The electrochemical oxidation of lithium-ammonia solutions
by John Edwin Bennett

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in CHEMICAL ENGINEERING
Montana State University
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Abstract:
The electrochemical oxidation of lithium-ammonia solutions has been successfully studied by the methods of single and cyclic sweep solid electrode voltammetry. The oxidation reaction which occurs is actually that of the solvated electron, and cyclic voltage scans confirm its reversibility.

Complete oxidation waves have been obtained up to a concentration of 0.2 moles/liter by single sweep voltammetry. These curves show a linear relationship between peak current and concentration, and some reach current densities of 1000 ma/cm^2. Unfortunately, because of instrumental limitations, complete curves could not be obtained in the concentrated region.

Polarization studies were carried out up to a concentration of 2.0 moles/liter. Solutions in the "bronze" or concentrated region showed a potential deviation of only about 3 mV at a current density of ma/cm^2.

Other tests showed current efficiencies to be at least 92%, with the majority of losses probably being caused by non-electrochemical reactions.

The electrochemical oxidation of lithium in liquid ammonia is a powerful reaction which appears to be well suited for application in an electrical power generating device such as a fuel cell and further development toward this goal is recommended.

18

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June, 1968

ACKNOWLEDGMENT

The author is indebted to many persons for the completion of this project. Particular acknowledgment is given to the following:

Dr. Michael J. Schaer for his guidance and encouragement throughout this investigation;

Mr. Silas Huso and Mr. James Tillery for construction and maintenance of equipment; and

Nancy Bennett, my wife, for her continual encouragement and endurance of my whims.

The author is also indebted to the National Science Foundation and to the Chemical Engineering Department of Montana State University for their financial support and the opportunity to undertake this investigation.

TABLE OF CONTENTS

Page

Vita ii

Acknowledgment iii

Table of Contents iv

List of Tables vi

List of Figures vii

Abstract ix

Introduction 1

A. Metal-Ammonia Solutions Background 3

B. Analytical Procedure Background 14

Statement of the Problem 17

Experimental Procedures 19

A. Electrode Catalysis Study 23

B. Three-Compartment Cell 24

C. One-Compartment Cell 29

D. The Scanning Instrumentation 30

Experimental Results 33

A. Electrode Catalytic Study 33

B. Voltage Scans 34

C. Potential Measurements 60

D. Current Efficiency Study 60

TABLE OF CONTENTS (continued)

Page

Summary 62

Appendix 64

Literature Cited 69

LIST OF TABLES

		Page
Table I	Equilibrium Potential in Lithium-Ammonia Solutions Measured vs. Lead/Lead Nitrate Reference	65
Table II	Peak Currents and Polarizations of Scans in the One-Compartment Cell on Platinum.	66
Table III	Peak Currents and Polarizations of Scans in the One-Compartment Cell on Various Electrode Materials	67
Table IV	Mean Molal Ionic Activity Coefficient of Lithium in Liquid Ammonia at -35^{o}C.	68

LIST OF FIGURES

Page

Figure 1 Ammonia Condensation Apparatus 21

Figure 2 Refrigeration System 22

Figure 3 Three-Compartment Cell 26

Figure 4 One-Compartment Cell 28

Figure 5 Chronopotentiostat Circuit 32

Figure 6 Cyclic Scan of Lithium-Ammonia Solution in the Three-Compartment Cell 35

Figure 7 Effect of Scan Rate on Reduction Waves in the Three-Compartment Cell 38

Figure 8 Oxidation Wave in the One-Compartment Cell. . . 40

Figure 9 Oxidation Wave in the One-Compartment Cell. . . 41

Figure 10 Oxidation Wave in the One-Compartment Cell. . . 42

Figure 11 Oxidation Wave in the One-Compartment Cell. . . 43

Figure 12 Oxidation Wave in the One-Compartment Cell. . . 44

Figure 13 Oxidation Wave in the One-Compartment Cell. . . 45

Figure 14 Oxidation Wave in the One-Compartment Cell. . . 46

Figure 15 A Plot of Concentration vs. Peak Current . . . 47

Figure 16 A Plot of Polarization/Milliamp vs. Concentration 50

Figure 17 Oxidation Wave at -60°C 52

Figure 18 Oxidation Wave Using an Aluminum Electrode. . . . 53

LIST OF FIGURES (continued)

Page

Figure 19 Oxidation Wave Using a Tungsten Electrode. . . . 54

Figure 20 Oxidation Wave Using a Palladium Electrode . . . 55

Figure 21 Oxidation Wave Using a Platinum-Iridium Electrode 56

Figure 22 Oxidation Wave in the Presence of Iron Impurities 58

ABSTRACT

The electrochemical oxidation of lithium-ammonia solutions has been successfully studied by the methods of single and cyclic sweep solid electrode voltammetry. The oxidation reaction which occurs is actually that of the solvated electron, and cyclic voltage scans confirm its reversibility.

