

where E_{Do}^{+o} is the dissociation energy at $0^{o}K$. The overall change in state for equations (5) and (6) is the same as that for equation (4), so that

$$E_{Do}^{+o} = (h\nu_{ip} - h\nu_c') - (E'(NH_3) - E_o^{\,o}(NH_3))$$

$$= 3.7_3 \pm 0.9 \text{ kcal/mole}^* \qquad (7)$$

*The accuracy is that of the measurement, $h\nu_{ip} - h\nu_c' = 6.5_7 \pm 0.9$ kcal/mole.

DISSOCIATION ENERGY OF $CsNH_3^+$ AT 298.15°K

This dissociation energy is calculated from

$$E_D^{+o} = E_{Do}^{+o} + 3/2RT^o + E_v^o(NH_3) - E_v^o(CsNH_3^+) \qquad (8)$$

In the evaluation, the last vibrational term is split into two parts, one for the $—NH_3$ and the other for the Cs—N—, where the dash indicates bonding to the other portion of the molecular ion. Interactions between the Cs and the H's are neglected and the fundamental vibrational frequencies, bond angles and N-H distances of NH_3(3) are used for those of the bonded $—NH_3$. Neglecting the nitrogen inversion term, the vibrational energy of the bonded $—NH_3$ is then equal to that of NH_3. In the analysis, the Cs—N— is treated as a diatomic molecule. Based on these approximations, equation (8) reduces to:

$$E_D^{+o} = E_{Do}^{+o} + 3/2RT^o - E_v^o(Cs—N) \qquad (9)$$

The fundamental vibrational frequency of Cs—N has been estimated by (i) Morse's relation $r_o^3\nu = 9\text{x}10^{-11}$, (ii) Moelwyn-Hughes' modification for CaO(4), $r_o^3\nu = 12.58\text{x}10^{-11}$, and (iii) Badger's relation, force constant $f = 1.86\text{x}10^5/(r_e - d_{ij})^3$, using 17.032 as the effective mass of N in Cs—N. The Cs-N distance has been taken as the sum of Pauling's values of the ionic radius of Cs (1.69 Å) and the covalent radius of N (0.70 Å)(5). The three calculated frequencies are (i) $6.59\text{x}10^{12}$, (ii) $9.22\text{x}10^{12}$, and (iii) $9.64\text{x}10^{12}$ cps, respectively. The average of the last two frequencies, $9.4\text{x}10^{12}$, has been used.*

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*As an example of the effect of an error in this value on the final results, an error of 50% in this frequency introduces an error in E_D^{+o} of 0.14 kcal/mole, in $S^o(CsNH_3^+)$ of 1.26 cal mole^{-1} °K^{-1}, and in ΔG^o for the dissociation of $CsNH_3^+$ of 0.24 kcal/mole.

The last term in equation (9) is equal to $Rh\nu k^{-1}(e^{h\nu/kT} - 1)^{-1}$. The dissociation energy calculated from this is

$$E_D^{+o} = 4.3_7 \pm 0.9 \text{ kcal/mole} \tag{10}$$

ENTROPY OF $CsNH_3^+$

The translational entropy of $CsNH_3^+$ (1 atm, 298.15°K) has been calculated using the Sackur-Tetrode equation and the constants in Kelley and King(6), $S^o_t = 40.93$ cal $^oK^{-1}$ mole^{-1}. The calculated moments of inertia are: $I_1 = 4.436\times10^{-40}$, $I_2 = I_3 = 1.543\times10^{-38}$ gram cm^2. From this, $S_r^o = 19.40$ cal $^oK^{-1}$ mole^{-1}. The vibrational entropies are calculated from $S_v = E_v/T - R\sum_i \ln(1 - e^{-h\nu_i/kT})$, using the numerical values in the preceding section. From this, $S_v^o(Cs—N) = 1.34$, $S_v^o(NH_3) = 0.13$, and $S_v^o(CsNH_3^+) = 1.47$ cal mole^{-1} $^oK^{-1}$. Adding the component entropies,

$$S^o(CsNH_3^+) = 61._8 \pm 1 \text{ cal/mole}^{-1}\ ^oK^{-1} \qquad (11)$$

HEAT AND FREE ENERGY OF FORMATION OF $CsNH_3^+ + e^-(T^o)$

In the calculation of the heat and free energy of formation, the electron is taken at 1 atm, 298.15°K; that is, it is under equilibrium in the system. Using the heats of formation, $\Delta H_f^o(Cs^+ + e^-) = 110.05$ and $\Delta H_f^o(NH_3) = -11.04$ kcal/mole,

$$\Delta H_f^o(CsNH_3^+ + e^-) = 94.0_5 \pm 0.9 \text{ kcal/mole} \tag{12}$$

$$\Delta G_f^o(CsNH_3^+ + e^-) = 102.4_1 \pm 0.9 \text{ kcal/mole} \tag{13}$$

THE DISSOCIATION CONSTANT OF $CsNH_3^+$

The increase in free energy for the dissociation of $CsNH_3^+$ into $Cs^+ + NH_3$ is

$$\Delta G^o = -2.3_7 \pm 0.9 \text{ kcal/mole} \tag{14}$$

and the dissociation constant $(Cs^+)(NH_3)/(CsNH_3^+)$ is $55 \times 10^{\pm 0.7}$ atm.

