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SELECTED PHYSICAL PROPERTIES OF SOLUTIONS OF CALCIUM IN LIQUID AMMONIA

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Special Thesis

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SELECTED PHYSICAL PROPERTIES OF SOLUTIONS OF CALCIUM IN LIQUID AMMONIA

Wa She Wong
(Ph.D. Thesis)

August 1966

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SELECTED PHYSICAL PROPERTIES OF SOLUTIONS OF CALCIUM IN LIQUID AMMONIA

Wa She Wong
Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

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ABSTRACT

The conductivity, viscosity, and density of calcium-ammonia solutions were measured in a temperature range from -35°C to -70°C. The liquid region of the phase diagram of calcium-ammonia solutions was determined by conductivity measurements.

The results may be summarized as follows:

(1) Over a very wide concentration range (approximately from 0.02 mole Ca/liter to 1.5 mole Ca/liter) the calcium-ammonia solutions separate into two liquid phases in good agreement with earlier results reported in literature.

(2) The equivalent conductance of a dilute calcium-ammonia solutions is much smaller than that of analogous alkali metal-ammonia solutions and increases with temperature, indicating that the fraction of calcium atoms in liquid ammonia dissociated into calcium ions and solvated electrons is much smaller than for analogous alkali metal-ammonia solutions.

The atomic conductance of concentrated calcium-ammonia solutions is of the same order of magnitude as for metals and increases rapidly as concentration of metal increases, a behavior similar to those demonstrated by concentrated alkali metal-ammonia solutions.

(3) The temperature coefficient of conductance of dilute calcium-ammonia solutions in the temperature range investigated is approximately +3.5% per degree centigrade. This is approximately twice the temperature coefficient of viscosity, which indicates an increase of degree of dissociation with temperature.

The temperature coefficient of conductance of the concentrated phase decreases from +0.39%/°C at 1.5 mole Ca/liter, and reaches constant value of +0.24%/°C beyond 2.1 moles Ca/liter.

(4) The excess volume of concentrated calcium-ammonia solutions is larger than that of analogous alkali metal-ammonia solutions and decreases much more rapidly with concentration increase than in alkali metal-ammonia solutions.

(5) The significant differences found in the conductance and excess volume behavior between solutions of calcium and of the alkali metals are largely due to the two valence electrons of calcium. The experimental findings are consistent with current theories on the structure of metal-ammonia solutions.

1. INTRODUCTION

Liquid ammonia exhibits a distinct advantage over water as a solvent in that it can dissolve the alkali and alkaline earth metals without an appreciable reaction*. The metal-ammonia solutions have the unusual feature that they act as electrolytes in dilute solutionsand preserve the metallic properties in concentration solutions.

Below the critical temperature all metal-ammonia solutions except cesium separate into two liquid phases, a concentrated one and a dilute one[9,43,91,92]. All dilute metal-ammonia solutions show a fine blue color. Their equivalent conductance is similar to that of an electrolytic solution, that is, it increases as concentration of metal decreases, and reaches a finite value in an infinitely dilute solution[51,66,67]. When current is passed through a dilute metal-ammonia solution , the positive metal ions migrate toward the cathode, but no new product is produced on the anode[30,63]. This fact indicates that the negative current carriers in dilute metal-ammonia solutions are electrons. On the other hand, the solutions show a positive excess volume** which is contrary to the behavior of ordinary electrolytic solutions[72,77].

The concentrated metal ammonia solutions show a luster resembling a copper or bronze color[67]. No migration of metal is found when current is passed in the concentrated metal-ammonia solutions[30,63]. The concentrated metal-ammonia solutions also show a remarkable positive excess volume[72,77].

Most of the experimental work concerning metal-ammonia solutions has been done in alkali metal-ammonia solutions. Based on these experimental

---

* Some other metals can also be dissolved in liquid ammonia (see Appendix A-1).

** Excess volume is defined in section 3-4-b.

data, many models have been suggested in an attempt to explain these unusual properties.

In the present work, the conductivity and density of calcium-ammonia solutions and the viscosity of liquid ammonia and dilute calcium-ammonia solutions were measured in a temperature range from -35°C to -70°C. The main purpose of this work was to determine the liquid region of the phase diagram of the calcium-ammonia solutions. The phase diagrams of sodium, potassium, lithium ammonia solutions have been established[55,61,70,91,92]. Fragmentary information on the behavior of the calcium-ammonia system indicates considerable differences from the sodium-ammonia case. On the basis of vapor pressure measurements, Kraus[62] found that at -32.5°C the saturation concentration of the dilute phase is 0.5 mole%, while that of the concentrated phase is 9 mole% in respect to calcium. The critical temperature for the solution appeared to be higher than room temperature (while that of the sodium-ammonia solutions is -41.5°C[70]). The work of Marshall and Hunt[79], again using vapor pressure measurements, indicated a very small two-liquid phase region in the temperature range of -45.4°C to -63.8°C. Because of the evolution of hydrogen due to the decomposition of the solutions of calcium in ammonia, the accuracy of these measurements may be subject to question (see appendix A-11). More recently, Jolly et al[39,56] determined the phase diagram of calcium-ammonia solutions by conductivity and vapor pressure measurements. Their results are markedly different from those of Kraus[62]. In the present work the liquid region of the phase diagram of calcium-ammonia solutions in the temperature range from -35°C to -70°C was determined by conductivity measurements which were affected to a much less degree by the decomposition reaction.

According to the phase rule, if three phases and two components are present, there is only one degree of freedom. If only one phase of calcium-ammonia solution in the two-liquid phase region is used for the conductivity measurements, the specific conductance is constant at constant temperature. However, in the one-liquid phase region the specific conductance will decrease as the concentration of calcium decreases. The breaking point on the curve of the specific conductance vs concentration plot was interpreted to be the concentration at which the phase separation occurred.

The equivalent conductance, and temperature coefficient of conductance, of calcium-ammonia solution in the single liquid phase region were calculated from the experimental conductivity measurements and the excess volume was calculated from density data. The results are discussed in the later sections and compared with those of alkali metal-ammonia solutions.

The results indicate that the physical properties of calcium-ammonia solutions determined in this work are quite different from those of alkali metal-ammonia solutions. It is possible that these differences are caused by the liberation of two valence electrons per atom when calcium is dissolved in liquid ammonia.

2. EXPERIMENTAL PROCEDURE

2-1. Conductivity Measurements in Dilute Calcium-Ammonia Solutions.

Conductances of the dilute calcium-ammonia solutions were determined by measuring the resistance of the calcium-ammonia solutions in a conductivity cell using an A-C Wheatstone bridge (Figure 2-1). The resistance and the capacitance of the calcium-ammonia solutions in the conductivity cell were balanced by a decade resistor (±1 ohm) and a condenser having a precision of 1 μ μ f. This A-C Wheatstone bridge had a precision of 0.1% for the resistance measurements made*.

The conductivity cell and the calcium-ammonia solutions "preparation cell" are shown in Figures 2-2 and 2-3. The conductivity cell was U-shaped so that if two liquid phases were formed inside the cell, the less dense, more concentrated phase would float to the top of the arms and not substantially affect the measurement. Both electrodes were smooth platinum disks, connected to tungsten wires. All tungsten inside the cell was covered with uranium glass so that only the platinum came in contact with the solutions.

The calcium-ammonia solution was prepared in the "preparation cell" by the following procedure: After the calcium-metal and a magnetic stirring bar were put into the preparation cell, the whole apparatus was immediately connected to the vacuum line and evacuated. Then the preparation cell and the conductivity cell were immersed into the cold bath. After stopcock (e) was closed (Figure 2-2), ammonia was condensed into the preparation cell from the stainless steel ammonia cylinder. The

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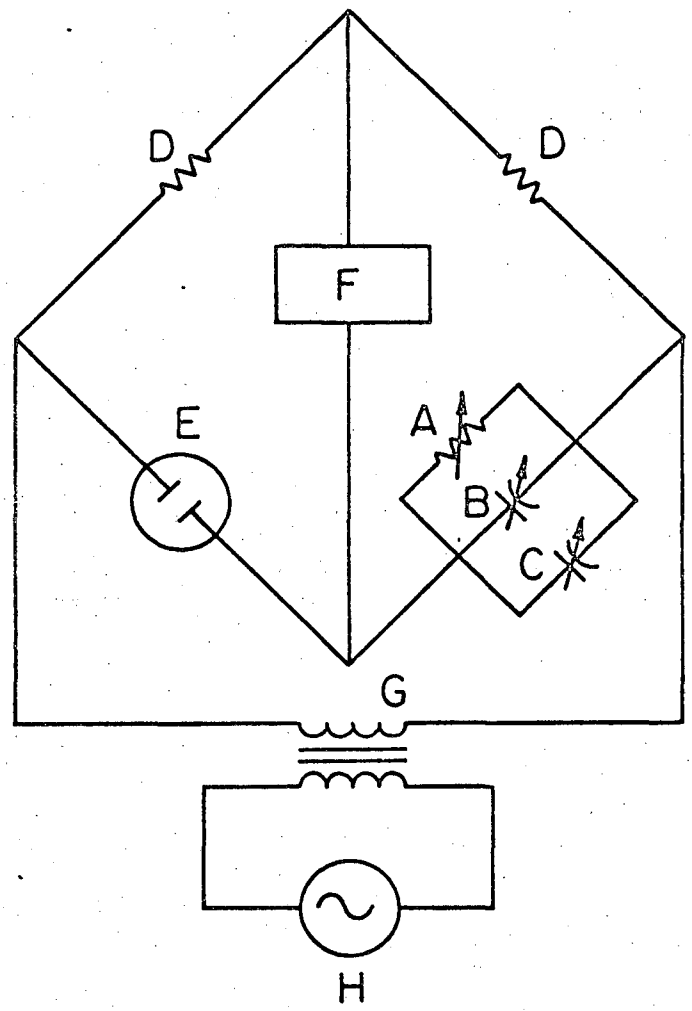
* In the latter part of this work a better Wheatstone bridge with a precision of 0.01% was used. This bridge is a product of Electro Scientific Industries, including an Impedance Bridge Type 290A and an A-C Generator Detector Type 861A.



A: Decade Resistance 100 K ohm 5 steps.

B: Decade Condenser 1 μ.f. 5 steps. General Radio Co. Type 219-M.

C: Precision Condenser 1100 μ.μ.f. General Radio Co. Type 722-N.

D: 1000 ohm Resistance.

E: Conductivity Cell.

F: Unit Null Detector. General Radio Co. Type 1212-A.

G: Isolation Transformer.

H: Test Oscillator. Hewlett Packard Model 650-A.

Figure 2-1. A-C Wheatstone Bridge.

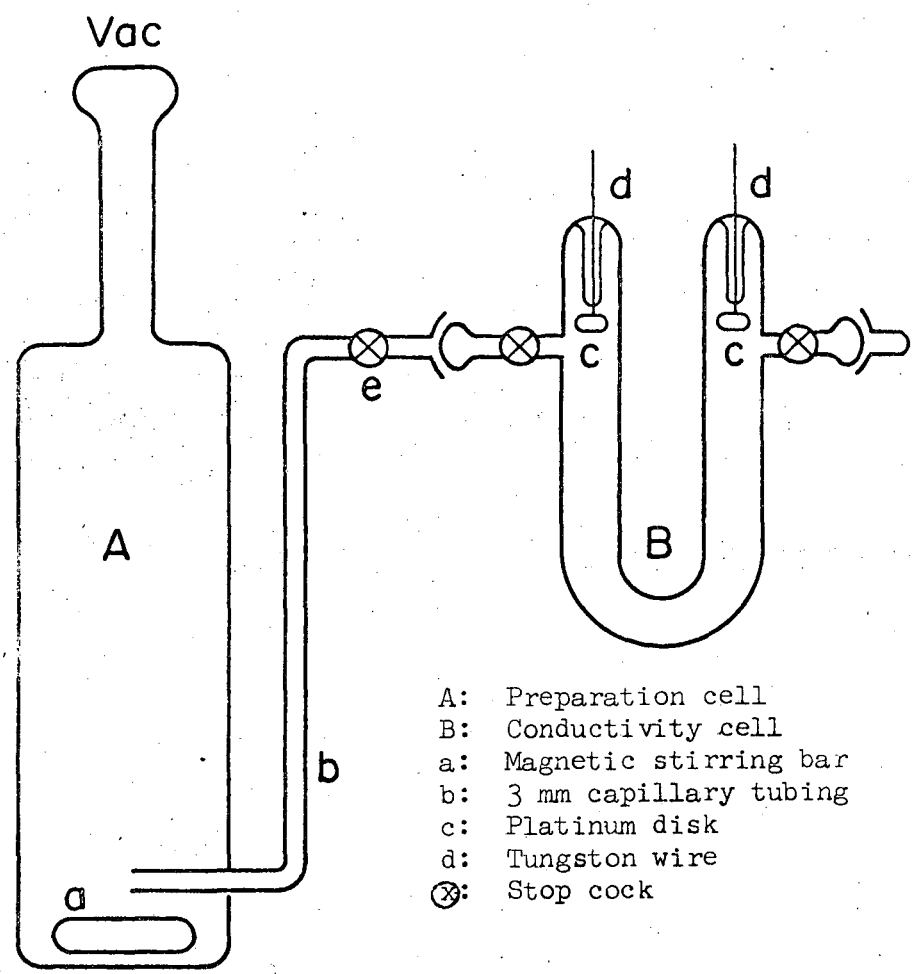


Figure 2-2.

Conductivity Cell for Dilute Calcium-Ammonia Solutions.

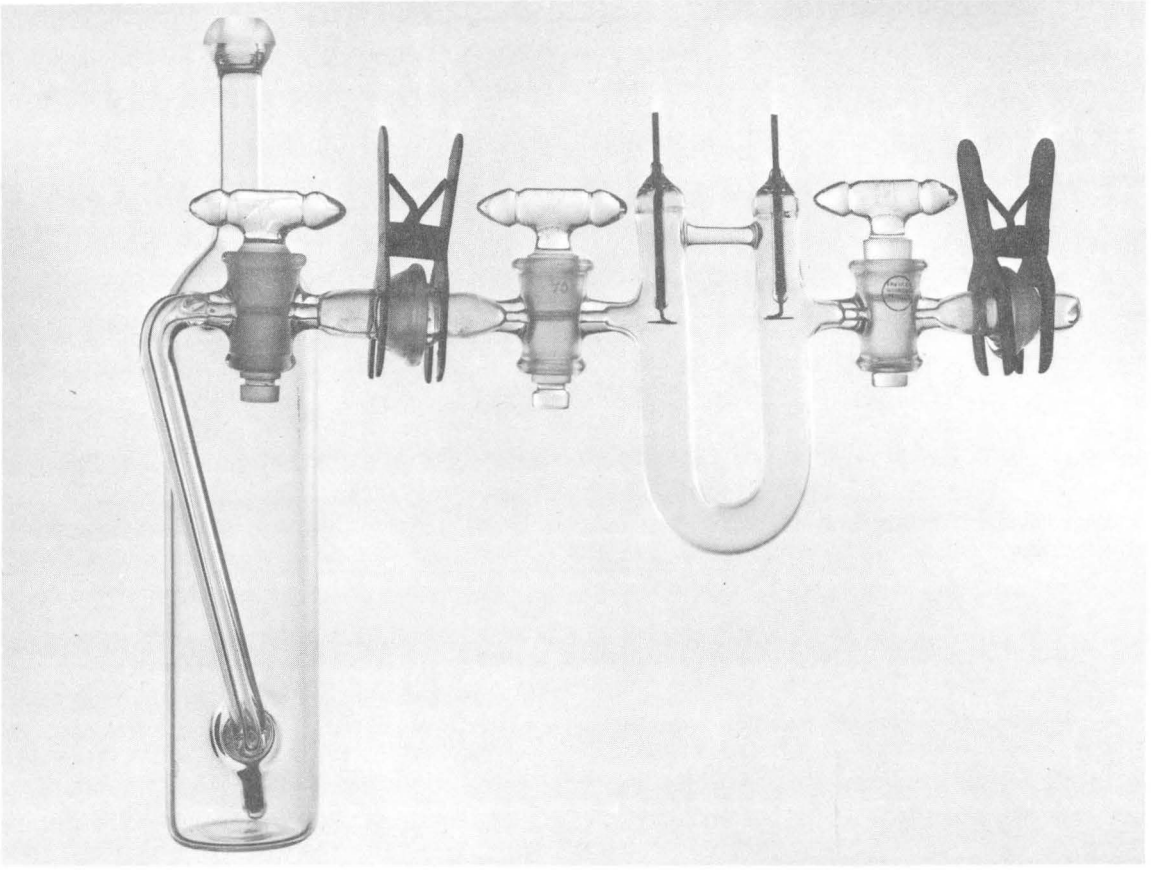


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Figure 2-3
Conductivity Cell for Dilute Calcium-Ammonia Solutions.

weight of the calcium metal and ammonia used was determined by the method described in appendix D. The measurements were made at 1 K cycles per second and 2.2V (R.M.S.).

To minimize the error due to decomposition reaction (see appendix C),

$$Ca + 2NH_3 \rightarrow Ca(NH_2)_2 + H_2 \qquad (2\text{-}1)$$

it is decided that each individual run should not last for more than four hours. Therefore, one sample of calcium-ammonia solution was used in the measurement at -35°C, another freshly prepared sample was used in the measurements covering the temperature range of -40°C to -51°C, and a third sample of -60°C to -70°C.

Since the conductance of calcium-ammonia solutions was not constant but decreased slowly due to the decomposition reaction, the following method was used for the conductivity measurements for the calcium-ammonia solutions in the one-liquid phase region: The measurements were started at the lowest temperature of the temperature range in which the sample of calcium-ammonia solution was to be used. The temperature was set at 1°C below the desired temperature. Using the temperature range of -40°C to -51°C as an example, the temperature of the cold bath was first set at -52°C. The calcium-ammonia solution in the preparation cell was transferred into the conductivity cell by applying argon pressure over the solution in the preparation cell and the temperature raised to -51°C slowly. The resistance measurements were started at -52°C and continued at two-minute intervals. The resistance of the calcium-ammonia solution first decreased due to the increase in temperature, then remained constant for approximately six to ten minutes, then increased again due to the decomposition reaction. The minimum value of the resistance was used

for the conductance calculation. After the conductivity measurement at -51°C was finished, the temperature was raised to -45.5°C, then to -40°C. The conductance of the calcium-ammonia solution at these two temperatures was then measured in the same manner as at -51°C.

Since the concentration of dilute calcium-ammonia solutions in the two-liquid phase region depends on the temperature, the method for the conductivity measurement was different from that for the calcium-ammonia solutions in the single liquid phase region. The measurement was begun at the highest temperature of the temperature range in which a calcium-ammonia solution was used. Again the temperature range from -40°C to -51°C is used as an example. The temperature of the cold bath was first set at -39.5°C. The calcium-ammonia solution in the preparation cell was stirred for 30 minutes to obtain equilibrium between the two liquid phases, then stirring was stopped to allow the two liquid phases to separate. The dilute calcium-ammonia solution was transferred into the conductivity cell from the center of the lower part of the preparation cell (see Figure 2-2) by applying argon pressure to the preparation cell. The temperature was then lowered to -40°C. The resistance measurements were started at -39.5°C and continued at two-minute intervals. The resistance increased very rapidly at the beginning because of the decrease of both the equivalent conductance and the concentration of the calcium in the dilute phase as temperature decreased. After equilibrium between the two-liquid phases were established, the resistance increased slowly due to the decomposition reaction. The transition point on the resistance vs time curve was taken for the conductance calculation. The conductance of the solution was then measured in the same manner at -45.5°C and at -51°C. The measurements in the other temperature ranges were made in the same manner.

The main sources of error in the conductivity measurement of the dilute calcium-ammonia solutions were due to:

(a) The decomposition of the calcium-ammonia solutions. Because platinum acts as a catalyst (appendix A-11), most of the decomposition reaction probably occurred on the electrode surface and a thin layer of lower conductivity was formed near the electrodes. The hydrogen generated from the decomposition reaction may have adhered to the electrode surface and altered the cell constant.

(b) The error in the determination of the concentration of calcium in the calcium-ammonia solutions. The amount of calcium metal used in these experiments ranged from 15 mg to 100 mg (in the one-liquid phase region). If the error in the amount of calcium metal used due to the weighing was 0.3 mg, it introduced a 0.3% to 5% error in the calculated calcium concentration. The impurities in the calcium metal (appendix C) also introduced some error in the concentration determination.

(c) In the two-liquid phase region, some solutions were used for the conductivity measurements at two or three temperature levels. As an example, after the measurement at -40°C was finished, the temperature was decreased to -45.5°C for the next measurement, and some concentrated phase separated out due to the temperature change. The concentrated solution may have adhered to the wall of the conductivity cell and formed a new electrical circuit parallel to that of the solution. In some experiments, some of the concentrated solution was unintentionally drawn into the conductivity cell from the preparation cell. A thin film covering the wall of the conductivity cell with the appearance of a golden mirror was then observed. In such cases the resistance dropped to a very low value*.

---

* The concentrated calcium-ammonia solutions have a very high conductivity, of the same order of magnitude as for metals (see section 3-3-a).

(d) The uncertainty in the temperature of ±0.2°C (due to the fluctuation of the cold bath temperature and due to the error in the reading of the thermometer) introduced an uncertainty of 0.7% in the conductivity measurement since the conductivity changes approximately by 3.5% per degree centrigrade (section 3-2-c).

2-2. Conductivity Measurements in Concentrated Calcium-Ammonia Solutions.

Conductances of the concentrated calcium-ammonia solutions were measured in a conductivity cell shown in Figures 2-4 and 2-5. In the conductivity cell the tubing between the electrodes is not horizontal but has a slope of approximately five degrees. In a case when the heavier dilute phase was formed in the tubing, it would flow down and be trapped in the leg of the conductivity cell below the electrodes. The electrodes were smooth platinum disks, built into the conductivity cell by the same method described in section 2-1. To avoid the error due to the contact resistance*, an A-C four pole method** was used to measure the resistance of concentrated calcium-ammonia solutions in the conductivity cell. The measuring device was a milliohmmeter, model 503, produced by Keithley Instruments.

The current passed through the conductivity cell was a square wave A-C current of 40 cycles per second.

---

* Because of the high conductivity of the concentrated calcium-ammonia solutions, the resistance of the calcium-ammonia solutions in the conductivity cell is of the same order of magnitude as the contact resistance.

** There were four electrodes in the conductivity cell. A known amount of current was passed between the outer electrodes and the ohmic potential drop was measured between the inner electrodes (see Figure 2-4).

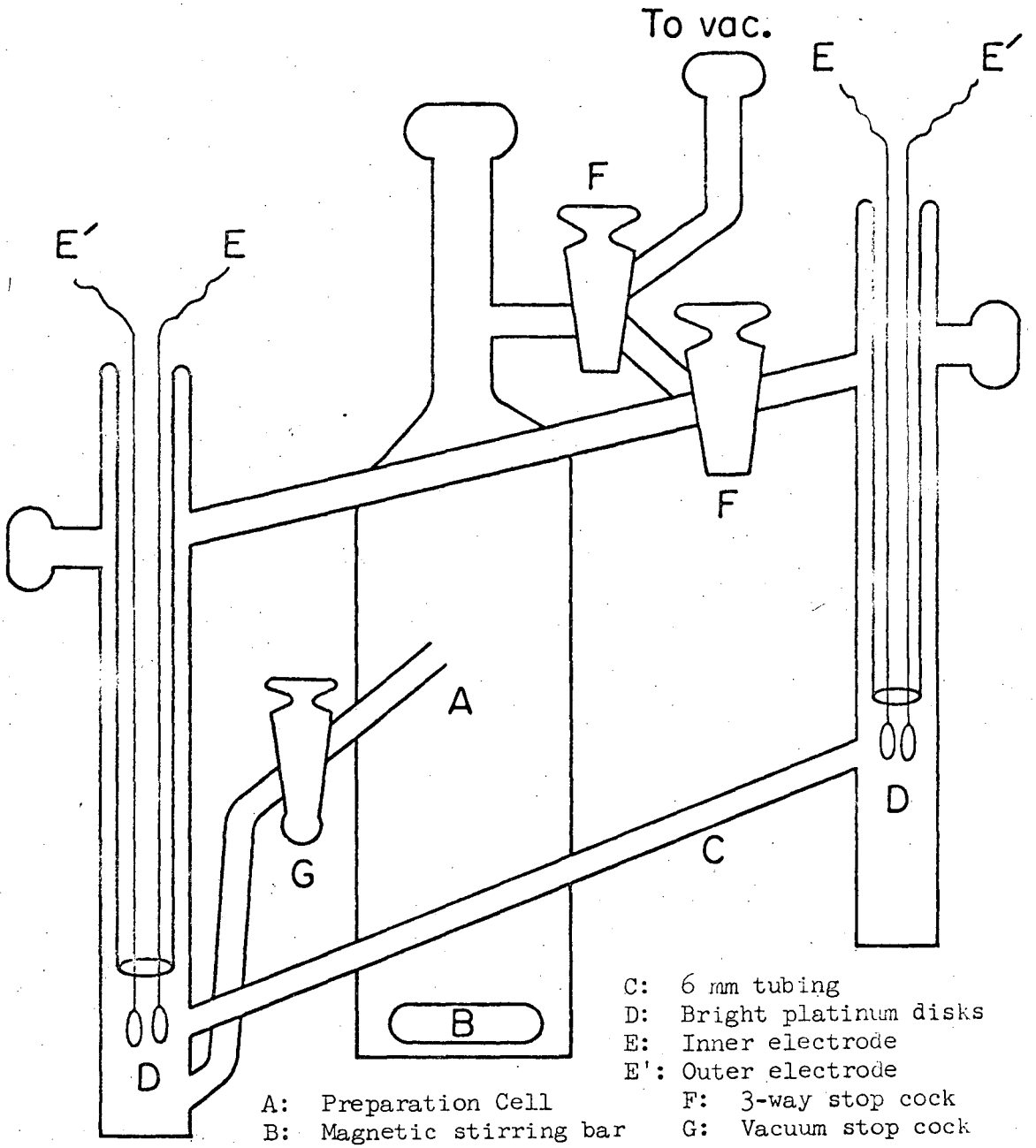

Figure 2-4.

Conductivity Cell for Concentrated Calcium-Ammonia Solutions.

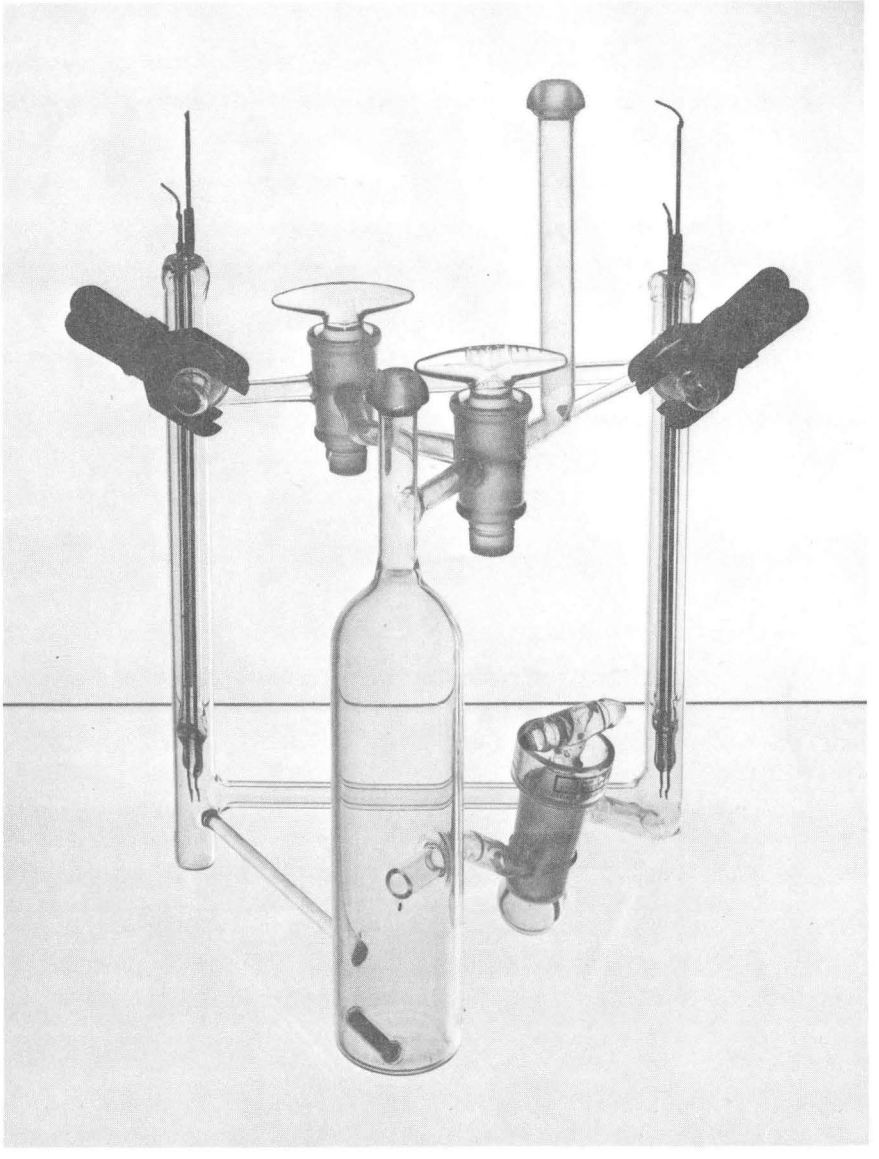

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Figure 2-5

Conductivity Cell for Concentrated Calcium-Ammonia Solutions.

The calcium-ammonia solution was prepared in the preparation cell by the method described in section 2-1. The solution was then transferred into the conductivity cell using argon pressure, from the upper part of the preparation cell so that if two liquid phases were presented, only the lighter concentrated phase was used for the measurement. For each concentration, two samples were used to cover the whole temperature range. One was used to cover the temperature range of -35°C to -51°C, the other was used for the measurements at -60°C and -70°C.

For a sample of calcium-ammonia solution, the measurements were begun at the highest temperature of the temperature range in which the measurements were taken. After this measurement was finished, the temperature of the cold bath was lowered to the next desired temperature and measurements were continued.

The main sources of error in the conductivity measurements in the concentrated solutions were due to:

(a) The decomposition reaction of calcium-ammonia solutions, which will change the concentration of calcium in the neighborhood of the electrodes. Since the measurements were always started from higher temperature, the error due to the decomposition reaction was most serious in the measurements at -51°C and -70°C.

(b) The uncertainty in the temperature of ±0.2°C of the cold bath. Since the temperature coefficient of conductivity of a concentrated calcium-ammonia solution is very small (see section 3-3-d), the error due to this source was not serious.

(c) The most important source of error was due to the accuracy of the measuring device. Since the accuracy of the milliohmmeter used in these measurements is only 1% of full scale, the uncertainty in the measured resistance was approximately 2%.

2-3. Density Measurement in Calcium-Ammonia Solutions.

The density of the calcium-ammonia solutions in the temperature range of -35°C to -70°C was measured by a pycnometer. This consisted of a 100 cc flask connected to a 3 mm glass capillary by a ground-glass ball joint (Figures 2-6 and 2-7). A red mark was made on the lower part of the capillary. Calcium metal and a magnetic stirring bar were placed into the pycnometer through the ball joint. The apparatus was connected to the vacuum line and evacuated. Ammonia was condensed into the pycnometer from the stainless steel cylinder at -70°C. A copper cylinder container containing acetone and dry ice was put into the cold bath to maintain this low temperature*. After the proper amount of ammonia had been condensed into the pycnometer, the temperature was raised to the desired temperature, causing the level of the calcium-ammonia solution to rise into the capillary by thermal expansion. The height of the level of the calcium-ammonia solution in the capillary above the red mark was measured by a cathetometer through the window of the cold bath. The vapor pressure** of the calcium-ammonia solution was measured by a McLeod manometer. Stopcock (e) (Figure 2-8) was then closed and more ammonia added to the vacuum line until the ammonia pressure was brought up to 600 mm Hg**. In the density measurement of concentrated calcium-ammonia solutions, some intert gases were in the pycnometer***. Since the inert gases could escape only

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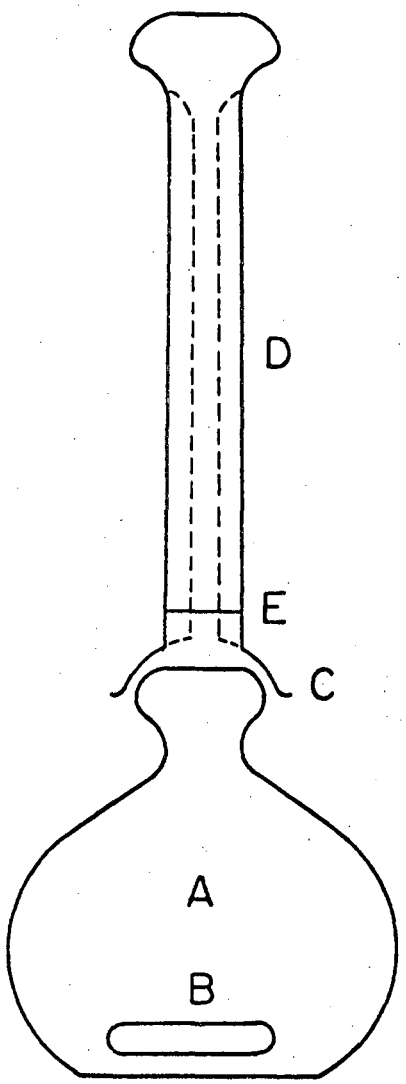
* The lowest temperature obtained by this cooling system was -55°C. Another cooling system was used for the experimental work in the temperature range from -60°C to -70°C (see appendix B).

