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**INFRARED ABSORPTION SPECTRA OF
METAL-AMMONIA SOLUTIONS**

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INFRARED ABSORPTION SPECTRA
OF METAL-AMMONIA SOLUTIONS

Marvin Gold
(Ph.D. Thesis)

February 1962

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ABSTRACT

The infrared absorption spectra of liquid ammonia solutions of lithium, sodium, potassium, cesium, and calcium have been studied from 6000 to 25,000 Å in the concentration range 0.005 to 0.2 M. Up to 0.03 M Beer's Law is very nearly obeyed for the alkali metals at all wavelengths. Above 0.03 M positive deviations occur at the long-wavelength tail of the band.

The similar behavior of the various alkali metals and the relatively constant extinction coefficients indicate that the electron-in-a-cavity, which is responsible for the absorption in very dilute solutions, remains intact as the concentration is increased. We propose that the associated species present in moderately concentrated solutions are ion pairs in which the electron cavity is not seriously distorted by the metal ion, and quadrupoles consisting of an assembly of two ion pairs in which the electron spins are paired.

It is shown that this model is consistent with many of the physical properties of alkali metal-ammonia solutions and, in particular, resolves the apparent contradiction between the magnetic and spectral data.

I. INTRODUCTION

The nature of the species present in solutions of alkali metals and alkaline earth metals in various nonaqueous solvents has been the subject of considerable investigation for the past half century. Although most of the work has been devoted to liquid ammonia solutions, studies have been made also of solutions in various amines, ethers, and a few other solvents. Much of this work has been summarized by Jolly in a recent review,¹ and the reader is referred there for a more thorough discussion of the results of these investigations. Our particular interest was with alkali metal-ammonia solutions, and we discuss some of the unusual properties of these systems that led us to undertake the investigation reported here.

It is generally agreed that in very dilute solutions the metal is completely ionized, forming ammoniated metal ions and ammoniated electrons:



There are three lines of evidence for this: (a) The equivalent conductance² in dilute solutions is higher than that of any electrolyte in any solvent. The transference number of the negative carrier is about seven times that of the positive carrier. These results point to the existence of a very mobile electron. (b) The molar susceptibility^{3,4} of dilute solutions is very high, and approaches, at infinite dilution, the value for a mole of free spins. (c) The infrared absorption spectra of dilute solutions of alkali metals in liquid ammonia⁵⁻⁷ are identical, indicating that the same species is responsible for the absorption at low concentrations.

An examination of the magnetic susceptibility data in the more concentrated solutions shows that Reaction (1) cannot be the only equilibrium of importance. The molar susceptibility decreases rapidly as one goes from very dilute to moderately concentrated solutions. For sodium at -33° , the molar susceptibility at 0.01 M is about half the value for an infinitely dilute solution. Therefore, there must be an equilibrium that accounts for the pairing of electron spins in moderately concentrated solutions.

The equivalent conductance also decreases with increasing concentration, but reaches a minimum at about 0.05 M and rises rapidly again at high concentrations. The equivalent conductance of a saturated sodium solution is about seven times that of liquid mercury.⁸

There is general agreement that in very dilute solutions (below about 0.001 M), electrons and metal ions exist as independent solvated ions, while in very concentrated solutions (above about 0.5 M) interaction of these species is considerable and properties are exhibited similar to those of a liquid metal. Our attention was focused on the intermediate-concentration range, where there is an equilibrium between a paramagnetic and a diamagnetic species. Although the existence of a diamagnetic species is inferred from susceptibility data, no direct observation of such a species had been made at the start of this work. Absorption spectrophotometry provides a sensitive method for studying the disappearance of one absorbing species and the simultaneous appearance of a new absorbing species. In dilute solutions, the broad absorption band at about $15,000 \text{ \AA}$ is responsible for the blue color of these solutions. Since metal-ammonia solutions are blue at all concentrations, it is reasonable to expect the diamagnetic species to absorb in the red or

near-infrared region, just as is observed in dilute paramagnetic solutions. In fact, diamagnetic solutions of alkali metals in various amines and ethers exhibit one or more absorption bands in the wave-length region from about 7000 to 13,000 Å.^{5,9,10}

The spectral data for metal-ammonia solutions available when this work was begun were rather limited. There are two reasons for this. First, the extinction coefficient of the 15,000-Å peak is very large, requiring the use of optical cells with exceedingly short path lengths. For example, according to the Beer-Lambert equation $A = \epsilon cl$, we see that for $A \approx 2$, $\epsilon \approx 4.5 \times 10^4$, and $l = 0.01$ cm, the upper concentration for observance of the band maximum is about 4.5×10^{-3} M. Second, alkali metals react slowly with liquid ammonia to form the corresponding alkali metal amide and hydrogen. This has often been an obstacle to accurate quantitative studies of the spectral variations that occur as the concentration of the solution is changed.

Thus, with the exception of two papers which appeared in the literature during the course of this work (and which will be referred to later), the spectral data were confined to the shapes of the absorption bands in very dilute solutions and one quantitative study of the variation of absorbance with concentration.¹¹ The latter investigation was of the short-wavelength tail of the 15,000-Å absorption band in the concentration range from about 0.001 to 0.1 M, and Beer's Law was found to be obeyed for all wavelengths investigated.

Several models have been proposed to account for the observed variations of electrical conductance and magnetic susceptibility with concentration. On the basis of electrolysis experiments,¹² Kraus proposed that the metal ionizes as shown in Eq. (1). This picture was not

quite complete, as no magnetic susceptibility data were available at that time. Huster was the first to measure the susceptibility, and proposed the following equilibrium to account for the pairing of electron spins:



Later, Freed and Sugarman proposed that single unpaired electrons are in equilibrium with two electrons with paired spins, a situation analogous to F and F' centers in crystals,



It was further proposed by Ogg that these electrons existed in solvent cavities created by electronic polarization of the ammonia dielectric.¹³ This model has been elaborated by Hill,¹⁴ Lipscomb,¹⁵ and Kaplan and Kittel.¹⁶

Becker, Lindquist, and Alder rejected the cavity model and gave detailed descriptions of the atoms and molecules of Eqs. (1) and (2).¹⁷ They proposed a neutral species, called a "monomer," consisting of an alkali metal ion surrounded by approximately six oriented ammonia molecules and with an electron circulating around the metal ion on the protons of the ammonia molecules. Two of these monomers are in equilibrium with a "dimer" in which the electron spins are paired,



In dilute solution the monomer dissociates into solvated metal ions and electrons.

According to either of the above models, one would expect to observe a change in the spectrum over the concentration range where spin-pairing

is appreciable. As stated previously, Beer's Law was obeyed for the visible tail of the sodium spectrum. This significant result seemed incompatible with the existing susceptibility data, but since only the tail of the band was observed, it was clear that a more thorough study was needed. Thus the primary purpose of this research was to make an accurate quantitative study of the variation of absorbance as a function of concentration over the entire spectral region at concentrations as high as several hundredths molar.

II. EXPERIMENTAL METHODS

It has been mentioned that the main difficulties in obtaining spectra of metal-ammonia solutions are the very large extinction coefficients and the instability of the solutions with respect to formation of amide ion and hydrogen. For sodium, the reaction is

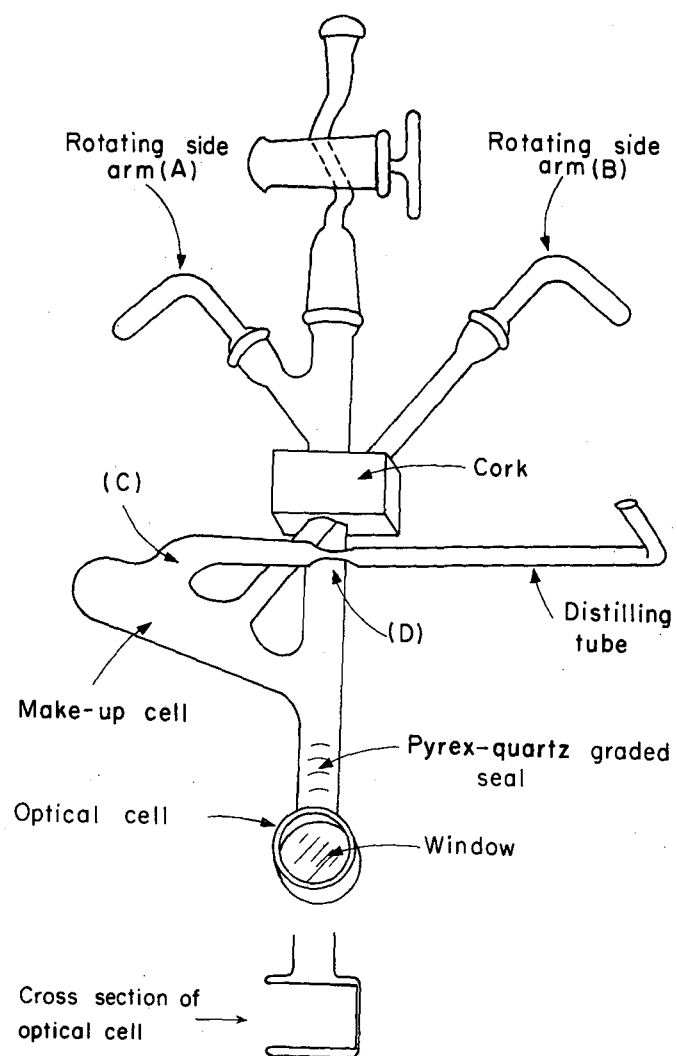


Rigorous cleaning of the apparatus and purity of materials are necessary, since the decomposition is catalyzed by certain foreign matter such as rust and heavy metals. Since the rate of this reaction increases with increasing temperature, we decided to work at low temperatures in ordinary vacuum-line equipment rather than use high-pressure equipment at room temperature. In order to observe the absorption peak of solutions which are 0.01 to 0.02 M in metal, it is necessary to have a light path of approximately 0.025 mm. The problem of mixing in a cell of this size is considerable. Previous experience had shown us that good mixing could be achieved in a 0.5-mm cell by adding sodium to ammonia which is refluxing under a dry ice - acetone cold bath.¹⁸ However, when a similar apparatus and a 0.02-mm cell were used, complete mixing could not be obtained between the optical windows. It was apparent that an apparatus was necessary in which the solution could be prepared in one section and then be transferred to the optical cell. These considerations led to the design of the equipment used in this research.

Description of Equipment

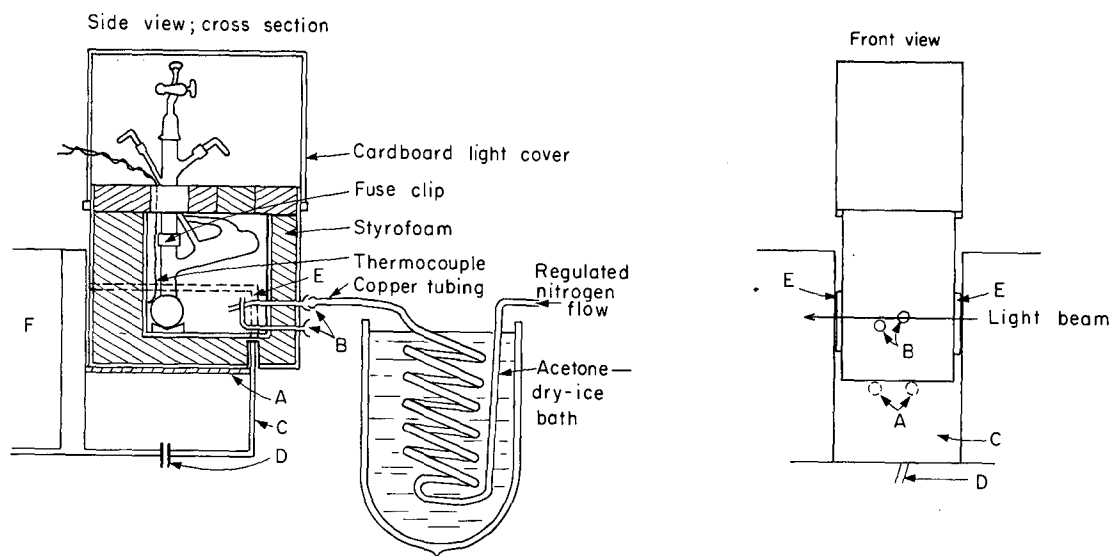
The vessel containing the optical cell is shown in Fig. 1. The optical cell is made of quartz and the rest of the vessel is pyrex. The cell was constructed in the glass shop of this Laboratory by using a piece of 1-mil copper foil to separate the two quartz windows which were fused to the cylindrical walls of the cell. The copper was then dissolved out with hot nitric acid. Two rotating side arms were attached with standard taper joints near the top of the vessel.