At the low partial pressures generally used in seeded gases, the partial pressure of $CsNH_3^+$ will be very low. For example, if the partial pressure of Cs^+ and NH_3 are both 1 torr, then under equilibrium conditions the partial pressure of $CsNH_3^+$ at 298.15°K will be $2 \times 10^{-5} \times 10^{\pm 0.7}$ torr. On the other hand, if the partial pressure of ammonia is raised to an atmosphere, that is, ammonia is used as the carrier gas, and the partial pressure of Cs^+ is relatively low, then the partial pressure of $CsNH_3^+$ will be $2 \times 10^{\pm 0.7}$% of that of the Cs^+.

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SOLVATION OF Cs^+ IN LIQUID AMMONIA*

by

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ABSTRACT

The free energies of solvation for $Cs^+ + (NH_3)_n = Cs - (NH_3)_n^+$ have been calculated for n = 1, 2, 8, 27, 64 and 125 using the standard state: gas at 239.76°K and 1 mole/liter. The effects of the dielectric constant on these ion-molecule processes are neglected. All of the evaluated species are mono-solvated cesium ions coordinated to one nitrogen. The ammonia clusters which are held together by hydrogen bonds, are those found in the liquid state.

The concentrations of clusters in liquid ammonia have been calculated using the estimate that one-third of all hydrogen bonds are broken at the boiling point of liquid ammonia and the approximation that the distribution of hydrogen bonds in the liquid state is random.

From the free energies of solvation and the cluster concentrations, the state of the cesium ions is determined; the values being approximately, 88% unsolvated Cs^+; 12% $CsNH_3^+$; and 1% coordinated to ammonia clusters. From these values, the solvation number for equilibrium processes is 0.12, and for transport properties 0.097. Some of the implications of these results are discussed briefly

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*Work supported by Office of Saline Water under Contract OSW 14-01-0001-424 and National Aeronautics and Space Administration under Contract NAS 7-437.

INTRODUCTION

The ionization of CsCl in liquid ammonia has been examined(1) using the approach of Fowler and Guggenheim(2). In this approach, the dielectric constant of the solvent is inserted into the statistical equations for the ionization of CsCl into Cs^+ and Cl^-, the species being treated as perfect gases. Then the free energy of solvation of the positive ion is introduced. It is found that the predicted ionization constant using this approach is too large by two orders of magnitude. In order to remove this discrepancy, an additional property of the liquid state is introduced, namely that of hydrogen bonding, which leads to the association, polymerization or clustering of the solvent molecules. To take this into account, the thermodynamic properties of mono-solvated Cs^+ singly-bonded to a variety of ammonia clusters have been evaluated. In the analysis, the effects of the dielectric constant on ion-molecule processes are neglected. The reaction considered is

$$Cs^+ + (NH_3)_n \rightleftharpoons Cs\text{-}(NH_3)_n^+ \tag{1}$$

where the dash in the product indicates that there is one Cs-N bond. The standard states are ideal gases at the boiling point of liquid ammonia, 239.76°K, and 1 mole/liter.

FREE ENERGY OF FORMATION OF $Cs\text{-}NH_3\text{--}NH_3^+$

The gaseous species $Cs\text{-}NH_3\text{--}NH_3^+$, where the double dash indicates hydrogen bonding, simulates the simplest solvated species partially hydrogen bonded into the liquid. Assuming that the Cs-N and the hydrogen bond energies in $Cs\text{-}NH_3\text{--}NH_3^+$ are equal to those in $CsNH_3^+$ and $NH_3\text{--}NH_3$, then the solvation energy is given by

$$\Delta E_2 = \Delta E_1 = -4.28 \pm 0.9 \text{ kcal/mole}^{(1)} \qquad (2)$$

where the subscript "1" refers to the process in equation (1) for n = 1, i.e. monomeric ammonia, and "2" to that for dimeric ammonia.

In the evaluation of the entropy increase, ΔS_2, the sum of the symmetry number terms is zero. Treating the Cs-N and the hydrogen bonds as diatomic molecules, and assuming that the fundamental frequencies of these bonds and the properties of NH_3 are the same in the various species, then the increase in vibrational entropy for n = 2 is just that for n = 1, so that

$$\Delta S_2 = \Delta S_1 + 3/2R \ln \frac{2m_1 + m_2}{2(m_1 + m_2)}$$

$$+ 1/2R \ln \frac{(I_1 I_2 I_3)_{NH_3} \times (I_1 I_2 I_3)_{Cs(NH_3)_2^+}}{(I_1 I_2 I_3)_{(NH_3)_2} \times (I_1 I_2 I_3)_{CsNH_3^+}} \qquad (3)$$

where m_1 is the molecular weight of NH_3 and m_2 that of Cs^+, and the I's are the various principal moments of inertia.