Complete oxidation waves have been obtained up to a concentration of 0.2 moles/liter by single sweep voltammetry. These curves show a linear relationship between peak current and concentration, and some reach current densities of 1000 ma/cm^2. Unfortunately, because of instrumental limitations, complete curves could not be obtained in the concentrated region.

Polarization studies were carried out up to a concentration of 2.0 moles/liter. Solutions in the "bronze" or concentrated region showed a potential deviation of only about 3 mV at a current density of ma/cm^2.

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INTRODUCTION

Fuel cells have been a subject of investigation since the early part of the twentieth century, but it has only been in the past decade that this work has become intense (1,2). Fuel cells are an attractive source of power for several reasons. They can presently be made to operate at nearly 80% efficiency compared to about half that figure for steam turbines and generators, which are limited by the Carnot cycle. Fuel cells produce no noxious fumes or objectionable combustion products. Noise and maintenance are minimized because there are no moving parts. Beyond ten hours operating time, fuel cells become the best systems by far in terms of power-per-unit-volume and power-per-unit-weight. Because of these factors, fuel cells are finding important uses in military and space applications today, and significant commercial applications are believed to be less than ten years away.

Even more recent has been the study of lithium as a possible source of electric power. This interest has been primarily because of its favorable position on the potential scale, and because of its light weight. Thus, lithium could prove advantageous for space application or any other use where weight is critical.

Most of the work with lithium to date has been done using a high temperature fused salt electrolyte. One such program (3) culminated in the operation of a lithium-hydrogen cell with a current density of 1300 ma/cm^2 at a potential of 0.325 volts. Fused salt is a logical choice as an electrolyte since, in addition to having favorable electrical properties, it is inert to the highly reactive lithium. There are, however, serious disadvantages to such high temperature operation. These include corrosion problems, operating problems, and construction problems.

As a possible solution, we have chosen to study the lithium/lithium ion reaction in a liquid ammonia electrolyte. Alkali metals dissolve in ammonia to form unique stable solutions which have been laboratory curiosities since the latter part of the nineteenth century.

Ammonia, itself, is second only to water as a general solvent. (4,5). To quote from an article by Franklin and Kraus (6):

> "Of all known liquids, ammonia most closely approaches water in all those properties which give water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents."

There are few anhydrous solvents, either inorganic or organic, which can compete with liquid ammonia as a solvent on the basis of cost. The use of ammonia offers no great experimental difficulties and is used widely in organic and inorganic synthetic chemistry today.

Our primary concern here is the ability of ammonia to form unique solutions with the alkali metals. The solutions of alkali and alkaline earth metals all possess a characteristic deep blue color in the dilute concentration ranges; the more soluble alkali metals give a coppery-bronze lustre in the more concentrated region.

The metal ammonia solutions possess varying stability. If solutions of lithium or sodium are prepared with enough care, they may be stored for weeks or even months without appreciable decomposition. The decomposition reaction

$$Li + NH_3 \longrightarrow LiNH_2 + 1/2\ H_2$$

is unfortunately catalyzed by most electrode materials. Burgess and Kahler (7) investigated qualitatively the catalytic action of a few materials, but this seems to be one field in which a great deal more investigation is necessary.

A. Metal-Ammonia Solutions Background

Weyl (8) made the first investigation of metal-ammonia solutions in 1864. Weyl reported both blue and bronze solutions of sodium and potassium, and attributed the phenomena to the ammonia substituted radicals $NaNH_3$ and KNH_3. A few scattered investigations in the years following confirmed the observations reported by Weyl.

It was not until the turn of the century that Charles A. Kraus began his significant series of investigations. Even though Kraus completed his conductance and vapor pressure experiments over sixty years ago, his data is still used today. Everyone familiar with non-aqueous solvents is aware of Kraus' exceptional work with metal-ammonia solutions.