An insulated cold box and cooling arrangement made up the rest of the apparatus (Fig. 2). The cold box consisted of an inner and an outer box, both made of $\frac{1}{4}$ -inch plywood and separated by Styrofoam insulation. The outer box was designed to fit the sample compartment of the Cary Model 14 recording spectrophotometer. The lengths, widths, and heights of the inner and outer boxes were $5\text{-}1/8 \times 2\text{-}1/2 \times 5\text{-}1/8$ in. and $8\text{-}1/2 \times 5 \times 7\text{-}3/8$ in., respectively. Part of the front wall of the sample compartment had to be removed and a slot cut from the bottom of the box in order for it to rest on the cylindrical rods in the compartment which normally support the cell holder. The windows of the box were 22-mm quartz tubes, evacuated and sealed off near one end. The spaces between the outer box and the compartment walls were flushed with nitrogen to keep the windows free of moisture. Two wood strips, $3/8$ in. wide, were glued to the box just above the windows in order to exclude light and minimize exposure of the windows to atmospheric moisture. An ordinary fuse clip fastened to the wall of the inner box held the cell in a vertical position and two V-shaped steel knife edges at the base provided a firm support for the cylindrical optical cell. Two 8-mm glass tubes extended from outside the box to the inside chamber, one



MU-24807

Fig. 1. Vessel



MU-24806

Fig. 2. Experimental arrangement for recording spectra

- A. Cylindrical support rods
- B. Cold nitrogen ports
- C. Front wall of sample compartment
- D. Warm nitrogen inlet
- E. Wood strips
- F. Reference compartment

pointing at the optical cell and one at the make-up cell of the vessel. One tube served as an entry for cold nitrogen, the other as an exit. Several peices of Styrofoam, placed around a square piece of cork cemented to the vessel, formed an insulating cover for the box.

Cooling was accomplished with dry high-pressure nitrogen which was precooled by passing through a copper coil immersed in a large Dewar flask of dry ice and acetone. The nitrogen flow was adjusted with the aid of a flowmeter to maintain temperatures of -45° , -55° , or -65° in the cold box. Temperature was measured with a Rubicon portable potentiometer and a copper-constantan thermocouple taped to the side of the optical cell. Fluctuations of temperature could be kept to $\pm 0.3^{\circ}$.

Use of Filters

The highest absorbance that can be read with the Cary Model 14 is 2.0. This corresponds to 1% transmitted light. However, if a filter is placed in the reference beam one can measure absorbancies greater than 2.0. This of course cuts down the amount of light reaching the photocell and decreases the sensitivity of the instrument. But, since the spectra of interest are quite broad, it was felt that this would not be a serious handicap.

A partially exposed photographic plate proved to be a satisfactory filter for our purpose. The absorbance of the filter used varied only from about 1.85 at 9,000 A to 1.96 at 25,000 A. The filter was calibrated by measuring the absorbance of some suitable material in the sample beam, then placing the filter in the reference beam and noting the decrease in absorbance. This decrease was taken as the apparent absorbance of the filter. It was necessary to have the filter in the

same position each time it was used, since the apparent absorbance changed somewhat when the position of filter was altered. In fact, the choice of material in the sample beam (other exposed photographic plates, "German" filters, etc.) seemed to affect the apparent absorbance of the reference filter although the variations were not greater than about 0.05 unit on the absorbancy scale. In view of these uncertainties, the filter values were determined during the run in which the filter was used. When the absorbance of a particular metal-ammonia solution was close to 2.0, the instrument was stopped and the filter inserted in the reference compartment. This decreased the recorded absorbance to about 0.1 and the recording was continued. In this way the absorbance of the filter was determined at two wavelengths of the spectrum, one on each side of the peak. Values for the intermediate wavelengths were interpolated. When a number of such runs provided several filter values at various wavelengths, it was estimated that these interpolations were correct to ± 0.02 absorbancy unit. This is a maximum error of about 1.2% in the absorbance of the solute.

By this method, absorbancies as high as about 3.7 could be measured. The loss of light could be compensated for by increasing the "slit control" which amplifies the phototube signal over a 100-to-1 range.

Calibration of the Optical Cell

The light path of the cell was calibrated with alkaline potassium chromate solutions of several concentrations. The solutions were prepared by adding potassium hydroxide pellets to aqueous potassium dichromate solutions until the color change from dichromate to chromate was evident. The amount of base added is not critical, as neither ion absorbs at

3700 Å. The filter previously described was used at the high absorbancies. When absorbancies of the 3700-Å peak were plotted as a function of concentration, the curve showed a negative deviation from Beer's Law (Fig. 3). The effective light path decreased about 10% on going from an absorbance of about 0.5 to 3.0, and another 10% from 3.0 to 3.45. This is most likely because a portion of the light beam is scattered by the sides of the cell and eventually reaches the phototube. At high concentrations, this "stray" light is a considerable fraction of the light reaching the phototube, causing the absorbance to level off; i.e. the amount of light reaching the phototube is approaching a constant value.

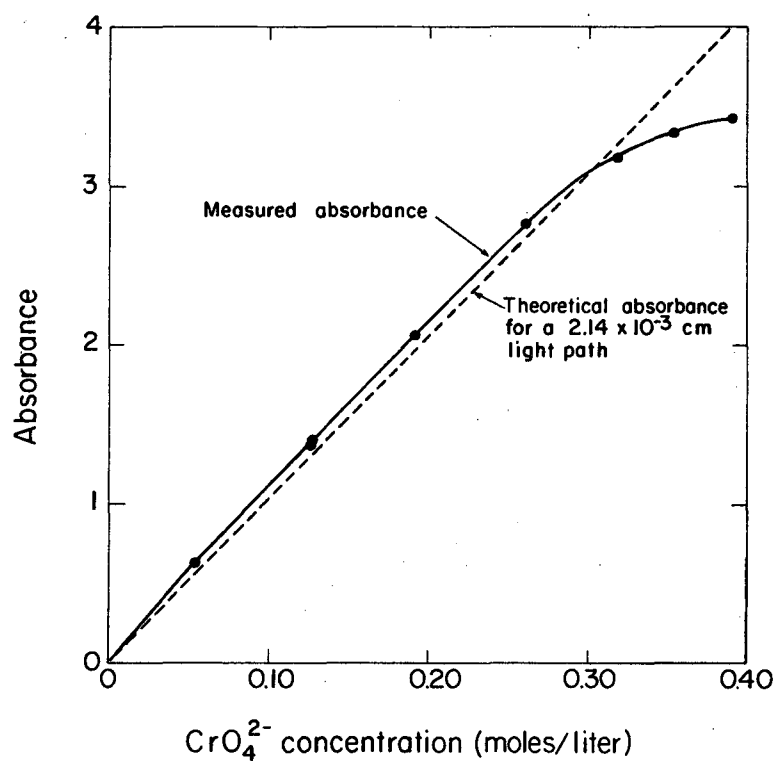
Since chromate ion is known to obey Beer's Law, a correction was calculated for each measured absorbance and these corrections were applied to the metal-ammonia solution spectra. The light path was taken as 2.14×10^{-3} cm, with an estimated uncertainty of $\pm 5\%$.

The infrared source had sufficient intensity at 3700 Å to be used for the calibration. This was fortunate, since the optics are reversed when the ultraviolet or visible sources are used and this is likely to affect the scattering.

Experimental Procedure

Prior to use, the optical cell and make-up cell were cleaned with hot aqua regia. Rinsing between the windows was facilitated by applying a vacuum with the optical cell immersed in boiling water. Every effort was made to keep insoluble matter from getting into the cell.

The solutions were prepared in the make-up cell with the vessel connected to the vacuum line in a horizontal position. Some ammonium



MU-26233

Fig. 3. Calibration of optical cell

chloride was placed in side arm A to be used later in determining the concentration. The volume of metal used varied from about 0.2 to 33 mm³, depending on the particular metal and the concentration desired.

The various materials used were prepared as follows.

Sodium and Potassium:

Approximate quantities of these metals were obtained by extruding the wire through a 1-mm-diameter hole of a hand press. This operation was done in the atmosphere and took about 1 minute. The metal was then put into the distilling tube, which was sealed off near the inlet end, and the vessel was evacuated. The vessel was then flamed below the cork for a few minutes. The metal was distilled to point C and the tube sealed off at D.

Cesium:

Obtaining rough quantities of cesium was more difficult because of its semiliquid state and extreme reactivity. The metal was heated slightly in a 12-mm evacuated tube and poured into 2-mm capillaries which were sealed onto the larger tube. When the desired amount of cesium was obtained, the capillary was sealed off. Under a stream of argon, the capillary was broken and introduced into the distilling tube, which was rapidly sealed off and the vessel was evacuated. The metal was transferred to C as described above.

Lithium and Calcium:

These metals cannot be distilled in a glass and were used undistilled. The lithium was cut in a polyethylene bag flushed with dry argon, and placed in rotating side arm B and capped in the bag. The side arm was quickly attached to the vessel and evacuated. The surface of the lithium remained shiny throughout the operation. Calcium is sufficiently

unreactive in the atmosphere and could be cut under a stream of argon. The metal is rather hard and had to be cut by pounding a sharp knife with a hammer. The uncut surfaces were scraped free of oxide with a razor blade. The piece of metal was placed in the rotating side arm which was then attached to the vessel and evacuated. The calcium also remained shiny during this operation. As with the previous metals, the vessel was well flamed below the cork.

Sodium iodide:

It was of interest to record the spectra of several solutions of sodium with added sodium iodide. The salt was dried in vacuo for several hours at about 180° . The container was put in a polyethylene bag flushed with dry nitrogen, and a pellet of sodium iodide was made with a small hand-operated pill press. The pellet was placed in the rotating side arm B, which, with its cap, had been previously weighed. These were weighed again and the weight of the salt determined. At this point sodium was admitted to the distilling tube, the tube sealed off, the side arm with sodium iodide attached, and the whole vessel evacuated. Great care must be taken to dry the sodium iodide thoroughly and to minimize its exposure to atmospheric moisture after it has been dried.

Ammonia:

The gas was dried by condensing it into an evacuated tube containing sodium metal. The dry ammonia was distilled into another evacuated tube and any hydrogen in the system was pumped out. (It was important that no hydrogen be in the vessel at the start of a run because the accumulation of hydrogen in the vessel is a measure of the amount of decomposition that occurs during the run). The make-up cell was immersed in a liquid nitrogen bath and about 3 ml of ammonia was distilled

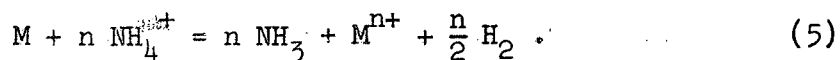
in. All mercury in the vacuum line was closed off while ammonia was being distilled. To be sure that no mercury contaminated the solution, some gold foil was placed in the tubing connecting the vessel to the vacuum line. The liquid nitrogen was then replaced by a dry ice-acetone bath and the ammonia allowed to melt.

The metals that had been distilled were dissolved by shaking ammonia into the distilling tube. The other metals or sodium iodide were added from side arm B. The vessel was then put in the cold box with the make-up cell still pointing down and the Styrofoam cover pieces were put into place. The cold nitrogen was directed at the make-up cell and the box was cooled to about -60° . At this point the optical cell was a few degrees warmer than the make-up cell. If the solution was poured into the optical cell at this time, excessive boiling occurred. Therefore, the nitrogen flow was directed at the optical cell for a few seconds to lower its temperature a little. It was important that this cooling not be excessive, since, if the optical cell were colder than the solution, ammonia would condense between the windows. The box was turned 90° , allowing the solution to run into the optical cell, and then placed in the sample compartment of the spectrophotometer. The nitrogen flow was again directed at the optical cell and cooling continued to about -70 to -72° , which was the lower limit. The solution was allowed to warm to -65° and the temperature maintained until the absorbance remained constant at a given wavelength. The spectrum was then recorded and the procedure repeated to record the spectra at -55 and -45° . It was found that best results were obtained if the solution was warmed, rather than cooled to the desired temperature. When cooling, other glass surfaces in the vessel may cool more rapidly than the solution, causing ammonia to condense there and concentrate the solution in the optical cell.