** These processes were for the determination of the amount of ammonia remaining in the vacuum line (appendix E-4).

*** Some inert gas which was produced by the reaction of the moisture in the sodium-ammonia and in the steel cylinder was carried by the ammonia gas into the pycnometer (see appendix D) and some inert gas was probably produced by the deomposition reaction (see appendix C).



A: 100 cc flask
B: Magnetic stirring bar
C: 18/9 ball joint
D: 3 mm capillary tubing
E: Red mark

Figure 2-6.

Pycnometer.

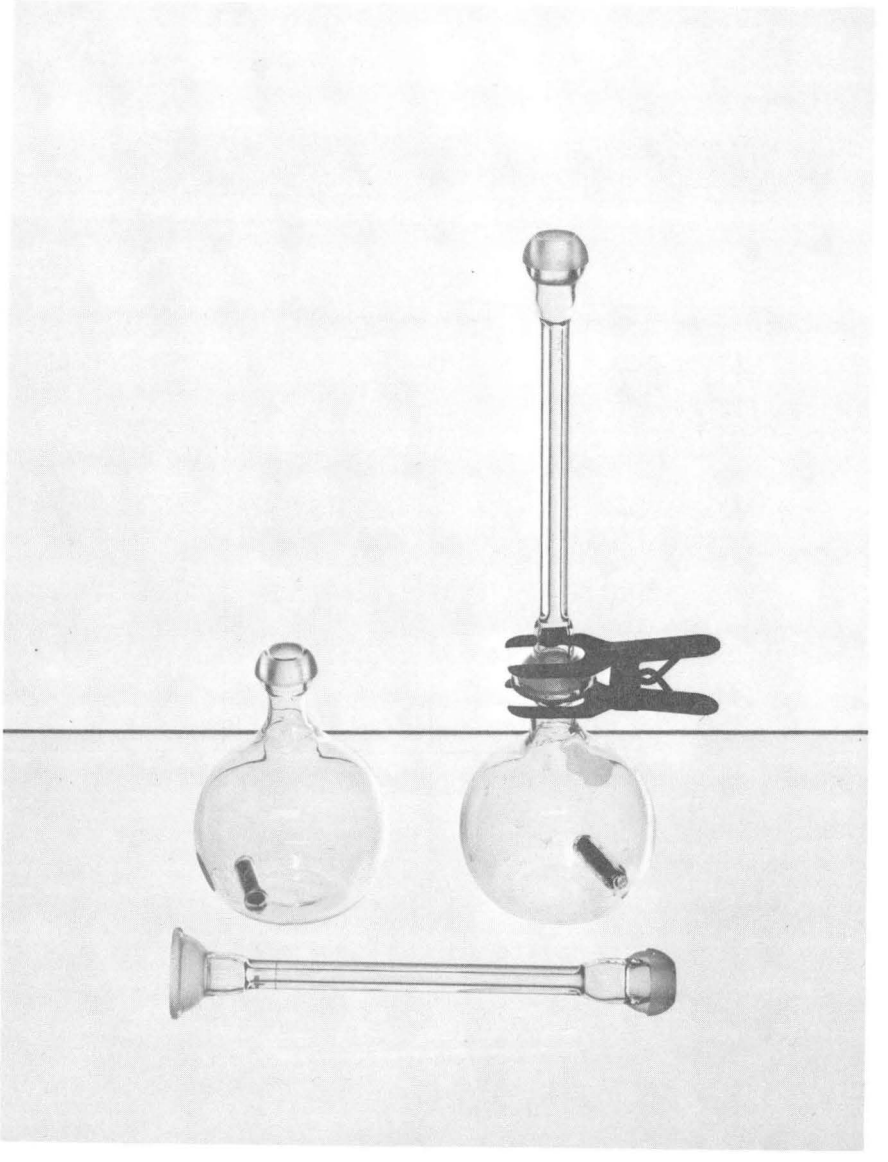


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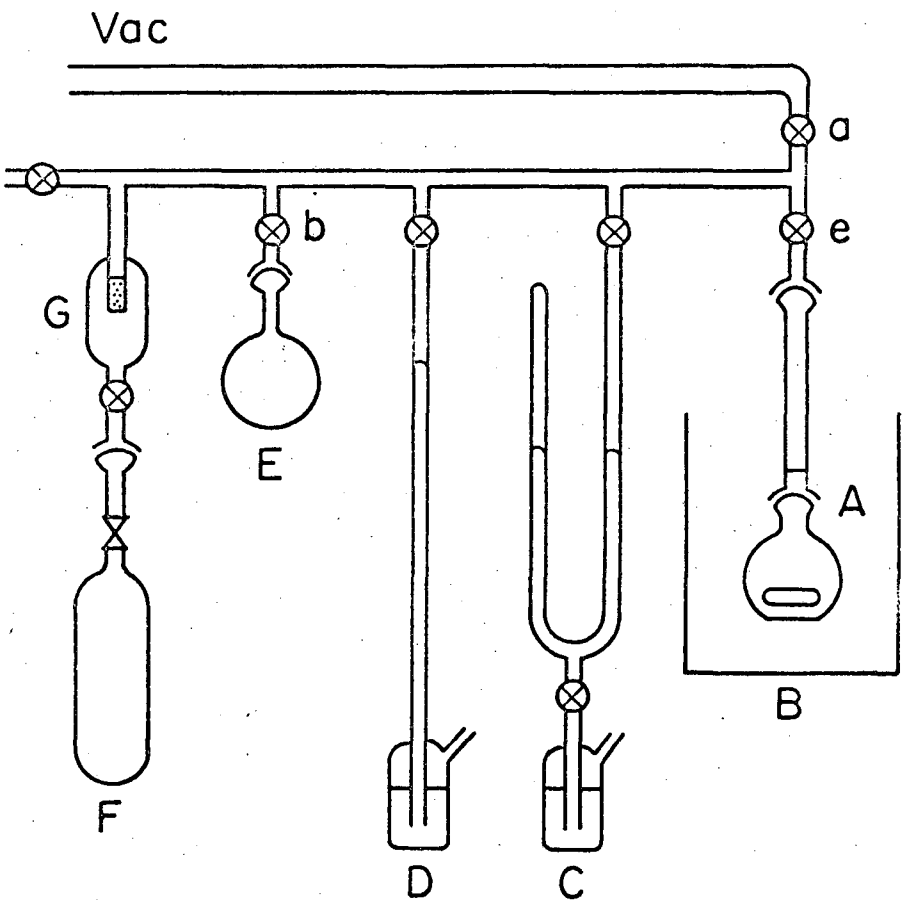
Figure 2-7
Pycnometer



A: Density cell
B: Cold bath
C: McLeod manometer
D: Safety valve
E: 1-liter flask
F: Stainless steel NH_3 cylinder
G: Sintered glass filter
VAC: To vacuum pump
⊗: Stopcock
X: Hoke needle valve

Figure 2-8.

Pycnometer and Vacuum Line.

through the capillary by diffusion, they were compressed into a small volume creating a high pressure when the condensation of ammonia was nearly completed. Therefore the inert gases had to be removed before more ammonia could be condensed. A one-liter flask attached to the vacuum line (Figure 2-8) was used for this purpose. The inert gases with some ammonia were transferred into the one-liter flask by opening stopcock (b) very slowly. The one-liter flask was filled with ammonia to a pressure of 600 mm Hg after the condensation of ammonia was completed. The amount of calcium metal and ammonia used was determined by the method described in appendix D. For each concentration, two samples were used to cover the temperature range from -35°C to -51°C. One sample was used for the measurements at -35°C, and another was used for the measurements at -40°C, -45.5°C, and -51°C. In the latter case, after the density measurement at -40°C was finished, the temperature of cold bath was lowered to -70°C again. More ammonia was condensed into the pycnometer to determine the density of the calcium-ammonia solution at -45.5°C, then at -51°C by the same method.

Another cooling system from which a lowest possible temperature of -72°C could be obtained was used in the density measurements of calcium-ammonia solutions at -60°C and -70°C. Since the lowest possible temperature that could be obtained by this cooling system was not much lower than -70°C, the liquid level of the calcium-ammonia could not be raised over the red mark by thermal expansion. The 3 mm capillary tubing, therefore, was replaced by a 7 mm tubing so that ammonia could be condensed into the pycnometer until the liquid level was above the red mark on the tubing. The experimental procedures were the same as that described above.

In order to estimate the accuracy of the density measurements of the

calcium-ammonia solutions, the density of liquid ammonia was also measured at different temperatures and compared to the data given in the literature [17,48]. The results tabulated in Table 2-1 and plotted in Figure 2-9 show that the average deviation from the literature values is ±0.031% and the maximum deviation of an individual run is ±0.085%*.

The accuracy of the density measurements of calcium-ammonia solutions in the dilute region is believed to be the same as that of liquid ammonia, less than ±0.05%. However, in the concentrated region, more error was introduced because of the large amount of inert gases evolved. When the inert gases escaped from the density cell, occasionally some of the calcium-ammonia solution was carried along into the capillary. This would wet the wall and introduce some error in the determination of the level of the calcium-ammonia solution in the capillary. The accuracy of the density measurement decreases at lower temperatures of the temperature range in which a sample of calcium-ammonia solution was used for the measurements because of the accumulation of errors due to the estimation of the amount of ammonia remaining in the vacuum line and also due to the decomposition of the calcium-ammonia solutions because of the longer residence time of the calcium metal in the solutions.

2-4. Viscosity Measurements in Liquid Ammonia and Dilute Calcium-Ammonia Solutions.

In order to better understand the temperature coefficient of conductance of calcium-ammonia solutions, the temperature coefficient of viscosity of liquid ammonia had to be obtained. Literature research

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* The density data of liquid ammonia given by Cragoe et al[17] is believed to be too low. For example, one may compare the density of liquid ammonia at -33.7°C measured by Hutchison et al[47] (0.6828 gm/cc) to that given by Cragoe et al (0.6822 gm/cc) and that calculated from the equation given by Keyes[48] (0.68285 gm/cc).

Table 2-1.

Densities of Liquid Ammonia (gm/cm^3)

Temp	Present Work	Average of Present Work	I.C.T. (Keyes[48])	Deviation from Keyes Data (%)	Cragoe et al[17]	Deviation from Cragoe's Data (%)
-35	0.68511 0.68475	0.68493	0.68448	+0.073		
-40	0.69088 0.69116 0.69078	0.69094	0.69069	+0.0362	0.6900	+0.136
-45	0.69648 0.69724 0.69658	0.69677	0.69682	-0.0072	0.6960	+0.1106
-50	0.70258 0.70308 0.70259	0.70275	0.70288	-0.0185	0.7020	+0.1068
-51	0.70430 0.70427	0.70429	0.70408	+0.0289		
-55	0.70836 0.70897 0.70855	0.70863	0.70884	-0.0295	0.7090	+0.1031
-60	0.71468 0.71476	0.71472	0.71473	-0.0014		
-70	0.72574 0.72600	0.72587	0.72626	-0.0537		

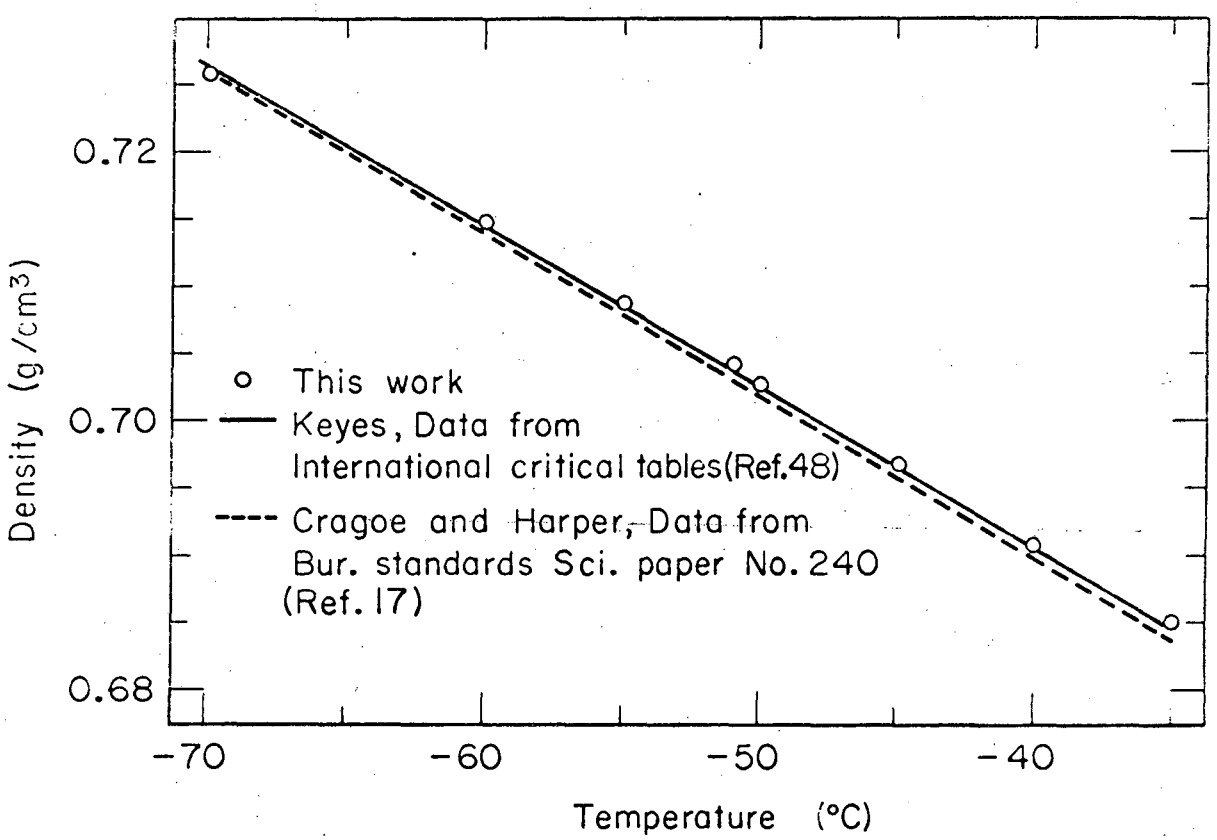


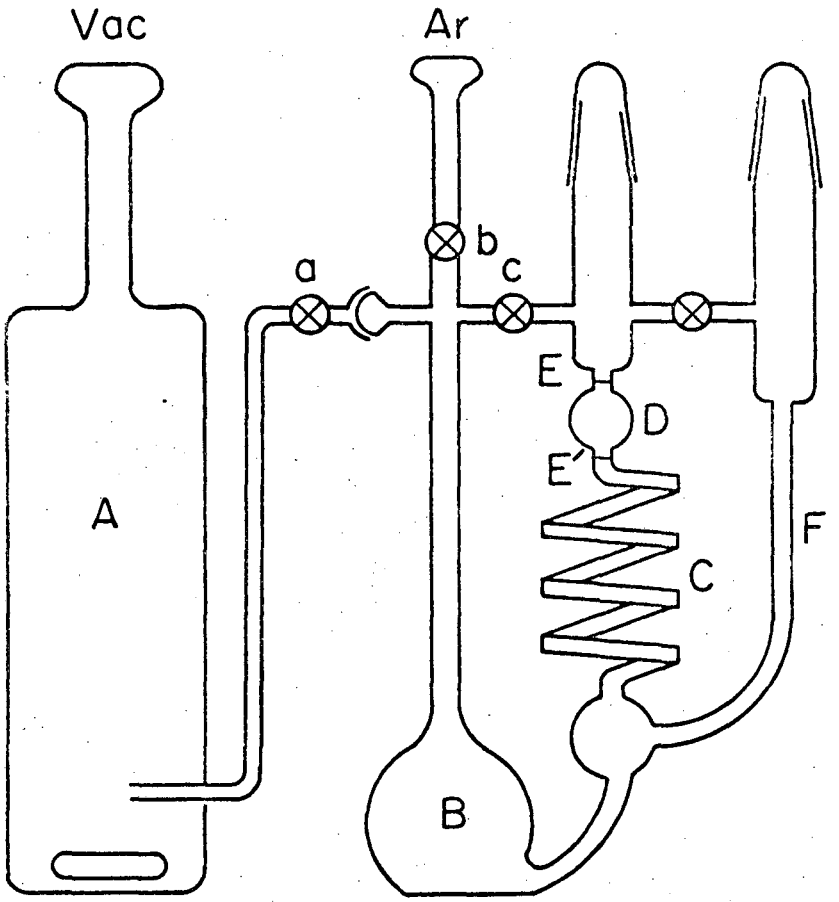
Figure 2-9.

Density of Liquid Ammonia.

revealed that no viscosity data of liquid ammonia at low temperature (below -34°C) were available. Therefore, the viscosity of liquid ammonia and dilute calcium-ammonia solutions in the temperature range of -35°C to -70°C was measured.

An Ubbelohde viscometer[26] adapted for low pressure operation (Figures 2-10 and 2-11) was used for these measurements. Calcium-ammonia solutions were prepared in the preparation cell by the method described in section 2-1. The weight of calcium metal and ammonia used was determined by the method described in appendix D. Approximately 30 cc of the calcium-ammonia solution were transferred into the 50 cc flask (B)(Figure 2-10) by introducing argon into the preparation cell and opening the stopcock (a). The calcium-ammonia solution was drawn from the central part of the bottom of the preparation cell so that if two liquid phases were present, only the dilute phase would be used for the measurement. After stopcocks (a) and (c) (Figure 2-10) were closed, argon was applied to the 50 cc flask (B) through stopcock (b) which forced the calcium-ammonia solution into the legs (C) and (F) until the liquid level was above the red mark (E). Then stopcock (b) was closed and (c) was opened to equalize the pressure between the 50 cc flask (B) and the legs (C) and (F). The calcium-ammonia solution then flowed back to the 50 cc flask through the four-turn capillary coil made of 0.5 mm capillary tubing. The diameter of the coil was 2 cm. The time (t) for the liquid level to move from the red mark (E) to (E') was measured.

As in the case of conductivity measurements, at each concentration two samples of calcium-ammonia solutions were used to cover the whole temperature range. One was used in the measurement in the temperature range of -40°C to -51°C, the other was used in the measurements at -60°C



A: Preparation cell
B: 50 cc flask
C: Capillary coil
D: 4.2 cc bulb
E: Red mark
F: 6 mm tubing
⊗: Stopcock
Vac: To vacuum line
Ar: To argon tank

Figure 2-10.

Ubbelohde Viscometer.

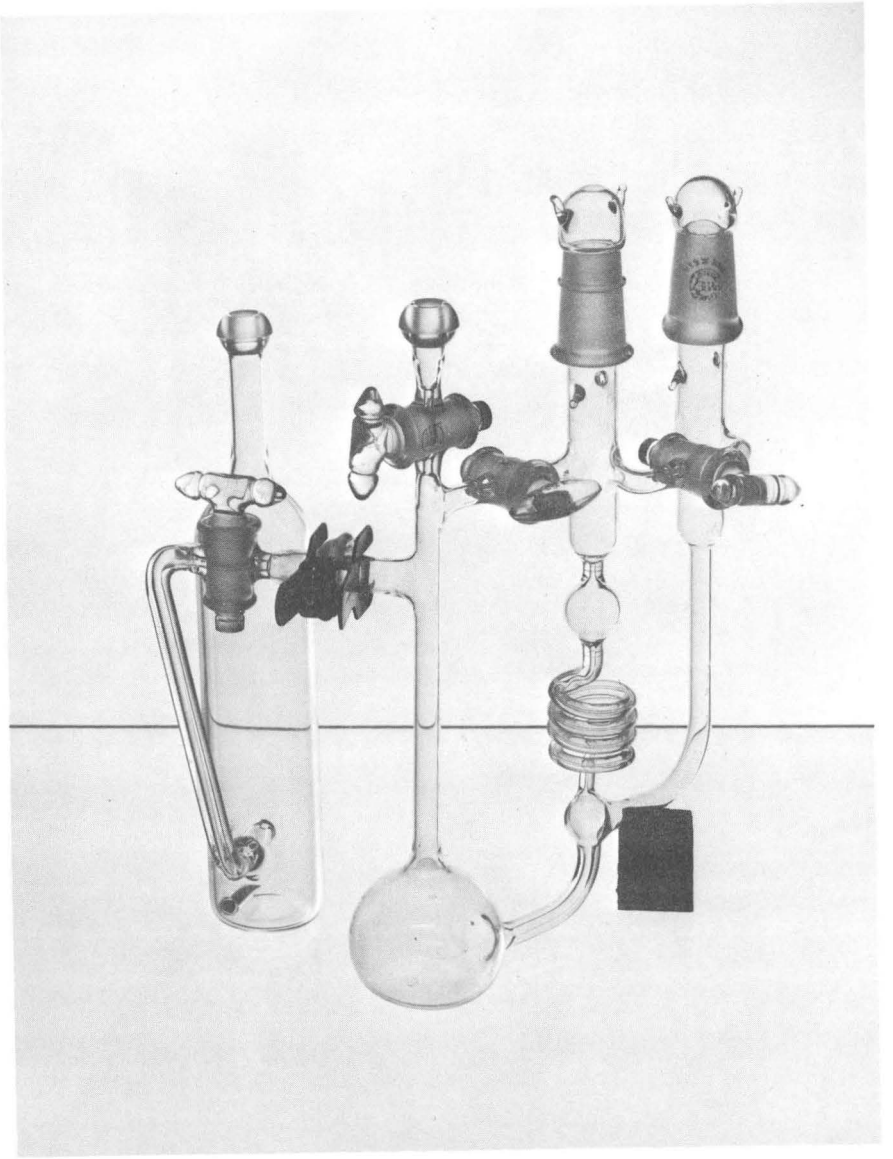


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Figure 2-11
Ubbelohde Viscometer.

and -70°C. The viscosity of liquid ammonia was measured by the same method. The viscosity was calculated by the equation[26]

$$\nu = Ct - B/t \tag{2-2}$$

$$\eta = \nu d \tag{2-2a}$$

where ν = kinematic viscosity (centistoke)

η = viscosity (centipoise)

d = density (gm/cm^3)

t = time for the liquid level to move from the red mark (E) to (E') (second)

C and B are constants with units of (centistoke per sec) and (centistoke-sec), respectively.

In the case of liquid ammonia, the Reynolds number of liquid ammonia flowing inside the capillary coil was approximately 80. At such a "high" Reynolds number, some turbulence would be expected. Bending the capillary tubing into the form of a coil* made the inside diameter nonuniform which would also have disturbed the laminar flow of the liquid inside the capillary coil. In equation (2-2), the last term (B/t) was used for the correction for turbulent flow. However, (B) is a function of Reynolds number, and it can be assumed constant only at low Reynolds numbers.

The error in the viscosity measurement of liquid ammonia was estimated to be less than 1%. However, the calcium-ammonia solutions had a tendency to cling to the glass wall, which may have introduced some additional error into the viscosity measurement because of the change of the diameter of the capillary.

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* A capillary coil was used because the cold bath was not deep enough to use a straight capillary tubing.

3. EXPERIMENTAL RESULTS AND DISCUSSION*

3-1. Viscosity of Liquid Ammonia and Dilute Calcium-Ammonia Solutions.

In order to interpret the temperature coefficient of conductance of calcium-ammonia solutions, the temperature coefficient of viscosity of liquid ammonia had to be obtained. Literature research revealed that no viscosity data for liquid ammonia at low temperature (below -35°C) were available. The viscosity of liquid ammonia measured in the present work and previous data taken from the literature[25,32,60,85,90] are tabulated in Table 3-1 and plotted in Figure 3-1. According to the "hole" theory of liquid, the relation between viscosity and temperature is

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta F^{\ddagger}_{vis}}{RT}\right) \qquad (3\text{-}1\text{-}1)$$

where η is the viscosity of the liquid (centipoise)

V is the molar volume (cm^3/mole)

N is Avogadro's number

h is Plank's constant (erg-sec) and

$\Delta F^{\ddagger}_{vis}$ is the free energy of activation for viscous flow (cal/mole).

Equation (3-1-1) shows that if the logarithm of viscosity is plotted against the reciprocal of absolute temperature, a straight line should result if the free energy of activation for viscous flow is constant. In Figure 3-1, it is shown that the viscosities measured in this study fall on a nearly straight line. However, the slope of this line is not identical with the one representing Kikuchi's data[60] or the one representing Plank and Hunt's data[90] for higher temperatures. In fact for the -35 to -70°C temperature interval, the data points are best

* The lines in the various figures in this section represent the best fit of experimental data by visual inspection.

Table 3-1.

Viscosities of Pure Liquid Ammonia.

Temperature (°C)	Viscosity (centipoise)	$1/T \times 10^3$	Source
30	0.1317	3.300	Kikuchi[60]
20	0.1442	3.413	
10	0.1577	3.534	
0	0.1746	3.663	
-10	0.1941	3.802	
-20	0.2178	3.953	
-30	0.2469	4.115	
25	0.1350	3.354	Plank and Hunt[90]
15	0.1457	3.470	
5	0.1618	3.595	
-33.5	0.254	4.173	Elsey[25]
-33.5	0.266	4.173	Fitzgerald[32]
-33.5	0.2532	4.173	Hutchison and O'Reilly[85]
-35	0.2590	4.202	Present work
-40	0.2742	4.289	
-45.5	0.3010	4.393	
-51	0.3286	4.501	
-56	0.3596	4.605	
-60	0.3908	4.695	
-70	0.4843	4.926	

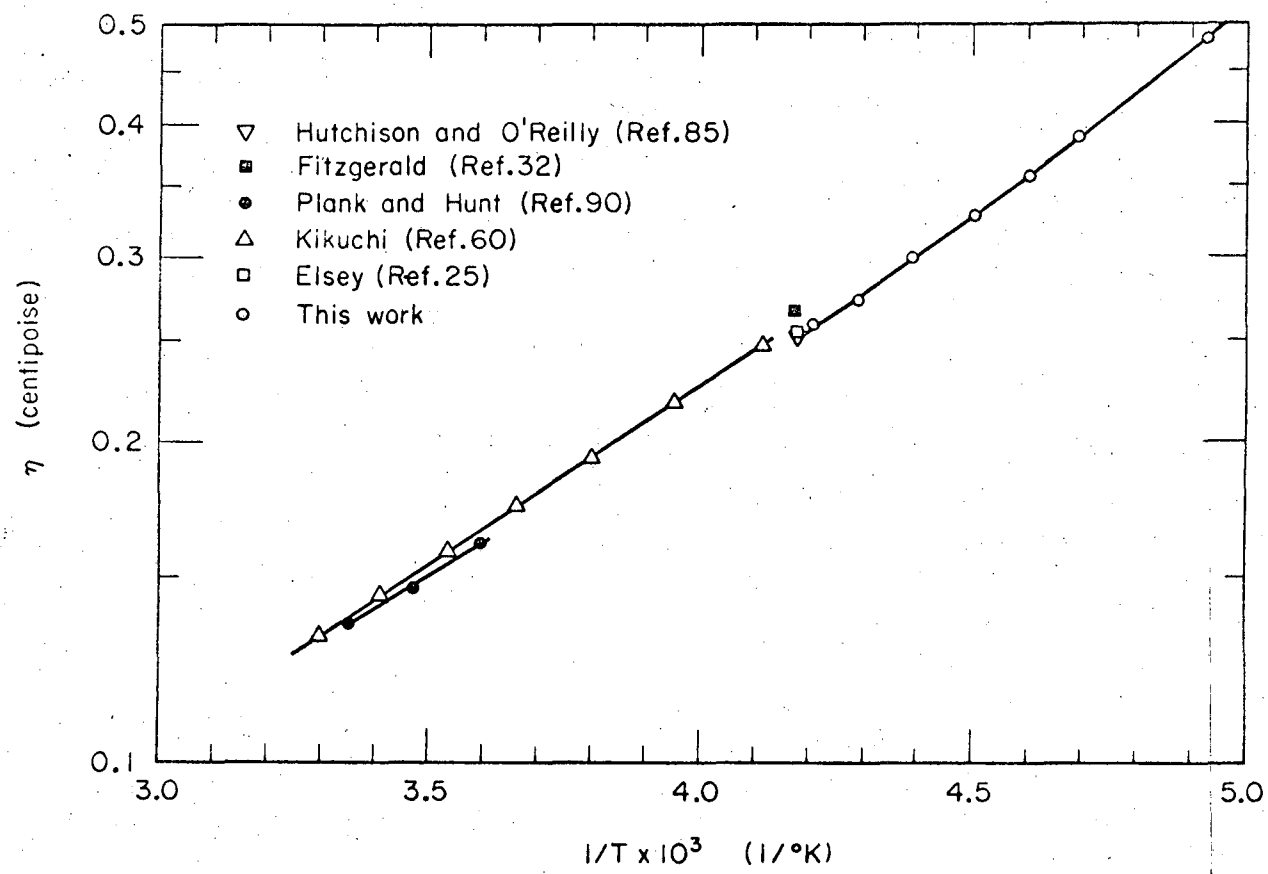

Figure 3-1.

Viscosities of Liquid Ammonia.

represented not by a straight line, but rather by one that curves slightly upward. The line appears to be more consistent with Plank and Hunt's data that with Kikuchi's data. It is interesting to note that these workers also calibrated their apparatus by CS_2 and CCl_4 as in the present work (see appendix E-5), while Kikuchi used distilled water for the purpose.

The free energy ofactivation of the viscous flow of liquid ammonia calculated from the slopes of the lines in Figure 3-1 is tabulated in Table 3-2.

Table 3-2.

Free Energy of Activation for Viscous Flow of Liquid Ammonia.

Activation Energy $\Delta F^{\ddagger}_{vis}$ (Kcal)	Temperature Range (°C)	Source
1.933	-35 to -70	Present work
1.545*	-30 to 30	Kikuchi[60]
1.285*	5 to 25	Plank and Hunt[90]
1.320	---	O'Reilly[85]

* These values have been calculated by the author and were not reported in the original articles.

In Table 3-2, it is shown that the free energy of activation of the viscous flow increases as temperature decreases. This may be due to the fact that liquid ammonia is a polar liquid, and because of the increasing hydrogen bondings, its free energy of activation for viscous flow should also increase with decreasing temperature. The viscosity behavior of

other polar liquids - among other, water, methanol, and ethanol - shows the same trend.

The integral temperature coefficient of viscosity of liquid ammonia is calculated by the equation

$$\alpha_t = \frac{\eta_{t_1} - \eta_{t_2}}{\eta_t (t_1 - t_2)} \times 100 \qquad (3\text{-}1\text{-}2)$$

where α_t is the integral temperature coefficient of viscosity of liquid ammonia at temperature t; η_t is the viscosity of liquid ammonia at temperature indicated; t_1 to t_2 is the temperature range which the viscosity data are taken for the calculation. Results are tabulated in Table 3-3 and plotted in Figure 3-2. The data in Table 3-3 show that the absolute value of the temperature coefficient of viscosity of liquid ammonia increases as the temperature decreases.

The viscosity of the dilute calcium-ammonia solutions was calculated from the measured kinematic viscosity assuming the density of a dilute calcium-ammonia solution to be the same as that of liquid ammonia. The results of the calculations are tabulated in Table 3-4 and plotted in Figure 3-3. The straight lines in Figure 3-3 represent the viscosity of liquid ammonia at the temperature indicated; the points are the experimental data for calcium-ammonia solutions. Figure 3-3 shows that the viscosity of a dilute calcium-ammonia solution does not change noticeably with concentration*. The viscosity of dilute calcium-ammonia solutions was the same as that of liquid ammonia, the difference being less than the experimental error in these measurements. The calcium-ammonia solutions had a tendency to wet and cling to the wall of the capillary of the viscometer. Also, the density of the dilute calcium-ammonia solutions is slightly less less than that of liquid ammonia.

*The concentration range of this experiment is up to the two liquid phase region (see section 3-5).

Table 3-3.

Integral Temperature Coefficients of Viscosity of Liquid Ammonia.