To simplify the analysis of the moments without affecting the general conclusions, $NH_3\text{--}NH_3$ and $Cs\text{-}NH_3\text{--}NH_3^+$ are treated as linear. On evaluation,

$$\Delta S_2 = -24.5 \pm 1 \text{ cal } {}^{o}K^{-1} \text{ mole}^{-1} \tag{4}$$

and

$$\Delta G_2 = 1.11 \pm 0.9 \text{ kcal/mole} \tag{5}$$

FREE ENERGY OF FORMATION OF $Cs\text{-}(NH_3)_n^+$

Much of the ammonia in the liquid state is present in the form of large clusters. The bonding of such clusters to Cs^+ will now be examined.

Although, from an examination of the electron distribution in $CsNH_3^+$, the tendency for hydrogen bonding of the H's in $CsNH_3^+$ is greater than that of the H's in NH_3 itself, in the analysis it is assumed that the bonding within a cluster is unchanged when a cesium ion bonds to an ammonia on the cluster. The increase in internal energy for solvation of Cs^+ by clusters (eq. 1) is as follows: $\Delta E_t = -3/2RT$; $\Delta E_r = 0$; and $\Delta E_v = E_v(Cs\text{-}N)$. The total increase in internal energy is then given by

$$\Delta E_n = E_{Do}^{+o} + E_v(Cs\text{-}N) - 3/2RT$$

$$= 44.28 \pm 0.9 \text{ kcal/mole} \qquad (6)$$

In the above, the Cs-N bond has been treated as a diatomic molecule. The value of E_{Do}^{+o}, the dissociation energy (eq. 1) at 0°K, is assumed to be equal to the dissociation energy for $CsNH_3^+$ at 0°K(1)*.

The calculation of the entropies for this model is conventional, the equation for the translational energy being

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*If one distinguishes between bond energies and enthalpies, E_{Do}^{+o} is the Cs-N bond energy at 0°K.

$$\Delta S_t = -3/2R \ln \mu - 3/2R \ln T - R \ln 10^3 - 5/2R + 16.042$$

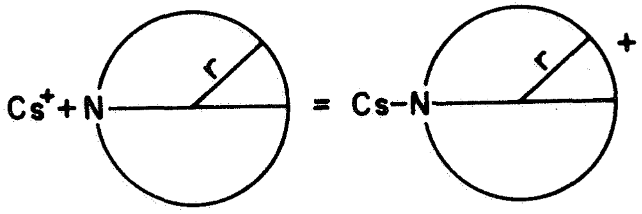
$$= 3/2R \ln \mu - 18.988 \qquad (7)$$

where μ is the reduced mass, i.e., $\mu = M_1 . m_2/(M_1 + m_2)$, and M_1 and m_2 are the cluster and cesium ion masses respectively. The increase in rotational entropy is

$$\Delta S_r = 1/2R \ln \frac{(I_1 I_2 I_3)_{Cs-C}}{(I_1 I_2 I_3)_C} - R \ln \frac{\sigma_{Cs-C}}{\sigma_C} \qquad (8)$$

where the subscript C represents the cluster, and Cs-C the solvated species.

In the calculation of the moments, it is assumed that the clusters are spherical and that the properties throughout the spheres are uniform. Neglecting the possibility of increased hydrogen bonding of the H's on the $CsNH_3^+$, the process being considered is



(9)

With the principal axis as in the figure above,

$$\Delta S_r = R \ln \frac{(I_2)_{Cs-C}}{(I_2)_C} + R \ln \frac{\sigma_C}{\sigma_{CsC}} \qquad (10)$$

For this configuration, the ratio of moments of inertia is $1 + 2.5\,\mu/M_1$.

Using the same analysis as for $CsNH_3^{+(1)}$, the increase in vibrational entropy is

$$\Delta S_v = S_v(Cs\text{-}N) = 0.161 \text{ cal mole}^{-1}\ {}^{o}K^{-1} \qquad (11)$$

The overall increase in entropy is

$$\Delta S_n = -3/2R \ln \mu + R \ln \left(1 + \frac{5\mu}{2M_1}\right) + R \ln \frac{\sigma_C}{\sigma_{CsC}} - 18.827 \qquad (12)$$

The entropies in table 1 for the clusters n = 8 to 125 have been calculated using $\sigma_C/\sigma_{Cs-C} = 1$, which is correct for the large majority of ammonia clusters.

TABLE 1

SOLVATION CONSTANTS FOR $Cs^+ + (NH_3)_n = Cs\text{-}(NH_3)_n^{\ +}$

It is assumed that the hydrogen bonding in the cluster is not affected by the solvation process so that ΔE = -4.28 ± 0.9 kcal/mole. Letting C represent cluster and σ its symmetry number, then $\sigma_C = \sigma_{Cs-C} = 3$ for n = 1, 1 for n = 2, and 1 for n $\geq$ 8 (since this is true for most of the species making up each composite n). Non-significant figures are retained throughout the calculations to better show the effects of the treatment under consideration.

n	ΔS, cal $^oK^{-1}$ mole^{-1}	ΔG, kcal mole^{-1}	K_n, moles^{-1} liter
1	-18.1 ± 1	-0.41 ± 0.9	2.4
2	-24.5	+1.11	9.8×10^{-2}
8	-29.8	+2.38	6.8×10^{-3}
27	-31.8	+2.86	2.5×10^{-3}
64	-32.6	+3.06	1.6×10^{-3}
125	-32.9	+3.12	1.4×10^{-3}