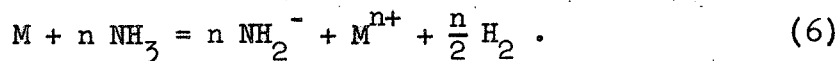
Since the absorption of the solvent and cell could not be measured at the time the solution spectra were recorded, it had to be measured separately. The spectrum of ammonia in the cell and the base line of the instrument (air vs air) were recorded. Then, each time a solution spectrum was obtained, the base line was also recorded. In this way the ammonia absorption needed to be obtained only once, although it was checked again several months later.

Concentration Determination

If ammonium chloride is added to a metal-ammonia solution, a stoichiometric amount of hydrogen is liberated according to the reaction



Hydrogen is also liberated by the slow decomposition of the solution:



The ratio of hydrogen produced from Reaction (5) to the total hydrogen from Reactions (5) and (6) is a measure of the uncertainty in the concentration at the time the spectrum was recorded. This analytical method is of great value when working with these relatively unstable solutions. Of course, this method is insensitive to any excessive decomposition of the thin film between the cell windows. This decomposition can be detected only by means of the spectra.

Procedure:

After the spectra were recorded, the vessel was removed from the cold box and immediately immersed in a dry ice-acetone bath. The vessel was then attached to the vacuum line, at the other end of which was a

Toepler pump connected to a gas buret for measuring the hydrogen. The buret had two calibrated volumes separated by a stopcock. With the stopcock closed, the smaller volume (about 2 cm^3) was used for the less concentrated solutions and with the stopcock open, the total volume (about 25 cm^3) was used for the more concentrated solutions. Two liquid nitrogen traps were maintained between the solution and Toepler pump to prevent any ammonia from reaching the gas buret. Hydrogen was released from the vessel by exposing the solution to an evacuated section of the line. With the stopcock of the vessel closed, the Toepler pump was used to pump the hydrogen into the gas buret. This procedure was repeated until a thermocouple vacuum gauge attached to the line between the solution and buret showed that all the hydrogen was in the buret. The mercury level was then adjusted to the proper level and the hydrogen pressure was recorded. The ammonium chloride was then added to the solution and the total hydrogen was pumped off and measured in the same manner.

The ammonia was absorbed in a flask containing 40 ml of 80% sulfuric acid, the flask being weighed before and after the absorption of ammonia. A magnetic stirrer was used and the flask was kept cool with an ice bath.

Source of Materials

Sodium - Baker and Adamson (Reagent)

Potassium - Baker and Adamson (Technical)

Lithium - Metal Hydrides (Technical)

Cesium - Fisher Scientific Co.

Calcium - Baker and Adamson, Turnings

Ammonia - Matheson, anhydrous

Ammonium chloride - J. T. Baker (Reagent)

Sodium iodide - Mallinckrodt (Reagent)

III EXPERIMENTAL RESULTS

The spectra of lithium, sodium, potassium, cesium, and calcium were recorded from 6000 to 25000 Å at concentrations from about 0.005 to 0.2 M. Up to 0.03 M the absorption peak was observed, but above this concentration only the tails of the band were visible.

Aside from the decomposition of the solutions, there was one other experimental difficulty which sometimes made the concentration of a particular solution uncertain: During the process of dissolving metals that had been distilled, some solution occasionally got trapped in the tip of the sealed-off distilling tube (D in Fig. 1) and would not wash down. However, this ammonia could not be excluded from the analysis and thus its volume, usually about 0.05 ml, was subtracted from the total measured volume. Table I shows the concentrations of the various solutions studied. Where only one figure appears, there was no decomposition and no volume correction. Where decomposition occurred, the lower limit of the concentration is underlined to indicate that this is the most likely concentration. This is to say that all the decomposition occurred during the cooling and transfer of the solution, before the spectra were recorded. Where a volume correction has been made, the higher concentration is underlined.

Owing to liquid-liquid phase separation, calcium solutions more concentrated than 0.02 M could not be observed. Such solutions always showed two phases between the windows of the optical cell. Even in solutions less concentrated than 0.02 M, two phases appeared when the calcium was added to the ammonia. The less dense, more concentrated phase tended to cling to the walls of the make-up cell even after

Table I. Concentrations (moles/liter) of metal solutions at -65° .

<u>Sodium</u>	<u>Lithium</u>
<u>0.00800-0.00855</u>	0.0117
<u>0.0105-0.0112</u>	0.0325
<u>0.0118-0.0121</u>	0.143
<u>0.0133-0.0135</u>	
<u>0.0229-0.0234</u>	
0.0295	
<u>0.0374-0.0379</u>	<u>Cesium</u>
<u>0.0442-0.0452</u>	<u>0.00483-0.00506</u>
0.0454	<u>0.0101-0.0110</u>
0.0476	<u>0.0590-0.0599</u>
0.0805	<u>0.131-0.134</u>
0.142	
<u>0.184-0.190</u>	
 <u>Potassium</u>	 <u>Calcium</u>
0.00846	<u>0.00298-0.00357</u>
0.0194	<u>0.00739-0.00786</u>
<u>0.104-0.107</u>	<u>0.0194-0.0202</u>
<u>0.222-0.226</u>	

persistent shaking. However, when the more dilute solutions were transferred to the optical cell, a uniform film was obtained between the windows and good spectra were recorded. Visual observation of the solution in the optical cell, while showing no signs of two phases, did show numerous small dark particles which were barely detectable in the dark blue solution. These phenomena were not further investigated, but their occurrences make the accuracy of the calcium data subject to some doubt.

The density of pure liquid ammonia¹⁹ at -65° was used to calculate the volumes of the solutions. The measured absorbancies at -55° and -45° were then corrected for the density differences between these temperatures and -65° .

Concentration Dependence

From 6000 Å to about 18,000 Å, sodium obeys Beer's Law within an average experimental uncertainty of $\pm 5\%$ at all concentrations investigated. The other alkali metals follow closely the behavior of sodium, although the deviation is about $\pm 10\%$ from the average sodium value at a given wavelength. Calcium shows a noticeably different behavior at all wavelengths. Values of the absorbancies and extinction coefficients at selected wavelengths are shown in Tables II through IV. Plots of absorbance vs concentration at -65° are shown in Figs. 4 through 10. In Figs. 4, 5, 9, and 10 the potassium, lithium, and cesium points below 0.015 M have been omitted for the sake of clarity, since they practically coincide with the sodium points here. At the high-wavelength tail of the absorption band there is a positive deviation from Beer's Law, as shown in the plots at 21,000 and 24,000 Å. Unfortunately, the absorption

Table II. Absorbancies (A) and extinction coefficient (ϵ) at -65° .

	concentration (moles/liter)	$\lambda = 7500 \text{ \AA}$		$\lambda = 10,000 \text{ \AA}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.065	3800	0.160	9350
	0.0105	0.085	3780	0.240	10700
	0.0118	0.090	3560	0.250	9900
	0.0133	0.105	3690	0.280	9830
	0.0229	0.185	3770	0.55	11200
	0.0295	0.230	3640	0.67	10600
	0.0379	0.285	3510	0.85	10500
	0.0452	0.315	3250	0.96	9930
	0.0454	0.335	3450	1.04	10700
	0.0476	0.355	3480	1.09	10700
	0.0805	0.59	3420	1.83	10600
	0.142	1.05	3450	3.52	11600
	0.190	1.32	3240		
Potassium	0.00846	0.080	4410	0.195	10800
	0.0194	0.165	3970	0.455	11000
	0.107	0.88	3840	2.72	11900
	0.226	1.60	3310		
Lithium	0.0117	0.070	2790	0.230	9180
	0.0325	0.210	3020	0.68	9780
	0.143	1.01	3300	3.51	11500
Cesium	0.00483	0.030	2900	0.100	9670
	0.0101	0.070	3230	0.20	9260
	0.0599	0.385	3000	1.26	9830
	0.134	0.92	3210	2.95	10300
Calcium	0.000298	0.04	6300	0.12	18800
	0.00739	0.09	5700	0.27	17000
	0.0194	0.19	4600	0.57	13700

Table II (Continued)

	concentration (moles/liter)	$\lambda = 13,000 \text{ A}$		$\lambda = 15,250 \text{ A}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.50	29200	0.67	39100
	0.0105	0.76	33800	1.05	46700
	0.0118	0.78	30900	1.09	43100
	0.0133	0.91	32000	1.30	45700
	0.0229	1.58	32200	2.29	46700
	0.0295	1.88	29800	2.84	45000
	0.0379	2.41	29700		
	0.0452	2.70	27900		
	0.0454	3.07	31600		
Potassium	0.0476	3.41	33400		
	0.00846	0.58	32000	0.78	43100
Lithium	0.0194	1.35	32500	1.86	44800
	0.0117	0.73	29100	1.02	40700
Cesium	0.0325	2.05	29500	3.07	44100
	0.00483	0.33	31900	0.420	40600
Calcium	0.0101	0.66	30500	0.92	42600
	0.00298	0.37	58000	0.475	74500
	0.00739	0.80	50500	1.06	67100
	0.0194	1.56	37600	2.00	48100

Table II (Continued)

	concentration (moles/liter)	$\lambda = 18,000 \text{ \AA}$		$\lambda = 21,000 \text{ \AA}$	
		$\text{\AA}$	ϵ	$\text{\AA}$	ϵ
Sodium	0.00800	0.41	24000	0.110	6430
	0.0105	0.66	29400	0.185	8240
	0.0118	0.69	27300	0.190	7520
	0.0133	0.84	29500	0.230	8070
	0.0229	1.50	30600	0.455	9280
	0.0295	1.82	28800	0.57	9010
	0.0379	2.36	29100	0.69	8500
	0.0452	2.57	26600	0.81	8370
	0.0454	2.86	29400	0.91	9360
	0.0476	3.24	31800	0.98	9610
	0.0805			1.66	9640
	0.142			3.90	12800
Potassium	0.00846	0.49	27000	0.140	7740
	0.0194	1.26	30400	0.37	8910
	0.107			2.79	12200
Lithium	0.0117	0.66	26300	0.195	7790
	0.0325	2.02	29000	0.63	9050
	0.143			4.1-4.2	13500
Cesium	0.00483	0.245	23700	0.070	6770
	0.0101	0.60	27700	0.170	7860
	0.0599			1.25	9750
Calcium	0.00298	0.26	40800	0.075	11700
	0.00739	0.62	39200	0.200	12600
	0.0194	1.25	30100	0.460	11100

Table II (Continued.)

	concentration (moles/liter)	$\lambda = 24,000 \text{ \AA}$	
		A	ϵ
Sodium	0.00800	0.020	1170
	0.0105	0.035	1560
	0.0118	0.040	1580
	0.0133	0.045	1580
	0.0229	0.115	2350
	0.0295	0.145	2300
	0.0379	0.180	2200
	0.0452	0.200	2070
	0.0454	0.245	2520
	0.0476	0.260	2550
	0.0805	0.54	3130
	0.142	1.25	4110
	0.190	1.89	4650
Potassium	0.00846	0.030	1660
	0.0194	0.095	2280
	0.107	0.99	4320
	0.226	2.76	5700
Lithium	0.0117	0.050	2000
	0.0325	0.160	2300
	0.143	1.25	4080
Cesium	0.00483	0.020	1940
	0.0101	0.045	2080
	0.0599	0.330	2570
	0.134	1.17	4080
Calcium	0.00298	0.0030	4700
	0.00739	0.075	4740
	0.0194	0.195	4700

Table III. Absorbancies (A) and extinction coefficients (ϵ) at -55° .