Temperature (°C)	Temperature Range in which the Data is taken (°C)	Temperature Coefficient (%/°C)	Source of Data
20	10 to 30	-0.90	Kikuchi[60]
10	0 to 20	-0.96	
0	-10 to 10	-1.04	
-10	-20 to 0	-1.11	
-20	-30 to -10	-1.21	
15	5 to 25	-0.92	Plank and Hunt[90]
-40	-45.5 to -35	-1.46	Present work
-45.5	-51 to -40	-1.64	
-51	-60 to -40	-1.77	
-56	-60 to -51	-1.92	
-60	-70 to -51	-2.10	

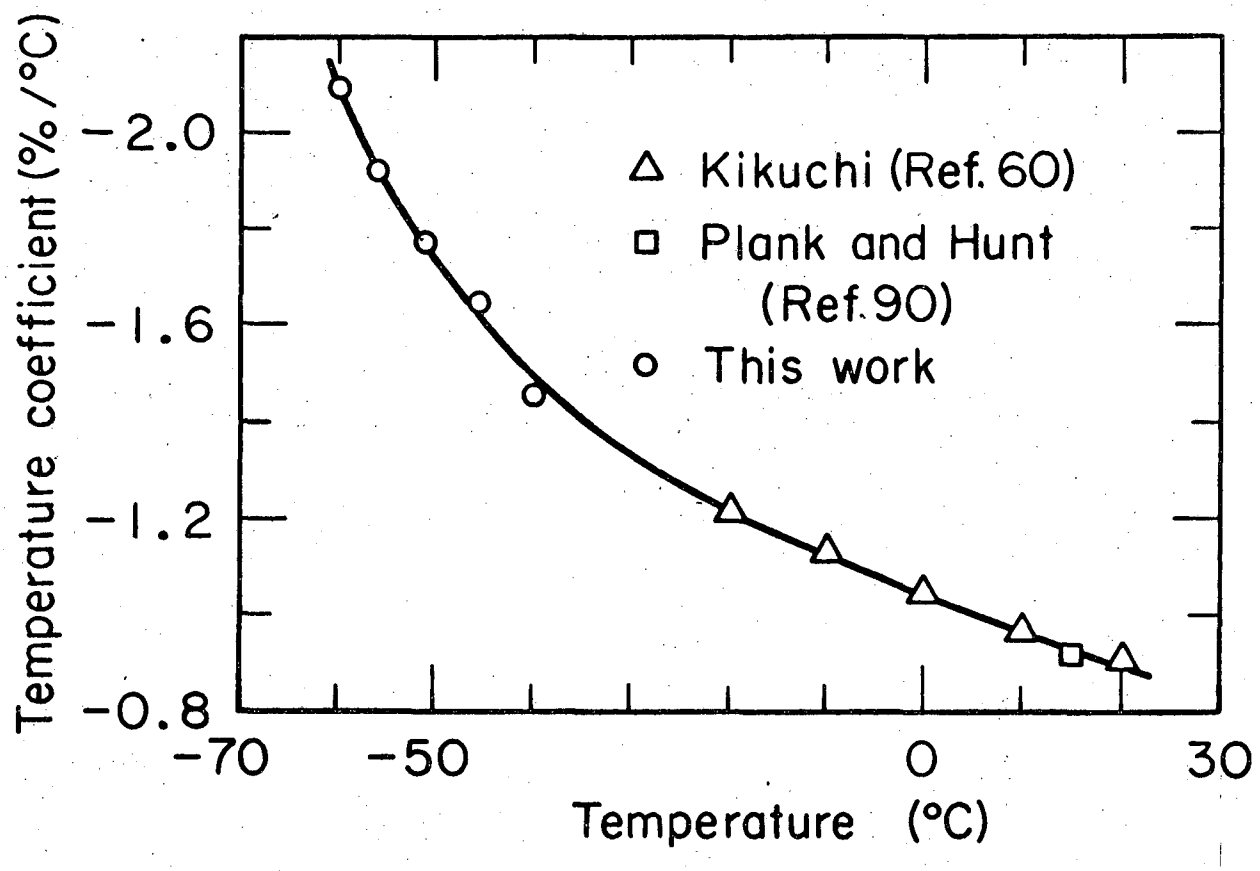

Figure 3-2.

Temperature Coefficients of Viscosity of Liquid Ammonia.

Table 3-4-a.

Viscosities of Dilute Calcium-Ammonia Solutions at -40°C.

Concentration (mole % Ca)	Viscosity (centipoise)
0.818×10^{-2}	0.277
1.516×10^{-2}	0.280
2.345×10^{-2}	0.277
4.706×10^{-2}	0.278
6.017×10^{-2}	0.277

Table 3-4-b.

Viscosities of Dilute Calcium-Ammonia Solutions at -45.5°C

Concentration (mole % Ca)	Viscosity (centipoise)
0.818×10^{2}	0.303
1.516×10^{-2}	0.302
2.345×10^{-2}	0.301
2.723×10^{-2}	0.302

Table 3-4-c.

Viscosities of Dilute Calcium-Ammonia Solutions at -51°C.

Concentration (mole % Ca)	Viscosity (centipoise)
0.818	0.332
1.516	0.333
2.345	0.335
4.480	0.331
6.017	0.331

Table 3-4-d.

Viscosities of Dilute Calcium-Ammonia Solutions at -60°C.

Concentration (mole % Ca)	Viscosity (centipoise)
0.900	0.393
1.434	0.396
2.236	0.393

Table 3-4-e.

Viscosities of Dilute Calcium-Ammonia Solutions at -70°C.

Concentration (mole % Ca)	Viscosity (centipoise)
0.900	0.492
1.434	0.492
2.236	0.488

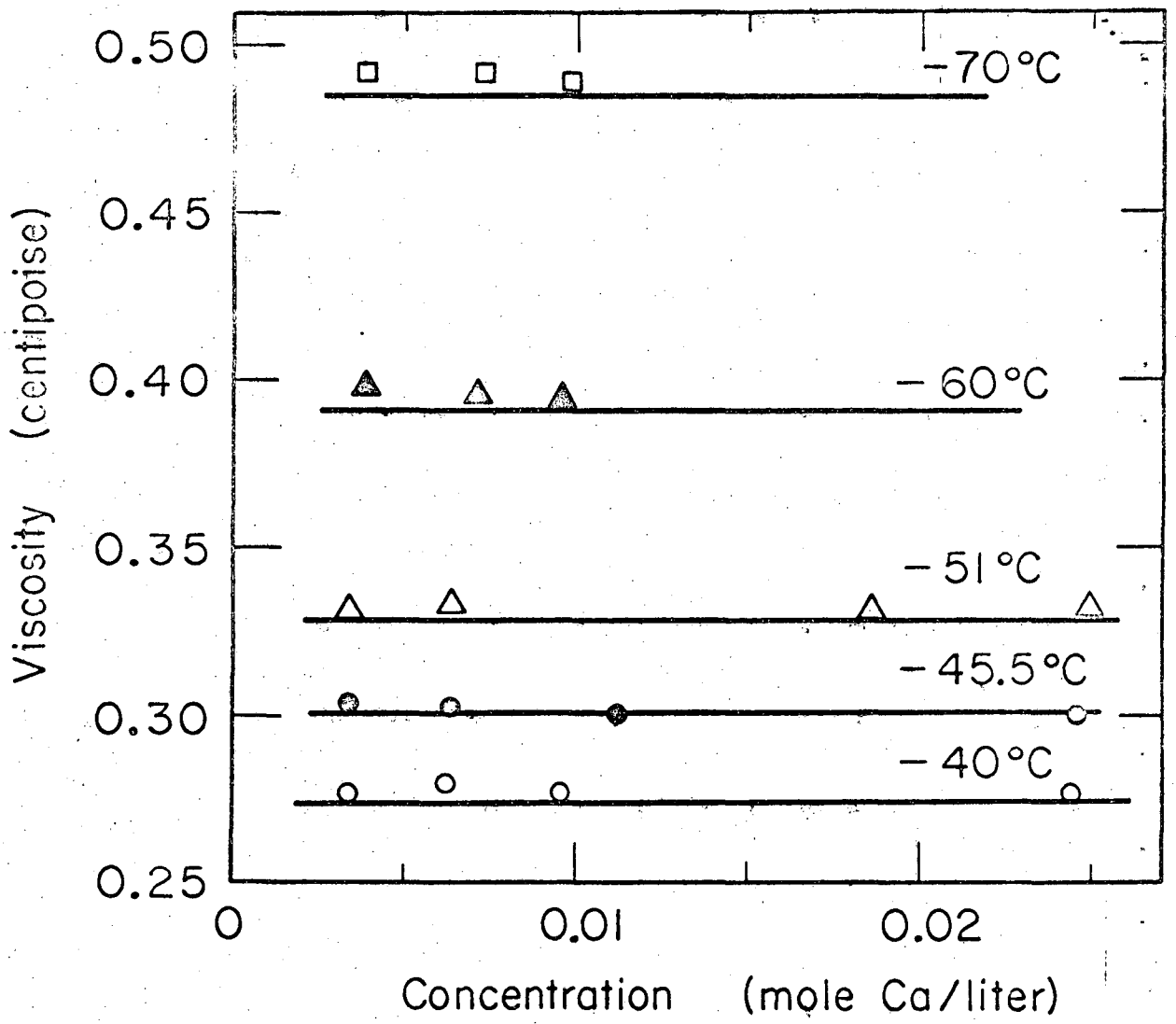

Figure 3-3:
Viscosities of Dilute Calcium-Ammonia Solutions.

3-2. Conductivity of Dilute Calcium-Ammonia Solutions.

3-2-a. Specific conductance of dilute calcium-ammonia solutions:

The specific conductance of the dilute calcium-ammonia solutions was calculated from the equation

$$x = \ell/A \frac{1}{R} \qquad (3\text{-}2\text{-}1)$$

where x is the specific conductance ($ohm^{-1}cm^{-1}$)

ℓ/A is the cell constant of the conductivity cell (cm^{-1})

R is the measured resistance (ohm).

The results are tabulated in Table 3-5 and plotted in Figure 3-4. The concentration of calcium (mole Ca/liter) in Figure 3-4-b was calculated based on the assumption that the density of dilute calcium-ammonia solutions is the same as that of liquid ammonia*.

According to the phase rule, if three phases are present in a calcium-ammonia solution (two liquid phases and a vapor phase), there is only one degree of freedom. Therefore the concentration of calcium in both dilute and concentrated phases is constant at constant temperature. In the two-liquid phase region, since only the dilute calcium-ammonia solution was used in the measurements, the specific conductance was constant at a constant temperature in spite of the change in overall concentration. In the one-liquid phase region, however, the specific conductance decreases as concentration decreases. The point of intersection of the two curves indicates the concentration at which the phase separation occurs. The concentration of the dilute calcium-ammonia solutions in the

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* This assumption is very good for the dilute calcium-ammonia solutions in the one-liquid phase region; however, it cannot be used in the two-liquid phase region because the density of the concentrated phase is much smaller than that of liquid ammonia (see section 3-4).

Table 3-5-a.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -35°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
7690.50	0.0130	0.005226	1.6553×10^{-3}
5215.77	0.0192	0.007706	2.1597×10^{-3}
4466.33	0.0224	0.009000	2.3459×10^{-3}
4261.76	0.0235	0.009431	3.0222×10^{-3}
3257.78	0.0307	0.012337	3.2254×10^{-3}
2922.20	0.0342	0.013754	3.8707×10^{-3}
2361.70	0.0423	0.017019	4.3379×10^{-3}
2055.25	0.0486	0.019558	5.1261×10^{-3}
1694.62	0.0590	0.023712	5.9692×10^{-3}
1425.10	0.0701	0.028203	6.4512×10^{-3}
1257.27	0.0795	0.031975	5.9692×10^{-3}
911.79	0.1096	0.044081	6.2123×10^{-3}
608.30	0.1641	0.066106	6.2509×10^{-3}

Table 3-5-b.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -40°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
13726.7	0.0073	0.00295	0.693×10^{-3}
12452.1	0.0080	0.00326	0.894×10^{-3}
9223.0	0.0108	0.00440	1.137×10^{-3}
8638.8	0.0116	0.00469	1.196×10^{-3}
8024.5	0.0120	0.00505	1.134×10^{-3}
6832.5	0.0146	0.00593	1.405×10^{-3}
5506.3	0.0181	0.00736	1.595×10^{-3}
4864.1	0.0206	0.00833	1.933×10^{-3}
4351.5	0.0230	0.00932	1.972×10^{-3}
3944.8	0.0253	0.01028	2.233×10^{-3}
3163.6	0.0316	0.01284	2.469×10^{-3}
3024.0	0.0331	0.01340	2.823×10^{-3}
2675.9	0.0374	0.01514	3.406×10^{-3}
2633.6	0.0380	0.01539	3.479×10^{-3}
2384.0	0.0419	0.01700	3.451×10^{-3}
2179.1	0.0459	0.0188	3.675×10^{-3}
1816.5	0.0550	0.02231	4.776×10^{-3}
1704.9	0.0586	0.02379	4.993×10^{-3}
1461.9	0.0684	0.02775	5.042×10^{-3}
1250.2	0.0799	0.03244	5.024×10^{-3}
998.2	0.1001	0.04063	5.173×10^{-3}
754.4	0.1324	0.5376	5.376×10^{-3}
523.7	0.1906	0.7744	5.320×10^{-3}

Table 3-5-c.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -45.5°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
13726.7	0.0073	0.00298	0.592×10^{-3}
12452.1	0.0080	0.00329	0.759×10^{-3}
9223.0	0.0108	0.00444	0.981×10^{-3}
8638.8	0.0116	0.00474	1.008×10^{-3}
8024.5	0.0120	0.00510	0.966×10^{-3}
6832.5	0.0146	0.00599	1.187×10^{-3}
5506.3	0.0181	0.00743	1.401×10^{-3}
4864.1	0.0206	0.00842	1.618×10^{-3}
4351.5	0.0230	0.00941	1.739×10^{-3}
3944.8	0.0253	0.01038	1.915×10^{-3}
3163.6	0.0316	0.01295	2.206×10^{-3}
3023.9	0.0331	0.01353	2.358×10^{-3}
2675.9	0.0374	0.01529	2.897×10^{-3}
2633.6	0.0380	0.01554	2.957×10^{-3}
2384.0	0.0419	0.01716	2.947×10^{-3}
2179.1	0.0459	0.01877	3.090×10^{-3}
1815.6	0.0550	0.02253	4.003×10^{-3}
1704.8	0.0586	0.02402	4.123×10^{-3}
1461.7	0.0684	0.02802	4.430×10^{-3}
1250.2	0.0799	0.03276	4.411×10^{-3}
998.2	0.1001	0.4103	4.089×10^{-3}
754.4	0.1324	0.5429	4.093×10^{-3}
532.7	0.1906	0.07688	4.038×10^{-3}

Table 3-5-d.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -51°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
13726.7	0.0073	0.00301	0.489×10^{-3}
12452.1	0.0080	0.00332	0.621×10^{-3}
9223.0	0.0108	0.00448	0.802×10^{-3}
8638.8	0.0116	0.00479	0.834×10^{-3}
8024.5	0.0120	0.00515	0.795×10^{-3}
6832.5	0.0146	0.00605	0.975×10^{-3}
5506.5	0.0181	0.00751	1.205×10^{-3}
4864.1	0.0206	0.00850	1.325×10^{-3}
4351.5	0.0230	0.00950	1.465×10^{-3}
3944.8	0.0253	0.01047	1.628×10^{-3}
3163.6	0.0316	0.01307	2.027×10^{-3}
3023.9	0.0331	0.01366	1.948×10^{-3}
2675.9	0.0374	0.01544	2.433×10^{-3}
2633.6	0.0380	0.01568	2.474×10^{-3}
2384.0	0.0419	0.01733	2.477×10^{-3}
2179.0	0.0459	0.01895	2.590×10^{-3}
1705.0	0.0586	0.02426	3.078×10^{-3}
1461.9	0.0684	0.02828	3.01×10^{-3}
998.2	0.1001	0.04142	2.986×10^{-3}
754.4	0.1324	0.05480	2.971×10^{-3}
523.7	0.1906	0.07894	2.925×10^{-3}

Table 3-5-e.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -60°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
8734.5	0.01145	0.004805	0.555×10^{-3}
7358.68	0.01359	0.005703	0.647×10^{-3}
6157.57	0.01624	0.006816	0.782×10^{-3}
6047.2	0.01653	0.006940	0.907×10^{-3}
5221.9	0.01915	0.008037	0.887×10^{-3}
4490.0	0.02227	0.009347	1.040×10^{-3}
4222.7	0.02368	0.00994	1.106×10^{-3}
3604.9	0.02773	0.01164	1.176×10^{-3}
3324.5	0.03007	0.01312	1.468×10^{-3}
2585.08	0.03867	0.016235	1.462×10^{-3}
2031.24	0.04920	0.02066	1.546×10^{-3}
1368.27	0.07301	0.03067	1.451×10^{-3}

Table 3-5-f.

Specific Conductances of Dilute Calcium-Ammonia Solutions at -70°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % of Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)
8734.5	0.01145	0.004880	0.366×10^{-3}
7358.68	0.01359	0.005792	0.434×10^{-3}
6157.57	0.01624	0.006922	0.524×10^{-3}
6047.2	0.01653	0.007048	0.577×10^{-3}
5221.92	0.01915	0.008162	0.591×10^{-3}
3727.04	0.02682	0.01144	0.7056×10^{-3}
2528.92	0.03953	0.01685	0.7105×10^{-3}
1618.07	0.06176	0.02634	0.7471×10^{-3}
1344.67	0.07431	0.03170	0.7105×10^{-3}

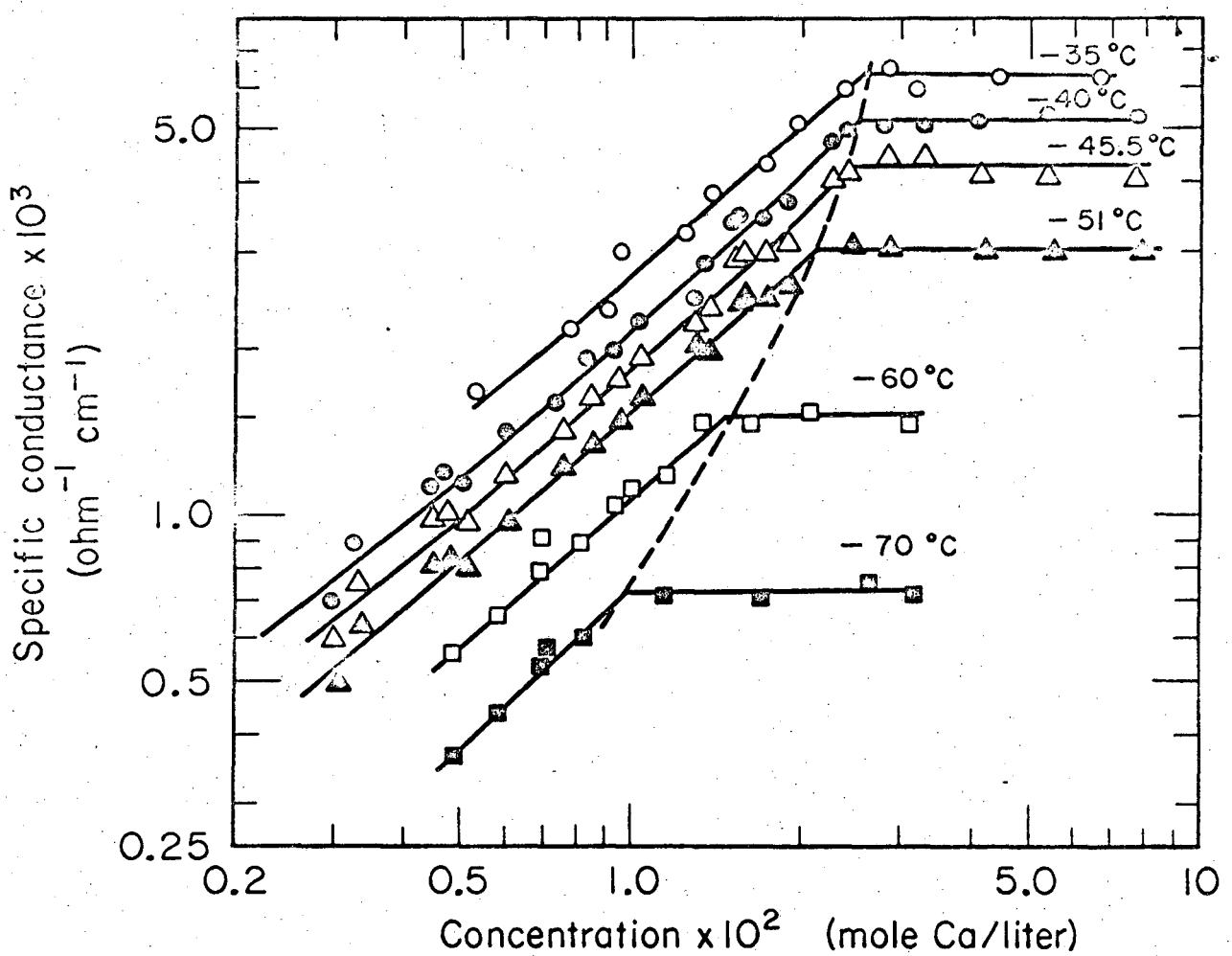

Figure 3-4-a.

Specific Conductances of Dilute Calcium-Ammonia Solutions.

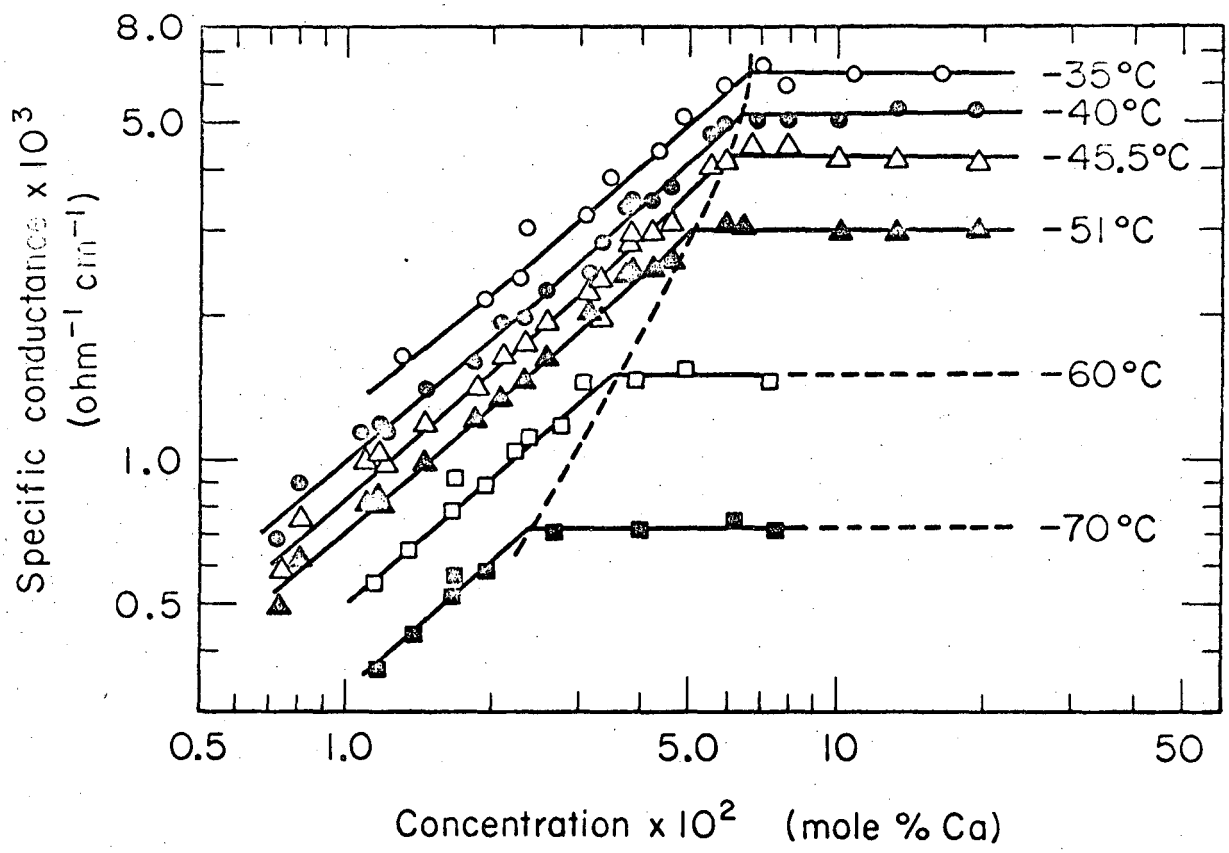

Figure 3-4-b.

Specific Conductances of Dilute Calcium-Ammonia Solutions.

two-liquid phase region was determined by this method from Figure 3-4 and is tabulated and plotted in section 3-5.

3-2-b. Equivalent conductance of dilute calcium-ammonia solutions: The equivalent conductance of dilute calcium-ammonia solutions was calculated from the equation

$$\Lambda = \frac{x}{2c} \times 1000 \qquad (3\text{-}2\text{-}2)$$

where Λ is equivalent conductance (cm^2/equiv-ohm)

x is specific conductance ($ohm^{-1}cm^{-1}$)

c is concentration of calcium (mole Ca/liter).

The results are tabulated in Table 3-6 and plotted in Figure 3-5. In Figure 3-5-a, the equivalent conductance at each temperature is plotted separately to avoid the overlapping of experimental points. The smooth curves from Figure 3-5-a are put together in Figure 3-5-b for comparison. The points in Figure 3-5-a were calculated directly from the experimental data reported in section 3-2-a, and the curves were calculated from the smoothed curves in Figure 3-4-b.

The equivalent conductance of calcium in dilute solutions increases as concentration decreases and is much smaller than that of sodium in liquid ammonia. At -33.8°C the equivalent conductance of sodium-ammonia solutions increases from 480 cm^2/equiv Na-ohm to 600 cm^2/equiv-Na-ohm in the concentration range of 0.045 equiv Na/liter to 0.01 equiv Na/liter[66], while at -35°C for the same concentration range, the equivalent conductance of calcium-ammonia solutions increases only from 124 cm^2/equiv-Ca-ohm to 161 cm^2/equiv-Ca-ohm. In Figure 3-5-a the equivalent conductance of calcium-ammonia solutions is plotted against the square root of concentration. It is shown that the curves are not straight lines as predicted for a completely dissociated electrolyte in very dilute solutions. These

Table 3-6-a.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -35°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.005226	0.0723	1.6553×10^{-3}	158.37
0.007706	0.0878	2.1597×10^{-3}	140.13
0.009000	0.0949	2.3459×10^{-3}	130.33
0.009431	0.0971	3.0222×10^{-3}	160.23
0.012337	0.111	3.2254×10^{-3}	130.72
0.013754	0.117	3.8707×10^{-3}	140.71
0.017019	0.131	4.3379×10^{-3}	127.44
0.019558	0.140	5.1261×10^{-3}	131.05
0.023712	0.154	5.9692×10^{-3}	125.87

Table 3-6-b.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -40°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.00295	0.0544	0.6929×10^{-3}	117.28
0.00326	0.0571	0.8941×10^{-3}	137.25
0.00439	0.0661	1.1374×10^{-3}	129.37
0.00469	0.0681	1.1955×10^{-3}	127.35
0.00505	0.0711	1.1343×10^{-3}	112.24
0.00593	0.0772	1.4052×10^{-3}	118.41
0.00736	0.0858	1.5953×10^{-3}	108.35
0.00833	0.0914	1.9328×10^{-3}	115.96
0.00932	0.0966	1.9716×10^{-3}	105.83
0.01028	0.1014	2.2328×10^{-3}	108.65
0.01284	0.1125	2.4694×10^{-3}	96.18
0.01340	0.1158	2.8228×10^{-3}	105.32
0.01514	0.123	3.4062×10^{-3}	112.47
0.01537	0.124	3.479×10^{-3}	113.06
0.0170	0.1303	3.451×10^{-3}	101.53
0.01867	0.1379	3.675×10^{-3}	97.95
0.02231	0.1493	4.7764×10^{-3}	107.05

Table 3-6-c.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -45.5°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.00298	0.0546	0.5917×10^{-3}	99.18
0.00329	0.0574	0.7593×10^{-3}	115.47
0.00444	0.0666	0.9806×10^{-3}	110.46
0.00474	0.0688	1.0079×10^{-3}	106.34
0.00510	0.0715	0.9663×10^{-3}	94.7
0.00599	0.0775	1.1866×10^{-3}	99.02
0.00743	0.0863	1.4005×10^{-3}	94.2
0.00842	0.0918	1.6176×10^{-3}	96.12
0.00941	0.097	1.7385×10^{-3}	92.42
0.01038	0.1018	1.9149×10^{-3}	92.29
0.01295	0.1138	2.2057×10^{-3}	85.16
0.01353	0.1161	2.3583×10^{-3}	87.14
0.01529	0.1233	2.8966×10^{-3}	94.72
0.01554	0.1246	2.9368×10^{-3}	95.16
0.01716	0.1308	2.947×10^{-3}	85.86
0.01877	0.1373	3.09×10^{-3}	82.31
0.02253	0.1501	4.003×10^{-3}	88.85

Table 3-6-d.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -51°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.00301	0.0549	0.489×10^{-3}	81.2
0.00332	0.0576	0.6214×10^{-3}	93.59
0.00448	0.0666	0.8015×10^{-3}	89.42
0.00479	0.0692	0.8339×10^{-3}	87.14
0.00515	0.0718	0.7949×10^{-3}	77.18
0.00605	0.0779	0.9745×10^{-3}	80.06
0.00751	0.0867	1.205×10^{-3}	80.26
0.00850	0.0921	1.3245×10^{-3}	77.95
0.00950	0.0975	1.4648×10^{-3}	77.13
0.01047	0.1023	1.6281×10^{-3}	77.72
0.01307	0.1146	2.0273×10^{-3}	77.56
0.01366	0.1195	1.9482×10^{-3}	71.31
0.01544	0.1244	2.4329×10^{-3}	78.8
0.01568	0.1252	2.474×10^{-3}	78.87
0.01733	0.1316	2.477×10^{-3}	71.48
0.01895	0.1375	2.59×10^{-3}	68.33

Table 3-6-e.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -60°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.004805	0.0693	0.555×10^{-3}	57.77
0.005703	0.0755	0.647×10^{-3}	56.74
0.006816	0.0825	0.782×10^{-3}	57.33
0.006940	0.0833	0.907×10^{-3}	65.36
0.008037	0.0896	0.887×10^{-3}	55.20
0.009347	0.0967	1.040×10^{-3}	55.63
0.00994	0.0997	1.106×10^{-3}	55.62
0.01164	0.1078	1.176×10^{-3}	50.51
0.01312	0.1145	1.468×10^{-3}	55.95

Table 3-6-f.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions at -70°C.

Concentration (mole Ca/liter)	$\sqrt{c}$ (mole Ca/liter)$^{\frac{1}{2}}$	Specific Conductance ($ohm^{-1}cm^{-1}$)	Equivalent Conductance (cm^2/equiv-ohm)
0.004880	0.0699	0.366×10^{-3}	37.45
0.005792	0.0761	0.434×10^{-3}	37.43
0.006922	0.0832	0.524×10^{-3}	37.83
0.007048	0.0840	0.577×10^{-3}	40.95
0.008162	0.0903	0.591×10^{-3}	36.17

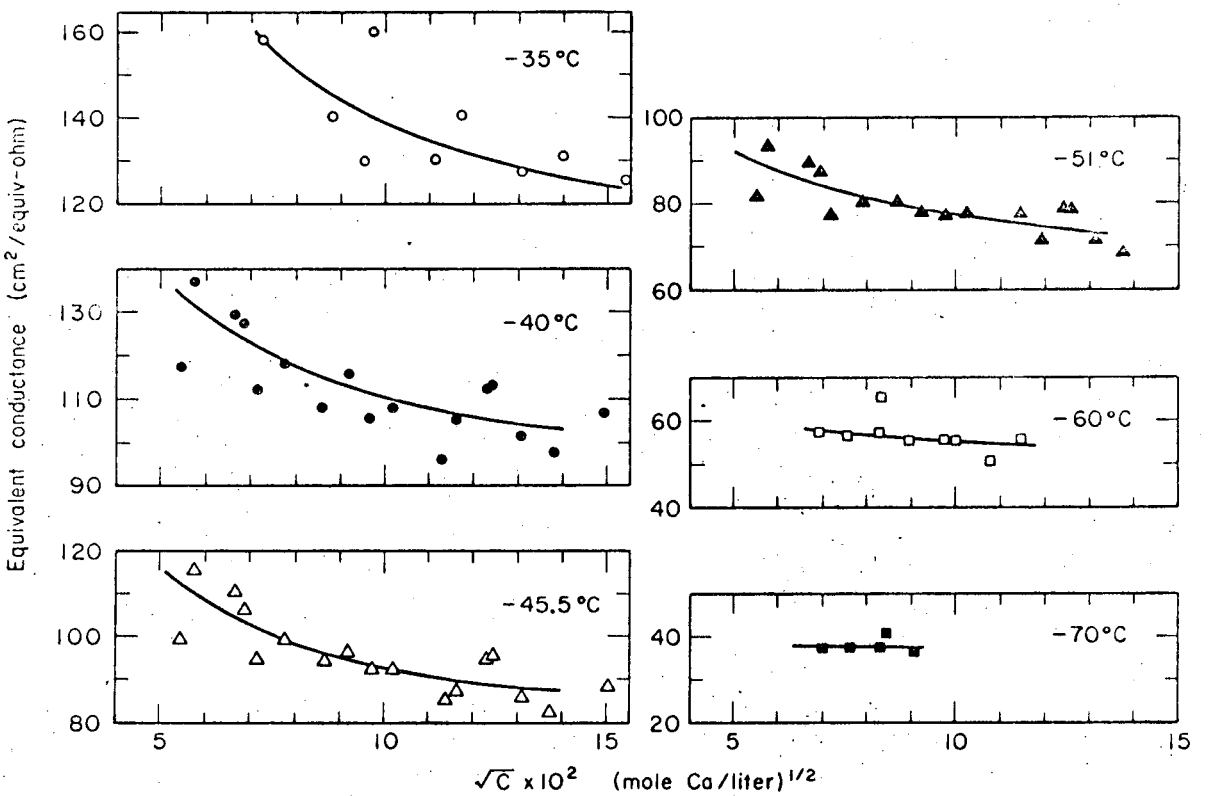

Figure 3-5-a.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions.