CONCENTRATIONS OF CLUSTERS IN LIQUID AMMONIA

To complete the analysis, the concentrations of the various ammonia polymers in liquid ammonia are needed. These will be combined with the solvation constants to provide the concentrations of each of the solvated species. Taft and Sisler(3) have deduced that one-third of all hydrogen bonds are broken at the boiling point of liquid ammonia. The assumption that the distribution of hydrogen bonds in liquid ammonia is random is sufficient to establish the concentrations of the various polymers. Thus in liquid ammonia in which the formal concentration of ammonia is 40 moles/liter, the concentration of the monomer and dimer are, respectively, 5.49×10^{-2} and 2.16×10^{-2} moles/liter. The results for $n = 3$, 4, and 5 are in Table 2. The product of solvation constant K_n and cluster concentration C_n is now negligible (Table 2). Therefore, for the larger species, a mean value of n is used and it is assumed that this is adequately represented by $n = 27$ molecules per cluster. This leads to the concentration of the average large cluster of $40/27 = 1.48$ moles/liter. For smaller n, the concentrations of the more symmetrical species are much higher than those of the less symmetric ones, and for larger n, the species with intermediate symmetry are the most abundant (because on the average 2 out of 6 hydrogen bonds are broken).

TABLE 2

THE RATIO OF CONCENTRATIONS OF SOLVATED SPECIES TO UNSOLVATED Cs^+, K_n'

n	K_n, moles/liter	C_n, moles/liter	K_n'*
1	2.4	0.055	0.132
2	0.098	0.011	0.001
3	1.1×10^{-1}	0.022	0.002
	3.5×10^{-2}	0.0009	0.000
4**	1.9×10^{-2}	0.1086	0.002
5**	1.3×10^{-2}	0.1114	0.001
27**	2.5×10^{-3}	1.48***	0.004
		Total	0.142

*$K_n' = (NH_3)_n \cdot K_n = (Cs(NH_3)_n^+)/(Cs^+)$.

**There are a variety of species present with this value of n.

***Assuming that the remainder of solution can be treated as $(NH_3)_{27}$, then $\bar{C}_{27} = 40/27 = 1.48$ moles/liter.

THE RATIO OF CONCENTRATIONS OF $Cs(NH_3)_n^+$ to Cs^+

The calculations on which Table 2 is based are as follows. The equilibrium constants without symmetry number are obtained from a plot of log K_n vs 1/n. Then the symmetry number is determined for the most abundant species and K_n calculated therefrom. In the cases of $n = 3$, $\sigma_C/\sigma_{Cs-C} = 3$ for the more abundant species and unity for the other. The concentrations of species with $\sigma_C > 1$ of the remainder of the species are relatively small, so that for $n > 3$, $\sigma_C = 1$ is used.

K_n', the product of K_n and $(NH_3)_n^+$ $((NH_3)_n^+)$, is the ratio of concentration of Cs^+ solvated with the polymer n to that of unsolvated Cs^+, i.e. $(Cs\text{-}(NH_3)_n^+)/(Cs^+)$. It is seen (Table 2) that about 93% of the solvated Cs^+ species are of the form $CsNH_3^+$ and that this concentration is only about 13% of that of unsolvated Cs^+, which is therefore the principal cesium ion species in solution.

The values of K_n' for the larger aggregates and clusters are probably an upper limit. This arises because a cesium bond to a nitrogen precludes hydrogen bonds to this nitrogen. If the solvation process takes place with hydrogen bond breaking, then the energetics are less favorable than that in eq. (1). In the case of the highly symmetrical clusters which involve about four hydrogen bonds on the average per molecule, there are very few places for cesium to bond without hydrogen bond breaking. These types of clusters are the most abundant of the large clusters.

There is a counter effect in that the $CsNH_3^+$ tendency to hydrogen bond is greater than that of NH_3 itself.

In summary, of the solvated species, $CsNH_3^+$ is the most favored thermodynamically (Table 1), the tendency for solvation decreasing as the cluster size increases (Table 2). This implies that in a solvent in which NH_3 is present in its monomeric form the solvating effect of the NH_3 should be larger than expected from its behavior in liquid ammonia itself.

SOLVATION NUMBER FOR EQUILIBRIUM PROCESSES, n_s

The solvation number is given by

$$n_s = \frac{0\ C_o + 1\ C_1 + \cdots}{C_o + C_1 + \cdots} = \frac{C_1}{C_o + C_1} \tag{13}$$

where C_o is the concentration of unsolvated Cs^+ and C_1 is the total concentration of the various monosolvated ions. From table 2,

$$n_s = \frac{0.142}{1.142} = 0.12 \tag{14}$$

This value is of reasonable order of magnitude.