Kraus (9) first demonstrated by vapor pressure determinations that no compounds existed in the cases of sodium, potassium, and lithium, and they were true solutions. Calcium, he reported, associated with ammonia in the compound $Ca(NH_3)_6$. Today it is well known that calcium, lithium, and the alkaline earths, unlike the other alkali metals, form definite compounds. Lithium forms $Li(NH_3)_4$, but only at extremely low temperatures, and is of no concern in this work.

Previously, Cady (10) had first measured some electrical properties of alkali metals in liquid ammonia and reported an excellent conductivity. He also noticed that passage of current in bronze solutions involved little or no mass transport, but in dilute solutions a passage of current resulted in an increase of metal concentration at the cathode. Cady also reported that the electrodes acted reversibly with respect to electrode processes.

Kraus (11) found the conductance-temperature coefficient to be positive, and later showed (12) that the cation of the metal was identical to the same cation of ordinary salts. The anion, however, appeared to be a new species for which he coined the term "solvated electron".

From EMF measurements carried out in concentration cells (12), he determined the relative speeds of these ions. Mobility of the positive cation remains relatively constant, but the negative species is seven times more effective in dilute solutions, and 280 times more effective in bronze solutions. Thus, the solvated electron carries 87% of the current in dilute solutions and nearly 100% in concentrated solutions.

Further studies by Kraus (13,14,15) reveal the following:

1. The electrical conductivity is higher for these solutions than that found for any known salt in any known solvent.
2. The conductance for the alkali metals in ammonia goes through a minimum and then increases sharply with increasing concentration.
3. Conductance in the concentrated region is very high. Near saturation, a sodium solution has a specific conductance one-half that of mercury even though there are over five molecules of ammonia for each atom of metal at this point. This seems to indicate metallic conductance of some kind.

Let us consider Dr. Kraus' analysis for a moment. He summarized the nature of metal-ammonia solutions as follows (13):

> "These solutions therefore constitute a connecting link between metallic and electrolytic conductors. In dilute solutions the process is, at least in part, electrolytic. A portion of the current is carried by

the positive carriers as they appear in solution of the common salts. The negative carrier is chemically uncombined, but is associated with one or more molecules of the solvent. These carriers are identical for solutions of all metals, and when discharge takes place, the only material process which takes place is that a portion of the solvent is left behind in the immediate vicinity of this electrode. As the concentration of the solution increases, the nature of phenomena changes only insofar as the combination of the negative carrier with ammonia is affected. At higher concentrations the negative carriers are free from association with the ammonia molecules to a greater and greater extent. Since under these conditions the negative carrier is associated with no matter of atomic dimensions, it follows that all the material effects cease so far as these carriers are concerned. It is not to be understood that these carriers are free from association with the solvent molecules for any considerable period of time. Certainly an equilibrium must exist between the free carriers, combined carriers, and ammonia which results in a constant interchange between free and bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in metals. As the concentration is increased, the number must be relatively small, since at higher concentrations their equivalent conductance reaches values one hundred times as great as that at one normal concentration. It is not possible to determine the actual number of carriers in the more concentrated solutions. In the more dilute solutions, however, it appears that the number of carriers decreases with increasing concentration, just as it does in the case of normal electrolytes in ammonia.

"There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radioactive and other phenomena."

Kraus, therefore, assumed the following equilibria to exist in solution:

$$M^{o} + n\ NH_3 \longrightarrow M^{+} + e^{-}(NH_3)_n$$

$$e^{-}(NH_3)_n \rightleftharpoons e^{-} + n\ NH_3$$

Because of its simplicity and workability, this model is often referred to in this paper. One should certainly be aware, however, of a great many other models. Many become very complicated in their effort to explain the behavior of metal solutions. It is not the primary purpose of this paper to propose or substantiate any physical model. For this reason, only brief descriptions of the more significant models are given. The proposals are many and varied, yet none sufficiently explains all aspects of the unusual metal-ammonia solutions.

A concentrated solutions model was first proposed by Farkas (16) and later extended by Jolly (17). Farkas assumed that the metal ions form a well-ordered structure in the concentrated region. This structure provides a periodic potential field in which the electrons reside in square potential wells. The higher the concentration, the closer these wells are to one another. Jolly postulated that at concentrations less than one molar the potential wells are too widely separated to permit quantum tunneling, but an appreciable amount of conduction may occur by thermal excitation of bound electrons to the conductance band. In very concentrated solutions, the electrical conductivity is of both types, excitation of the bound electron to the conductance level, and quantum tunneling from potential well to potential well in the bound state.