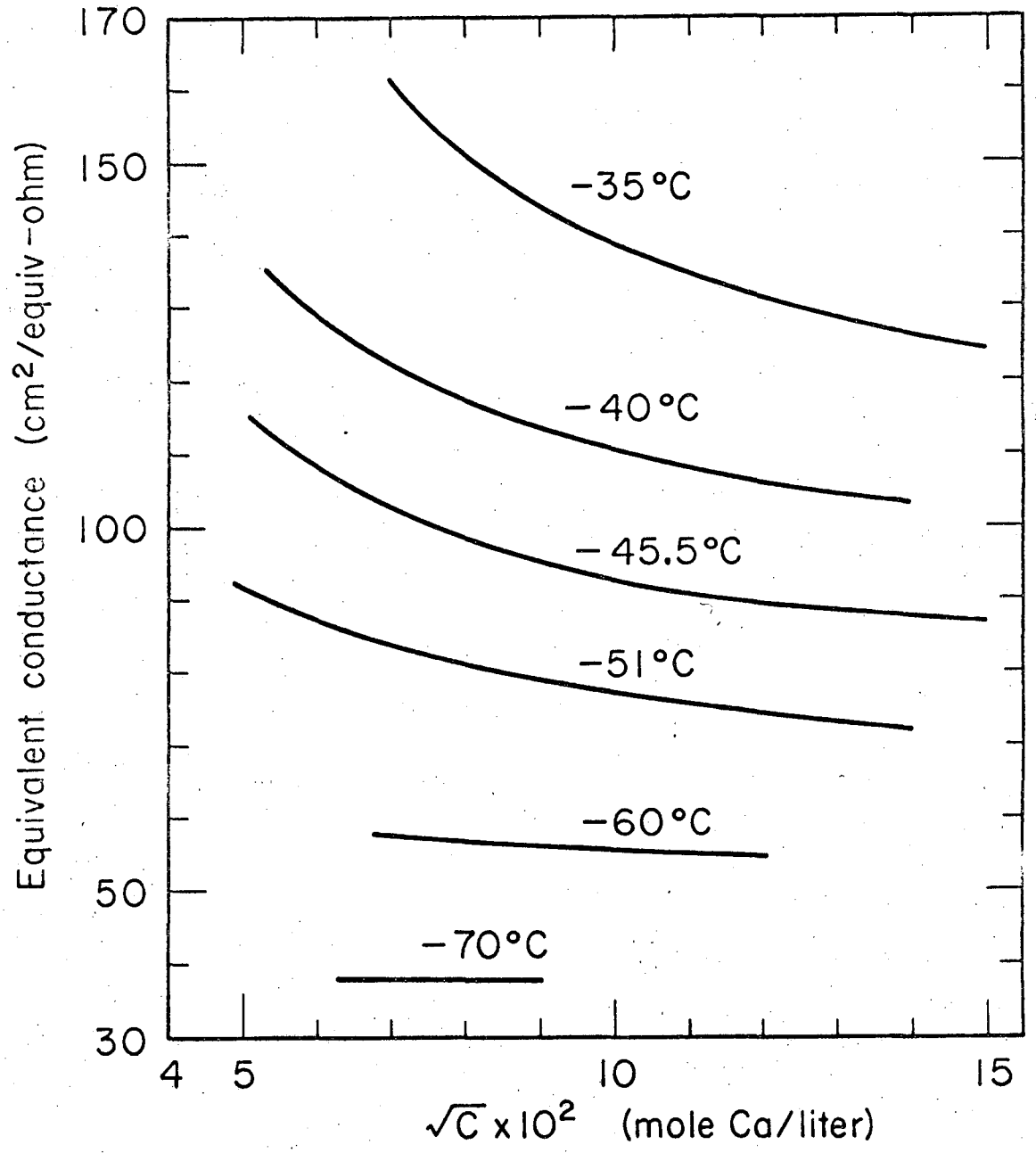

Figure 3-5-b.

Equivalent Conductances of Dilute Calcium-Ammonia Solutions.

two facts indicate that the calcium molecules in these solutions are not completely dissociated.

The limiting equivalent conductance (Λ_o) of calcium-ammonia solutions could not be determined in these experiments because of the small concentration range available up to saturation and the scattering of the experimental data in the most dilute region covered.

The limiting equivalent conductance of sodium-ammonia solution at -33.8°C has been extrapolated to be 1020 cm^2/ohm equiv[66]. Applying the temperature coefficient of conductance (1.52%/°C)[69], the limiting equivalent conductance of sodium-ammonia solution at -35°C, -40°C, -45°C, -51°C, -60°C and -70°C can be estimated to be 1003, 927, 849, 778, 672, and 552 cm^2/equiv-ohm, respectively*. Since 7/8 of total current is carried by electrons[66], the limiting equivalent conductance of all metal-ammonia solutions should be about the same as that of sodium-ammonia solution**. Based on this estimate, the ratio of the equivalent conductance to that at infinite dilution, Λ/Λ_o, for calcium-ammonia solutions was calculated at different concentrations. The results are tabulated in Table 3-7. The values of Λ/Λ_o of sodium-ammonia solution at -33.8°C and at the same concentrations were also calculated for comparison. Table 3-7 shows that the fraction of calcium dissociated into ions and electrons in calcium-ammonia solutions is much smaller than that for sodium-ammonia solutions. This is notunreasonable because of the high ionization energy

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* This is only a qualitative estimate since the temperature coefficient of conductance is not independent of temperature[69,71].

** The limiting equivalent conductance of lithium-ammonia solutions was determined recently to be 5587 ± 15.9 cm^2/equiv-Li-ohm[29] at -71°C, showing good agreement with this estimate.

Table 3-7-a.

Λ/Λ_o of Calcium-Ammonia Solutions at -35°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.007	147.9	0.148
0.01	138.6	0.138
0.013	133	0.133

Table 3-7-b.

Λ/Λ_o of Calcium-Ammonia Solutions at -40°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.004	144	0.155
0.007	123	0.133
0.01	111	0.120
0.013	104.5	0.113

Table 3-7-c.

Λ/Λ_o of Calcium-Ammonia Solutions at 45.5°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.004	115.5	0.136
0.007	101.3	0.119
0.01	93.2	0.110
0.013	89	0.105

Table 3-7-d.

Λ/Λ_o of Calcium-Ammonia Solutions at -51°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.004	95	0.122
0.007	86	0.111
0.010	78	0.100
0.013	73	0.0938

Table 3-7-e.

Λ/Λ_o of Calcium-Ammonia Solutions at - 60°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.007	56.5	0.0841
0.01	55.2	0.0821
0.013	54.2	0.0806

Table 3-7-f.

Λ/Λ_o of Calcium-Ammonia Solutions at -70°C.

Concentration (mole Ca/liter)	Equivalent Conductance $(\Lambda)^*$ (cm^2/equiv Ca-ohm)	Λ/Λ_o
0.007	38.6	0.0700

Table 3-7-g.

Λ/Λ_o of Sodium-Ammonia Solutions at -33.8°C.

Concentration (mole Ca/liter)	Equivalent Conductance (Λ)** (cm^2/equiv Na-ohm)	Λ/Λ_o
0.004	715	0.701
0.007	643	0.630
0.010	600	0.588
0.013	557	0.546

* Data from Figure 3-5-a.

** Data from Kraus, J.A.C.S. 43, 749, 1921.

of the calcium atom. The degree of dissociation of calcium atoms into ions and electrons increases as temperature increases and also as the concentration of calcium decreases.

3-2-c. Temperature coefficient of conductance of dilute calcium-ammonia solutions: The integral temperature coefficient of conductance in a temperature range from t_1 to t_2 for a calcium-ammonia solutions at constant concentration was calculated from the equation

$$\beta_c = \frac{2(x_{t_1} - x_{t_2})}{(x_{t_1} + x_{t_2})(t_1 - t_2)} \times 100 \qquad (3\text{-}2\text{-}3)$$

where β_c is the temperature coefficient of conductance (%/°C),

x is the specific conductance of the calcium-ammonia solution at the concentration and temperatures indicated (cm^{-1}-ohm^{-1}).

Equivalent conductance in the one-liquid phase region taken from the smoothed data in Figure 3-4 were used for these calculations. The results are tabulated in Table 3-8. The temperature coefficient of conductance of dilute calcium-ammonia solutions varies from 2.67 % per degree to 4.25 % per degree. The dependence of the temperature coefficient of conductance on temperature and on concentration could not be determined by the present work because of the uncertainty of the experimental data.

The temperature coefficient of conductance of very dilute sodium and potassium-ammonia solution is +1.52% per degree and +1.42% per degree, respectively[69,71*], at -33.8°C. This may be compared to the temperature

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* In the other article[66] Kraus reported that the temperature coefficient of conductance of a very dilute sodium-ammonia solution is 2.25% per degree at -33.8°C. By Gibson et al's measurements[34], the temperature coefficient of a very dilute sodium-ammonia solution (approximately 0.01 mole Na/liter) at -33.5°C is only slightly different from the value 1.52% per degree.

Table 3-8.

Integral Temperature Coefficients of
Conductivity of Dilute Calcium-Ammonia Solutions.

Concentration (mole Ca/liter)	Temperature Coefficient in the Indicated Temperature Interval (%/°C)				
	-35°C to -40°C	-40°C to -45.5°C	-45.5°C to -51°C	-51°C to -60°C	-60°C to -70°C
0.0075	4.25	2.672	4.196	3.33	3.611
0.010	3.577	3.270	3.861	3.790	
0.0125	2.87	3.331	3.593	3.831	
0.015	3.513	3.003	3.795	3.831	
0.0175	3.532	2.903	3.814		
0.02	3.723	2.905	3.888		
0.0225	3.707	2.733			

coefficient of viscosity of liquid ammonia at the same temperature which is 1.38% per degree (Figure 3-2), indicating that temperature coefficient of conductance of the dilute sodium and potassium-ammonia solution is due mainly to the viscosity change.

The temperature coefficient of conductance of calcium-ammonia solutions determined by present work is much larger than that for the viscosity of liquid ammonia. Therefore, conductance is not only governed by the viscosity change, but also by the fraction of calcium atoms dissociated into metal ions and electrons.

3-2-d. The mechanism of conductance of dilute metal-ammonia solutions: The mechanism of conductance of dilute metal-ammonia solutions is still not very clear. When current passes through a dilute sodium-ammonia solution, the positive metal ions migrate toward the cathode and the "blue color" moves toward the anode, but no new product is formed on the anode[30,63]. Based on this fact, Kraus[63] concluded that the metal atoms in liquid ammonia dissociate into ionic form, and the negative ions are electrons surrounded by an envelope of ammonia molecules. Ogg[80] suggested that an electron can dig a hole in liquid ammonia by polarizing the solvent molecules to form an electron cavity. He determined the radius of an electron cavity to be approximately 10Å, which was later on shown to be too high due to experimental error. Lipscomb[75] based on experimental data of density of sodium-ammonia solutions[59] and after considering size of the sodium atoms and sodium ions, determined the radius of an electron cavity to be 3.2Å. The mobility of the electron cavity is approximately seven times larger than that of the sodium ions[66]. Since the size of an electron cavity is so large (an electron cavity in liquid ammonia displaces two to four ammonia molecules) there is a question as to how the electron

cavities can move so fast in liquid ammonia. Kaplan and Kittel[57], comparing the mobility of an electron cavity (approximately 0.01 cm^2/volt-sec) to the minimum mobility of an electron in the conduction band (approximately 2 cm^2/volt-sec for a mean free path of 1Å) concluded that the conductivity of electrons in liquid ammonia is not due to a conduction band process. They also pointed out that even though the mobility of an electron cavity in liquid ammonia is approximately ten times higher than that of a typical ion of the same size (estimated by Stoke's law), the electron cavities may pass through ammonia more easily than typical ions. A lowering of the ammonia barrier energy by a factor of two can produce such a high mobility. The other suggestion[3,21] is that electrons in liquid ammonia can jump out of one cavity and form a new cavity among the neighboring ammonia molecules (tunneling mechanism). The temperature coefficient of the limiting conductance of sodium and potassium-ammonia solutions and also the similarity of the Walden product ($\Lambda_o \eta_o$) of sodium-ammonia solution at -35°C, lithium-ammonia solution at -71°C[29] and lithium-methylamine solution at -78°C[6] (2.6, 2.8, and 2.1, respectively). show that the mobility of solvated electrons is nearly completely viscosity dependent. This fact supports Kaplan and Kittle's suggestion.

The equilibrium constants of the dissociation and dimerization reactions of alkali metal in liquid ammonia:

$$Me_{(am)} \rightarrow Me^{+}_{(am)} + e^{-}_{(am)} \qquad (3\text{-}2\text{-}4)$$

$$2Me_{(am)} \rightarrow Me_{2(am)} \qquad (3\text{-}2\text{-}5)$$

have been determined for sodium-ammonia solutions at -34°C[27]* and for

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* These equilibrium constants determined by conductivity data do not agree with those determined by magnetic susceptibility data. Therefore Arnold et al[2] suggested that there should be another association reaction in alkali-metal ammonia solutions (see appendix A-10): $Me_{(am)} + e^{-}_{am} \rightarrow Me^{-}_{(am)}$.

lithium-ammonia solutions at -71°C[29*] from conductivity data. Because no accurate value for the limiting equivalent conductance and the transference number is available, the calculation of an equilibrium constant for the dissociation reaction in dilute calcium-ammonia solutions is not possible at the present time. However, based on the current theories[5], there should be only one dissociation reaction (see appendix A-10)

$$Ca_{(am)} \rightarrow 2Ca^{++}_{(am)} + 2e^{-}_{(am)}. \qquad (3\text{-}2\text{-}6)$$

3-3. Conductivity of Concentrated Calcium-Ammonia Solutions.

3-3-a. Specific conductance of concentrated calcium-ammonia solutions: The specific conductance of concentrated calcium-ammonia solutions calculated from equation (3-2-1) is tabulated in Table 3-9 and plotted in Figure 3-6. In Figure 3-6 there are two different lines. Based on the agreement in section 3-2-a, one can see that the inclined curves in Figure 3-6 represent the specific conductance of concentrated calcium-ammonia solutions in the single-liquid phase region, in which the specific conductance increases as concentration of calcium increases. The horizontal straight lines in Figure 3-6 represent the specific conductance of the concentrated calcium-ammonia solutions in the two-liquid phase region which is independent of the overall concentration. The concentration at the point of intersection of these two curves is that of the concentrated calcium-ammonia solutions in the two-liquid phase region. The concentration of the concentrated calcium-ammonia solutions[**] in the two-liquid phase region determined by this method from Figure 3-6 is tabulated and plotted in section 3-5.

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* These equilibrium constants determined by conductivity data do not agree with those determined by magnetic susceptibility data. Therefore Arnold et al[2] suggested that there should be another association reaction in alkali-metal ammonia solution (see appendix A-10): $Me_{(am)} + e^{-}_{am} \rightarrow Me^{-}_{(am)}$.

** The concentration of the concentrated calcium-ammonia solution was calculated from the density data of the present work (see section 3-4).

Table 3-9-a.

Conductivities of Concentrated Calcium-Ammonia Solution at -35°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)	Atomic Conductance (cm^2/mole-ohm)
37.200	2.6178	0.975	0.50347×10^3	
36.960	2.6343	0.980	0.49959×10^3	
35.440	2.7442	1.025	0.50152×10^3	
32.189	3.0130	1.125	0.49916×10^3	
30.34	3.1908	1.182	0.49959×10^3	
28.34	3.4083	1.253	0.51139×10^3	0.4081×10^6
26.92	3.5817	1.314	0.59043×10^3	0.4493×10^6
25.923	3.7143	1.360	0.66956×10^3	0.4923×10^6
25.048	3.8391	1.405	$0.7[illegible]929 \times 10^3$	0.5262×10^6
23.966	4.0054	1.459	0.82175×10^3	0.5632×10^6
21.386	4.4671	1.608	0.99156×10^3	0.6168×10^6
21.280	4.4883	1.616	1.0309×10^3	0.6379×10^6
18.09	5.2383	1.866	1.39072×10^3	0.7453×10^6
16.616	5.6766	2.002	1.5918×10^3	0.7951×10^6
16.455	5.7290	2.017	1.63181×10^3	0.809×10^6
15.204	6.1713	2.155	1.90764×10^3	0.8852×10^6
14.778	6.3379	2.213	1.8880×10^3	0.8531×10^6
14.5345	6.4371	2.247	2.022×10^3	0.8999×10^6
12.34	7.4963	2.571	2.77475×10^3	1.0792×10^6

Table 3-9-b.

Conductivities of Concentrated Calcium-Ammonia Solutions at -40°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)	Atomic Conductance (cm^2/mole-ohm)
37.200	2.6178	0.991	0.51978×10^3	
36.963	2.6343	0.996	0.53252×10^3	
35.440	2.7442	1.034	0.51954×10^3	
32.189	3.0130	1.127	0.52377×10^3	
30.340	3.1908	1.188	0.51954×10^3	
28.340	3.4083	1.264	0.51545×10^3	
26.920	3.5817	1.322	0.57475×10^3	0.4348×10^6
25.923	3.7143	1.368	0.65603×10^3	0.4796×10^6
25.048	3.8391	1.410	0.72019×10^3	0.5108×10^6
23.966	4.0054	1.460	0.80322×10^3	0.5502×10^6
21.386	4.4671	1.616	0.97226×10^3	0.6016×10^6
21.280	4.4883	1.622	1.03090×10^3	0.6356×10^6
18.090	5.2383	1.876	1.38185×10^3	0.7366×10^6
16.616	5.6766	2.014	1.58407×10^3	0.7865×10^6
16.455	5.7290	2.030	1.62367×10^3	0.7998×10^6
15.204	6.1713	2.172	1.88520×10^3	0.8680×10^6
14.778	6.3379	2.222	1.88799×10^3	0.8497×10^6
14.535	6.4371	2.260	2.0030×10^3	0.8863×10^6
12.340	7.4963	2.588	2.7275×10^3	1.0539×10^6

Table 3-9-c.

Conductivities of Concentrated Calcium-Ammonia Solutions at -51°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohn^{-1}cm^{-1}$)	Atomic Conductance (cm^2/mole-ohm)
37.200	2.6178	1.010	0.60698×10^3	
36.960	2.6343	1.013	0.60136×10^3	
35.440	2.7442	1.045	0.59584×10^3	
32.189	3.0130	1.142	0.59043×10^3	
30.340	3.1908	1.203	0.59043×10^3	
28.340	3.4083	1.282	0.59043×10^3	
26.920	3.5817	1.344	0.60698×10^3	
25.923	3.7143	1.390	0.63055×10^3	0.4536×10^6
25.048	3.8391	1.435	0.68921×10^3	0.4803×10^6
23.966	4.0054	1.492	0.75944×10^3	0.509×10^6
21.386	4.4671	1.645	0.93990×10^3	0.5714×10^6
21.280	4.4883	1.651	1.00072×10^3	0.6061×10^6
18.090	5.2383	1.896	1.35306×10^3	0.7136×10^6
16.616	5.6766	2.033	1.54636×10^3	0.7606×10^6
16.455	5.7290	2.050	1.58795×10^3	0.7746×10^6
15.204	6.1713	2.200	1.84158×10^3	0.8371×10^6
14.778	6.3379	2.250	1.86629×10^3	0.8295×10^6
14.535	6.4371	2.280	1.96014×10^3	0.8595×10^6
12.340	7.4963	2.618	2.69314×10^3	1.0287×10^6

Table 3-9-d.

Conductivities of Concentrated Calcium-Ammonia Solutions at -60°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)	Atomic Conductance (cm^2/mole-ohm)
32.659	2.9710	1.138	0.75408×10^3	
31.064	3.1188	1.194	0.75586×10^3	
29.350	3.2949	1.259	0.73929×10^3	
27.123	3.5558	1.347	0.74100×10^3	
24.533	3.9165	1.477	0.76034×10^3	0.5148×10^6
22.781	4.2050	1.575	0.86500×10^3	0.5492×10^6
21.577	4.4293	1.647	0.98303×10^3	0.5969×10^6
19.799	4.8079	1.770	1.1612×10^3	0.656×10^6
17.884	5.2955	1.924	1.4275×10^3	0.7419×10^6
16.611	5.6783	2.051	1.5826×10^3	0.7716×10^6
16.547	5.6990	2.057	1.6435×10^3	0.7990×10^6
16.311	5.7766	2.082	1.6237×10^3	0.7799×10^6
16.024	5.8741	2.115	1.7230×10^3	0.8147×10^6
15.236	6.1592	2.209	1.8687×10^3	0.8459×10^6
14.408	6.4901	2.313	1.9662×10^3	0.8501×10^6
14.155	6.5985	2.349	2.1654×10^3	0.9218×10^6
13.601	6.8489	2.428	2.3393×10^3	0.9635×10^6
12.942	7.1726	2.529	2.5335×10^3	1.0018×10^6

Table 3-9-e.

Conductivities of Concentrated Calcium-Ammonia Solutions at -70°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Concentration (mole Ca/liter)	Specific Conductance ($ohm^{-1}cm^{-1}$)	Atomic Conductance (cm^2/mole-ohm)
32.659	2.9710	1.164	0.84227×10^3	
31.064	3.1188	1.215	0.83351×10^3	
29.350	3.2949	1.274	0.85462×10^3	
27.123	3.5558	1.364	0.84896×10^3	
24.533	3.9165	1.489	0.84560×10^3	
22.781	4.2050	1.586	0.85805×10^3	0.541×10^6
21.577	4.4293	1.660	0.95953×10^3	0.578×10^6
19.799	4.8079	1.785	1.1466×10^3	0.6424×10^6
17.884	5.2955	1.951	1.3874×10^3	0.7111×10^6
16.611	5.6783	2.072	1.5334×10^3	0.7401×10^6
16.547	5.6990	2.077	1.6186×10^3	0.7793×10^6
16.024	5.8741	2.134	1.6912×10^3	0.7925×10^6
15.236	6.1592	2.225	1.8209×10^3	0.8184×10^6
14.408	6.4901	2.331	1.8633×10^3	0.7994×10^6
14.155	6.5985	2.365	2.0676×10^3	0.8742×10^6
13.601	6.8489	2.446	2.2974×10^3	0.9392×10^6
12.942	7.1726	2.550	2.4844×10^3	0.9743×10^6

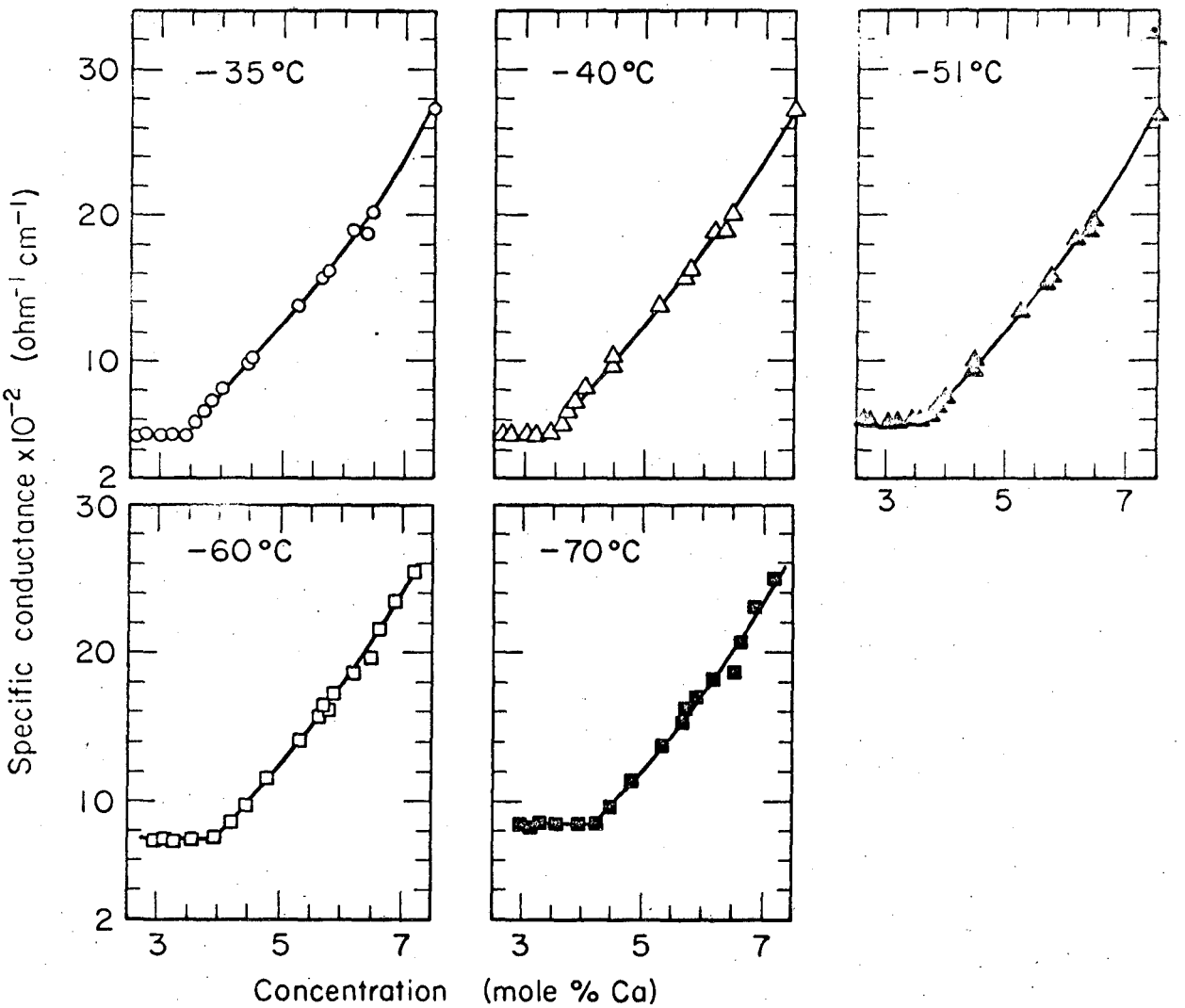

Figure 3-6-a.

Specific Conductances of Concentrated Calcium-Ammonia Solutions.

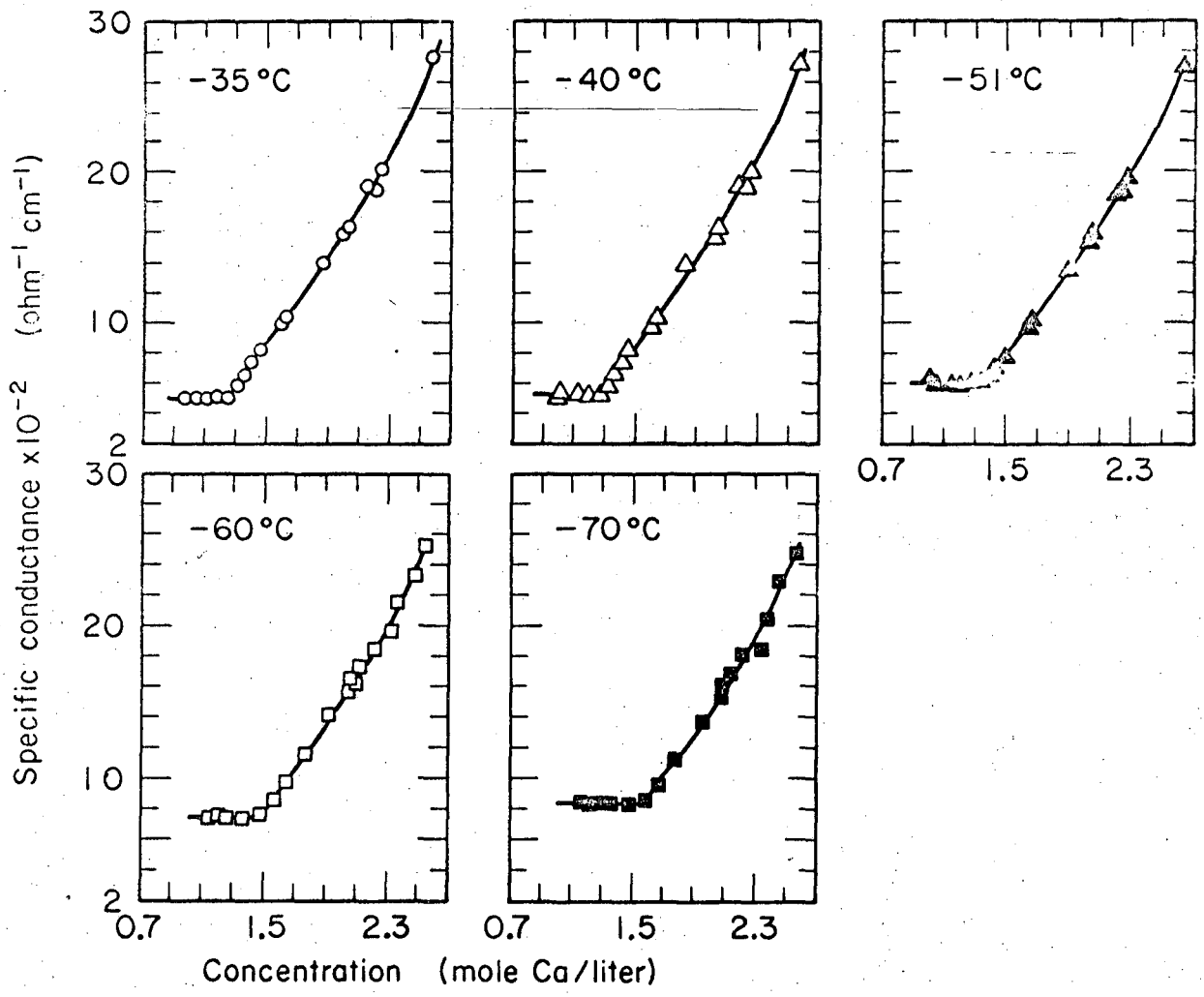

Figure 3-6-b.

Specific Conductances of Concentrated Calcium-Ammonia Solutions.

3-3-b. Atomic conductance of concentrated calcium-ammonia solutions: The atomic conductance of concentrated calcium-ammonia solutions was calculated from the equation

$$\Lambda' = \frac{x}{c} \times 1000 \qquad (3\text{-}3\text{-}1)$$

where Λ' is the atomic conductance (cm^2/mole Ca-ohm),

x is the specific conductance ($ohm^{-1}cm^{-1}$), and

c is the concentration of calcium (mole Ca/liter).