SOLVATION NUMBER FROM MOBILITIES η_μ

In the experimental determination of transport solvation numbers, the specific conductivity σ of a solution is measured, and the solvation number η_μ calculated from this. In effect, it is assumed that there is only one positive ionic species in the solution such that

$$\sigma^+ = n^+ e\, \mu^+ \tag{15}$$

where n^+ is the number density of the positive ion, e its charge, and μ^+ its mobility. It is also assumed that the product $\mu^+ r_s$ is a constant k (Stokes' Law), where r_s is the effective diameter of the positive ion. The ionic volume V_s is given by

$$V_s = \frac{4\pi r_s^{\,3}}{3} = v_2 + \eta_\mu v_1 \tag{16}$$

where v_2 and v_1 are, respectively, the volumes of the solute ion and a solvent molecule in the solvated ion. Hence, the experimentally determined conductivity is interpreted as follows

$$\sigma^+ = \left[\frac{\overset{o}{A} ek(4\pi/3)^{1/3}}{10^3}\right] \frac{C^+}{(v_2 + \eta_\mu v_1)^{1/3}} \tag{17}$$

where $\overset{o}{A}$ is Avogadro's number and C^+ is the formal concentration of the positive ion.

In the present approach, which is based on the binding energy of the solvent molecule to the positive ion, it is assumed that there is a distribution of species such that

$$\sigma^+ = \sum_{o}^{m} n_n\, e\, \mu_n^{\,+} \tag{18}$$

Using the same approach as for the conventional analysis,

$$\sigma^+ = \left[\frac{\mathring{A}ek(4\pi/3)^{1/3}}{10^3}\right] \sum_o^m \left[\frac{C_n}{(v_2 + nv_1)^{1/3}}\right] \tag{19}$$

Eliminating σ^+ and solving for η_μ

$$\eta_\mu = \varphi\left[\sum_o^m \frac{K_n{}'/\sum_o^m K_n{}'}{(1 + n/\varphi)^{1/3}}\right]^{-3} - \varphi \tag{20}$$

where $\varphi = v_2/v_1$ and $K_o{}' = 1$. This result is evaluated for two different values of φ, the ratio of volume of Cs^+ to that of one NH_3 in the solvated ion, and for seven clusters, namely, $n = 0, 1, 2, 3, 4, 5$ and 27. The result is insensitive to φ, at least in the range considered. Thus, for $\varphi = 4.66$, $\eta_\mu = 0.098$ and for $\varphi = 2.33$, $\eta_\mu = 0.096$.

DISCUSSION

In an analysis(1) carried out in conjunction with this one, it was found that introduction of the dielectric constant and solvation into the statistical ionization constant equations gave a value of the ionization constant of CsCl too large by two orders of magnitude. It was surmised that the difficulty lay in the use of the formal concentration of ammonia in its liquid state in the evaluation of the effective ionization constant.

In the present analysis, the effects of hydrogen bonding on the state of Cs^+ in ammonia have been examined. The deductions from this analysis are satisfying in two respects, first, they give a reasonably small (0.12) rather than large (0.99) solvation number for Cs^+ in ammonia and, second, they lead to a value of the ionization constant that is of the same order of magnitude as expected from available experimental data(1).

In addition, the results permit an interesting excursion into the field of solvation numbers. The present analysis is based on energies in contrast to the standard methods which are often based on a variety of secondary properties such as mobilities. It is shown in the two preceding sections that the weight factors for determining solvation numbers vary with the experimental parameters. This may be seen by comparing eqs. (13) and (20). In the case of Cs^+, which is weakly solvated, the effects are small. It is seen that the predicted solvation number determined from mobilities, 0.097, is smaller than that determined from equilibrium properties, 0.12. For a species that was more strongly solvated than Cs the differences may be more marked.

Another interesting aspect is that of the situation at infinite dilution. Even though the substance is completely ionized, some of the ions are solvated to such large clusters that they are effectively immobile. Thus, complete ionization does not mean that all of the ions are mobile. In other words, the effective number density of ions contributing to conductivity can be smaller than that contributing to equilibrium processes such as vapor pressure depression.

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THE IONIZATION OF CsCl IN LIQUID AMMONIA*

by

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ABSTRACT

The ionization of CsCl in liquid ammonia at its boiling point (239.76°K) is calculated from the thermodynamic properties of gaseous $CsNH_3^+$ using the approach of Fowler and Guggenheim. For the standard state; perfect gas, 1 mole/liter and 239.76°K, the ionization constant K is 7×10^{-99} moles/liter. Introduction of the dielectric constant D of liquid ammonia (22.4) into the statistical equations increases K to 1.1×10^{-3} moles/liter. Introducing solvation, $CsCl + NH_3 = CsNH_3^+ + Cl^-$, leads to $K = 2.7 \times 10^{-3}$. For comparison, the formal concentration of NH_3 in the liquid state, 40 moles/liter is used to calculate the effective ionization constant $K' = (NH_3) \cdot K = 1.1 \times 10^{-1}$ moles/liter. This is two orders of magnitude larger than the ionization constant of CsCl projected from the available experimental data. To resolve this discrepancy, a third liquid-state property is introduced, clustering. K_Σ is calculated for $CsCl + \sum_{o}^{m} (NH_3)_n = \sum_{o}^{m} Cs(NH_3)_n^+ + Cl^-$. The effective ionization constant K_Σ', which is $K_\Sigma \cdot \left[\sum_{o}^{m} ((NH_3)_n) \right]$, is equal to $1.3 \times 10^{-3 \pm 0.4}$ moles/liter. Thus, when the effect of solvation is introduced, it is necessary to introduce also clustering in order to obtain satisfactory agreement with experimental data.