	Concentration (moles/liter)	$\lambda = 15,500 \text{ A}$		$\lambda = 18,000 \text{ A}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.75	43800	0.54	31500
	0.0105	1.12	49900	0.80	35600
	0.0118	1.20	47500	0.91	36000
	0.0133	1.39	48800	1.05	36900
	0.0229	2.45	50000	1.86	37900
	0.0295	3.07	48600	2.30	36400
	0.0379			2.95	36300
	0.0452			3.37	34800
	0.0454				
	0.0476				
Potassium	0.00846	0.85	47000	0.63	34800
	0.0194	2.02	48600	1.57	37800
Lithium	0.0117	1.09	43500	0.81	32300
	0.0325	3.47	49900	2.55	36600
Cesium	0.00483	0.445	43000	0.300	29000
	0.0101	1.00	46200	0.75	34700
Calcium	0.00298	0.505	78900	0.33	51700
	0.00739	1.14	72100	0.79	50000
	0.0194	2.19	52700	1.55	37400

Table III. (Continued)

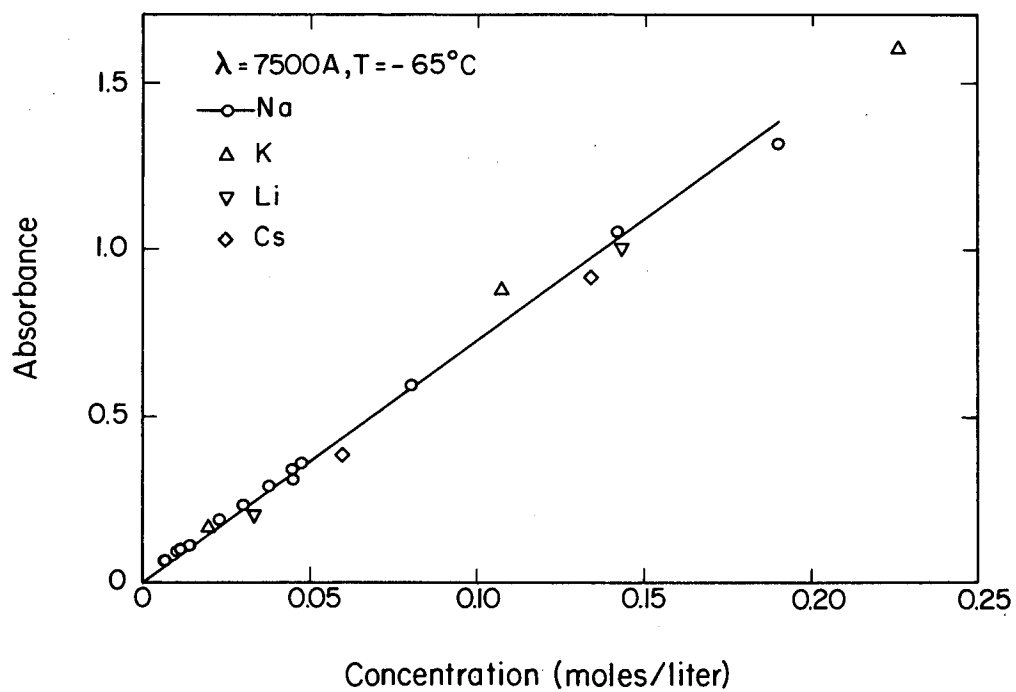
	Concentration (moles/liter)	$\lambda = 21,000 \text{ A}$		$\lambda = 24,000 \text{ A}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.190	11100	0.050	2920
	0.0105	0.285	12700	0.080	3560
	0.0118	0.310	12300	0.085	3360
	0.0133	0.365	12800	0.100	3510
	0.0229	0.73	14900	0.205	4180
	0.0295	0.89	14100	0.270	4270
	0.0379	1.16	14300	0.365	4500
	0.0452	1.34	13800	0.420	4340
	0.0454	1.40	14400	0.470	4830
	0.0476	1.53	15000	0.525	5150
	0.0805	2.41	14000	0.84	4870
	0.142			1.98	6520
	0.190			3.12	7670
Potassium	0.00846	0.225	12400	0.060	3310
	0.0194	0.64	15400	0.205	4940
	0.107			1.47	6410
Lithium	0.0117	0.290	11600	0.090	3590
	0.0325	1.01	14500	0.300	4310
	0.143			2.03	6630
Cesium	0.00483	0.110	10700	0.035	3380
	0.0101	0.270	12500	0.085	3930
	0.0599	1.93	15000	0.64	4990
	0.134			1.88	6550
Calcium	0.00298	0.120	18800	0.040	6270
	0.00739	0.285	18000	0.115	7280
	0.0194	0.66	15900	0.230	5540

Table IV. Absorbancies (A) and extinction coefficients (ϵ) at -45°

	Concentration (moles/liter)	$\lambda = 15,750 \text{ \AA}$		$\lambda = 18000 \text{ \AA}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.82	47900	0.66	38500
	0.0105	1.21	53900	0.98	43600
	0.0118	1.31	51900	1.11	44000
	0.0133	1.50	52600	1.26	44300
	0.0229	2.67	54500	2.17	44300
	0.0295	3.41	54000	2.82	44600
	0.0379			3.79	46700
Potassium	0.00846	0.94	51900	0.77	42500
	0.0194	2.25	54200	1.92	46300
Lithium	0.0117	1.18	47100	0.97	38700
	0.0325			3.18	45600
Cesium	0.00483	0.480	46400	0.36	34800
	0.0101	1.11	51300	0.92	42600
Calcium	0.00298	0.565	88600	0.43	67500
	0.00739	1.26	79700	0.99	62600
	0.0194	2.60	62600	2.02	48600

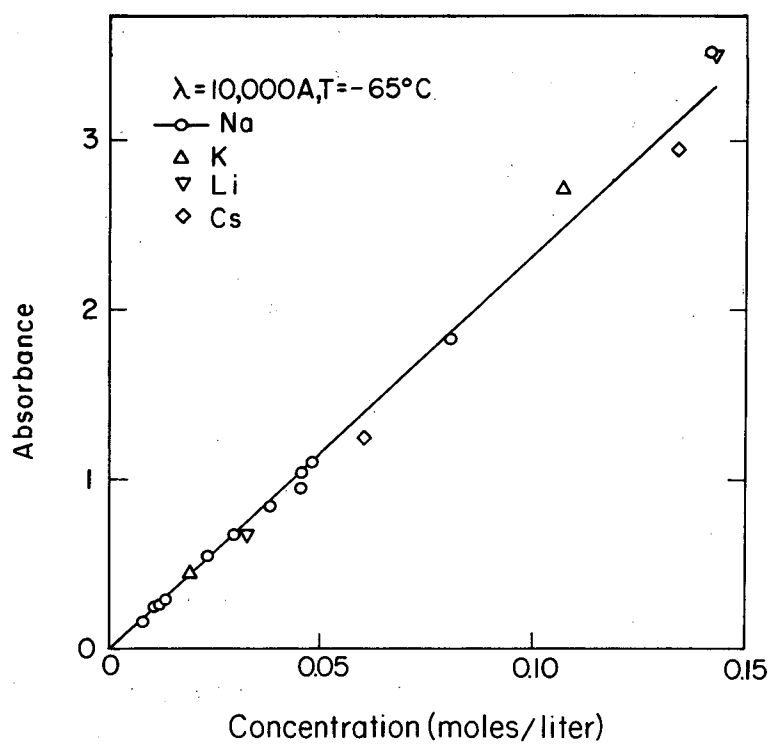
Table IV. (Continued)

	concentration (moles/liter)	$\lambda = 21,000 \text{ \AA}$		$\lambda = 24,000 \text{ \AA}$	
		A	ϵ	A	ϵ
Sodium	0.00800	0.275	16100	0.090	5260
	0.0105	0.430	19100	0.155	6900
	0.0118	0.490	19400	0.170	6740
	0.0133	0.495	17400	0.180	6320
	0.0229	1.03	21000	0.350	7140
	0.0295	1.29	20400	0.455	7200
	0.0379	1.59	19600	0.60	7400
	0.0452	-	-	0.74	7640
	0.0454	2.10	21600	0.78	8030
	0.0476	2.12	20800	0.82	8040
	0.0805	4.16	24200	1.34	7780
	0.142			3.13	10300
Potassium	0.00846	0.325	17900	0.110	6080
	0.0194	0.92	22100	0.315	7590
	0.107			2.38	10400
Lithium	0.0117	0.425	17000	0.155	6190
	0.0325	1.46	21000	0.540	7760
	0.143			3.35	10900
Cesium	0.00483	0.160	15500	0.055	5320
	0.0101	0.420	19400	0.160	7400
	0.0599	2.83	22100	1.08	8440
	0.134			2.72	9490
Calcium	0.00298	0.180	28200	0.065	10200
	0.00739	0.445	28100	0.180	11400
	0.0194	0.97	23400	0.400	9630