The results are tabulated in Table 3-9 and plotted in Figure 3-7 and 3-8. For the same reason mentioned in section 3-2-b, the atomic conductance at each temperature is plotted separately in Figure 3-7, and then put together (without experimental points) in Figure 3-8 for comparison. In Figure 3-8 the curve for atomic conductance of calcium in liquid ammonia at -51°C is omitted because it is very close to that at -60°C. Figure 3-8 also shows that the curves have nearly the same shape, but the separation between them is not proportional to the temperature difference. This is due to experimental uncertainty, especially due to the decomposition reaction of calcium-ammonia solutions. Although the decomposition reaction was minimized by carefully cleaning the metal surface (see appendix C), some decomposition still occurred, especially on the electrode surface because platinum can serve as a catalyst. Thus a thin layer of less conductive liquid could have formed. In the conductivitiy measurements of concentrated calcium-ammonia solutions, one sample was used to cover the temperature range from -35°C to -51°C, and another to cover the temperature range from -60°C to -70°C. The measurements were always taken at the higher temperature first. The time for an individual run was approximately 4 hours (see section 2-2). Therefore, when the conductivity measurements

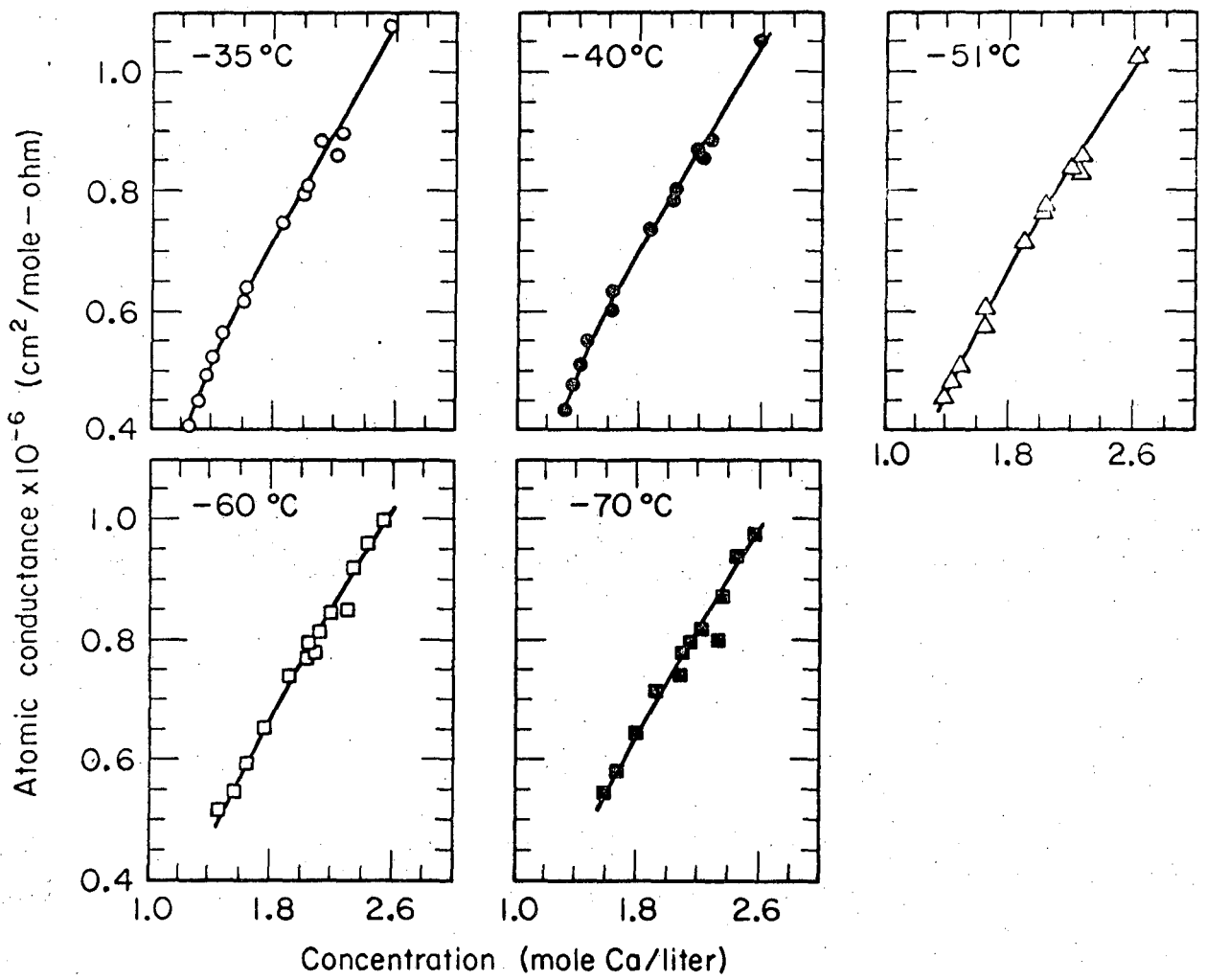

Figure 3-7.

Atomic Conductances of Concentrated Calcium-Ammonia Solutions.

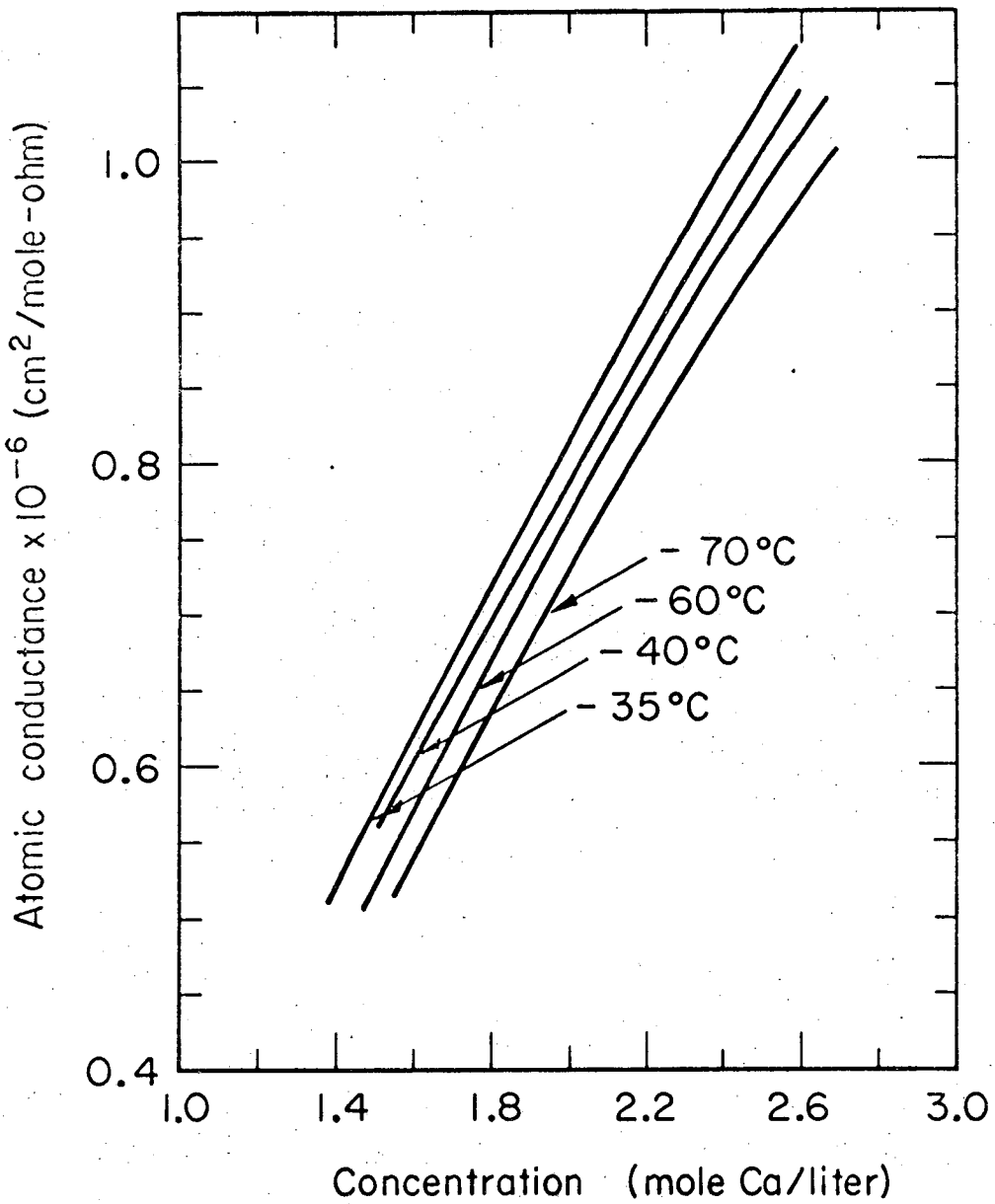

Figure 3-8.

Atomic Conductances of Concentrated Calcium-Ammonia Solutions.

at -51°C were being made, some calcium had already decomposed. Since the tmperature coefficient of conductance of concentrated calcium-ammonia solutions is very small (approximately 0.3%/°C - see next section), even a little decomposition of calcium in the sample used for the higher temperature range will cause the conductance curve at -51°C to overlap with that of -60°C.

The equivalent conductance* of calcium-ammonia solutions at -35°C is plotted in Figure 3-9 with that of sodium and of potassium ammonia solutions at -33.6°C[78]. Figure 3-9 shows that at a concentration of 5 equivalent metal/liter, the equivalent conductance of calcium in liquid ammonia is approximately half that of sodium in liquid ammonia. At a lower concentration (2.55 equiv-metal/liter), the equivalent conductance of calcium-ammonia is 80% of that of sodium-ammonia solutions.

3-3-c. <u>Mechanism of conductance of concentrated metal-ammonia solutions</u>: Based on current theories[5], the metal atoms in concentrated metal-ammonia solutions are surrounded by ammonia molecules with their nitrogen atoms pointing toward the metal atom, and their "protons" pointing outward to form a "proton shell" surrounding the whole complex (a monomer unit, see appendix A-10). The valence electron of the metal atom will jump into this "proton shell" and form a new orbital. The mechanism of conductance is similar to the case of a metal. The valence electrons jump from one energy well into the conductance band and move through the space filled with ammonia molecules into another energy well. Since a calcium ion has two

---

* The equivalent conductance is defined as:

$$\Lambda \left(\frac{cm^2}{\text{equiv Ca-ohm}}\right) = \frac{x}{\text{equiv Ca}} \times 1000 = \frac{\Lambda'}{2}, \qquad (3\text{-}3\text{-}2)$$

where Λ' is the atomic conductance (cm^2/mole Ca-ohm).

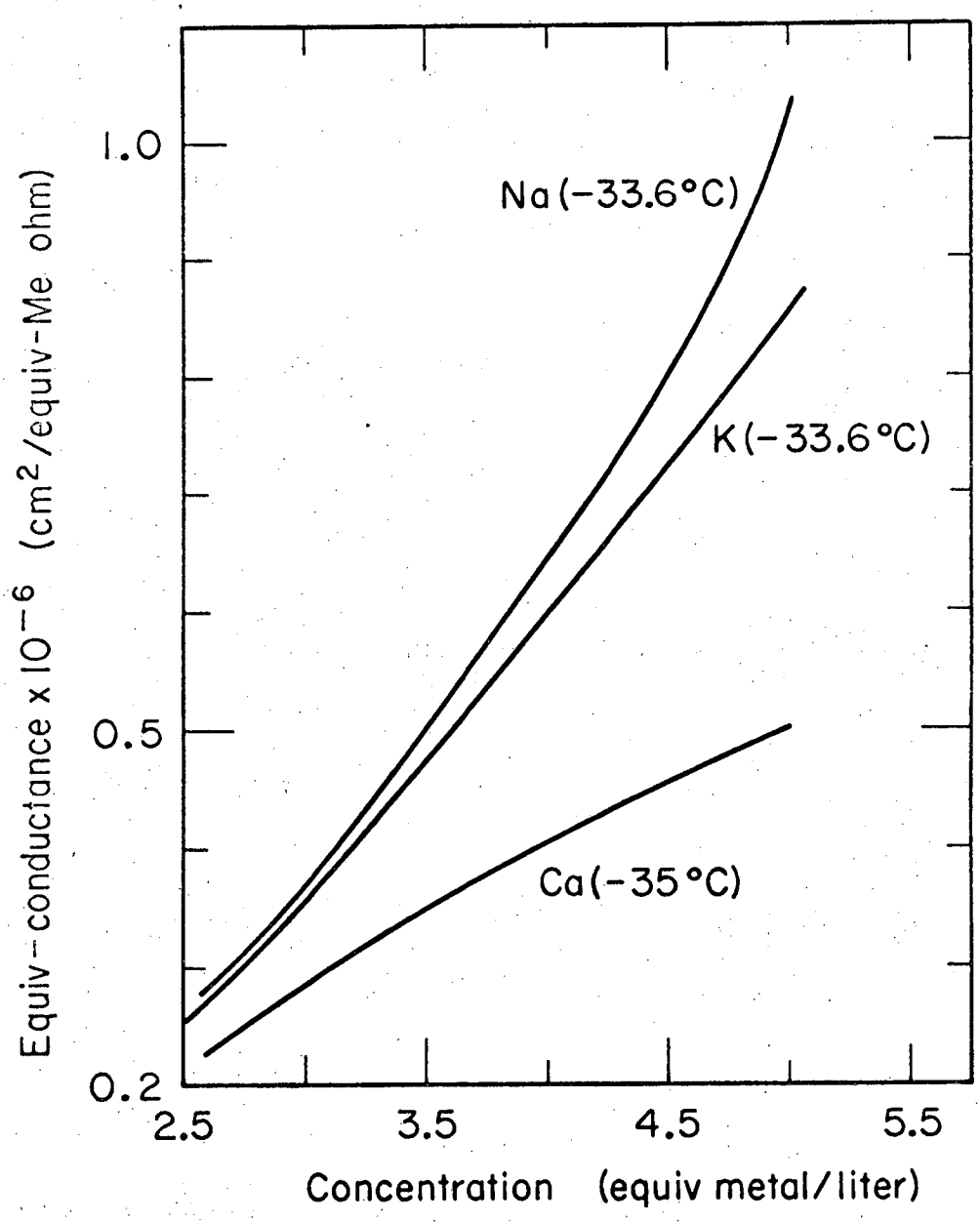

Figure 3-9.

Equivalent Conductances of Concentrated Metal-Ammonia Solutions.

charges it will produce a deeper energy well than that produced by sodium ions. Therefore, the equivalent conductance of a concentrated calcium-ammonia solution is much smaller than that of an analogous sodium-ammonia solution as in the case of pure metal[68].

3-3-d. Temperature coefficient of conductance of concentrated calcium-ammonia solutions: To avoid the possible error due to the decomposition reaction of the calcium-ammonia solution (see section 3-3-b), only the specific conductance data at -35°C and -60°C were used to calculate the temperature coefficient of conductance of concentrated calcium-ammonia solutions. The integral temperature coefficient of the concentrated calcium-ammonia solutions were calculated from the equation:

$$\beta_c = \frac{2(x_{-35} - x_{-60})}{(x_{-35} + x_{-60}) \times 25} \times 100 \qquad (3\text{-}3\text{-}3)$$

where β_c is the temperature coefficient at the concentration indicated(%/°C),

x is the specific conductance of calcium-ammonia solution at the same concentration and at the temperature indicated ($ohm^{-1}cm^{-1}$), and the number 25 represents the temperature difference between -35°C and -60°C (°C).

The specific conductance data taken from the smooth curves in Figure 3-9 were used for the calculation. The results are tabulated in Table 3-10.

The integral temperature coefficient of conductance of concentrated calcium-ammonia solutions is smaller than that of analogous concentrated sodium or potassium-ammonia solutions. The temperature coefficient of conductance of a calcium-ammonia solutions decreases as concentration of calcium increases in the concentration range from 1.5 mole Ca/liter to 2.1mole Ca/liter. However, it remains constant at more concentrated solutions. In the case of concentrated sodium and potassium-ammonia solutions,

Table 3-10.

Integral Temperature Coefficients of Conductivity of Concentrated Calcium-Ammonia Solutions in the Temperature Interval of -35°C to -60°C.

Concentration mole Ca/liter	Temperature Coefficient (%/°C)
1.5	0.39
1.6	0.34
1.7	0.31
1.8	0.30
1.9	0.27
2.0	0.25
2.1	0.24
2.3	0.24
2.4	0.25
2.5	0.24

the temperature coefficient of conductance decreases continuously as concentration of metal increases up to the saturated solutions.

3-4. Density of Calcium-Ammonia Solutions.

3-4-a. Overall density of calcium-ammonia solutions: The overall density of calcium-ammonia solutions is tabulated in Table 3-11 and plotted in Figure 3-10 and Figure 3-11. In Figure 3-10 the overall density of calcium-ammonia solutions is plotted against the overall concentration of calcium in the solution using the unit of mole% Ca. In the two-liquid phase region, since the density and the concentration of each phase are constant, the overall density depends only on the amount of each phase present. In the one-liquid phase region the density changes with concentration of calcium in a different manner. Figure 3-10 shows the curves of overall density plotting against overall concentration have an inflection point. The portion of the curves which is concave downward represents the overall density of calcium-ammonia solution in the two-liquid phase region. The portion of the curves which is concave upward represents the overall density of calcium-ammonia solutions in the one-liquid phase region. The inflection point of the curve, which represents the boundary of the two-liquid phase region, could not be determined accurately from Figure 3-10 because of the uncertainty of the experimental data. When the overall density of calcium-ammonia solutions is plotted against the overall concentration using units of mole Ca/liter (Figure 3-11), two different portions are observed. The portion which is a curve represents the density of concentrated calcium-ammonia solutions in the one-liquid phase region. The portion which is a straight line represents the overall density of the calcium-ammonia solutions in the two-liquid phase region as predicted by

Table 3-11-a.

Overall Densities of Calcium-Ammonia Solutions at -35°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
144.04	0.6895	0.27255	0.67944
94.74	1.0445	0.40933	0.67656
62.46	1.5758	0.60885	0.67207
41.44	2.3563	0.89135	0.66476
34.27	2.8353	1.06145	0.66199
29.2	3.3113	1.22165	0.65641
27.2	3.5461	1.30426	0.65635
25.2	3.8168	1.3955	0.65482
23.1	4.1494	1.5058	0.65095
19.8	4.8077	1.7214	0.64934
17.358	5.4472	1.9241	0.64611
17.31	5.4615	1.9344	0.64780
16.47	5.7241	2.0184	0.64693
14.157	6.5976	2.2956	0.64544
12.75	7.2727	2.50684	0.64482
11.575	7.9523	2.71536	0.64409

Table 3-11-b.

Overall Densities of Calcium-Ammonia Solutions at -40°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
3699.1	0.0270	0.01097	0.69129
2683.0	0.0373	0.01511	0.69102
1192.2	0.0838	0.03392	0.69007
609.8	0.1637	0.6621	0.69023
275.2	0.3621	0.14561	0.68837
263.0	0.3788	0.15219	0.68776
173.8	0.5721	0.2288	0.68644
161.4	0.6158	0.24596	0.68577
155.8	0.6378	0.25436	0.68502
144.2	0.6887	0.27437	0.68480
98.0	1.0101	0.39897	0.68179
60.0	1.6393	0.63743	0.67637
45.13	2.1678	0.83019	0.67139
36.68	2.6539	1.0058	0.66864
30.9	3.1348	1.1721	0.66381
28.09	3.4376	1.2762	0.66167
24.76	3.8820	1.4264	0.65871
23.67	4.0535	1.4824	0.65702
23.18	4.1356	1.5016	0.65694
21.06	4.5331	1.6410	0.65451
20.84	4.5788	1.6558	0.65155
17.24	5.4825	1.9528	0.65155
16.2	5.8140	2.0611	0.65133
14.89	6.2933	2.2143	0.65008
13.82	6.7496	2.3575	0.64920
10.52	8.6805	2.9424	0.64510
10.25	8.8889	2.9994	0.64364

Table 3-11-c.

Overall Densities of Calcium-Ammonia Solutions at -45.5°C

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
3713.1	0.0269	0.01101	0.69684
2707.0	0.0369	0.01511	0.69730
1202.0	0.0832	0.0340	0.69664
616.1	0.1621	0.60134	0.69657
277.9	0.3586	0.1456	0.69455
265.4	0.3754	0.1522	0.69403
175.3	0.5672	0.22896	0.69258
145.9	0.6807	0.27384	0.69123
98.8	1.0020	0.3982	0.68610
60.47	1.6268	0.6372	0.68171
46.38	2.1106	0.81677	0.67793
35.02	2.7762	1.0552	0.67161
31.55	3.0720	1.1585	0.66889
29.56	3.2723	1.2273	0.66700
26.33	3.6590	1.3576	0.66375
25.12	3.8285	1.4186	0.66362
25.08	3.8344	1.4211	0.66391
24.48	3.9246	1.4499	0.66251
23.95	4.0080	1.4763	0.66132
21.16	4.5126	1.6438	0.65821
20.45	4.6620	1.6969	0.65871
20.27	4.7015	1.7080	0.65801
16.43	5.7372	2.0462	0.65442
16.30	5.7804	2.0593	0.65423
13.94	6.6934	2.3538	0.65311
13.61	6.8446	2.3963	0.65163
12.64	7.3314	2.5489	0.65066
10.91	8.3963	2.8135	0.64928

Table 3-11-d.

Overall Densities of Calcium-Ammonia Solutions at -51°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
3749.7	0.0266	0.01101	0.70371
2732.0	0.0366	0.01512	0.70404
1212.1	0.0824	0.0340	0.70329
620.8	0.1608	0.0626	0.70318
280.3	0.3555	0.1456	0.70089
267.4	0.3726	0.1525	0.70022
177.2	0.5612	0.2286	0.69901
147.2	0.6748	0.2736	0.69689
99.65	0.9935	0.4009	0.69369
60.82	1.6176	0.6374	0.68577
46.93	2.0864	0.8148	0.68384
37.32	2.6096	1.0043	0.67863
31.39	3.0874	1.1712	0.67302
28.88	3.3467	1.2641	0.67236
26.67	3.6140	1.3547	0.66964
25.19	3.8183	1.4250	0.66854
24.68	3.8941	1.451	0.66784
23.59	4.0667	1.5087	0.66650
21.18	4.5086	1.655	0.66318
20.36	4.6817	1.7169	0.66179
17.56	5.3879	1.943	0.65892
17.41	5.4318	1.955	0.65811
16.86	5.5991	2.0126	0.65849
16.36	5.7604	2.0624	0.65720
15.10	6.2112	2.2111	0.65704
12.77	7.2622	2.5466	0.65574
11.01	8.3264	2.8737	0.65400
10.67	8.5690	2.9409	0.65238

Table 3-11-e.

Overall Densities of Calcium-Ammonia Solutions at -60°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
218.537	0.4555	0.18859	0.70944
147.246	0.6746	0.27744	0.70684
80.687	1.2242	0.49570	0.70100
58.585	1.6783	0.67154	0.69692
39.785	2.4519	0.9598	0.68871
29.810	3.2457	1.23920	0.67876
29.090	3.3234	1.26808	0.67903
26.729	3.6063	1.36504	0.67607
25.762	3.7366	1.41101	0.67559
22.127	4.3240	1.61026	0.67123
21.609	4.4230	1.64492	0.67126
19.152	4.9623	1.82282	0.66758
18.138	5.2252	1.90853	0.66602
17.287	5.4684	1.98807	0.66496
15.497	6.0617	2.17983	0.66256
15.235	6.1595	2.21177	0.66248
14.120	6.6138	2.3564	0.66108
13.886	6.7177	2.39112	0.66128
13.110	7.0871	2.50528	0.65973
12.928	7.1798	2.53687	0.66061
12.840	7.2254	2.55548	0.66120
12.604	7.3508	2.5877	0.65916
12.160	7.5988	2.66885	0.65962
11.580	7.9491	2.78237	0.66021
11.045	8.3022	2.88777	0.65863

Table 3-11-f.

Overall Densities of Calcium-Ammonia Solutions at -70°C.

Mole Ratio (mole NH_3/mole Ca)	Mole % Ca	Overall Concentration (mole Ca/liter)	Overall Density (gm/cm^3)
221.844	0.4487	0.18882	0.72091
149.848	0.6629	0.27747	0.71921
81.867	1.2068	0.49575	0.71104
59.520	1.6523	0.67089	0.70691
40.406	2.4151	0.9599	0.69894
30.329	3.1919	1.23933	0.68930
29.576	3.2705	1.26502	0.68787
27.110	3.5575	1.36569	0.68525
26.131	3.6858	1.41116	0.68455
22.401	4.2733	1.61044	0.67889
21.869	4.3727	1.64510	0.67862
19.380	4.9068	1.82301	0.67457
18.406	5.1530	1.90336	0.67291
17.524	5.3984	1.98524	0.67204
15.383	6.1039	2.21201	0.66813
14.256	6.5548	2.35668	0.66659
14.109	6.6186	2.37855	0.66685
13.209	7.0378	2.49911	0.66528
13.067	7.1088	2.53414	0.66548
12.804	7.2443	2.57619	0.66499
11.811	7.8058	2.75482	0.66452
11.138	8.2386	2.8881	0.66355

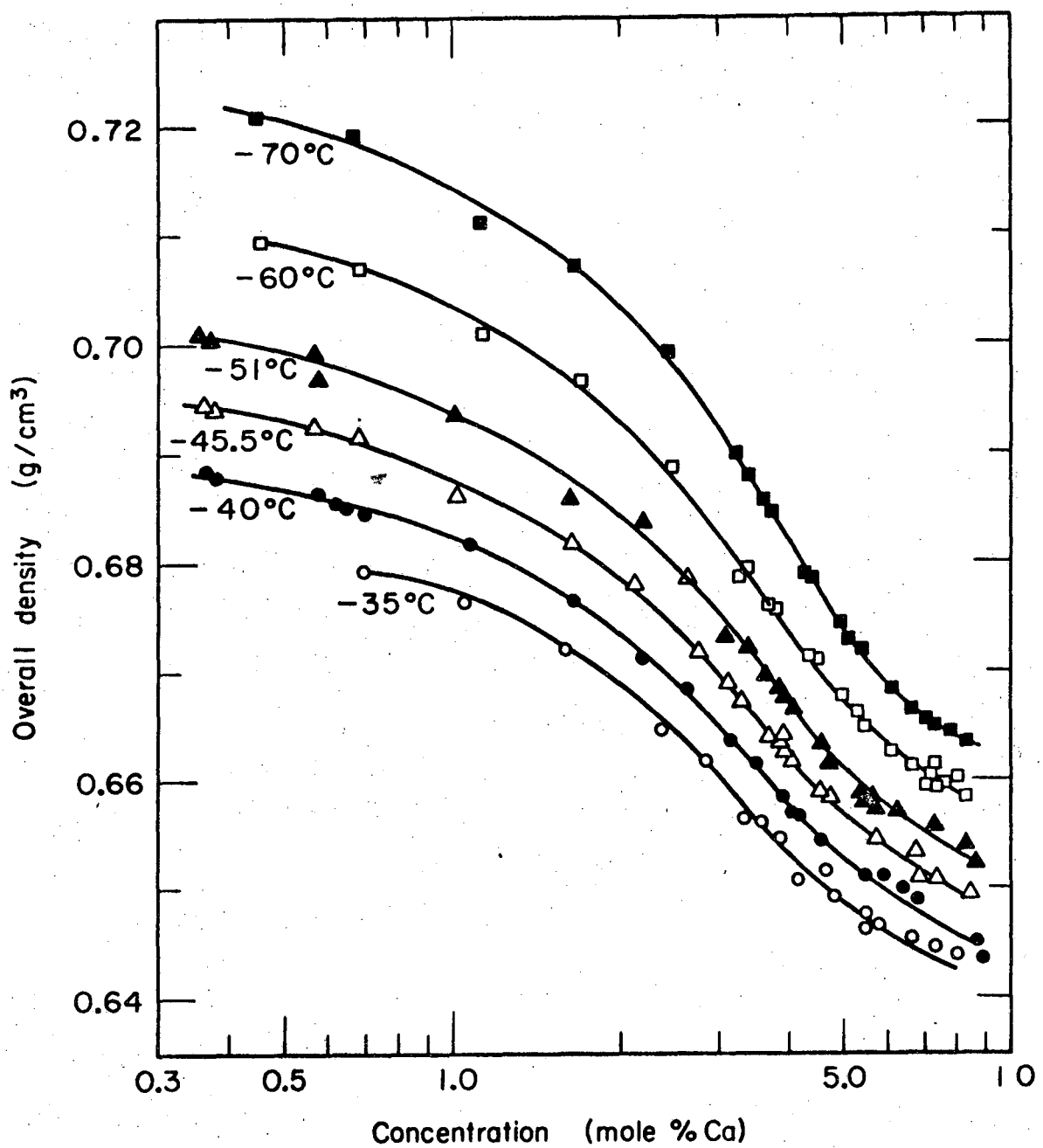

Figure 3-10.

Overall Densities of Calcium-Ammonia Solutions.

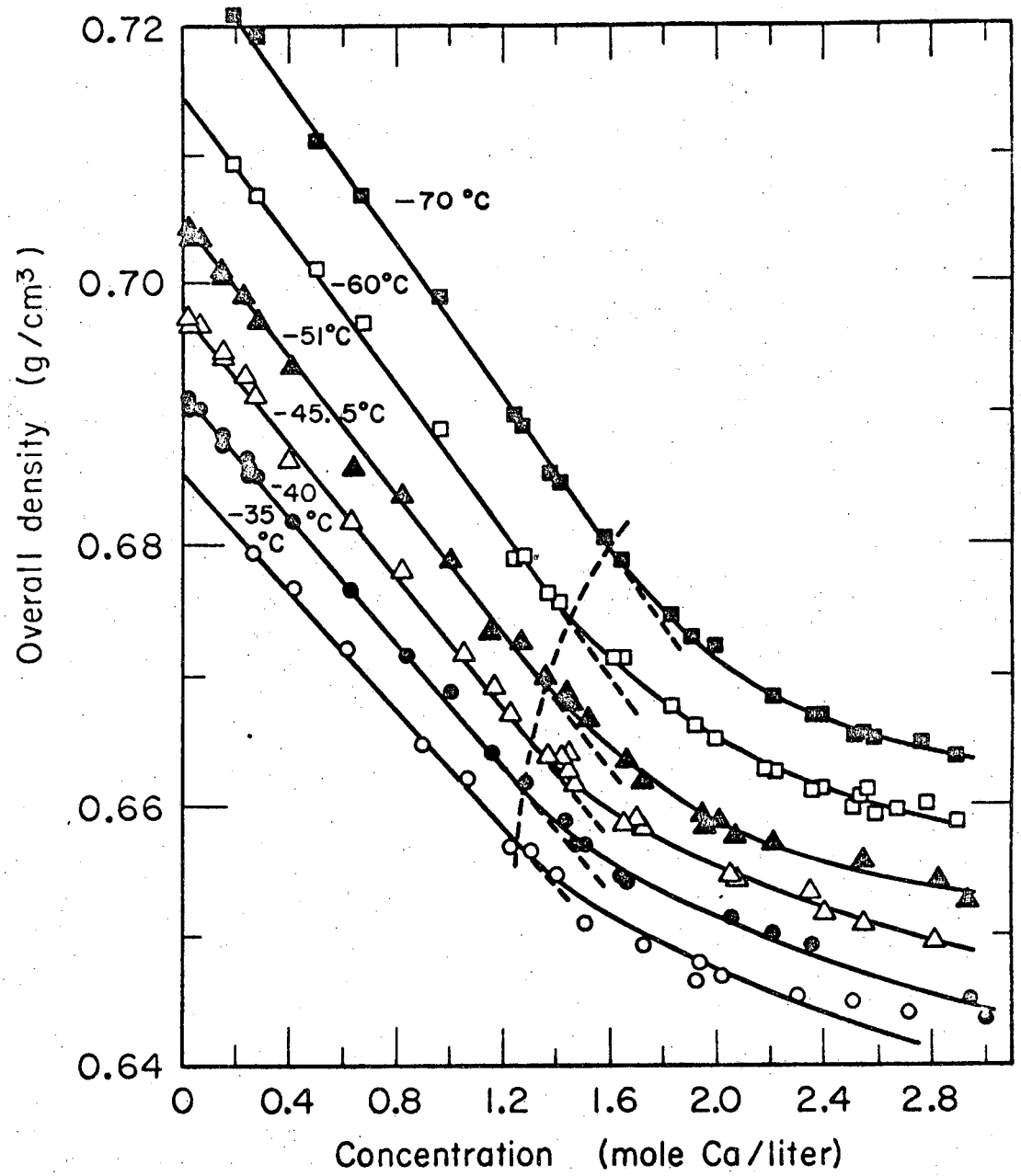

Figure 3-11.

Overall Densities of Calcium-Ammonia Solutions.

the following relation.

For one liter of a calcium-ammonia solution in the two-liquid phase region:

Let d = overall density (g/cm^3)

z = overall concentration (mole Ca/liter)

In the dilute phase:

d' = density of the dilute phase (g/cm^3)

z' = concentration of the dilute phase (mole Ca/liter)

w' = the weight of the dilute phase (g)

In the concentrated phase:

d'' = density of the concentrated phase (g/cm^3)

z'' = concentration of the concentrated phase (mole Ca/liter)

w'' = the weight of the concentrated phase (g)

Then

$$1000z = \frac{w'}{d'} z' + \frac{w''}{d''} z'' \qquad \text{(a)}$$

$$\frac{w'}{d'} + \frac{w''}{d''} = 1000 \qquad \text{(b)}$$

$$w' + w'' = 1000d \ . \qquad \text{(c)}$$

By combining equations (a), (b) and (c), one gets:

$$d = z \frac{d'' - d'}{z'' - z'} + d' - z' \frac{d'' - d'}{z'' - z'} \qquad (3\text{-}4\text{-}1)$$

which is an euqation of a straight line because d', d'', z' and z'' are constants. The point of intersection of these two portions represents the boundary of the two-liquid phase region. The concentration of the concentrated calcium-ammonia solution in the two-liquid phase region as determined by this intersection from Figure 3-11 was 1.25 ± 0.03 mole Ca/liter, 1.27 ± 0.03 mole Ca/liter, 1.31 ± 0.03 mole Ca/liter, 1.36 ± 0.03 mole Ca/liter, 1.46 ± 0.3 mole Ca/liter and 1.59 ± 0.03 mole Ca/liter at

temperatures -35°C, -40°C, -45.5°C, -51°C, -60°C and -70°C, respectively. These results agree very well with those determined by conductivity measurements (see section 3-5).

The only information about the density of calcium-ammonia solutions in the literature is that reported by Coulter[15]. He reported that density of a saturated calcium-ammonia solution (7 mole NH_3/mole Ca) at -35°C was 0.651 gm/cm^3. This value is approximately 2% higher than that estimated from the present work (0.639 ± .001 gm/cm^3). However, the concentration of the saturated calcium-ammonia solution in his report may not be reliable. It is not mentioned how he obtained this value. The concentration of a saturated calcium-ammonia determined by Kraus[62] by vapor pressure measurements is 7 mole NH_3/mole Ca but the accuracy is questionable (see section 3-5). The concentration of a saturated calcium-ammonia solution at -36°C has been determined by Jolly et al[56] to be 10.7 mole% Ca (8.35 mole NH_3/mole Ca) also from vapor pressure measurements.