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*Work supported by Office of Saline Water under Contract OSW 14-01-0001-424 and National Aeronautics and Space Administration under Contract NAS 7-437.

INTRODUCTION

Fowler and Guggenheim(1), in their examination of the nature of electrolytic solutions, have demonstrated that the most important property of the liquid solvent is its dielectric constant. In the case of NaCl in the ideal gas state at room temperature, the increase of dielectric constant from unity to 80 (that of liquid water) increases the ionization constant from 10^{-79} to 7. To account for the residual gap between this result and complete ionization in liquid water, they introduce the solvation of Na^+.

In the following, this procedure is carried out for CsCl in liquid ammonia. After insertion of the dielectric constant of liquid ammonia into the statistical equations, the thermodynamic functions for the solvation of Cs^+ by NH_3 in the ideal gaseous state(2) are introduced and their effect on the ionization of CsCl calculated. It is found that the calculated ionization constant is too large by two orders of magnitude. Therefore a third liquid property is introduced, the clustering of the solvent molecules(3), which brings the calculated ionization constant into agreement with experimental data.

IONIZATION OF CsCl

For the ionization of CsCl in its standard state as a perfect gas at the boiling point of ammonia (239.76°K) and 1 mole/liter,

$$CsCl = Cs^+ + Cl^-, \qquad (1)$$

ΔE^o is deduced from $\Delta H^o_{298.15} = 110$ kcal/mole(4) using the fundamental vibrational frequency of 210 cm^{-1} (5). The entropy of CsCl is calculated using this value and $I = 3.92 \times 10^{-38}$ gram cm^2 (5). The results are recorded in Table 1.

It is assumed that all of the internal energy in the Cs-Cl bond is due to coulombic ion-ion interactions. The bond energy (the sum of the bond energy at 0°K and vibrational energy at the boiling point of ammonia) is then divided by the dielectric constant. The other terms, such as rotational and translation energies, $\Delta(pV)$, and energies of molecule-ion interactions, are not, so that

for D = 1; $$\Delta E = \Delta E_o^{\,o} - E_v(CsCl) + 1/2\ RT, \qquad (2)$$

and for D = 22.4; $$\Delta E = \left[\Delta E_o^{\,o} - E_v(CsCl)\right]/D + 1/2\ RT. \qquad (3)$$

ΔG is calculated assuming that ΔS^o is independent of dielectric constant. It is seen in Table 1 that the introduction of dielectric constant 22.4 produces a decrease in ΔG for the ionization of cesium chloride of 104 kcal/mole.

TABLE I

IONIZATION CONSTNATS OF CsCl

The standard state is 239.76°K and 1 mole/liter in the perfect gas state.

Process	Dielectric Constant	ΔE, kcal/mole	ΔS, cal °K^{-1} mole^{-1}	ΔG, kcal/mole	K	K$'$,* moles/liter
$CsCl = Cs^+ + Cl^-$	1	109.57 ± 10**	9.87 ± 0.5	107.68 ± 10	$7.08 \times 10^{-99 \pm 9}$ moles/liter	
	22.4	5.12 ± 0.4	9.87 ± 0.5	3.23 ± 0.4	$1.1 \times 10^{-3 \pm 0.4}$ moles/liter	
$CsCl + NH_3 = CsNH_3^+ + Cl^-$	1	105.29 ± 11	-8.2 ± 1	107.27 ± 11	$1.7 \times 10^{-98 \pm 10}$	$6.7 \times 10^{-97 \pm 10}$
	22.4	0.8 ± 1.0	-8.2 ± 1	2.82 ± 1.0	$2.7 \times 10^{-3 \pm 0.9}$	$1.1 \times 10^{-1 \pm 0.9}$

*Taking the concentration of NH_3 as the formal concentration in the liquid state, namely 40 moles/liter,

$$K' = 40K = (CsNH_3^+)(Cl^-)/(CsCl).$$

**Nonsignificant figures are retained throughout the calculations to better show the effects of the treatment under consideration.

EFFECT OF SOLVATION ON THE IONIZATION OF CsCl

The simplest approach to solvation is now introduced, namely

$$Cs^{+} + NH_3 = CsNH_3^{+}. \qquad (4)$$

Conversion of the thermodynamic data for this process(2) to 239.76°K and 1 mole/liter, yields

$$\Delta S = -18.1 \pm 1 \text{ cal mole}^{-1}\ {}^{o}K^{-1} \qquad (5)$$

$$\Delta H = -4.76 \pm 0.9 \text{ kcal mole}^{-1} \qquad (6)$$

$$\Delta G = \Delta H - T\Delta S = -0.41 \pm 0.9 \text{ kcal mole}^{-1} \qquad (7)$$

$$K_s = (CsNH_3^{+})(Cs^{+})^{-1}(NH_3)^{-1} = 2.4 \times 10^{1\pm0.9} \text{mole}^{-1} \text{ liter} \qquad (8)$$

In this approach, the effect of the change in dielectric constant from unity to 22.4 on the ion-molecule solvation process is neglected. If the formal concentration of NH_3 is the liquid state, 40 moles/liter, is inserted into the expression for K_s, then the ratio of solvated to unsolvated cesium ions is

$$K_s' = 40K_s = (CsNH_3^{+})/(Cs^{+}) = 9.6 \times 10^{1\pm0.9} \qquad (9)$$

where the brackets indicate concentration. From this, the solvation number n_s is

$$n_s = \frac{(CsNH_3^{+})}{(Cs^{+}) + (CsNH_3^{+})} = \frac{K_s'}{1 + K_s'} = 0.99 \qquad (10)$$

This result appears to be too large, since in water the solvation number of Cs^{+} is generally considered to be about zero.