One of the most popular proposals is the cavity model first proposed by Ogg (18) and later extended by several authors. Ogg postulated that the solvated electron in liquid ammonia is trapped in a spherical cavity created by the solvent molecules. The electrons may be confined in these cavities either singly or paired, according to the equilibrium:

$$2e_1^- \rightleftharpoons e_2^=$$

At infinite dilution the electrons should all be in singly occupied cavities, while at higher concentrations the energetically favored paired sites should predominate.

Hill (19), Lipscomb (20), and Stairs (21) improved the primitive cavity model proposed by Ogg. The basic concept was retained, but mathematical treatment was improved to make the model more compatible with experimental observations.

Kaplan and Kittel (22) made a major contribution giving credence to the idea of a cavity model. They proposed the complete ionization of the alkali metal at all concentrations with the electrons located in solvent cavities as before. These cavities would have approximately the volume of two to four ammonia molecules. Furthermore, the electrons in the cavities are regarded as being in molecular orbital states on the protons of the adjacent ammonia molecules. A mathematical treatment of this model compares well with most experimental results, but does not appear to be compatible with electrical conductivity data.

The Becker, Lindquist, and Alder (23), or BLA model, is another proposal which has received considerable attention. The BLA model proposes an equilibrium between four solute species: the solvated metal ion, the electron, a monomer, and a dimer. The metal ion is solvated by a sheath of about six molecules of ammonia, with the electron moving around the hydrogen atoms which form the outer surface. The dimer is a unit composed of two monomers bound together principally by exchange forces.

Symons (24) proposed a hybrid model, postulating that in dilute solutions the electron resides in a cavity while at higher concentrations, dimer formation of the BLA type occurs.

Gold, Jolly, and Pitzer (25) introduced a model which incorporates a solvated cation and an electron in a cavity. As the concentration is increased, the solvated metal ion and the electron in a cavity form an ion pair.

Extensions of these models and other models have been advanced by several authors since 1940 (26-31).

The optical properties of metal-ammonia solutions have been a subject of interest ever since investigators first noticed the intense blue color which appears. This blue color for dilute solutions arises from the existence of an adsorption maximum in the infrared with a tail extending into the red region of the visible spectrum.

Jolly (32) reported the absorption peak maximum at 6666 cm^{-1}. Jolly proposed that this energy, equivalent to 0.83 volts, is the energy needed for the excitation of the unpaired "solvated" electron in the solution into a conductance band. The electron, once in the conductance band, is free to move without becoming trapped by solvent molecules.

Blades and Hodgins (33) investigated the absorption spectra in greater detail and learned that the peak's maximum and width depended strongly on temperature and metal concentration. These environmental changes point to a dynamic equilibrium existing between species of some kind. The postulated equilibrium in this case is

$$2e_1^- \rightleftharpoons e_2^=$$

as proposed by the cavity model.

Some knowledge of more concentrated solutions was gained by Beckman and Pitzer (34), who made reflection spectral studies on the sodium-ammonia system.

Photoelectric measurements complement the spectral data by providing some information about the nature of the binding between the various species present in metal-ammonia solutions. Studies in this area appear to be somewhat conflicting, however (35-37).

Based on X-ray studies, Schmidt (38) supported the BLA rather than the cavity model. But similar X-ray studies by Brady and Varimbi (39) appear to be conflicting.

Until magnetic susceptibility measurements were made, the Kraus (13) model for metal-ammonia solutions provided an adequate explanation for the physical properties of these solutions. Freed and Sugarman (26) determined that molar magnetic susceptibility was dependent on metal concentration. This is contrary to the behavior predicted by the simple Kraus model.

Nuclear magnetic resonance (40) and electron spin resonance (41) studies have also supplied useful information concerning the physical nature of the metal-ammonia solutions.

None of the models proposed to date accurately describes the metal-ammonia solutions in all respects, and there is considerable debate concerning which of the proposed models is best. The true metal-ammonia system must be a complicated equilibrium, indeed.