The difference between the density of dilute calcium-ammonia solutuions in the one-liquid phase region and that of liquid ammonia at the same temperature is very small and could not be determined in the present work. Theoretically, equation (3-4-1) can be used to calculate the density of the saturated dilute calcium-ammonia solutions in the two-liquid phase region if the overall density data in the two-liquid phase region are very accurate. By applying the method of least squares, equation (3-4-1) was determined to be

$$d = -0.02381z + 0.68626 \quad \text{at } -35°C \tag{3-4-1a}$$

$$d = -0.02335z + 0.69136 \quad \text{at } -40°C \tag{3-4-1b}$$

$$d = -0.02485z + 0.69767 \quad \text{at } -45°C \tag{3-4-1c}$$

$$d = -0.02597z + 0.70428 \quad \text{at } -51°C \tag{3-4-1d}$$

$$d = -0.02388z + 0.71509 \quad \text{at } -60°C \tag{3-4-1e}$$

$$d = -0.03026z + 0.72697 \quad \text{at } -70°C\ . \tag{3-4-1f}$$

The concentration of a saturated dilute calcium-ammonia solution in the two-liquid phase region is 0.02 ± 0.01 mole Ca/liter in this temperature range (see section 3-5). Applying these concentrations to the equations (3-4-1a) to (3-4-1f), it was determined that the difference between the density of a saturated dilute calcium-ammonia solution in the two-liquid phase region and that of liquid ammonia is less than 0.1% of the density of liquid ammonia at the same temperature.

3-4-b. Excess volume of the concentrated calcium-ammonia solutions: The excess volume of a metal-ammonia solution is defined as

$$\Delta V = \frac{V_{sol'n} - N_m V_m - N_a V_a}{N_m} \tag{3-4-2}$$

where ΔV is the excess volume (cm^3/mole metal)

$V_{sol'n}$ is the total volume of the metal-ammonia solution (cm^3)

V_m is the molar volume of pure metal (cm^3/mole metal)

V_a is the molar volume of liquid ammonia (cm^3/mole NH_3)

N_m is the number of moles of metal in the solution

N_a is the number of moles of ammonia in the solution.

The excess volume of the concentrated calcium-ammonia solutions in the one-liquid phase region calculated from the density of calcium-ammonia solutions and the molar volume of calcium[40] is tabulated in Table 3-12 and plotted in Figure 3-12 and Figure 3-13. The results show that the excess volume of calcium-ammonia solutions decreases as temperature increases and also as concentration of calcium increases.

Table 3-12-a.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -35°C.

Mole % of Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
3.5461	1.30426	64.21
3.8168	1.3955	63.75
4.1494	1.5058	65.32
4.8077	1.7214	62.53
5.4472	1.9241	61.82
5.4615	1.9344	60.40
5.7241	2.0184	59.88
6.5976	2.2956	57.54
7.2727	2.50684	55.82
7.9523	2.71536	54.43

Table 3-12-b.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -40°C

Mole % Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
3.8820	1.4264	64.63
4.0535	1.4824	65.05
4.1356	1.5016	64.51
4.5331	1.6410	64.08
4.5788	1.6558	64.23
5.4825	1.9528	61.87
5.8140	2.0611	59.80
6.2933	2.2143	58.72
6.7496	2.3575	57.59
8.6805	2.9424	54.56
8.8889	2.9994	54.88

Table 3-12-c.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -45.5°C

Mole % Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
3.6590	1.3576	67.15
3.8285	1.4186	65.79
3.8344	1.4211	65.43
3.9246	1.4499	66.15
4.0080	1.4763	66.68
4.5126	1.6438	65.82
4.6620	1.6969	64.34
4.7015	1.7080	64.71
5.7372	2.0462	61.75
5.7804	2.0593	61.69
6.6934	2.3538	58.61
6.8446	2.3963	59.02
7.3314	2.5489	57.92
8.3963	2.8135	55.65

Table 3-12-d.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -51°C.

Mole % Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
3.8183	1.4250	66.46
3.8941	1.451	66.55
4.0667	1.5087	66.45
4.5086	1.655	66.17
4.6817	1.7169	66.17
5.3879	1.943	64.62
5.4318	1.955	64.64
5.5991	2.0126	63.24
5.7604	2.0624	63.40
6.2112	2.2111	61.28
7.2622	2.5466	58.02
8.3264	2.8737	55.83
8.5690	2.9409	56.05

Table 3-12-e.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -60°C.

Mole % Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
4.3240	1.61026	67.93
4.4230	1.64492	67.19
4.9623	1.82282	66.40
5.2252	1.90853	65.92
5.4684	1.98807	65.24
6.0617	2.17983	63.64
6.1595	2.21177	63.27
6.6138	2.3564	62.07
6.7177	2.39112	61.49
7.0871	2.50528	60.93
7.1798	2.53687	60.04
7.2254	2.55548	59.52
7.3508	2.5877	60.26
7.5988	2.66885	59.11
7.9491	2.78237	57.63
8.3022	2.88777	57.41

Table 3-12-f.

Excess Volumes of Concentrated Calcium-Ammonia Solutions at -70°C.

Mole % Ca	Concentration (mole Ca/liter)	Excess Volume (cm^3/mole Ca)
4.2733	1.61044	69.55
4.3727	1.64510	68.92
4.9068	1.82301	68.13
5.1530	1.90336	67.69
5.3984	1.98524	66.71
6.1039	2.21201	65.32
6.5548	2.35668	64.01
6.6186	2.37855	63.59
7.0378	2.49911	62.61
7.1088	2.53414	62.19
7.2443	2.57619	61.92
7.8058	2.75482	60.04
8.2386	2.8881	59.09

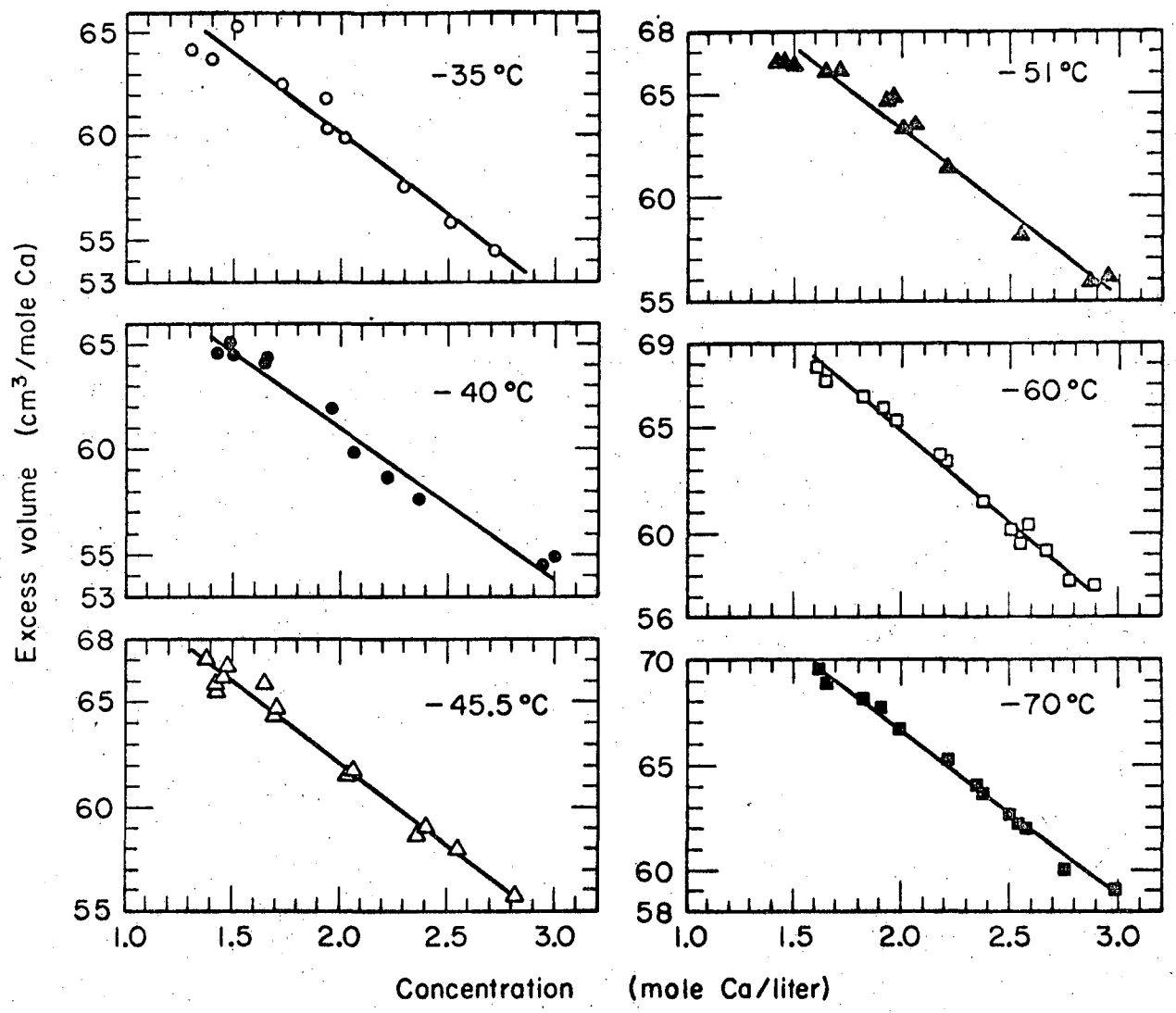

Figure 3-12.

Excess Volume of Concentrated Calcium-Ammonia Solutions.

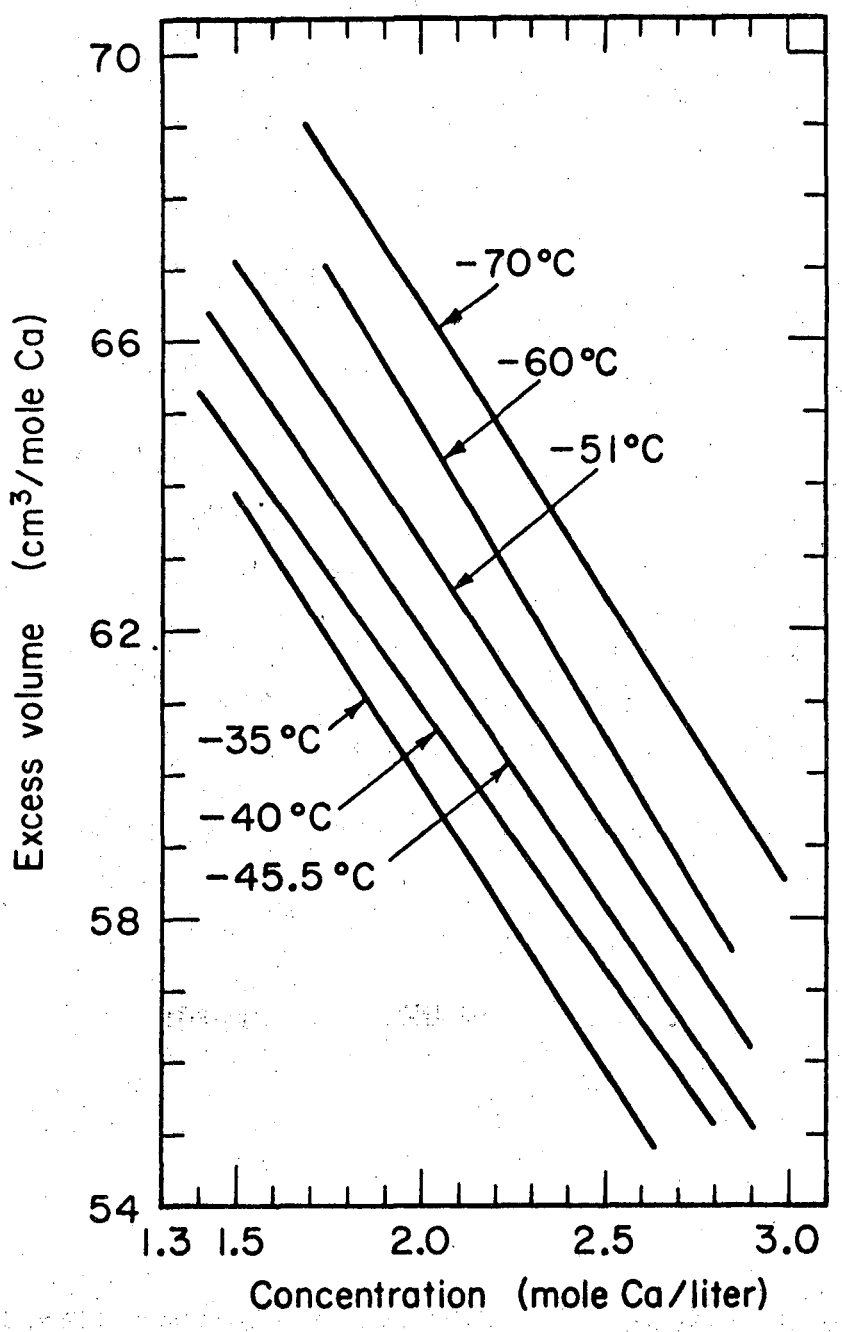

Figure 3-13.
Excess Volume of Concentrated Calcium-Ammonia Solutions.

3-4-c. Comparison of the excess volume of calcium-ammonia solutions to those of alkali metal ammonia solutions: Compared to those of alkali metal-ammonia solutions[52,54,72,77] (Figure 3-14), the excess volume of concentrated calcium-ammonia solution is larger than those of alkali metal-ammonia solutions at the same concentration. This is due to the face that the calcium-ammonia complex in the calcium-ammonia solutions (appendix A-10) has two valence electrons in the "proton shell". The effect will be to stretch the N-H bond in the ammonia molecule and weaken the hydrogen bonding with other ammonia molecules. This effect is greater for calcium-ammonia solutions than for alkali metal-ammonia solutions because there is only one valence electron in the "proton shell" of the alkali metal-ammonia complex (monomer).*

The excess volume of a concentrated calcium-ammonia solution decreases as concentration of calcium increases as in alkali metal-ammonia solution. The rate of decrease for calcium-ammonia solution is much larger than for alkali metal-ammonia solutions. Possibly the "clusters" of the metal-ammonia complex (appendix A-10) are more stable in the calcium-ammonia solution than in the alkali metal-ammonia solutions. This could be due to the fact that a calcium-ammonia complex contains six ammonia molecules and can be fitted into a crystal lattice[9,62]. It is known that a solid calcium-ammonia compound $[Ca(NH_3)_6]$ can be separated but no solid sodium or potassium-ammonia compounds were found (appendix A-2) so far.

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* The excess volume of lithium-ammonia solutions is larger than that of sodium-ammonia solutions which is larger than that of potassium-ammonia solutions[77]. These differences can be accounted for as the differences of the molar volume of alkali metals. The molar volume of calcium metal is between that of sodium and potassium, but the excess volume of calcium-ammonia solutions is much larger than that of sodium or potassium-ammonia solutions. This indicates that the differences are not due only to differences in the molar volume of the metals.

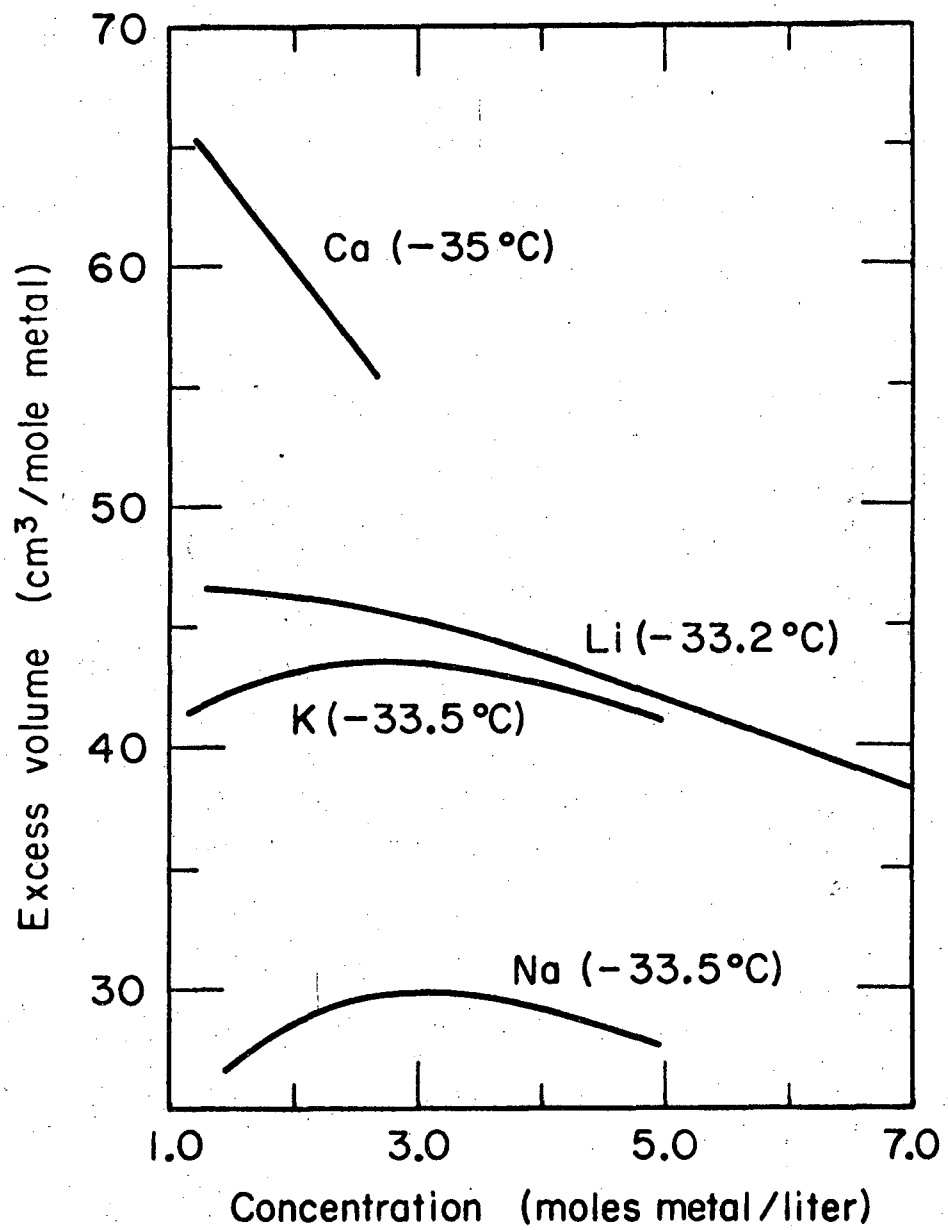


Figure 3-14.
Excess Volumes of Metal-Ammonia Solutions.

3-5. Liquid Region of the Phase Diagram of Calcium-Ammonia Solutions.

The concentrations of the dilute and concentrated calcium-ammonia solutions in the two-liquid phase region, as determined by conductivity measurements, are tabulated in Table 3-13 and plotted in Figure 3-15 and Figure 3-16, along with the data obtained from the literature[39,56,62].

Table 3-13 shows that there is some difference between the concentration of the dilute calcium-ammonia solution in the two-liquid phase region determined by the present work and that determined by Jolly et al[39,56] at -45°C. However, the absolute value of this difference is less than 0.008 mole Ca/liter. Since both data were not determined by direct measurement and also considering the difficulties involved in the experimental work with calcium-ammonia solutions, this agreement cannot be considered as poor. No experimental data other than graphical presentation of the conductivity measurements can be found in Jolly et al's report. In the present work, the main source of error of the conductivity measurement is the decomposition reaction. In Jolly et al's report[39] it was mentioned that there was 5 to 10% calcium decomposed during the course of the absorption spectra measurement. It is probable that the accuracy of their conductivity measurements also suffers from the decomposition reaction.

The concentration of the concentrated phase in the two-liquid phase region determined by the conductivity measurements agrees excellently with those determined by the density measurements (see section 3-4-a). There is, however, a small difference (less than 1 mole % Ca) between the present values and those of Jolly et al[56] as determined from the vapor pressure measurements.

The phase diagram determined by vapor pressure measurements is not

Table 3-13.

Concentration of Dilute and Concentrated Calcium-Ammonia Solutions in the Two-Liquid Phase Region.

Temp. (°C)	Concentration of Dilute Phase		Concentration of concentrated phase		Experimental Method	Source of Data
	Mole Ca / liter	mole % Ca	Mole Ca / liter	mole % Ca		
-32.5		0.5		9.0	vapor pressure measurements	Kraus[62]
+ 7		0.44			conductivity measurements	Jolly et al 39,56
- 4		0.32				
-45	0.032	0.078				
-63.8	0.013	0.031				
0				3.25	vapor pressure measurements	Jolly et al 56
-36				3.8		
-45				4.0		
-63.5				4.8		
-35	0.0263	0.066	1.242	3.36	conductivity measurements	Present work
-40	0.0255	0.0638	1.278	3.46		
-45.5	0.024	0.058				
-51	0.0208	0.051	1.362	3.66		
-60	0.0146	0.036	1.458	3.93		
-70	0.0095	0.0234	1.576	4.2		

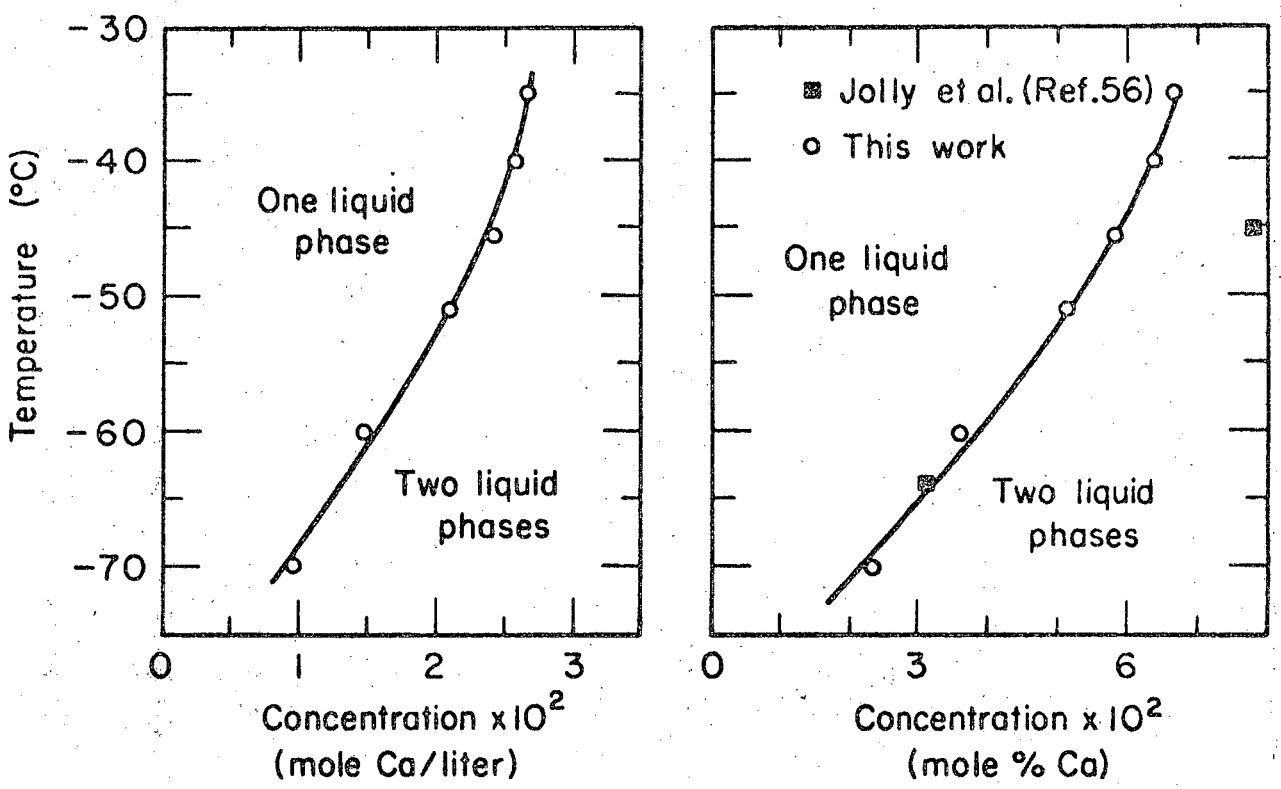


Figure 3-15.
Phase Boundaries of Dilute Calcium-Ammonia Solutions.

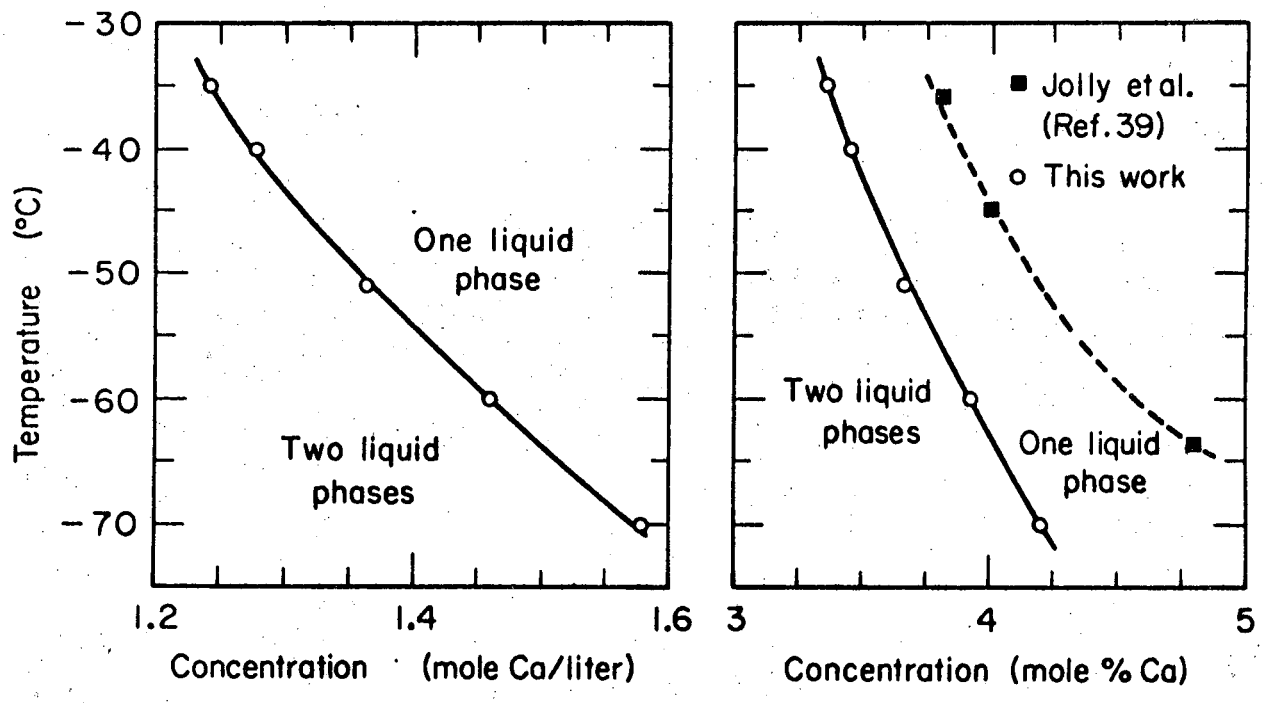


Figure 3-16.
Phase Boundaries of Concentrated Calcium-Ammonia Solutions.

believed to be accurate because the hydrogen gas generated from the decomposition reaction will shift the boundaries of the two-liquid phase region to the more concentrated side.

The phase diagram of calcium-ammonia solutions determined by the present work agrees with the results of Kraus' vapor pressure measurements[62] in order of magnitude only. The purpose of Kraus' work was to establish the existence of the solid calcium-ammonia compound $Ca(NH_3)_6$[62]. Only a graphical representation of vapor pressure of calcium-ammonia solution vs mole fraction of calcium was present and no experimental data were included. It was mentioned that some decomposition of calcium-ammonia solutions did take place during his experiment.

Marshall and Hunt[79] measured the vapor pressure of calcium-ammonia solutions at -45.3°C and -63.8°C. The results indicated that the concentration range of the two-liquid phase region was very small. However, when the vapor pressure data were plotted against the concentration, an irregular curve was obtained. Probably the accuracy of their experiments was decreased by the hydrogen gas generated from the decomposition reaction.

The logarithm of the ratio of the concentrations of the dilute and the concentrated calcium-ammonia solutions existing in the two-liquid phase region is plotted against the reciprocal of the absolute temperature in Figure 3-17. Based on the following relations, the slope of this curve represents the $\Delta E/Rx2.303$, where ΔE is the energy needed to transfer one mole of calcium from the concentrated phase to the dilute phase, and R is the gas constant. From figure of the energy state, one can see that the rates of transference of calcium atoms from one phase to the other are

$$-\frac{d\,C_d}{dt} = k_d\,C_d \exp - \frac{(E^{\ddagger} - E_d)}{RT}$$

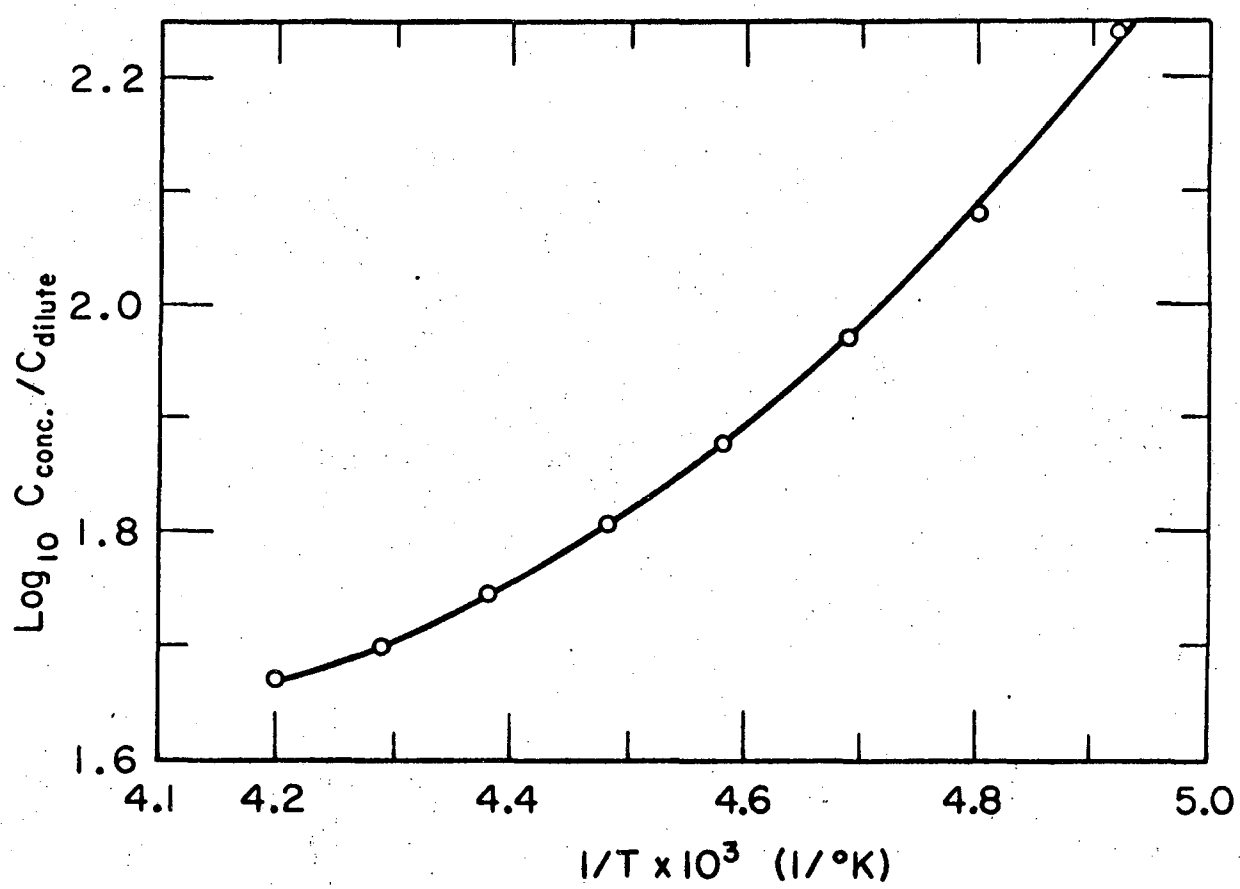
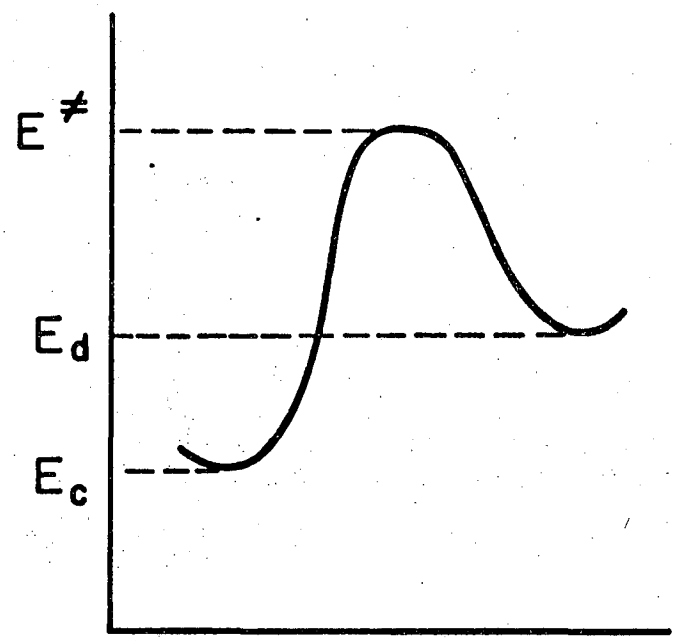

2.2
2.0
1.8
1.6
$\mathrm{Log}_{10}\ C_{conc.}/C_{dilute}$
4.1
4.2
4.4
4.6
4.8
5.0
$1/T \times 10^3$ (1/°K)

Figure 3-17.