The preceding results are now used to calculate the thermodynamic data for

$$CsCl + NH_3 = CsNH_3^+ + Cl^- \qquad (11)$$

which are the sum of those for eqs. (1) and (4). In the last column of Table 1, the formal concentration of NH_3 in liquid ammonia, 40 moles/liter, is inserted for (NH_3). K', which is equal to 40 K, is the effective ionization constant of CsCl in a medium in which the concentration of NH_3 is effectively constant.

On comparison of this value of K' (1.1×10^{-1} moles/liter) with the available experimental data in table 2, it is seen that K' is too large by two orders of magnitude.

TABLE 2

IONIZATION CONSTANTS OF ALKALI HALIDES IN LIQUID AMMONIA AT -34°C

The values are taken from Jolly and Hallada(5)

	K, moles/liter
KCl	0.94×10^{-3}
KBr	2.21×10^{-3}
KI	5.46×10^{-3}
NaBr	3.80×10^{-3}

EFFECT OF CLUSTERING OF AMMONIA ON THE IONIZATION OF CsCl

The approach of the last section will now be re-evaluated using the results of a detailed analysis of the effect of clustering on the solvation of Cs^{+}(3). In the present analysis, the concentrations of the various polymers of NH_3 will be used instead of the formal concentration of NH_3 in the liquid state used earlier. Introducing the various clusters and monosolvated species,

$$\mathrm{CsCl} + \sum_{0}^{m} (NH_3)_n = \sum_{0}^{m} \mathrm{Cs}\text{-}(NH_3)_n^{\;+} + \mathrm{Cl}^- \qquad (12)$$

and letting K_Σ represent the equilibrium constant of this process, then the effective ionization constant K_Σ' is given by

$$K_\Sigma' = K_\Sigma \cdot \left[\sum_{0}^{k} ((NH_3)_n) \right] = \left[\sum_{0}^{k} (\mathrm{Cs}\text{-}(NH_3)_n^{\;+}) \right] (\mathrm{Cl}^-)/(\mathrm{CsCl})$$

$$= 1.3 \times 10^{-3\pm0.4} \text{ moles/liter} \qquad (13)$$

DISCUSSION

The available experimental ionization constants of alkali halides in liquid ammonia at its boiling point are summarized in Table 2. Based on these values, that for CsCl appears to be of the order of, or smaller than, 1×10^{-3} moles/liter. The comparable equilibrium constants for $D = 22.4$ are K (for eq. (1) in which solvation is neglected), K' (for eq. (11) in which solvation is introduced), and K_{Σ}' (for eq. (12) in which clustering is introduced). The calculated ionization constant without solvation, K, is of the correct order of magnitude (1.1×10^{-3} moles/liter). In contrast, the calculated value of the ionization constant with solvation, K', is too large by two orders of magnitude (1.1×10^{-1} moles/liter), and the solvation number (eq. 10) is almost unity, which also appears to be too large. However, K_{Σ}' with solvation and clustering is of the correct order of magnitude, $(0.5$ to $3.2) \times 10^{-3}$ moles/liter, as is the corresponding solvation number (0.12)(3). Thus, in agreement with Fowler and Guggenheim, solvation does increase the calculated degree of ionization. However, unless clustering is accounted for, the calculated ionization constant may be excessively large.

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DISCUSSION AND CONCLUSIONS

Little is known about the potential usefulness of dense gaseous electrolytes for energy conversion. This program has uncovered facts pertinent to such applications as well as to understanding the basic nature of such electrolytes. Prior to this program, the principal known facts relating to such electrolytes were(1) solubilities of salts and metals, (2) conductivities of such solutions, (3) dielectric constant as a function of solvent density, and (4) ionization constants.

The first problem encountered in this program was poor electrochemical behavior. For this reason, measurements were undertaken to determine whether the electrolyte is well behaved under equilibrium and this was established. Thus, classical electrochemical investigations can be carried out in these gases. In addition, not only can the solute density be varied but that of the solvent can also be varied.

In order to obtain information on dynamic characteristics, such as overvoltages, special cells were constructed. These were required because the dense gaseous ammonia solutions have pressures in excess of about 110 atmospheresand temperatures above about 133°C. In addition, to keep the glass cells from rupturing, the cells were placed in a pressure vessel and external pressurization used. Because of the restrictions on the cell geometry, imposed by use of the pressure vessel, a four-probe DC technique was used for measuring conductivities. At the time of the measurements, all of the electrode systems tried (Pb, Zn, Tl, and Cd amalgam/insoluble salt) displayed such poor characteristics that appreciable current could not be drawn, and hence useful overvoltage studies could not be made. However, further work has shown the electrode half-cell (Ag/$AgNO_3$-NH_3) to be almost reversible, permitting reasonable currents to be passed. Some of the experimental difficulties have been lack of useable reference electrodes, high electrolyte resistance for most of the standard electrodes, and a tendency to bubble which has been severe in the liquid state in absence of a pressurizing gas as compared with the experiments in the literature.