Another interesting phenomenon is the remarkable volume expansion which occurs when an alkali metal is dissolved in liquid ammonia. This expansion is most marked for lithium and decreases with increasing atomic weight of the metal. A saturated lithium-ammonia solution, in fact, is the lightest known liquid at room temperature, having a density of only 0.477 g/cc.

Johnson (43) first pointed out in 1931 that saturated solutions of sodium and potassium in liquid ammonia are among the lightest known liquids. Johnson noted that the increase in volume cannot be attributed to the metal ions, but must be due to the negative electron associated with the solvent molecules.

Evers and Filbert (44) reported the volume change of sodium in liquid ammonia at -45°C. Their results show an expansion of about 41 cc/g-atom sodium near 1 n, decreasing to a minimum of 30 cc/g-atom at 0.04 n, and then increasing to a limiting value of 41 cc/g-atom at infinite dilution.

Gunn and Green (45,46) reported volume change data for sodium and lithium at 0°C and sodium at -45°C. This phenomenon is further evidence of the unique physical structure of the metal-ammonia solutions.

A very recent paper by Gordon and Sundheim (46) is of considerable interest in this discussion. They made a chronopotentiometric study of the anionic idffusion in potassium-ammonia solutions. These investigations were made at various temperatures both with and without potassium iodide as a supporting electrolyte. They report diffusion coefficients for the electron of approximately 5×10^{-5} $cm^2 sec^{-1}$, supporting the view that the electron in dilute solutions shows no evidence of any unique transport properties as compared with ordinary electrolytes. They obtained pseudo-diffusion coefficients of approximatel 1×10^{-5} in pure potassium-ammonia solutions. Diffusion coefficients obtained in this way refer to the electrolyte as a whole. They reported their investigations to a maximum concentration of 0.164 M. Further progress into the high concentration region was blocked by problems of "phase separations" and "Joulean heating". At the higher concentrations and higher current densities, the latter part of the chronopotentiograms appeared to show the onset of boiling. It should also be noted that their reproducibility was not very good, and the general morphology of the chronopotentiograms was poor.

This recent article by Gordon and Sundheim confirms the strong oxidation of the solvated electron at a potential within the range of liquid ammonia. This suggests the possibility of practical application of this oxidation in the form of electrical power generation.

This concludes the historical review presented here. The reader is reminded, however, that many excellent reviews (17,47,48, 49,50) are available on this fascinating subject.

B. Analytical Procedure Background

Solid electrode voltammetry, the principal analytical method used, has only recently found extensive use. Basically, this technique involves the linear change of potential between a stationary working electrode and a non-polarized reference electrode. Electrochemical reactions are observed in the form of current between the working electrode and a third electrode, the counter. This current-potential curve is recorded on an X-Y recorder. This method gives a better qualitative picture of the system than chronopotentiometry, or constant current operation, but is usually more difficult to treat quantitatively.

This method is analogous to polarography but the latter is generally applied to the branch of voltammetry in which a dropping mercury electrode is used as the working or polarized electrode. The dropping mercury electrode, or D.M.E., has been investigated more thoroughly and is generally considered more accurate and reproducible than solid electrodes. It is indeed unfortunate that the rapid amalgamation tendencies of alkali metals preclude its use here.

The first application of this method was made by Matheson and Nichols (51). Randles (52) was the first to consider the single scan method for a reversible reaction taking place at a plane electrode. The theory was later extended to totally irreversible charge transfer reactions by Delahay (53). Reinmuth (54,55) also contributed to the theory of both reversible and irreversible reactions taking place at flat electrodes. Unfortunately, even in cases involving complete diffusion control and plane electrodes, the theoretical treatment is relatively difficult, ultimately requiring some sort of numerical analysis.

Other electrode geometries become quite formidable mathematically. Despite its complexity, however, the theory of the single scan method has been extended to reversible reactions taking place at cylindrical electrodes (56) and at spherical electrodes (54,44).

Mathematical complexity has also prevented extensive study of the cyclic triangular wave methods, in spite of their value. Zublik (57) and Adams et al (58) discussed the cyclic method qualitatively. An excellent treatment of the theory of stationary electrode polarography was presented in a recent paper by Nicholson and Shain (59). They discuss both single scan and cyclic methods as applied to reversible, irreversible, and kinetic systems.

The reader is referred to Treatise on Analytical Chemistry by Kolthoff and Elving (60) for a more complete discussion of various electro-analytical techniques.