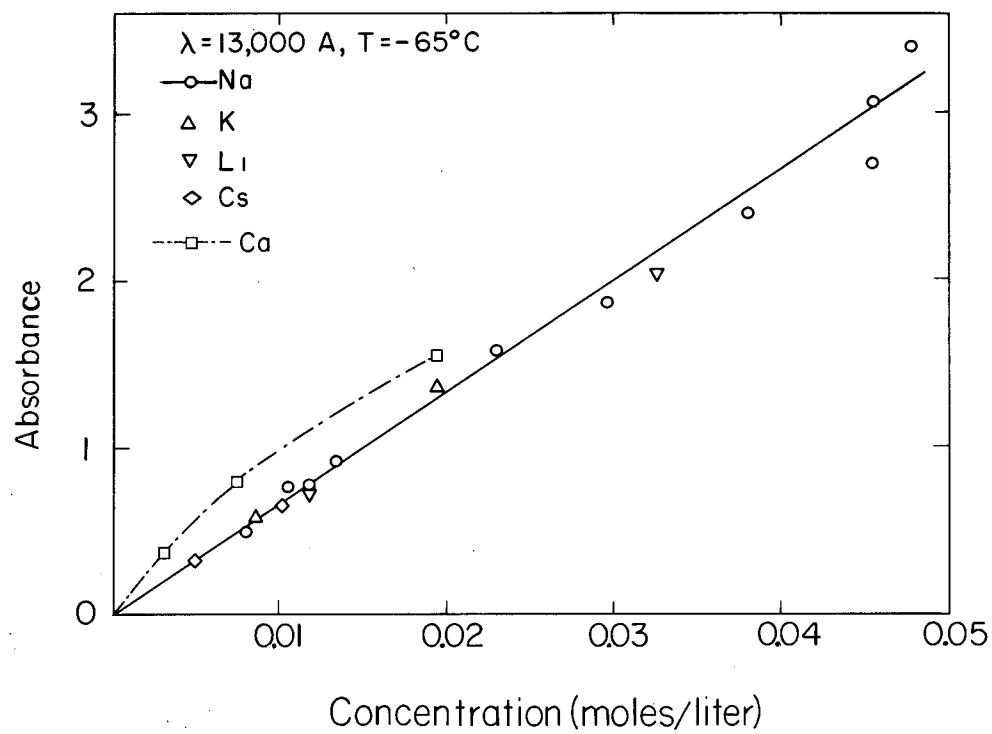
MU-25964

Fig. 4. Absorbance vs concentration at 7500 Å



MU-25965

Fig. 5. Absorbance vs concentration at 10,000 Å



MU-25966

Fig. 6. Absorbance vs concentration at 13,000 Å

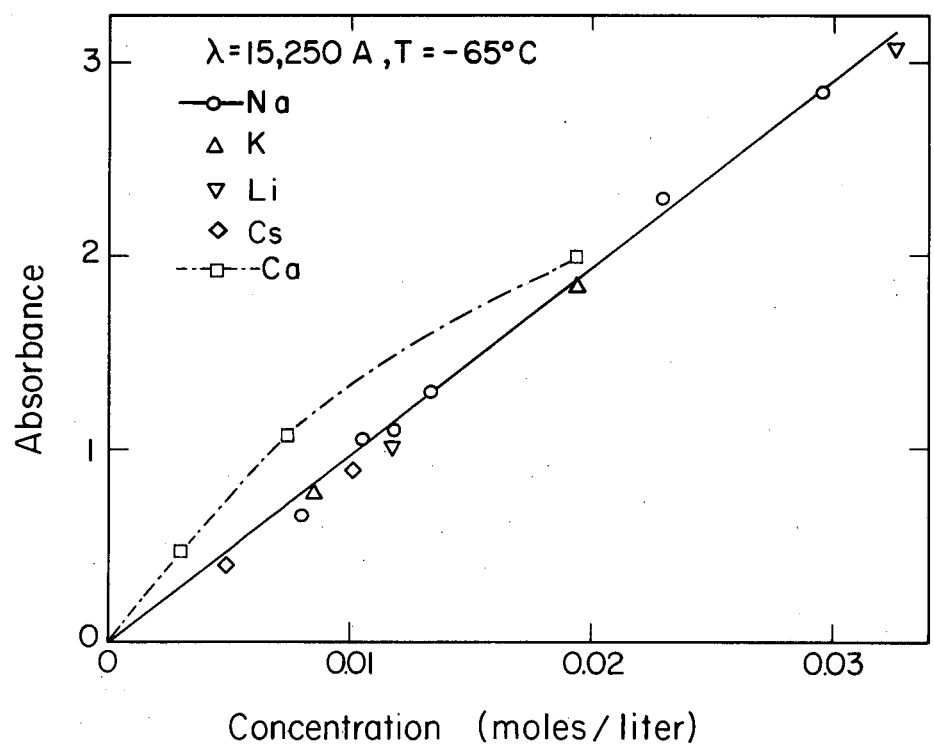
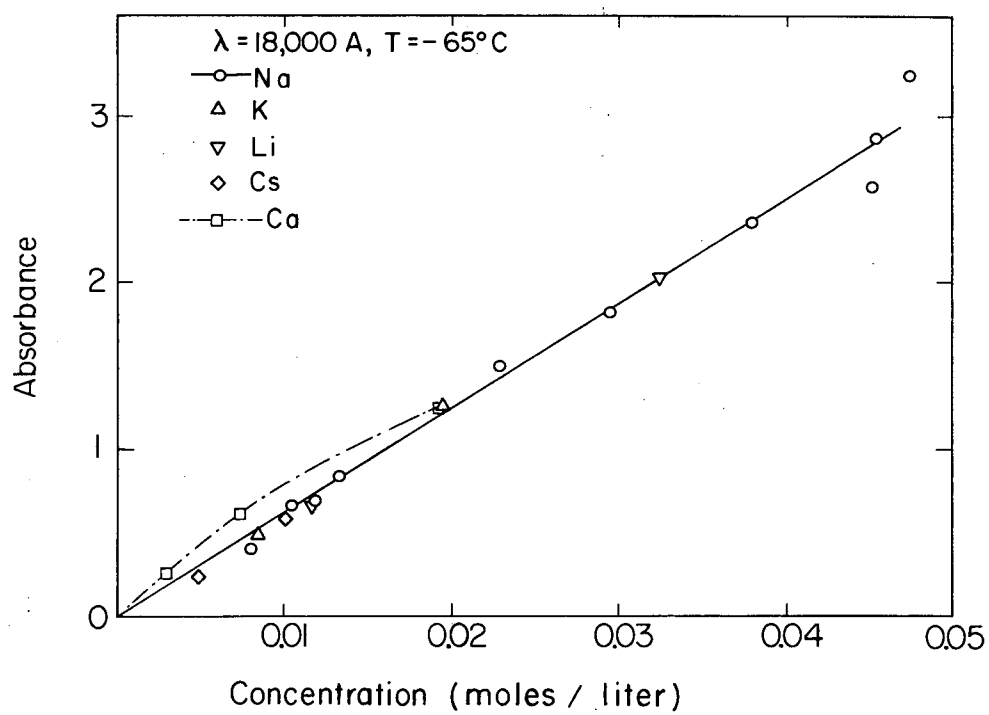
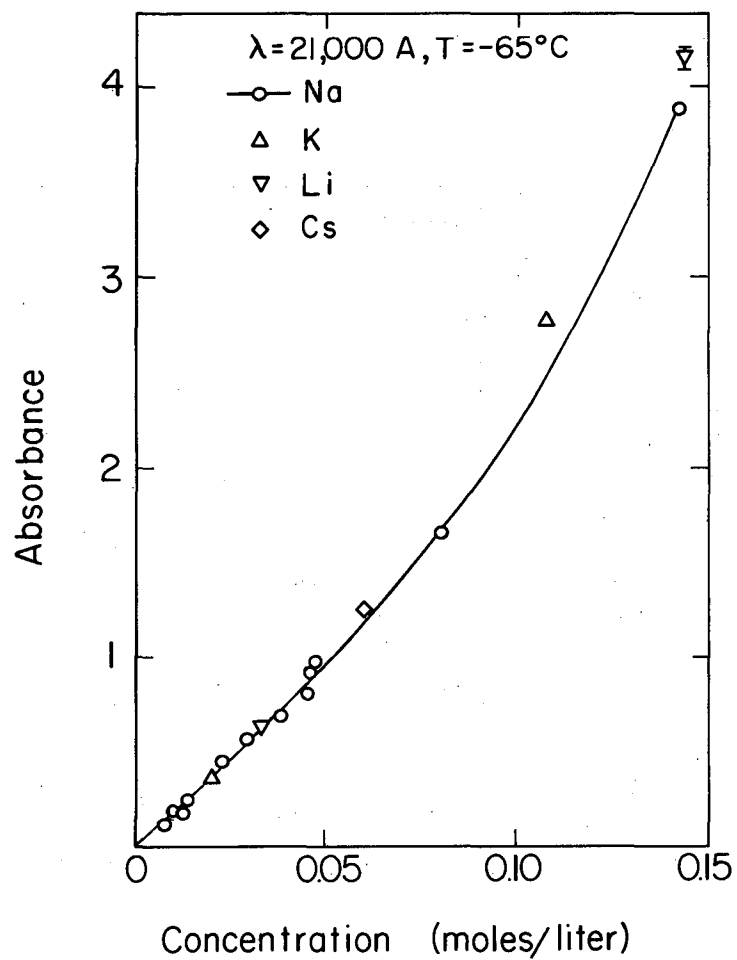


Fig. 7. Absorbance vs concentration at 15,250 Å



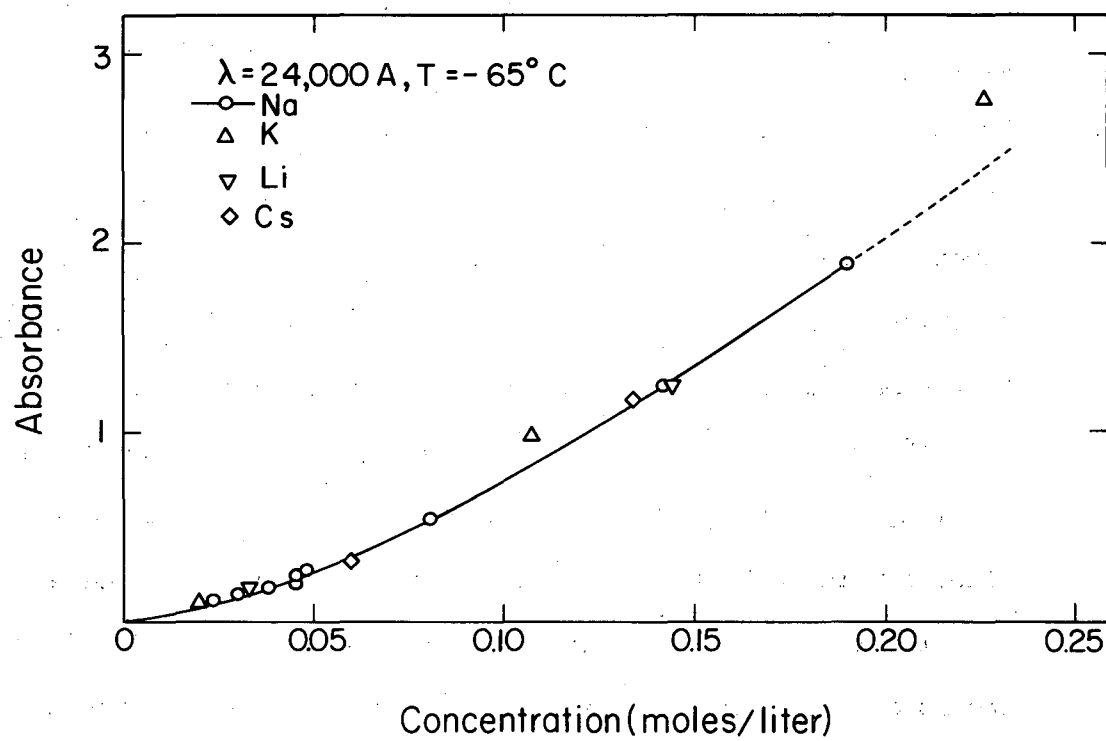
MU-25968

Fig. 8. Absorbance vs concentration at 18,000 $\text{\AA}$



MU-25969

Fig. 9. Absorbance vs concentration at 21,000 Å



MU-25970

Fig. 10. Absorbance vs concentration at 24,000 Å

peak could not be observed at concentrations greater than about 0.03 M, and one cannot know if this deviation is due to a shift of the whole absorption band or not. The spectra show no signs of a new band or a shoulder which might be responsible for the increase in the extinction coefficients in this region.

The shift of the peak position is very small over the concentration range from 0.005 to 0.03 M. These values are shown in Table V. A plot of $\nu_{\max}$ vs $A_{\max}$ is shown in Fig. 11 along with the work of Douthit and Dye on more dilute solutions. It is seen that below about 0.005 M the shift is much more pronounced and the two sets of data are in reasonable agreement where they overlap. Because the shift is so small for the solutions studies here, Fig. 7 is changed insignificantly if absorbance at the maximum is plotted instead of absorbance at 15,250 Å.

Since the absorption peaks are so broad, it was necessary to locate the wavelengths of the maxima by a standardized procedure. Several horizontal lines cutting both sides of the peak were drawn at various absorbancies. The midpoints of these lines formed a straight line which intercepted the absorption curve at the maximum. This operation could be done on the original spectrum, since the background was always horizontal within several thousand angstroms of the peak.

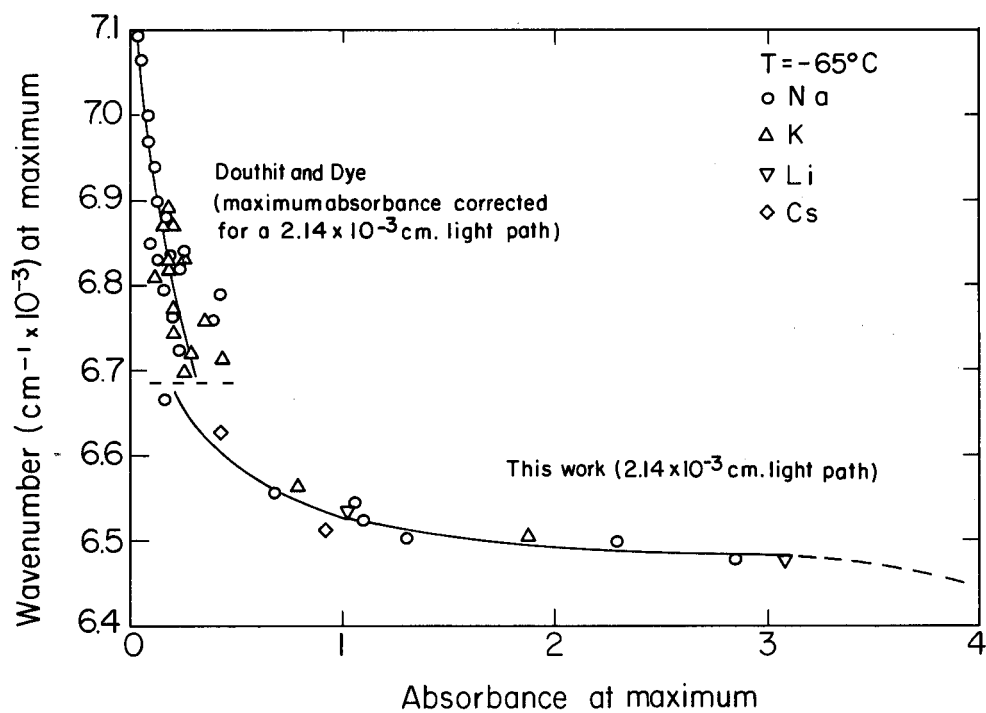
Temperature Dependence

An increase in temperature broadens the band and shifts the peak to longer wavelengths with an increase in the maximum absorbance. The temperature dependence of the spectrum is illustrated in Fig. 12, and absorbancies and positions of the maxima are listed in Table V. The average shift of the peak, for the alkali metals, is $-14.1 \text{ cm}^{-1} \text{ deg}^{-1}$ from -65 to -55° and $-11.3 \text{ cm}^{-1} \text{ deg}^{-1}$ from -55 to -45° .