E_c is the ground state energy of calcium in the concentrated phase.

E_d is the ground state energy of calcium in the dilute phase.

$E^{\ddagger}$ is the activation energy.

Energy State of Calcium in Two Liquid Phase Calcium-Ammonia Solutions.

$$-\frac{d\,C_d}{dt} = k_c\,C_c\,\exp - \frac{(E^{\ddagger} - E_c)}{RT}$$

where C_d and C_c are the concentrations of the dilute and concentrated calcium-ammonia solutions in the two-liquid phase region, respectively.

When the two-liquid phases coexist, they are in equilibrium

$$-\frac{d\,C_d}{dt} = -\frac{d\,C_c}{dt}$$

or

$$k_d\,C_d\,\exp - \frac{(E^{\ddagger} - E_d)}{RT} = k_c\,C_c\,\exp - \frac{(E^{\ddagger} - E_c)}{RT}$$

then

$$\ln\frac{k_c}{k_d} + \ln\frac{C_c}{C_d} = -\frac{E^{\ddagger} - E_d}{RT} + \frac{E^{\ddagger} - E_c}{RT} = \frac{E_d - E_c}{RT}\,. \qquad (3\text{-}5\text{-}1)$$

The energy needed to transfer one mole of calcium from the concentrated phase to the dilute phase in the two-liquid phase region as calculated from equation (3-5-1) and Figure 3-17 is tabulated in Table 3-14.

Table 3-14.
The Difference between Ground Energy State of the Dilute and Concentrated Calcium-Ammonia Solutions in the Two-Liquid Phase Region.

Temperature (°C)	ΔE (kcal/mole Ca)
-40	1.89
-45	2.54
-50	3.12
-55	3.65
-60	5.34

Table 3-14 shows that the energy needed to transfer one mole of calcium from the concentrated phase to the dilute phase increases as temperature decreases. This is because the concentration of the concentrated phase increases as temperature decreases. This will increase the strength of the metallic bonds between the calcium-ammonia complexes and also lower their ground energy state.

4. SUMMARY

Below -35°C, the two-liquid phase region of calcium-ammonia solutions covers a very wide concentration range. The liquid region of the phase diagram of calcium-ammonia solutions was determined by conductivity measurements. The concentrations of the dilute phase in the two-liquid phase region were: 0.0263 mole Ca/liter at -35°C; 0.0255 mole Ca/liter at -40°C; 0.0240 mole Ca/liter at -45.5°C; 0.0208 mole Ca/liter at -51°C; 0.0146 mole Ca/liter at -60°C; and 0.0095 mole Ca/liter at -70°C, which agree reasonably with those reported in the literature. The concentrations of the concentrated phase in the two-liquid phase region were: 1.242 mole Ca/liter at -35°C; 1.278 mole Ca/liter at -40°C; 1.362 mole Ca/liter at -51°C; 1.458 mole Ca/liter at -60°C; and 1.576 mole Ca/liter at -70°C. These results agree reasonably with literature values obtained by vapor pressure measurements, and agree very well with those determined by density measurements in the present work. The liquid region of the phase diagram determined by conductivity measurements is believed to be more accurate than that determined by vapor pressure measurements because the hydrogen gas generated from the decomposition reaction interferes with the vapor pressure measurements.

The viscosity of liquid ammonia was determined to be: 0.2590 centipoise at -35°C; 0.2742 centipoise at -40°C; 0.310 centipoise at -45.5°C; 0.3286 centipoise at -51°C; 0.3596 centipoise at -56°C; 0.3908 centipoise at -60°C; and 0.4843 centipoise at -70°C. These results show good agreement with those given in the literature for higher temperatures, even though extrapolation was necessary to compare the data. The absolute temperature coefficient of viscosity increases with temperature from 1.46% per degree

centigrade at -40°C to 2.1% per centigrade at -60°C.

The viscosity of dilute calcium-ammonia solutions in the single-liquid phase region was found to be only slightly different from that of liquid ammonia at the same temperature.

The equivalent conductance of dilute calcium-ammonia solutions is much smaller than that of analogous alaklai metal-ammonia solutions, and decreases as concentration of calcium increases. In the indicated concentration range, it has been determined to be: 161 cm^2/equiv-ohm to 124 cm^2/equiv-ohm (from 0.005 to 0.225 mole Ca/liter) at -35°C, 138 cm^2/equiv-ohm to 103 cm^2/equiv-ohm (from 0.0025 to 0.020 mole Ca/liter) at -40°C, 116 cm^2/equiv-ohm to 87 cm^2/equiv-ohm (from 0.0025 to 0.020 mole Ca/liter) at -45.5°C, 92 cm^2/equiv-ohm to 72 cm^2/equiv-ohm (0.0025 to 0.020 mole Ca/liter) at -51°C, 57 cm^2/equiv-ohm to 54 cm^2/equiv-ohm (from 0.005 to 0.012 mole Ca/liter) at -60°C and 38 cm^2/equiv-ohm (from 0.005 to 0.008 mole Ca/liter) at -70°C.

The temperature coefficient of conductance of dilute calcium-ammonia solutions in the investigated temperature and concentration range was determined to be approximately +3.5% per centigrade, which is about double of the absolute temperature coefficient of viscosity.

These facts indicate that the conductivity of dilute calcium-ammonia solutions is governed by the degree of dissociation of calcium atoms into calcium ions and solvated electrons. The degree of dissociation in calcium-ammonia solutions is smaller than that of analogous alkali metal-ammonia solutions.

The atomic conductance of concentrated calcium-ammonia solutions is of the same order of magnitude as that of calcium metal. In a concentration range from 1.4 mole Ca/liter to 2.6 mole Ca/liter, it ranges from

5.1×10^5 cm^2/mole-ohm to 10.7×10^5 cm^2/mole-ohm at -35°C; 4.95×10^5 cm^2/mole-ohm to 10.45×10^5 cm^2/mole-ohm at -40°C; 4.6×10^5 cm^2/mole-ohm to 10.0×10^5 cm^2/mole-ohm at -51°C; 4.7×10^5 cm^2/mole-ohm to 10.1×10^5 cm^2/mole-ohm at -60°C; and 4.4×10^5 cm^2/mole-ohm to 9.8×10^5 cm^2/mole-ohm at -70°C. The atomic conductance of concentrated calcium-ammonia solutions is smaller than that of analogous alkali metal-ammonia solutions, as in the case of the metals.

The integral temperature coefficient of conductance of concentrated calcium-ammonia solutions in a temperature range of -35°C to -60°C decreases continuously with concentration of calcium increase. In a concentration range from 1.5 mole Ca/liter to 2.1 mole Ca/liter it decreases from 0.39% per degree centigrade to 0.24% per degree centigrade. However, it remains constant in solutions with concentration more than 2.1 mole Ca/liter. The integral temperature coefficient of conductance of concentrated calcium-ammonia solutions is smaller than that of analogous alkali metal-ammonia solutions.

The excess volume of concentrated calcium-ammonia solutions in the single-liquid phase region was found to be larger than that of alkali metal-ammonia solutions and decreases as concentration of calcium increases. The rate of decrease for concentrated calcium-ammonia solutions is much larger than for alkali metal-ammonia solutions.

The physical properties of calcium-ammonia solutions determined by the present work are quite difference from thos of alkali metal-ammonia solutions. This indicates that a calcium atom does not release only one electron when it dissolves in liquid ammonia.

The physical properties of calcium-ammonia solutions found in the present work can be explained very well by the current theories of metal-ammonia solutions.

5. ACKNOWLEDGEMENTS

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APPENDICES

Appendix A: Previous Work

A-1. Solubility of Metals in Liquid Ammonia

Most of the alkali and alkaline earth metals dissolve in liquid ammonia. The metals which can be dissolved easily are: lithium, sodium, potassium, rubidium, cesium, calcium, barium, and strontium[61]. Magnesium [31,51,55] and aluminum[18] are slightly soluble. The other metals which can be dissolved in liquid ammonia solutions are europium, ytterbium, and rare earths which exhibit the plus two oxidation state[55].

The solubility of lithium in liquid ammonia does not change in the temperature range from -80°C to 0°C[50,53]. The solubility of potassium in liquid ammonia increases slightly as temperature increases, but that of sodium decreases slightly as temperature increases[51,53,61]. These results indicate that the heat of solution of alkali metals in liquid ammonia is very small[50].

The solubility of calcium in liquid ammonia has been investigated by Kraus[62] and Jolly et al[56]. It has been shown that a solid calcium-ammonia compound of a formula of $Ca(NH_3)_6$ is in equilibrium with the solution. The solubilities of alkali metals and calcium in liquid ammonia are listed in Table A-1.

A-2. Metal-Ammonia Compounds

Joannis first studied the compounds formed by metals with ammonia by analytical methods. He obtained the compounds $Na(NH_3)$ and $K(NH_3)$. Employing his method, Moissan discovered the compounds $Li(NH_3)$ and $Ca(NH_3)_6$ while Mentrel obtained the compound $Ba(NH_3)_6$ and Roedered identified

Table A-1.

Solubilities of Alkali Metals and Calcium in Liquid Ammonia (mole NH_3/mole metal)

Lithium

Temperature (°C)	0	-25	-33.4	-50	-80
Krauss and Johnson			3.61		
Ruff and Geisel	3.93	3.93	3.93	3.93	3.93

Sodium

Temperature (°C)	0	-33.9	-50	-70	-105
Kraus and Johnson		5.48			
Ruff and Geisel	5.78	5.48	5.39	5.2	4.98
Kraus and Lucasse		5.37			
Johnson and Meyer	5.79				

Potassium

Temperature (°C)	0	-33.5	-50	-100	
Kraus and Lucasse		4.84			
Ruff and Geisel	4.72		4.79	4.82	
Johnson and Meyer	4.68	4.95	5.05		

Calcium (mole % Ca)

Temperature (°C)	0	-33.8	-36	-40	-63.5
Kraus		12.5			
Jolly et al	11.0		10.7	10.5	10.0

$Sr(NH_3)_6$[62].* Kraus[62], using vapor pressure data and applying the phase rule, concluded that no solid metal-ammonia compounds of sodium, potassium or lithium should exist, but there should be a calcium-ammonia solid compound of the formula $Ca(NH_3)_6$. Birch[8] agreed with Jaffe's[49] observation that the solid lithium-ammonia compound of the formula $Li(NH_3)_4$ exists, but no solid sodium-ammonia compound is found. Biltz[7] showed that the compounds of ammonia with calcium, strontium, and barium are the hexamines.

Marshall and Hunt[79], by vapor pressure measurements of calcium-, strontium-, and barium-ammonia solutions at -45.3°C and -63.8°C, found that the solid which is in equilibrium with the liquid metal-ammonia solution contains a non-integral number of moles of ammonia per mole of metal.

From the literature mentioned above, it is concluded that all the metals dissolved in liquid ammonia form ammonia complexes but only the hexamine can be crystallized and separated.

A-3. Density of Metal-Ammonia Solutions.

The densities of metal-ammonia solutions have been measured for lithium[15,38,54], sodium[28,38,45,52,59,72,77,80,83,94], potassium[47,52,54,83] and cesium[42]. The density of metal-ammonia solutions is always less than that of liquid ammonia, and it decreases as the concentration of metal increases. The excess volume of sodium and potassium-ammonia solutions (defined in section 3-4-b) at moderate concentration increases as concen-

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* This information in this paragraph was obtained from reference 62. The original articles are:

Joannis, A., Compt. rent. 109, 900 (1889).
Moissan, H., Compt. rent. 127, 685 (1898).
Moissan, H., Compt. rent. 128, 26 (1899).
Mentrel, R. C., Compt. rent. 135, 790 (1902).
Roederer, G., Compt. rent. 140, 1252 (1905).

tration of metal increases, passes through a maximum and decreases again[77]. In the very dilute region two sets of experimental data which contradict each other were reported recently. Evers et al[83] found that there is a marked minimum in the excess volume of sodium- and potassium-ammonia solution at -45°C (at the concentration of 0.03N and 0.01N, respectively), while Gunn and Green[38] found that little change in the excess volume of a sodium-ammonia solution at 0°C over a concentration range from 0.01M to 0.35M.

The excess volume of lithium-ammonia solutions at the moderate and concentrated concentration range decreases continuously as concentration of metal increases[54]. On the other hand, cesium-ammonia solution shows opposite behavior, its excess volume increases with concentration of metal continuously as concentration of metal increases[42].

The behavior of the excess volume of metal-ammonia solutions can be explained by Alder's model of metal-ammonia which will be discussed later.

A-4. Conductivity of Metal-Ammonia Solutions.

According to Kraus'[67] measurements, the limiting equivalent conductance of an infinitely dilute sodium-ammonia solution at -33.8°C (which is above the critical temperature)(see appendix A-9) is 1020 cm^2/ohm-equivalent. The equivalent conductance of sodium-ammonia solutions decreases as concentration of sodium increases and passes a minimum of 475 cm^2-ohm^{-1}-equivalent at a 0.63 molar solution and then increases rapidly up to a value of 8 x 10^5 cm^2/ohm-equivalent* for the saturated solution. The

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* These values are based on the measurements of Kraus and Lucasse[68]. The calculations were made on the assumption that the density of metal-ammonia solution is the same as that of liquid ammonia, which will introduce some error.

specific conductance of a saturated sodium-ammonia solution at -33.8°C is approximately half that of mercury at 20°C[67]. Since the saturated sodium-ammonia solution contains only 14.93 mole per cent sodium, the atomic conductance*of sodium in the saturated sodium-ammonia solutions is more than 1/7 of that of metallic sodium and more than five times of that of mercury[67]. The equivalent conductance of a lithium-or potassium-ammonia solution is only slightly different from the corresponding sodium-ammonia solution[51,55,66] in the dilute region. The equivalent conductance of potassium-ammonia solutions is only slightly greater than that of a sodium-ammonia solution, but in concentrated solutions their atomic conductances are quite different. Using density values from Kraus and Johnson [52,72], Marshall and Hunt[78] recalculated the atomic conductance of concentrated sodium- and potassium-ammonia solutions from the conductivity data of Kraus and Lucasse[68]. They found that the atomic conductance of a saturated sodium-ammonia solution is approximately 20% greater than that of a potassium-ammonia solution at the same concentration.

A-5. Temperature Coefficient of Conductance of Metal Ammonia Solutions.

The conductance of a metal-ammonia solution increases as temperature increases at all concentrations[67,69,71]. In the dilute region, the temperature coefficient of conductance of sodium-ammonia solutions in the temperature range from -32°C to -40°C is constant at 1.52% per degree. As

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* The atomic conductance is defined as:

$$\Lambda' = \frac{x}{c} \times 1000$$

where Λ' is atomic conductance (cm^2-ohm^{-1}-g-atom)
x is the specific conductance (ohm^{-1}-cm^{-1})
c is the concentration of the metal (g-atom/liter).

concentration increases, it increases and passes a maximum of 3.8% per degree in a 0.87 molar solution and decreases rapidly to 0.66% per degree in the saturated solution[69]. For dilute potassium-ammonia solutions, the temperature coefficient of conductance is 1.4% per degree at the temperature range from -33°C to -45°C[71]. As concentration increases, it increases to a maximum of 4.4% per degree for a 1.1 molar solution, then decreases rapidly to 0.438% in the saturated solution[71]. Although the temperature coefficient of conductance of dilute metal-ammonia solutions is independent of temperature, in the concentrated region, the temperature coefficient of conductance depends markedly on temperature, increasing as temperature decreases[69,71].

A-6. Paramagnetic Susceptibility of Metal-Ammonia Solutions.

The macroscopic magnetic susceptibility of sodium-ammonia solutions has been measured by Huster[45], and Freed and Sugarman[98], by static field methods. Since they measured the sum of diamagnetic and paramagnetic susceptibilities, some correction for the diamagnetic effect is required if the data is used to predict the amount of paramagnetic species in the solutions. Hutchison and Pastor[46] calculated the paramagnetic susceptibilities of sodium- and potassium-ammonia solution from the results of their magnetic resonance absorption measurements, and obtained the following results:

(a) At all temperatures, the molar magnetic susceptibilities are relatively small at the higher concentration, increase as concentration of metal decreases, and reach something near the value of $N_{av}\beta^2/hT$.

(b) At all concentrations which were examined, the molar magnetic

susceptibilities increase with increasing temperature.

(c) At the higher concentrations, the molar susceptibilities calculated from the magnetic resonance absorption measurements are larger than those measured by the static field. The difference is small and approximately constant. In the dilute solutions the smooth curves drawn through the data points show the static field data for K slightly higher and the static field data for Na but slightly lower than those calculated from the magnetic resonance absorption data.

A-7. Nuclear Magnetic Resonance Measurements in Metal-Ammonia Solutions.

Nuclear magnetic resonance measurements in metal-ammonia solutions show the shift in resonance frequency which is informative and the principle cause of a shift is the presence of unpaired electrons near the nuclei of each type. The shift for sodium and nitrogen in sodium-ammonia solutions was measured at room temperature by McConnell and Holm[76], and over a range of temperatures by Acrivos and Pitzer[1]. The shift for proton resonance is very small[44]. Pitzer[89] observed two facts from the nuclear magnetic resonance data: (a) The ratio of the shift for nitrogen to that of the proton (k(N)/k(H)) is approximately constant over a wide range of concentration and temperature; and (b), in a dilute solution, when R is larger than 100, R k(N)/x(mole) is approximately constant where R is mole ratio of ammonia to sodium in the solution (mole NH_3/mole Ca), k(N) is the shift for nitrogen and x(mole) is molar susceptibility of the solution.

The nuclear magnetic resonance of Li, Na, Rb, Cs, and N in alkali metal-ammonia solutions was measured by O'Reilly[84]. He found that the shift for metals (k(m)) varies by a factor of 100, increasing from lithium to cesium, but for a given metal is nearly independent of concentration.

The shift for nitrogen appears to be independent of metal and dependent only on the metal concentration. It decreases linearly as the mole ratio of NH_3 to metal (R) increases. It is also found that both the shift for metal and for nitrogen decreases as temperature decreases.

A-8. Absorption Spectra of Metal-Ammonia Solutions.

The absorption spectra of dilute metal-ammonia solutions has been measured by many authors[10,13,22,33,36,39,56]. All the measurements agree that: (a) Within the experimental uncertainty, the absorption spectra of alkali metal-ammonia solutions at the same concentration are identical. There is an absorption peak in the neighborhood of 6700 cm^{-1}; (b) Beer's law is obeyed up to a relatively high concentration, about 0.03M, at the frequency of the absorption peak. Jolly et al[36,56] found that the absorption spectra of sodium-, potassium-, lithium-, and cesium-ammonia solutions obey Beer's law not only at the frequency of the absorption peak, but also over a wide frequency range (from 4150 to 25,000 cm). The absorption spectra of calcium-ammonia solutions also obeys Beer's law, and at the frequency in the vicinity of the absorption peak its extinction coefficient is twice those of alkali metal-ammonia solutions. These facts indicate that the absorption spectra of dilute metal-ammonia solutions is due to the solvated electrons and that a calcium atom yields two solvated electrons when it dissociates in liquid ammonia. Contradictory to Jolly et al's measurements, Douthit and Dye[22] found that in potassium-ammonia the absorption spectra shows a very marked deviation from Beer's law behavior at concentrations between 0.003 and 0.01M. He ascribes this deviation to the dimer formation (see appendix A-10). Clark, et al[13]

reported that when sodium iodide is added to sodium-ammonia solutions, the absorption spectra shows a shoulder at the frequency of 12500 cm^{-1}. However, this experiment has been repeated by Jolly et al[56] who failed to find the shoulder.

A-9. Coexistence of Liquid Phases in Metal-Ammonia Solutions.

The most unusual feature of metal-ammonia solutions is that they separate into two liquid phases at temperatures below the critical temperature. Comparing the phase diagrams of alkali metal-ammonia solutions (Figure A-1)[91], one can see that the curve for lithium is between those for sodium and potassium. It seems that the long range coulombic force of the metal ion is not the main reason for this phase separation. Pitzer[88] suggested that the two-phase separation in metal-ammonia solutions is like a vapor-liquid separation. In the dilute phase, the absence of metallic properties indicates that there are ions and molecules in the solution. On the other hand, in the concentrated phase the solvent molecules act as dielectric to fill the space between metal atoms. The valence electrons can pass through this dielectric. Birch and MacDonald[9] based on the vapor pressure data, suggested that the positive departure from Raoult's law of the dilute metal-ammonia solutions is due to the association of solute, and that the negative deviation at concentrated solutions is due to association of the solvent and solute molecules. Since they assumed that the phase separation could be regarded as a direct consequence of the aggregation vapor pressure phenomenon, they claim that a semi-quantitative approximation for the phase separation curve may be derived by use of van der Waal's equation and van't Hoff's law of osmotic pressure. Sienko[92] pointed out that unlike other carefully examined liquid-liquid separations,

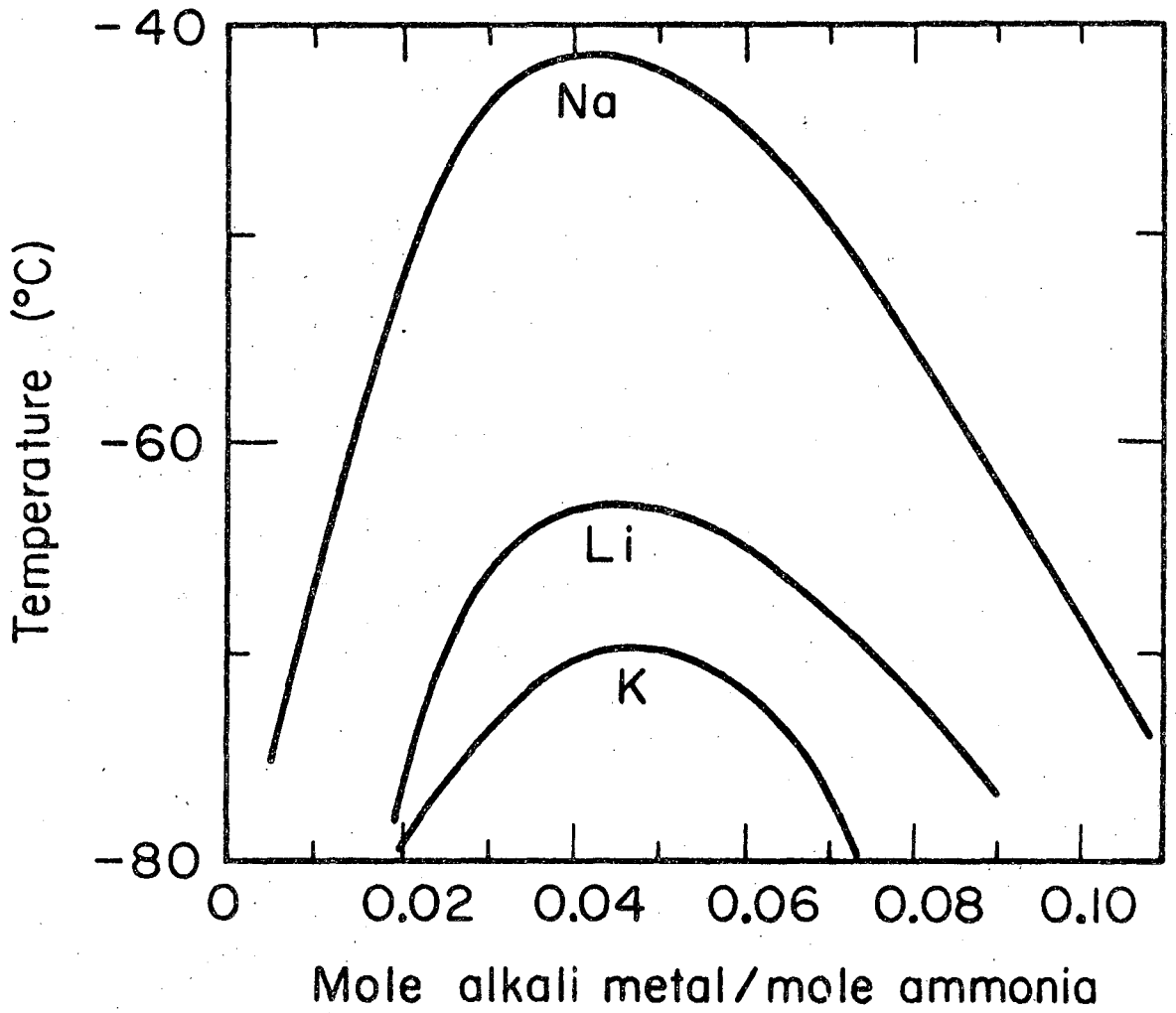

Figure A-1.
Phase Diagram of Alkali Metal-Ammonia Solutions.

and unlike the simple gas-liquid coexistence curves which are cubic, the phase separation curves of alkali metal-ammonia solutions are parabolic.* Based on the suggestion of Widom, Sienko expressed the phase separation curves in the form of

$$T_c - T = a(x_1 - x_2)^n$$

where T_c is the maximum critical temperature, a is a constant, x_1 and x_2 are mole fractions of metal in the coexistence phases of the metal-ammonia solutions. n comes out to be 2.1 ± 0.05 for the case of sodium-ammonia solutions, 2.1 ± .2 for the case of lithium-ammonia solutions and 2.0 ± 0.1 for the case of potassium-ammonia solutions.

A-10. Model of Metal-Ammonia Solutions.

The first ideas on metal-ammonia solutions are due to Kraus[64]. Based on conductance data, he suggested that the metal atoms dissociate into ionic form in metal-ammonia solutions. This hypothesis was based on two facts: (a) no new products are formed at the cathode when current is passed; and (b), the current carried by the negative carriers is approximately 7/8 of the total current in the infinitely dilute sodium-ammonia solutions[65]. He concluded that the negative carriers are electrons surrounded by an envelope of ammonia molecules, and have a mobility seven times that of the sodium ion. The size of the envelope decreases as the concentration of metal increases, thus increasing the mobility. Finally, in the saturated solutions, the ammonia envelope vanishes and the electrons are free to move in the metal-ammonia solutions as in the metal. In dilute metal-ammonia solutions, the equivalent conductance decreases as

* The phase separation curve for the case of calcium-ammonia obtained from the present work is not parabolic (see section 3-5).

concentration of metal increases, due to the decreased dissociation of the metal atoms into ions. However, Kraus did not suggest what this ammonia envelope looks like or how the size of this envelope can decrease continuously as the concentration of metal increases. Ogg[80,81] suggested that the solvated electrons in the metal-ammonia solutions existed in a "cavity". As in the case of a crystal[74], an electron can dig its own hole by polarizing the surrounding ammonia molecules. Two electrons may occupy a single "cavity". Peka[86] and Davydov[19] extended this concept and called an electron surrounded by a polarized medium a "polaron". Combining all these concepts, the picture of an "electron cavity" can be formed. An electron is surrounded by ammonia molecules with their protons pointing toward the electron. The electron moves along the "proton shell" forming an s-like orbital, and two electrons with opposite spin can occupy the same orbital.

The first completed model was suggested by Becker, Linguist and Alder[5]. They considered the metal atom in the metal-ammonia solutions to be associated with ammonia molecules. They pictured the ammonia molecules as surrounding the metal atom with the nitrogen atoms pointing toward the metal atom and the protons pointing outward, forming a "proton shell" surrounding the whole complex. The valence electron of the metal atom jumps into the "proton shell" and forms a new orbital. The whole complex looks like a large hydrogen atom and is called a monomer. As in the case of hydrogen atoms, two monomers can associate into a dimer. A monomer can also dissociate into a positive metal ion and an electron which becomes associated with ammonia molecules. The species in the metal-ammonia solution case: (a) ammoniated metal ions; (b) ammoniated electrons or "electron cavities"; (c) monomers; and (d) dimers, and are related by the following reactions:

$$Me_{(monomer)} \rightarrow Me^{+z}_{(am)} + ze^{-}_{(am)} \qquad (A\text{-}1)$$

$$Me_{(monomer)} \rightarrow \tfrac{1}{2}\, Me_{2(dimer)} \,. \qquad (A\text{-}2)$$

Most of the physical properties of metal-ammonia solutions can be explained by this model. The conductivity of a dilute metal-ammonia solution is due to the mobility of the ammoniated metal ions and electron cavities. The equivalent conductance decreases as concentration of metal increases because of the smaller degree of dissociation according to reaction (A-1). As concentration of metal increases further, the distance between the monomers decreases and finally reaches a critical value where the tunneling effect of the electrons jumping from a "proton shell" of one monomer (or dimer) to another becomes important. Thus the equivalent conductance will increase rapidly as concentration of metal increases and finally reaches a value comparable to that of a metal.

The positive excess volume of a dilute metal-ammonia solution is due to the large size of the electron cavity. The radius of an electron cavity has been calculated to be 3.2Å[75] from the excess volume data of an infinitively dilute sodium-ammonia solution. The formation of monomers and dimers also causes a positive excess volume. This positive excess volume is caused by the valence electrons in the "proton shell" which will weaken and stretch the N-H bonds of the ammonia molecules inside the "proton shell", and also weaken the hydrogen bonding with other ammonia molecules[5]. In concentrated metal-ammonia solutions, the distance between the dimers and monomers is small, so the valence electrons can jump from one monomer to the other. In such cases, metallic bonds are formed between monomers, and it is possible to form a cluster of monomers, instead of dimers. Thus the excess volume will decrease. This concept can explain

the fact that even in a very dilute metal-ammonia solution, there is a positive excess volume. As concentration of metal increases, the excess volume increases and reaches a maximum point and decreases again.

The paramagnetic susceptibility of metal-ammonia solutions also can be explained by Alder's model of the four species in the metal-ammonia solutions, the monomers and electron cavities are paramagnetic and the ammoniated metal ions and dimers are diamagnetic. The molar paramagnetic susceptibility decreases as concentration of metal increases[46] because of the formation of dimers. In very dilute metal-ammonia solutions, the dissociation of monomers into ammoniated metal ions and electron cavities is nearly complete. The only paramagnetic specie is the electron cavity. Therefore the molar paramagnetic susceptibility of a very dilute metal-ammonia solution will approach to the value of $N_{av}\beta^2/kT$.[46]

Even though there is little doubt of the existence of the four species mentioned above in metal-ammonia solutions, two questions are still unanswered:

(1) In what form do they exist, and (2), are there any other species existing in the metal-ammonia solutions? The first question is raised by the absorption spectra and nuclear magnetic resonance measurements. The absorption spectra measurements show that Beer's law is obeyed in a relatively large concentration range and also in a large range of frequency[36,56]. This indicates that the electrons have the same property concerning light absorption no matter if they are in the electron cavities or are connected to the metal ions. Based on this fact, Gold, Jolly and Pitzer[37] suggested that the $M_{e(am)}$ species in the metal-ammonia solutions is made up of normal ion pairs represented by $[Me^{+}_{(am)} \cdot e^{-}_{(am)}]$. Also the

$Me_{2(am)}$ species is a quadrupolar ionic assembly of $2Me^{+}_{(am)}$ and $2e^{-}_{(am)}$ which are held in a square or rhombic configuration. This suggestion is supported by the apparent molar volume of dilute sodium-ammonia solutions measured by Gunn and Green[38] which shows there is only a very small change in the excess volume of sodium-ammonia solutions over a concentration range from 0.01 to 0.35M at 0°C. However, contradictory to their measurements, the measurements of Evers and Filbert[28] show that the excess volume of sodium-ammonia solutions has a marked minimum around 0.03M at -45°C. The nuclear magnetic resonance of metal-ammonia solutions shows that the Knight shift of protons is very small[44]. In other words the valence electrons are not located in the protons. Pitzer[87] suggested that the valence electrons are located in a 3s-like orbital of nitrogen with a node at the position of the protons. Such an orbital would be 2p-like in the vicinity of the proton. Blumberg and Das[97], based on Alder's model, used two wave functions to calculate the Knight shifts of sodium-ammonia solutions and found the hydrogen shift is very small, which agrees with experimental fact.