STATEMENT OF THE PROBLEM

The unique "blue solutions" formed by the solution of alkali metals in liquid ammonia have been laboratory curiosities since their discovery in 1864. Their unusual properties have prompted considerable investigation but as yet practical applications are undeveloped. It has been established (46) that these solutions undergo a strong electrochemical oxidation which could be favorable if applied to the production of electrical energy.

This oxidation has long been known (10) to be nearly perfectly reversible due to extremely fast kinetic processes. This suggests that application of this reaction in a device such as a fuel cell could provide a system capable of very high current densities and low polarization. A complete electrochemical study of the characteristics of this oxidation would be the first step in the fabrication of such a fuel cell. It would be ideal to use a cell without transference for these studies, such as

$$\mathrm{Li(S)} \,\Big|\, \mathrm{Li(NH_3)} \,\Big|\, \text{inert metal}$$

$$\text{or} \quad \mathrm{Li(Hg)} \,\Big|\, \mathrm{Li(NH_3)} \,\Big|\, \text{inert metal}$$

Indeed, electrochemical studies have been conducted utilizing lithium as the anode in solvents of propylene carbonate (61) and cyclic esters (62), but not in liquid ammonia.

One cannot use the free metals as electrodes in ammonia because of their high solubility, nor can the amalgam electrodes be used because of the nearly complete extraction of the metals from ammonia into mercury. Inert electrodes, such as platinum, are then the logical approach to lithium-ammonia electrochemical studies. Unfortunately, most inert electrode materials catalyze an undesirable side reaction to lithium amide. This also seems to be a subject which has received little attention to date (7).

With these criteria in mind, an attempt was made to study the electrochemical oxidation of lithium in liquid ammonia. The objectives of this investigation were the following:

1. Observe the lithium oxidation reaction with single sweep voltammetry.
2. Make a systematic study of several electrodes and their effects on both the electrochemical reactions and catalyzing the undesirable amide reaction.
3. Compile quantitative electrochemical data.
4. Make recommendations concerning application of these results to further development of a lithium fuel cell at Montana State University.

EXPERIMENTAL PROCEDURES

In performing precise experiments on the quasi-stable metal-ammonia system, extreme care and purity are necessary. Because of this requirement, experimental procedures become involved and tedious.

Lithium samples were prepared and handled in an inert argon atmosphere contained by dry box model HE-43-2 manufactured by Vacuum/Atmospheres Corporation. The argon atmosphere was maintained pure by circulation through NaK-56 eutectic which was also contained inside the glove box. This simple purification system seemed adequate but proved bothersome and difficult to maintain.

In order to determine lithium concentrations, a small piece of lithium was cut and cleaned, placed in a small weighing bottle, removed from the dry box, weighed accurately to 1/10 of a milligram, and returned to the dry box. The empty weighing bottle was then removed and weighed again, containing only the argon atmosphere of the box. This known quantity of lithium was then placed in the electrolytic cell while in the dry box. The sealed cell could then be removed and the experiment performed. Care was taken in all cases to keep the cell completely sealed until the experiment had been completed.

The anhydrous ammonia was purchased from The Matheson Company in a commercial cylinder with a minimum purity analysis of 99.99%. The ammonia as supplied was found to be totally unsatisfactory.

Lithium blue solutions prepared with ammonia directly from the cylinder were unstable and usually decomposed to a white precipitate in less than an hour. The product is presumed to be lithium amide. Therefore, all ammonia referred to in this report was distilled from the cylinder into a glass condensing flask immersed in a dry ice-isopropanol bath (Figure 1). During the distillation into this flask, the flask was connected to a mercury manometer blowoff by means of Tygon tubing to prevent excessive pressure buildup. Pressure could be easily controlled by positioning a leveling bulb containing mercury. Application of a few millimeters of mercury pressure in this way facilitated the condensation of ammonia. Following the condensation, the liquid ammonia could be forced from the condensing flask through a dip tube and into the electrolytic cell by again applying pressure in this manner.

It should be noted that most investigators studying metal-ammonia solutions use more scrupulous purification procedures. Some, involved in precise quantitative determinations, distilled the ammonia several times over sodium to insure a minimum of impurities. In view of other factors limiting accuracy, however, this single distillation is considered adequate.

Low temperatures were maintained with a tandem refrigeration system (Figure 2). A conventional Freon refrigeration unit was used to cool a methanol bath contained in a large Dewar flask to approxi-