Table V. Absorbance at the maximum ($A_{\max}$) and position of the maximum ($\lambda_{\max}$: angstroms, $\nu_{\max}$: cm^{-1})

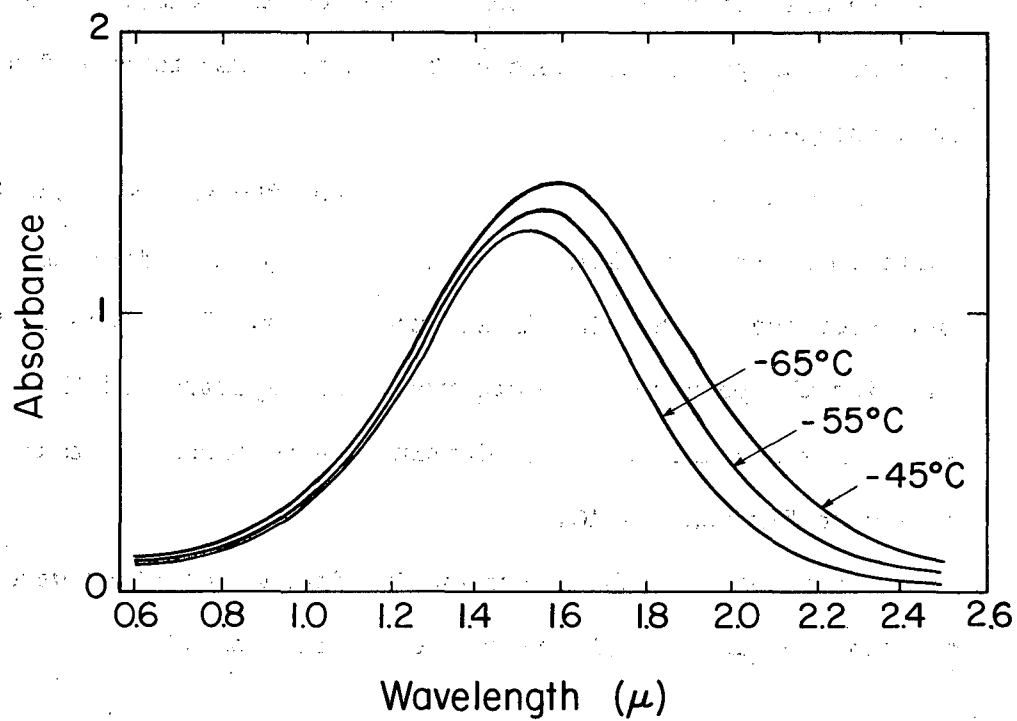
concentration (moles/liter)	-65°			-55°			-45°		
	$A_{\max}$	$\lambda_{\max}$	$\nu_{\max}$	$A_{\max}$	$\lambda_{\max}$	$\nu_{\max}$	$A_{\max}$	$\lambda_{\max}$	$\nu_{\max}$
Sodium									
unknown	0.16	15,500	6665	-	-	-	-	-	-
0.00800	0.67	15,250	6555	0.75	15,590	6415	0.82	15,820	6320
0.0105	1.05	15,280	6545	-	-	-	1.21	15,900	6290
0.0118	1.09	15,320	6525	1.20	15,620	6400	1.32	15,920	6280
0.0133	1.30	15,370	6505	1.39	15,670	6380	1.51	16,000	6250
0.0229	2.29	15,380	6500	2.47	15,780	6335	-	-	-
0.0295	2.85	15,430	6480	3.09	15,730	6355	3.44	16,100	6210
0.00591*	0.66	15,000	6665	0.71	15,300	6535	-	-	-
0.0203*	2.23	14,750	6780	2.46	15,120	6615	-	-	-
Potassium									
0.00846	0.78	15,230	6565	0.85	15,550	6430	0.94	15,800	6330
0.0194	1.86	15,370	6505	2.03	15,800	6330	2.22	16,090	6215
Lithium									
0.0117	1.02	15,300	6535	1.09	15,630	6400	1.18	15,910	6285
0.0325	3.08	15,440	6475	3.50	15,870	6300	-	-	-
Cesium									
0.00483	0.42	15,080	6630	0.44	15,340	6515	0.48	15,560	6425
0.0101	0.92	15,350	6515	1.00	15,690	6375	1.11	15,970	6265
Calcium									
0.00298	0.48	14,930	6700	0.50	15,250	6555	0.56	15,630	6400
0.00739	1.06	14,980	6675	1.14	15,330	6525	1.26	15,725	6360
0.0194	2.01	14,990	6670	2.19	15,410	6490	2.60	15,750	6350

* Sodium iodide added. See Table VI for concentrations



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Fig. 11. Peak position as a function of maximum absorbance.



MU-25972

Fig. 12. Temperature dependence of the spectrum.

Addition of Sodium Iodide

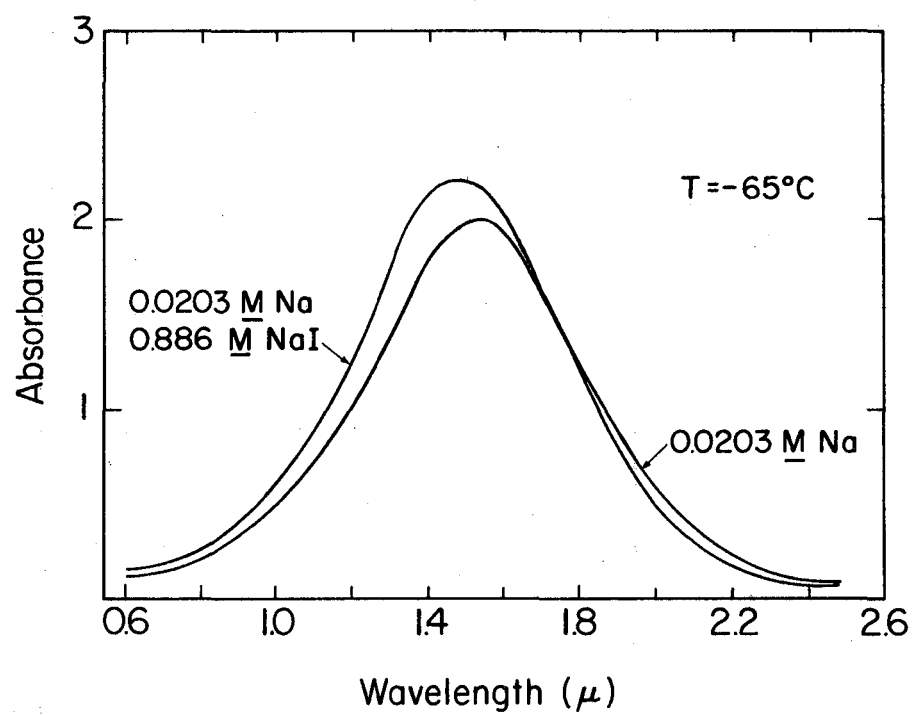
With the exception of solution No. 3 (Table VI), sodium solutions containing sodium iodide did not show any excessive decomposition during the several hours required for a run. In solutions Nos. 1 and 4, some hydrogen was evolved shortly after the solutions were prepared, presumably because of residual water in the sodium iodide. However, this hydrogen was pumped off before the spectrum was taken and should be of no consequence.

The addition of sodium iodide causes the entire absorption band to shift to shorter wavelengths with a corresponding increase in the maximum absorbance. This is illustrated in Fig. 13 for one of the two runs in which the peak could be observed. The spectrum of the 0.0203 M sodium solution was constructed by plotting the absorbancies taken from the curves in Figures 4 - 10.

The volumes of the sodium-sodium iodide solutions were calculated by using the density of sodium iodide solutions.²⁰

Table VI. Absorbancies (A) and extinction coefficients (ϵ) of sodium - sodium iodide solutions.

λ	Solution No.							
	1 ^a		2 ^a		3 ^a		4 ^a	
	A	ϵ	A	ϵ	A	ϵ	A	ϵ
<u>T = -65°</u>								
7500 A	0.07	5500	0.20	4660	0.46	3950	0.57+.05	3570-4250
10000	0.17	13400	0.57	13100	1.46	12500	1.73	11900
13000	0.49	38700	1.73	39800	-	-	-	-
15250	0.65	51400	2.19	50400	-	-	-	-
18000	0.34	26900	1.16	26700	3.22	27600	3.47	23800
21000	0.08	6300	0.27	6210	0.84	7210	1.05	7210
24000	0.03	2400	0.07	1610	0.26	2230	0.40	2740
<u>T = -55°</u>								
15500 A	0.70	55400	2.44	56100	-	-	-	-
18000	0.45	35600	1.52	35000	-	-	-	-
21000	0.14	11100	0.46	10600	1.27	10900	-	-
24000	0.05	3900	0.13	3000	0.42	3600	-	-
<u>T = -45°</u>								
15750 A	0.75	59300	-	-	-	-	-	-
18000	0.54	42700	-	-	-	-	-	-
21000	0.19	15000	-	-	1.61	13800	-	-
24000	0.06	4700	-	-	0.52	4470	-	-
^a Solution No. Sodium concentration Sodium iodide concentration								
(moles/liter) (moles/liter)								
1	0.00591-0.00625 (after vol. corr. $\approx$ 0.05 ml)					0.446		
2	0.0203 -0.0212					0.886		
3	0.0544 -0.0790 (after vol. corr. $\approx$ 0.05 ml)					1.49		
4	0.0671 -0.0681					0.923		



MU-25973

Fig. 13. Effect of sodium iodide on the spectrum.

IV. DISCUSSION

Both the electron-cavity model and the monomer-dimer model have been used to explain some of the physical properties of metal-ammonia solutions. Either model accounts quite satisfactorily for the magnetic susceptibility data. With regard to some of the other physical properties such as conductivity and chemical shift (as determined by nuclear magnetic resonance), the latter model is in better accord with the data.

1. Evers and Frank have calculated the conductances of sodium solutions,²¹ using the equilibria given by the monomer-dimer model, namely



They find excellent agreement with the experimental values obtained by Kraus.² To our knowledge, no attempt has been made to explain the large decrease in equivalent conductance on the basis of the electron-cavity model. It is not apparent why two electrons trapped in a single cavity should be less conducting than single electrons in cavities. The association of metal ions and electrons appears more plausible to account for the observed conductivity.

2. The results of nuclear magnetic resonance studies^{22,23} also lend support to the monomer model. The data are limited to concentrations greater than 0.04 M and it is found that the density of unpaired electrons on the sodium nuclei is somewhat less than 1% of that expected for isolated sodium atoms. This result, coupled with the large shift for nitrogen, is consistent with the picture of electrons in expanded orbitals on the oriented ammonia molecules. The cavity model cannot account for the observed sodium shifts.

Some recent spectroscopic studies on alkali metal-ammonia solutions have been influential in drawing further support for the monomer model.

1. Symons et al. reported that the spectrum of a sodium solution (5×10^{-4} M) containing sodium iodide (0.1 M) showed the appearance of shoulders at 8000 Å and 6700 Å, the former being more pronounced.²⁴ If equilibria (1) and (4) are correct, the effect of the common ion would be to form more M and M_2 , and these shoulders were accordingly attributed to these species.

2. Douthit and Dye made a quantitative study of the absorption spectra of sodium and potassium in the 10^{-3} M range.²⁵ They found that sodium followed Beer's Law up to 0.004 M but potassium showed a negative deviation. The latter effect was attributed to the removal of solvated electrons with corresponding monomer or dimer formation. Although no new bands were observed for these species, it was argued that the dependence of the spectra on the particular metal is consistent with the monomer model and inconsistent with the cavity model.