The second question is raised because the equilibrium constants for reaction (A-1) and (A-2):

$$K_1 = \frac{[Me^{+2}_{(am)}]\cdot[e^{-}_{(am)}]^{z}}{\text{Monomer}} \qquad \text{(A-1')}$$

$$K_2 = \frac{[Me_{2(dimer)}]^{\frac{1}{2}}}{Me_{monomer}} \qquad \text{(A-2')}$$

calculated from conductivity data[27], agree with those calculated from the transference number data[23] and from the activity coefficients data[24], but do not agree with those calculated from the paramagnetic susceptibility

data[5]. It is possible that there are other species in the metal-ammonia solutions which will affect the paramagnetic susceptibility measuremetns but not the conductivity measurements. Ogg suggested that two electrons may occupy the same electron cavity to form a diamagnetic species $e^{=}_{2(am)}$. Arnold and Patterson[3,4] suggested that two electrons can occupy an orbital of a monomer to form a $Me^{-}_{(am)}$ species. Therefore the physical properties of a metal-ammonia solution are governed by three reactions:

$$Me_{(am)} \rightleftarrows Me^{+}_{(am)} + e^{-}_{(am)}$$

$$2Me_{(am)} \rightleftarrows Me_{2(am)}$$

$$Me_{(am)} + e^{-}_{(am)} \rightleftarrows Me^{-}_{(am)} \ .$$

By selecting the equilibrium constants, they calculated conductivity and molar paramagnetic susceptibility of the dilute sodium-ammonia solutions which agrees very well with the experimental results.

A-11. Decomposition Reaction of Metal-Ammonia Solutions.

The metal-ammonia solutions are metastable and will decompose to hydrogen and the amide:

$$Me + n\ NH_3 \rightarrow n/2\ H_2 + Me(NH_2)n \quad .$$

The decomposition rate of metal-ammonia solutions decreases in the order: potassium, calcium, lithium, sodium[61]. If there is no impurity in the solutions, the decomposition rate is small, but trace impurities can catalyze the reaction and greatly increase the decomposition rate.

Kraus[61] found that the metallic oxides and hydroxides can act as catalysts, and the decomposition reaction can also be catalyzed by its own

product (metal amide). Burgess et al[11] studied the effect of different catalysts on the reaction between sodium or potassium and ammonia. They found that nearly any metal except aluminum can act as a catalyst. Platinized platinum, iron oxide, nickel and powdered ferrous oxide are the best. They also found that potassium amide does not change the effectiveness of the catalyst, but sodium amide poisons the catalyst. The mechanism of this reaction is not known. Ogg[82] suggested that the reaction is controlled by:

$$e^-_{(am)} + NH_3 \rightarrow NH^-_{2(am)} + H_{(am)}$$

and estimated the activation energy to be at least 30-40 Kcal/mole. He also suggested that the same reaction in aqueous solutions:

$$e^-_{(aq)} + H_2O \rightarrow OH^- + H_{(aq)}$$

is exothermic and probably has a negligible activation energy. This would mean that an electron cavity could not exist in aqueous solution. Watt et al[96] studied the catalytic action of metals and alloys and found the reaction to be zero order with respect to potassium, but it approaches first order as the concentration of potassium decreases. Corset and Lepoutre[14] also found that the decomposition reaction of dilute potassium ammonia solutions is first order with respect to the concentration of potassium.

Appendix B: Cooling System

The experimental work described here on calcium-ammonia solutions was carried out in a temperature range from -35°C to -70°C, thus a good cooling system was necessary (Figure B-1). Cooling media was cooled in storage tank B and then was circulated to an insulated secondary cold bath (C), located adjacent to the vacuum line. The secondary bath was equipped with a heater, a stirrer, a calibrated thermometer and a temperature controller.* The temperature of the secondary cold bath was first set by adjusting the flow rate or temperature of the incoming cooling media. The temperature controller and auxiliary heater was then used to control the bath to ± 0.1°C. Magnetic stirring motors placed beneath the secondary cold bath were used to stir the calcium-ammonia solutions. The secondary cold bath could be raised and lowered to accommodate a variety of types of apparatus and to assure easy access to the vacuum line.

Two systems were used to cover the whole temperature range. In the first system, the cooling media was trichloroethylene which was cooled by a refrigerator** to -60°C in a 50-gallon tank. The flow rate of the cooled trichloroethylene was controlled by a needle valve (G). Because of the high viscosity and the freezing point of the trichloroethylene, the lowest possible temperature in the secondary bath obtained from this system was -55°C. Therefore, a second cooling system was used to cover the temperature range from -60°C to -70°C. The second cooling system was a complete unit

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* Dynatrol 20: Dynatronics Instrument Corporation. Electronics Division/Lab-line Instrument, Incorporated.

** The refrigerator was constructed by G. D. Snider. A complete description of this equipment can be found in his thesis[93].

obtained from Landa Company*. Methanol used as cooling media was cooling in a five-gallon storage tank which is equipped with a temperature controller and a centrifugal pump to circulate the cooling media to the secondary cold bath. The temperature of methanol in the storage tank was adjusted to be 3°C below the temperature of the secondary cold bath. The flow rate of the methanol was not regulated.

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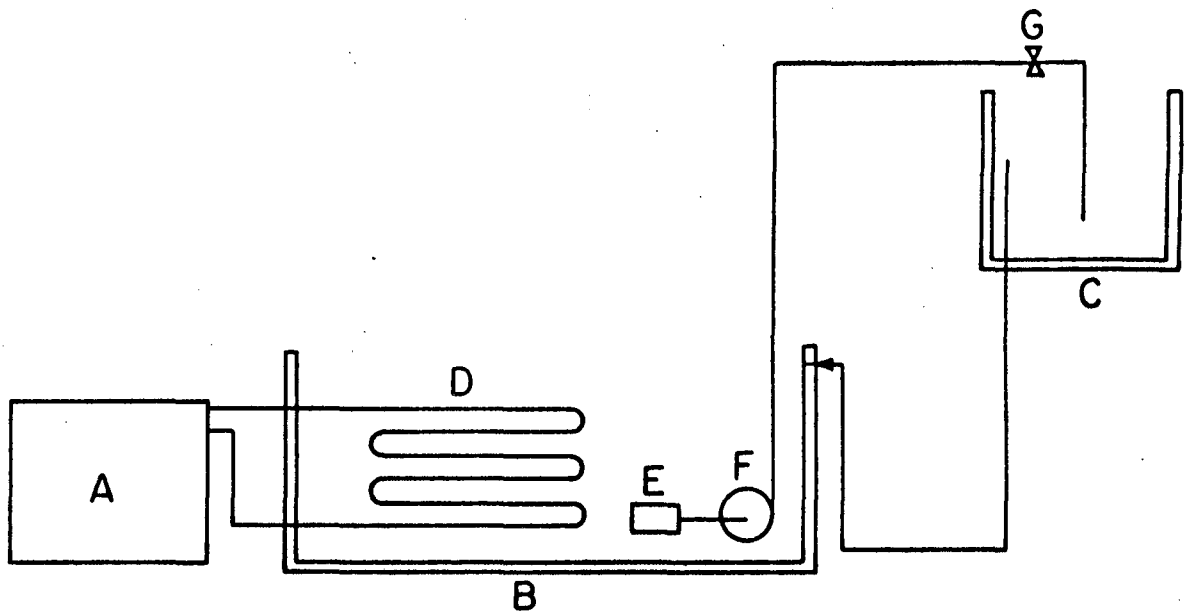
* Ultra Kryostate UK-60D.



A: Compressor
B: Trichloroethylene storage tank
C: Secondary cold bath
D: Cooling coil
E: Filter
F: Pump
G: Needle bath

Figure B-1.

Cooling System.

Appendix C: Decomposition Reaction of Calcium-Ammonia Solutions.

The decomposition rate of metal-ammonia solutions is very slow. However, a trace of impurities can act as a catalyst and greatly increases the decomposition rate. Due to its high melting and boiling points, calcium metal cannot be purified by vacuum distillation. In the experiments described elsewhere in this work, it was desired to obtain calcium-ammonia solutions which had the lowest possible decomposition rate. Therefore, preliminary experiments were made to determine which calcium metal from commercial sources yielded ammonia solutions having the lowest decomposition rate.

Commercially available calcium metal obtained from three different sources was investigated. These calcium metals are: (a) Comal Grade I - calcium metal in the form of granules. The brightest granules were picked under an argon atmosphere for this experiment. (b) Domal Grade II - calcium metal in an extruded form. The surface was freshly cut using a sharp knife under an argon atmosphere. And, (c) calcium metal obtained from United Chemical and Mineral Company in an extruded form. The surface was freshly cut under an argon atmosphere. However, there were some oxide layers inside the calcium metal which could not be removed by mechanical means.*

The amount of impurities of these calcium samples was determined by emission spectroscopy and by wet chemical analysis. The results are shown in Table C-1.

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* This calcium metal had been exposed to air for a long time before its use in this experiment.

Table C-1.

Impurities of Calcium Metals

Source of Metal	Impurities (wt %)						
	Mg	Sr	Al	Fe	$CO_3^=$	Cl^-	N
Domal Grade I	0.3	0.2	0.03	0.05	0.15	0.005	<0.01
Domal Grade II	0.3	0.2	<0.01	<0.01	0.03	0.002	0.79
United Chem. & Min. Co.	0.2	0.07	<0.01	<0.01	0.06	0.002	0.12

The decomposition rate of calcium-ammonia solutions was determined by measuring the vapor pressure change over the solutions (corresponding to the generation of hydrogen) at -45°C. To minimize the error caused by temperature fluctuation, the vapor pressure of calcium-ammonia solutions was measured against that of pure liquid ammonia. The apparatus is shown in Figure C-1. The U-tube manometer (D), manometer (E) and the safety valve (F) were filled with mercury. Calcium metal was prepared in a dry box under argon atmosphere (appendix D-1) and was placed into the empty Ca-NH_3 cell (B). The cell was connected to the vacuum line and the whole apparatus was evacuated immediately. Both the Ca-NH_3 cell (B) and NH_3 cell (C) were placed into the cold bath (A). All stopcocks except (a) were closed. Ammonia was condensed into the Ca-NH_3 cell (B) from the NH_3 cylinder (G). Stopcock (a) was closed and (b) was opened. Ammonia was condensed into the NH_3 cell (C). The concentration of the calcium-ammonia solution was determined by the weight of calcium and ammonia using the method described in appendix D. To eliminate the error caused by the inert gases* which were carried by the ammonia, both liquid ammonia and calcium solution were frozen at liquid nitrogen temperature and the whole

* Most of the inert gas was hydrogen which was generated by the reaction between metallic sodium and moisture in ammonia (see appendix D-2).

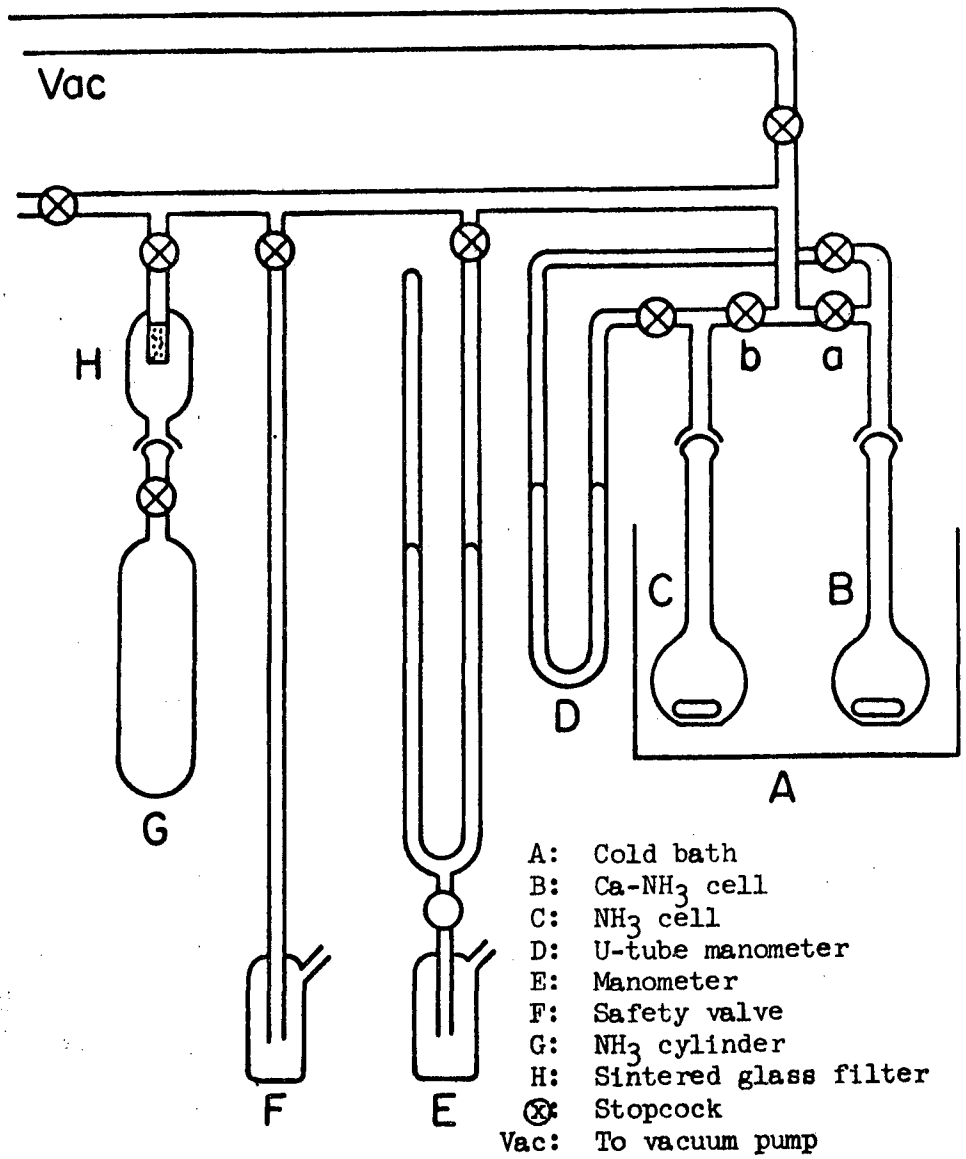

Figure C-1.

Apparatus for Decomposition Rate Measurement.

apparatus was evacuated by opening all the stopcocks. The solutions were then warmed up to -45°C after closing the stopcock (a). Solutions in both cells were stirred by magnetic stirring bars rotating at the same speed. The pressure difference between the liquid ammonia and the calcium-ammonia solution was measured by the U-tube manometer (D) and a cathetometer which had a precision of 0.05 mm. After the experiment, both cell (B) and (C) were cleaned with hot cleaning solution.

The rate of hydrogen generation (corresponding to the decomposition rate of the calcium-ammonia solution) was calculated from the rate of vapor pressure change over the solutions by applying the ideal gas law. The volume occupied by the hydrogen gas was estimated from the length and diameter of the glass tubing. In some experiments, the Ca-NH_3 cell was not completely filled and the void volume in the cell was estimated by subtracting from the total volume of the cell the volume occupied by the solution (assuming the density of the calcium-ammonia solutions to be the same as that of liquid ammonia). The temperature of the hydrogen in the part of the apparatus above the cold bath was assumed to be room temperature and that in the cold bath to be -45°C.

The measurement of the rate of hydrogen generation was made over a three-hour period. In some experiments, this measurement was extended to twenty-four hours. No change in the rate of hydrogen generation was observed. The rate of generation of hydrogen was constant for each individual run. However, the rate of hydrogen generation depended on the overall concentration of calcium*.

The results are tabulated in Table C-2 and plotted in Figure C-2.

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* Further experiments show that for the concentration range of these experiments, two liquid phases were in equilibrium.

Table C-2.

Decomposition Rate of Calcium-Ammonia Solutions at -45°C.

Domal Grade II

Mole Ratio (mole NH_3/mole Ca)	Decomposition Rate (% total Ca/hr)
255.5	0.0438
194	0.057
143	0.0711
124	0.1002
112	0.0602
106.2	0.053
91	0.0655
70	0.052
57.7	0.038
54.8	0.058
42	0.0635

Domal Grade I

Mole Ratio (mole NH_3/mole Ca)	Decomposition Rate (% total Ca/hr)
46.8	0.196
28.9	0.206

United Chem. and Min. Co.

Mole Ratio (mole NH_3/mole Ca)	Decomposition Rate (% total Ca/hr)
76.5	0.383
116.5	0.39

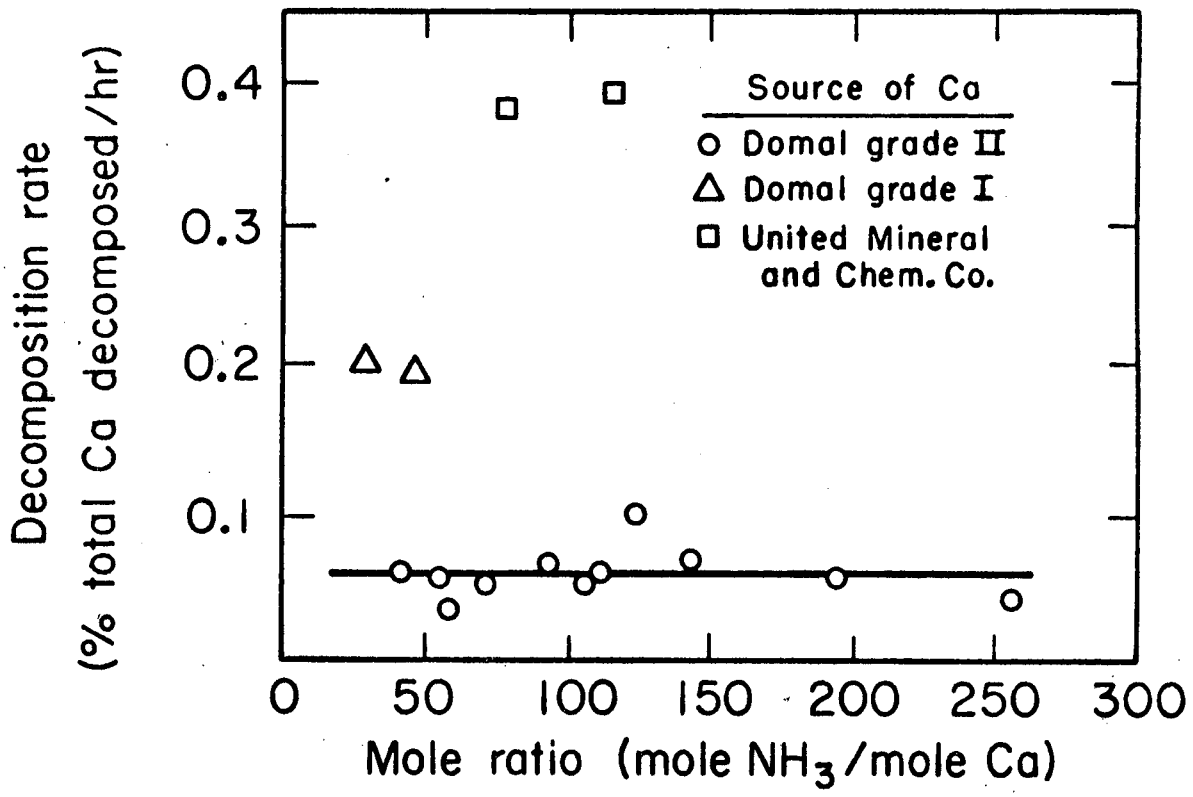

Figure C-2.
Decomposition Rate of Calcium-Ammonia Solutions at -45°C.

From these results, it appeared that the decomposition rate of calcium-ammonia solutions was highly dependent on the amount of oxide present. The Domal Grade II calcium metal with freshly cut surface had the lowest decomposition rate (approximately 0.06% of the total calcium in the solution per hour) in spite of its high content of impurities other than oxide. The reaction order could not be determined in this experiment because: (a) the reaction rate was small. Taking 0.06% of total calcium per hour, in a period of twenty-four hours, only 1.4% of total amount of calcium would be decomposed, so that the concentration of calcium in the solution is practically constant and (b) the concentration range of the calcium-ammonia solutions was in two-liquid phase region. From Figure C-2, one sees that the decomposition rate of a calcium-ammonia solutions is proportional to the concentration of calcium. However, since the amount of impurities was also proportional to the amount of the calcium, it is possible that the decomposition rate of calcium-ammonia solutions was proportional to the concentration of impurities.

Appendix D: Preparation of Materials

D-1. Preparation of Calcium Metal

Domal Grade II calcium metal* was suitable for the experimental work on calcium-ammonia solutions due to the low decomposition rate of the solutions prepared from it (appendix C). The Domal Grade II was in an extruded form having dimensions 1/4" x 1/4" x 3". The calcium metal was prepared in a dry box (Figure D-1) under an argon atmosphere by the following procedure: The working chamber (A) was first evacuated to 10^{-4} mm Hg pressure and then was filled with argon gas to atmospheric pressure. The argon gas from a steel cylinder was first passed through a U-tube (C) containing molecular sieves at acetone-dry ice temperature to remove any traces of moisture carried by the argon gas. Calcium metal and any needed equipment were put into the air lock (B). The air lock was evacuated and then was filled with argon gas. Valve (e) was opened to equalize the pressure between the working chamber and the air lock. The calcium metal and the equipment were transferred into the working chamber. The surface of the calcium metal bar was carefully removed by a sharp knife until the whole surface was bright shiny silver color. The calcium metal used in a single experiment was cut from the calcium metal bar and put into a small weighing bottle without applying stopcock grease. Then the small weighing bottle was put into a large weighing bottle and sealed with stopcock grease to prevent any air from diffusing into it. The calcium metal sample was removed from the dry box through the air lock. The calcium metal sample prepared by this method could be kept outside the dry box for several days without losing the bright shiny surface.

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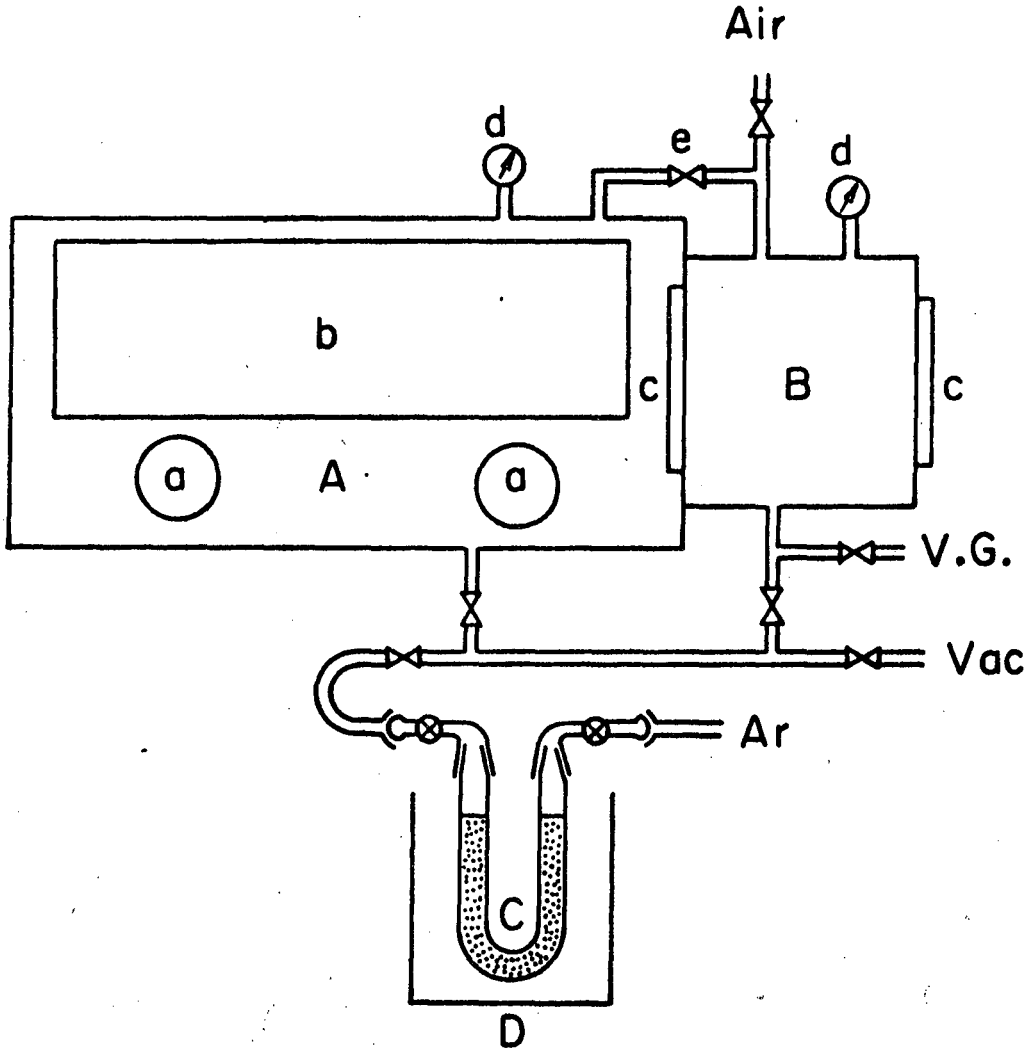
* In later part of this work, calcium bars obtained from Bram: Metallurgical-Chemical Company were used.



A: Working chamber
B: Air lock
C: U-tube
D: Acetone-dry-ice bath
a: Ports for rubber gloves
b: Glass window
c: Door
d: Vacuum gauge

e : Needle valve
○ : Stopcock
⋈: Needle valve
Vac: To vacuum pump
Ar: To Argon tank
Air: To atmosphere
V.G: To thermocouple vacuum gauge

Figure D-1.

Dry Box.

When the sample was to be used, the inside weighing bottle was removed, and the bottle plus the calcium metal were weighed to within 0.1 mg on an analytical balance. After the calcium metal had been transferred into the apparatus, the empty weighing bottle was weighed again to determine the weight of the calcium metal sample.

The working chamber of the dry box was evacuated and refilled with argon gas once a week. The molecular sieves were regenerated once a month by heating them to at least 300°C for six hours, then vacuum dried for another twelve hours.

D-2. Preparation of Ammonia

Commercial ammonia from a five-pound capacity cylinder was first condensed into a stainless steel cylinder, equipped with a Hoke needle valve and containing metallic sodium to remove the moisture carried by the ammonia. The capacity of the stainless steel cylinder was 70 grams of ammonia. The cylinder was warmed to room temperature and approximately three grams of ammonia were bled off to remove any inert gas. The stainless steel cylinder was connected to the vacuum line and the line was evacuated. Then the Hoke needle valve was opened and the ammonia released from the stainless steel cylinder and condensed into the cell which was immersed in the secondary cold bath. The temperature of the cold bath was maintained as low as possible (approximately -60°C). A sintered glass filter was used to remove the solid impurities* carried by the ammonia. The condensation rate of ammonia was controlled by the Hoke needle valve and the safety valve on the vacuum line so that no ammonia gas escaped from the

* Most of the solid impurities were NaOH which was formed by the reaction between the metallic sodium and the moisture carried by the ammonia.

system. The weight of ammonia used was determined by weighing the stainless steel cylinder before and after the condensation. An analytical balance having a precision of 2.5 mg was used.*

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* In the later part of this work an analytical balance produced by Mettler was used. This new balance has a precision of 0.2 mg.

Appendix E: Calibration of Apparatus

E-1. Thermometer

An alcohol thermometer with a temperature range of -100°C to +50°C was calibrated against the vapor pressure of liquid ammonia at several temperatures. The apparatus used for the calibration was the same as that used in the density measurement (Figure 2-6), except that the pycnometer was replaced by a 50 cc flask. Liquid ammonia was condensed into the 50 cc flask. The inert gases carried with the ammonia were removed by freezing the ammonia at liquid nitrogen temperature and the whole apparatus was evacuated. The bath temperature was then raised to the desired temperature. The vapor pressure of liquid ammonia was measured by the manometer and used to calibrate the thermometer. Cragoe et al's[16] vapor pressure of liquid ammonia was used for the calibration.

E-2. Conductivity Cell

The cell constant (ℓ/A) of the conductivity cell used to measure the conductivity of dilute calcium-ammonia solutions was determined by measuring the resistance of a standard 0.01 N KCl solution at 25 ± 0.01°C and applying the equation

$$\ell/A = R\chi.$$

The A.C. Wheatstone bridge described in section (2-1) was used for the calibration. The distilled water used to prepare the 0.01 N KCl solution was boiled for half an hour to remove the carbon dioxide, then cooled to room temperature under a nitrogen atmosphere. KCl salt was vacuum dried for at least three days before use. The amount of KCl salt used was weighed on an analytical balance having a precision of 0.1 mg. The 0.01 N solution was prepared in a one-liter volumetric flask.

The cell constant was calculated to be 10.3 ± 0.5% cm^{-1} from the average of five calibrations and the specific conductance of 0.01 N KCl solution[73] at 30°C.

The cell constant (ℓ/A) of the conductivity cells used to measure the conductivity of concentrated calcium-ammonia solutions were calibrated by measuring the resistance of pure mercury at 0°C. The milliohmmeter which was used to measure the conductivity of concentrated solution was also used for the calibration. For the two cells which were calibrated, the cell constant was calculated to be 64.10 and 64.95 cm^{-1}, respectively, using the specific conductance of mercury[35].

E-3. Pycnometer

The volume of the pycnometer was calibrated by using distilled water at room temperature. The empty pycnometer with a magnetic stirring bar in it was first weighed, then filled with distilled water to the red mark (Figure 2-6) and reweighed. Then more distilled water was added to bring the water level into the capillary above the red mark and weighed again. The height of the water level above the red mark was measured with a cathetometer. The volume of the pycnometer below the red mark and also the volume of the capillary per unit length* were calculated by using the density of water[12].

The volume of the pycnometer at the temperature used in the experiments was calculated by using the thermal expansion data of Pyrex glass (1.08 x 10^{-3} % cm^3/cm^3 per degree)[40].

Three pycnometers were calibrated. The volume below the red mark of each cell was determined by three calibrations. The maximum deviation

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* The diameter of the capillary was assumed to be uniform. Measurements at different heights of the water level were made. The average value was used.

was 0.01% from the average value. Nine calibrations were made to determine the volume of the capillary of each cell. The maximum deviation from the average value was 5% (corresponding to 0.0035% of the total volume of the density cell per cm capillary).

E-4. The Amount of Ammonia Remaining in the Vacuum Line

Because high accuracy was needed for the density measurements, the amount of ammonia remaining in the vacuum line had to be known.

The vacuum line was first evacuated. After stopcock (a) was closed (see Figure 2-8), the vacuum line was filled with ammonia to a pressure of 600 mm Hg (the pressure was measured with a mercury manometer). The weight of ammonia in the vacuum line was determined by weighing the ammonia cylinder before and after the ammonia was released into the vacuum line. Five calibration measurements were made. The maximum deviation from the average value (81.3 mg) was 0.5 mg (corresponding to an error of 8×10^{-4}% in the density measurement).

The amount of ammonia remaining in the portion of the vacuum line below stopcock (a)(Figure 2-8) was estimated by using the vapor pressure of the calcium-ammonia solution, the volume from the diameter and the length of the tubing and applying the ideal gas law. The temperature was assumed to be room temperature.

In the density measurements of concentrated calcium-ammonia solutions, a one-liter flask was used to remove the inert gases (section 2-3). The amount of ammonia contained in the one-liter flask was calibrated by the same method used in the calibration of the amount of ammonia remaining in the vacuum line. Four calibration measurements were made. The maximum

deviation from the average value (763 mg) was 2.5 mg (corresponding to an error of $4 \times 10^{-3}\%$ in the density measurement).

E-5. Ubbelohde Viscometer

The constants C and B used in the viscosity calculation (eequation (2-2)) were determined by the kinematic viscosity of carbon disulfide and carbon tetrachloride at 25°C, because these kinematic viscosities are close to that of liquid ammonia.

$$\nu = Ct - B/t.$$

The procedure for the calibration was the same as the experimental procedure described in section 2-4. Thorpe and Rodgers'[95] density and viscosity data of carbon disulfide and carbon tetrachloride were used for the calibration.

The constants C and B were calculated from three calibration measurements to be $3.947 \times 10^{-3} \pm 0.7\%$ centistoke/sec and $7.983 \pm 0.7\%$ centistoke-sec*, respectively. The cell constants of the Ubbelohde viscometer was assumed to be independent of temperature. This is a very good assumption because (1) the thermal expansion of Pyrex glass is very small ($3.6 \times 10^{-4}\%$ per degree for linear expansion) and (2), as temperature decreases, the bulb containing the solution and the length of the capillary tubing will decrease thus decreasing the flowing time. But the diameter of the capillary tubing decreases also, thus increasing the flowing time. These two errors will cancel each other. The temperature dependents of these two constants were calculated from the equations given in the literature[26] to be vanishing small.

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* In the viscosity measurements of liquid ammonia, the time ranged from 118 seconds to 143 seconds, so that the term B/t corresponded to a correction of $15 \pm 3\%$ in the kinematic viscosity determinations.

Appendix F: Material, Source and Purity

Material	Source	Purity
Ca Metal	Domal	Grade II Special
NH_3	Matheson Co., Inc.	Anhydrous
Argon gas	Lindo Co.	99.995% Ar
CS_2	Allied Chem. Co.	Reagent A.C.S.
CCl_4	Brothers Chem. Co.	Reagent A.C.S.
Hg	Masero Laboratories	Brillian Grade*
Molecule sieve	Lindo Co. Type 4A	

* Purity exceeds Triple Distilled A.C.S. Reagent Grade Instrument Grade.

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