Having established behavior of these electrolytes for equilibrium studies, dynamic studies were initiated to explore the differences in behavior between these solutions and liquid electrolytes. The electrodeposition of silver out of $AgNO_3$-NH_3 was studied as an example of the dynamic behavior at the dense gaseous electrolyte-electrode interface as compared with liquid electrolyte-electrode interface. Since, in the dense gaseous case, bubbles should not persist at the surface of the electrode, it was anticipated that significant differences in electrodeposition might be observed. It was found that on increasing the temperature from -78° to $145^{\circ}C$, the crystallinity increased. The low temperature deposits were very coarse, bulky, and dark. At about $100^{\circ}C$, the surface was metallic. The surface became sparkly above the critical point and a dendrite crystal growth was observed. It is suggested that this technique may be useable for preparation of single crystals or whiskers.

The conductivity of $AgNO_3$-NH_3 solution was measured to support the silver growth experiments. This conductivity was very high in the dense gas state. It is probable (cf. the experiments of Sourirajan and Kennedy on the solubility of sodium chloride in dense gaseous water) that under more extreme conditions, one might obtain conductivities well in excess of those obtainable in the corresponding liquids at room temperature.

Polarographic studies were planned. A special cell was designed and built for studying the properties of dense gaseous electrolytes. Preliminary experiments were undertaken. Definitive data have not yet been obtained.

In addition to the experimental program, a parallel theoretical effort was undertaken to extend the understanding of the nature of these dense gaseous electrolytes. In the first of these, data obtained on another program on the energy of attachment of NH_3 to Cs^+ were converted to the thermodynamic properties of $CsNH_3^+$ in the gaseous state. In the next, the solvation of Cs^+ in liquid ammonia was investigated using these results. This was then applied to the ionization of CsCl in NH_3 and a preliminary extension of the analysis to dense gaseous electrolytes has been initiated.

The approach of Fowler and Guggenheim has been somewhat extended and refined. When both dielectric constant and solvation were introduced into theoretical statistical equations using the experimental thermodynamic values for $CsNH_3^+$, the calculated ionization constant was too large by two orders of magnitude. For this reason a detailed analysis of the effect of the state of the solvent on the solvation process was carried out. As a result of this analysis, in addition to the two liquid properties, dielectric constant and solvation, association or hydrogen bonding must be introduced. When this is done, the calculated ionization constant of CsCl in NH_3 is in agreement with experimental data.

The preliminary analysis of the application of these results to the ionization of CsCl in dense gaseous ammonia showed that there are two opposing effects that tend to maintain the state of ionization. At low temperatures hydrogen bonding is strong so that dielectric constant is large and solvation small.

With increasing temperature, hydrogen bonds are broken so the dielectric constant becomes smaller, the fraction of monomeric solvent increases, and the extent of solvation increases. Insofar as conductivity is concerned, the larger (more solvated)ions at higher temperature encounter smaller viscosity (due both to lower density and lesser association), so that the increased solvation at higher temperatures is not adverse. The opposing effects do not counterbalance effectively since the decrease in dielectric constant has a much larger effect on ionization than does the increase in solvation. Thus, it can be seen that in spite of the lower dielectric constant in the dense gases as compared with the liquid state, there is increased solvation. There appears to be a tendency for the ionization constant in electrolytic solutions to remain somewhat constant as the two competing factors operate against each other.

APPENDICES

1. Electrodeposition of Silver

   A patent application has been filed by NASA on this crystal growing technique.

2. Special equipment developed in this program

   Some of the specialized equipment developed in this program are included in a paper to be presented at the meeting of American Vacuum Society, May 7 through 9, 1969. The equipment in that paper was developed both on this program and another NASA program, namely "Advanced Fuel Synthesis". An abstract follows.

3. The theoretical treatment in the paper on the $Cs(NH_3)^+$ species has been refined, additional terms having been introduced at the request of a referee. When the papers appear in publication, therefore, they will have a slightly different numerical value because of this.

AMERICAN VACUUM SOCIETY
SECOND ANNUAL SYMPOSIUM, MAY 7-9, 1969

VACUUM TECHNIQUES USED FOR THE SYNTHESIS OF MOLECULAR METALS*

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ABSTRACT

On a program involving the synthesis and isolation of molecular metals such as NH_4 and $N(CH_3)_4$, one of the approaches used here has been to synthesize these metals by the electrolysis of the corresponding halides in liquid ammonia at -78°C to transfer them, and then to concentrate and isolate them by pumping ammonia off frozen metal-containing solution.

The metals in solution are sensitive to traces of impurities such as water-like materials on the glass surfaces. The system is so designed that the initial solution or portions of subsequent solutions containing metal is used to flush the transfer lines and the electrolysis chamber. Several devices are described in detail, namely a salt adder, a rotary divider for liquids, and a cryopumped collection cell.

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*This work was sponsored by the National Aeronautics and Space Administration under contracts NAS7-551 and NAS7-326.