We have shown in the preceding section that, with the exception of the deviations that occur at long wavelengths, Beer's Law is obeyed for all the alkali metals at concentrations considerably higher than those studies by Douthit and Dye. In addition, we observed no new bands in sodium-sodium iodide solutions as reported by Symons et al. The insensitivity of the spectra to the concentrations of the solutions and to the particular metal used is strong evidence that neither the monomer-dimer model nor the electron-cavity model is correct. Since the absorption in very dilute solutions is presumably due to a hydrogenlike $1s \rightarrow 2p$ transition of a single electron in a cavity, one would expect a significant change in the spectrum if two electrons were trapped in one cavity or if

the electron were removed from the cavity to an expanded orbital of the metal ion.

The logical conclusion to be drawn is that the electron cavity is retained in all alkali metal-ammonia solutions. As the concentration is increased, metal ions and electrons associate to form ion pairs and, as the concentration is further increased, a quadrupolar ionic assembly consisting of two electron cavities and two solvated metal ions is formed.²⁶ These associated species account for the conductivity decrease and, since their formation may be represented by Equilibria (1) and (4), the quantitative calculations by Evers and Frank are just as applicable to these ion pairs and quadruplets as they are to the monomers and dimers of Alder et al. Our model also predicts the small chemical shift for sodium and the large shift observed for nitrogen.

There is another line of evidence which supports the contention that electron cavities remain intact over a wide concentration range. The apparent molar volume of sodium in ammonia²⁷ at 0° changes from 56.3 to 58.6 ml/mole from 0.0093 to 0.34 M. For lithium, the apparent molar volume is practically constant at about 50 ml/mole from 0.02 to 0.99 M. These data are quite consistent with our model but somewhat fortuitous on the basis of the other two models.

The necessity of accounting for the pairing of electron spins, in terms of equilibria such as (2), (3), or (4) had been somewhat of an obstacle so far as correlating the magnetic susceptibilities and spectral data is concerned. The fact that Jolly found Beer's Law to be strictly obeyed at the short-wavelength tail for sodium solutions from 0.001 to 0.1 M¹¹ indicated that the nature of the absorbing species is independent of concentration. These results seemed completely incompatible with

the existing susceptibility measurements, for we (and apparently others) had assumed that the latter work precluded the retention of cavities containing single electrons. Furthermore, it seemed unlikely that the energy levels of paired and unpaired electrons could be so similar as to have practically no effect on the absorption spectra. However, the results of this work required us to re-examine these concepts -- which were never theoretically justified, and which, perhaps, have too strongly influenced the formulation of a satisfactory model for these solutions.

It is not unreasonable that the wave functions of the electrons in the quadruplet, M_2 , overlap significantly and that the energy of the paired singlet state is lower than that of the unpaired triplet state by more than kT . From Fig. 11 we see that the position of the maximum shifts about 600 cm^{-1} ($\approx 4kT$) from the dilute paramagnetic solutions to the more concentrated diamagnetic solutions. When one considers the extreme broadness of the absorption band, it is not surprising that two maxima separated by only 600 cm^{-1} are not resolved. Also, there may be an intermediate band characteristic of ion pairs.

It may be argued that the absorption of the monomer and dimer of Alder et al. would not be expected to be very different from each other; however, we point out that either of these species should show a different absorption than a solvated electron. That the solvated electron and diamagnetic species show practically the same absorption band and extinction coefficient is our strongest argument in favor of the retention of electron cavities.

Temperature Dependence

Previous workers report a somewhat smaller temperature dependence of the peak position than was found by us. Blades and Hodgins report a value of $-9.1 \text{ cm}^{-1} \text{ deg}^{-1}$ for potassium in ammonia from -42° to -78° .⁵ Douthit and Dye report -9.7 and $-11.5 \text{ cm}^{-1} \text{ deg}^{-1}$ for sodium and potassium respectively from -37° to -65° .²⁴ These measurements were of much more dilute solutions than ours.

Jortner has calculated the energies of the 1s and 2p levels of an electron in a spherical cavity and has given a plausible explanation of the shift based upon the temperature dependence of the dielectric constant and cavity radius.²⁸ In addition, he finds $E_{2p} - E_{1s} \approx 0.8 \text{ ev}$ ($\approx 1.5\mu$), in good agreement with experiment. The similarity of the temperature dependence in paramagnetic and diamagnetic solutions is further indication that the nature of the absorbing species is not very sensitive to concentration changes.

Douthit and Dye found that the low-wavelength side of the band is also displaced toward higher wavelengths with increasing temperatures. However, they determined the displacements on the sides of the band from A/A_{max} rather than from the measured absorbance; i.e. because of an unknown amount of decomposition, they made the assumption that the maximum absorbance is the same for two different temperatures. It can be seen from Fig. 12 that such an assumption would produce a similar effect with our data.

Effect of Sodium Iodide

On the basis of the proposed model the addition of excess sodium ions would favor the formation of ion pairs and quadrupoles at the expense of free electrons. Thus, one might expect the absorption band to shift slightly to longer wavelengths, as when the concentration of a pure metal solution is increased. The shift to shorter wavelengths indicates that the energy-level separation between the electronic 1s and 2p states is increased by the addition of sodium iodide. Such a situation could be brought about by an increase in the potential field around the cavity due to the increased number of positive charges which would then be oriented around the electron cavities. This increased polarization would result in a deepening of the potential well of the electron, whose transition to the next higher level would now require a somewhat higher energy.

It is possible that the concentration of ion pairs and quadrupoles does in fact increase with sodium ion addition but that the small shift expected is overshadowed by the effect discussed above. On the other hand, species such as Na_2^+ may be forming. Since the latter species is paramagnetic and Na_2 is diamagnetic, it would be of interest to examine the electron spin resonance of sodium solutions with and without the added salt.

Deviations from Beer's Law

The increase of the extinction coefficients at the long-wavelength tail of the absorption band suggests that one or more new species are being formed. It is likely that these species may be higher polymers such

as M_3 , M_4 , ..., M_n , whose formation would be expected at higher concentrations. The sharp rise of the equivalent conductance above about 0.05 M indicates that the concentration of such "clusters" is becoming high enough to impart metallic properties to the solutions.

If we assume that the absorption is due to the contribution of two unresolved bands, a graphical method can be used to test this assumption. From the equation

$$\epsilon c l = (\epsilon_a c_a + \epsilon_b c_b) l$$

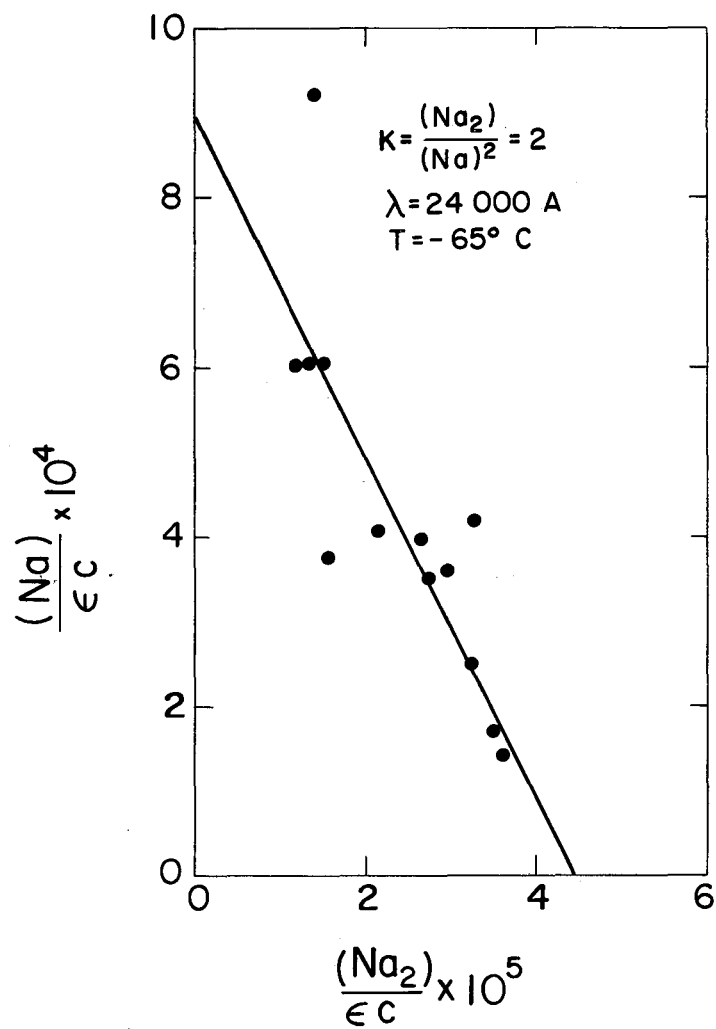
one obtains

$$\frac{c_a}{\epsilon c} = \frac{1}{\epsilon_a} - \frac{\epsilon_b}{\epsilon_a} \cdot \frac{c_b}{\epsilon c},$$

where ϵ is the measured extinction coefficient, c is the total metal concentration, ϵ_a and ϵ_b are the extinction coefficients for the low- and high-concentration species, respectively, and c_a and c_b are the concentrations of these species. If one knew the true reaction and its equilibrium constant, one would expect a plot of $\frac{c_a}{\epsilon c}$ vs $\frac{c_b}{\epsilon c}$, for a given wavelength, to yield a straight line of negative slope, the intercepts determining the values of ϵ_a and ϵ_b .

To test a particular reaction, an equilibrium constant was assumed and values for c_a and c_b were calculated by a series of approximations for each sodium concentration. Several equilibrium constants were tried until the best straight line was obtained.

The results of several plots are shown in Figs. 14 - 17. As can be seen, reasonable plots can be obtained for several equilibria, and the correct one cannot be chosen solely on the basis of this graphical method. It is interesting to point out, however, that although one obtains a



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Fig. 14. Trial plot for the reaction $2Na = Na_2$ (24000 Å)

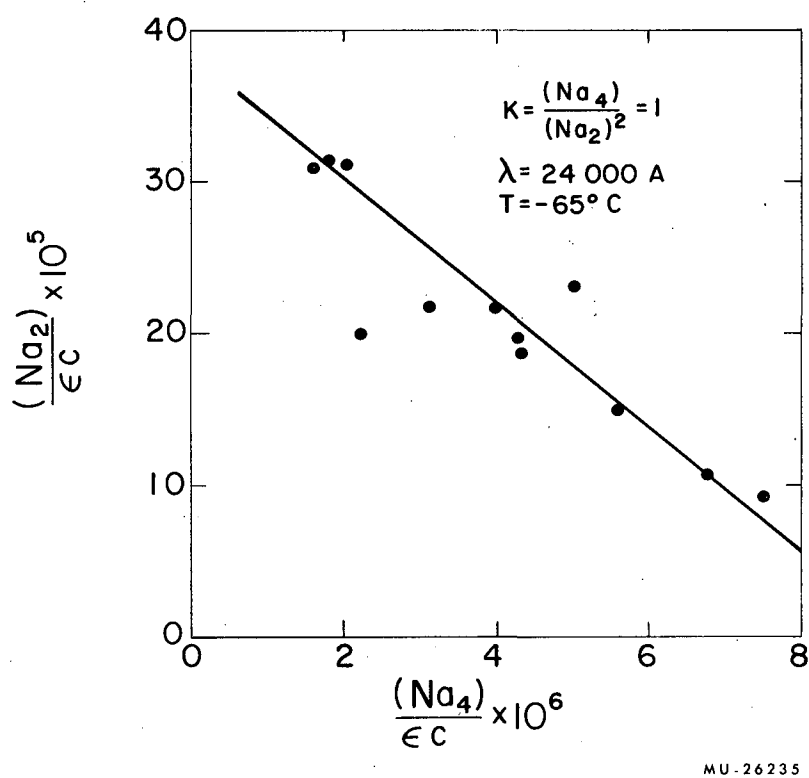
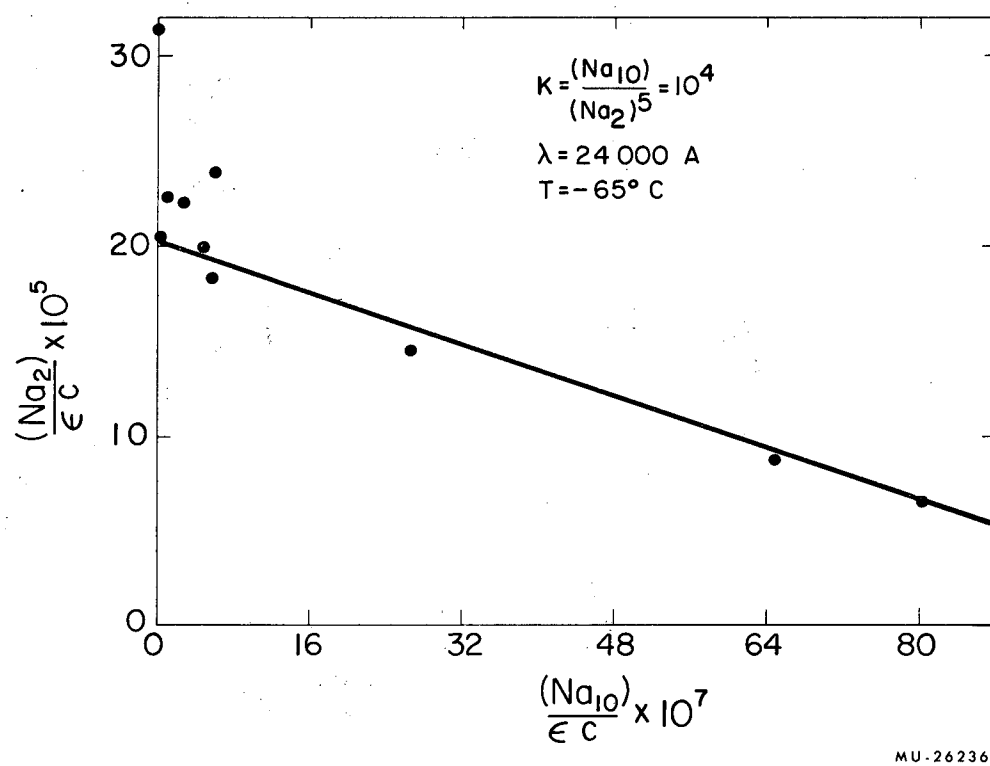
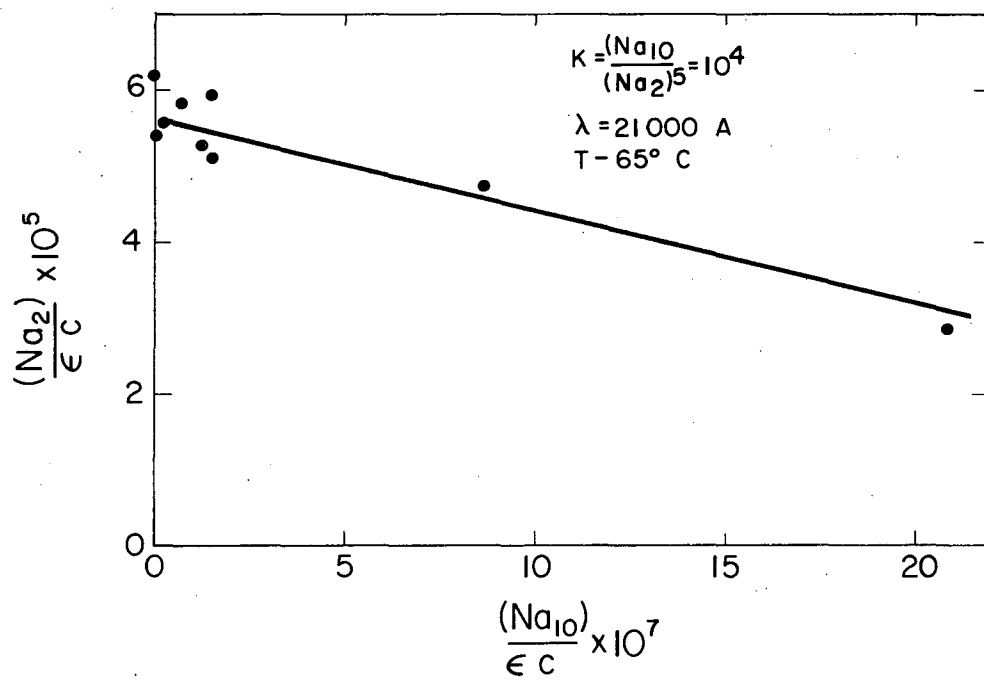


Fig. 15. Trial plot for the reaction $2Na_2 = Na_4$ (24000 A)



MU-26236

Fig. 16. Trial plot for the reaction $5Na_2 = Na_{10}$ (24000 A)



MU-26237

Fig. 17. Trial plot for the reaction $5Na_2 = Na_{10}$ (21000 A)

straight-line plot for the reaction $2\text{Na} = \text{Na}_2$ (which in this method is indistinguishable from $2e^- = e_2^-$), the values used for c_{Na} and c_{Na_2} are inconsistent with magnetic data; i.e., at 0.01 M all the metal is in the Na (paramagnetic) form, whereas susceptibility data show that the spins are about half paired at this concentration.

We suggest that polymers are forming at high concentrations, and the plot obtained for the reaction $5\text{Na}_2 = \text{Na}_{10}$ is at least consistent with this interpretation. The value of K has no real meaning, as there are probably many equilibria operating and many different polymers being formed. There must be some Na present at the lower concentration (for reasons just given), and the species on the left side of the above reaction is only an approximation of the true situation, as also is the species on the right side.

The values for ϵ_{Na_2} and $\epsilon_{\text{Na}_{10}}$ obtained from the intercepts are as follows:

$$\begin{array}{ll} 24,000 \text{ \AA} & \epsilon_{\text{Na}_2} = 5.0 \times 10^3, \\ & \epsilon_{\text{Na}_{10}} = 8.3 \times 10^4; \\ 21,000 \text{ \AA} & \epsilon_{\text{Na}_2} = 1.8 \times 10^4, \\ & \epsilon_{\text{Na}_{10}} = 2.1 \times 10^5. \end{array}$$

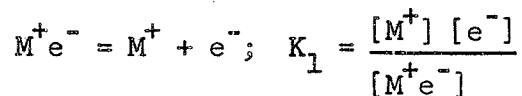
The extinction coefficients per sodium atom are thus several times as great for Na_{10} as for Na_2 in this wavelength region.

Estimation of Equilibrium Constants Based on the Proposed Model

It is possible to make a rough estimate of the equilibrium constants for ion-pair and quadrupole formation based on a simple electrostatic picture. We felt that it would be interesting to compare the results of

such an empirical calculation with the equilibrium constants obtained from various experimental methods.

For the dissociation of the ion pair,



we are interested in the free energy change when the separation of the ions is increased from a distance r to infinity. The work done in this process is given by²⁹

$$\Delta F = \int_r^\infty \frac{e^2}{\epsilon r^2} dr = \frac{e^2}{\epsilon r} \text{ ergs/molecule,}$$

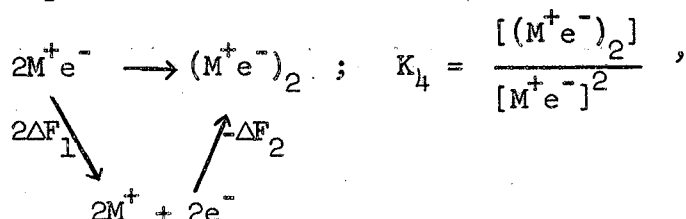
where e is the electronic charge, ϵ is the dielectric constant, and r is the ionic separation in the ion pair. For a calculation of this order of magnitude we take $\epsilon = 22$, the bulk dielectric constant for ammonia at -34° .

The value for r is estimated as follows: The electron cavity radius is about $3.3 \text{ \AA}$,²⁶ and the H-N distance is about $1 \text{ \AA}$. Alder et al. estimate the distance from the sodium to the nitrogen of a coordinated ammonia molecule to be about $2.2 \text{ \AA}$.¹⁶ The H-N distance between two hydrogen-bonded ammonia molecules is about $2.4 \text{ \AA}$ in the pure liquid. In the ion pair this distance is probably somewhat shortened. A maximum value for r is thus about $10 \text{ \AA}$. Table VII lists the values of the dissociation constant calculated for various values of r , along with some values obtained by others from experimental data.

Table VII. Ion pair dissociation constants.

	<u>r</u> <u>(A)</u>	<u>k₁</u> <u>(x 10³)</u>
<u>Calculated(this work)</u>		
	7.0	11.0
	8.0	19.5
	9.0	30.2
	10.0	42.7
<u>Derived from experimental data</u>		
Conductance, Na in NH ₃ (-34°)(Ref. 21)		7.23
Transport, Na in NH ₃ (-37°) (Ref. 30)		9.2
Activity, Na in NH ₃ (-37°) (Ref. 31)		9.6
Magnetic Susceptibility } (-34°) (Ref. 17)		30
K in NH ₃ } (-34°) (Ref. 32)		7.9

The free energy change for the formation of quadrupole, M_2 , was calculated in two steps:



where ΔF_1 is the free energy change previously calculated for ion-pair dissociation and ΔF_2 is evaluated from the expression

$$\Delta F_2 = \frac{e^2}{\epsilon} \left(4 \cdot \frac{1}{r} - \frac{1}{r_e} - \frac{1}{r_m} \right) ,$$

where r is the distance between metal ions and electrons, r_e is the electron-electron distance, and r_m is the distance between metal ions. In the presumed diamondlike structure, all the metal-electron distances are identical. For a given r , a value of r_e was assumed from which r_m could be calculated. These results are given in Table VIII.

It is seen that the calculated values are in fairly good agreement with the experimental values, especially considering the crudeness of the calculation. These results support the argument that the physical properties of alkali metal-ammonia solutions are consistent with simple ion-pair and quadrupole formation. In this connection it may be noted that the dissociation constants³³ for several alkali metal halides in liquid ammonia are also of the same magnitude as the values listed in Table VII, indicating that dilute metal solutions follow normal electrolyte behavior.

Some Comments on the Calcium Spectra

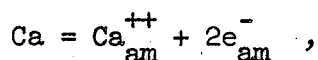
We have pointed out that the calcium data cannot be considered nearly as reliable as the data obtained for the alkali metals. Also, the

Table VIII. Quadrupole formation constants

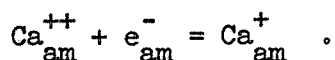
	r (A)	r_e (A)	r_m (A)	K_4 —
Calculated (this work)	6.6	8.9	9.8	20.9
		10.0	8.6	19.5
		12.2	5.0	2.0
	8.0	10.1	12.4	9.0
		11.0	11.6	10.0
		13.0	9.3	7.9
	10.0	12.0	15.8	5.6
		14.0	14.6	6.6
		16.0	12.0	5.5
<u>Derived from experimental data</u>				
Conductance, Na in NH_3 (-34°) (Ref. 21)				27.0
Transport, Na in NH_3 (-37°) (Ref. 30)				18.5
Activity, Na in NH_3 (-37°) (Ref. 31)				23.0
Magnetic Susceptibility, $\left\{ \begin{array}{l} (-34^\circ) \text{ (Ref. 17)} \\ (-34^\circ) \text{ (Ref. 32)} \end{array} \right.$				98
K in NH_3				99

negative deviation is determined essentially by one point: that of the highest concentration. However, we believe that the trend observed permits some qualitative statements to be made regarding the possible structure of calcium solutions.

It is likely that in very dilute solutions the calcium extinction coefficients are twice as high as those of the alkali metals although, for the lowest concentration reported here, this ratio is somewhat less than 2. Thus we may write



with the electrons existing in cavities in the solvent. If, as the data indicate, the extinction coefficients do decrease with increasing concentration, this is presumably due to the removal of electrons from cavities, and suggests the reaction.



When all the calcium is in the Ca^{+} form, the situation is analogous to an alkali metal solution, since in our model the undissociated electron would not contribute to the observed absorption band. The similarity of the extinction coefficients near 0.02 M tempts one to draw this conclusion although, in view of the experimental uncertainties, there must be some doubt remaining.

Solutions of barium and strontium in liquid ammonia may be more suitable for spectroscopy, and such experiments should yield some very interesting results.

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