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# Absorption Spectra of Metal–Ammonia Solutions

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The absorption spectra of solutions of lithium, sodium, potassium, and cesium in liquid ammonia have been measured up to 0.03 *M* at the absorption maximum and up to 0.2 *M* at other wave lengths. The spectra of calcium solutions have been measured up to 0.02 *M*. The alkali metal spectra are practically identical and follow Beer's law from 3500 to 18,000 Å. for all concentrations investigated. At longer wave lengths, the extinction coefficients increase with increasing concentration beyond ~0.03 *M*. A revised model for alkali metal–ammonia solutions is proposed to explain the spectra. Calcium gave abnormally low extinction coefficients which are explained in terms of colorless $Ca_2^{+2}$ ions.

## Introduction

The study of the species which exist in solutions of metals in non-aqueous solvents has occupied the attention of many investigators in the past half century. The most stable metal solutions are those in liquid ammonia; consequently, such solutions have received the most attention.[2] It is well established that, in extremely dilute solutions of alkali metals in liquid ammonia, the metal is completely dissociated into ammoniated metal ions and ammoniated electrons. Each electron is believed to exist in a large cavity in the solvent and to be stabilized by the orientation of the ammonia dipoles on the periphery of the cavity. The decrease in the equivalent electrical conductance of these solutions as the concentration is increased to about 0.05 *M* indicates that ion pairing or assembly into larger aggregates takes place. The decrease of the molar paramagnetic susceptibility of the solutions with increasing concentration indicates that the ammoniated electrons associate to form species containing electron pairs. These effects have been explained in several different ways.

Long before the paramagnetic susceptibility data became available, Kraus[3] proposed that electrons and metal ions combine to form atoms

$$M^+ + e^-_{am} = M \qquad (1)$$

Of course this equilibrium alone does not account for the susceptibility data.

Huster[4] suggested that electrons and sodium ions combine to form diatomic molecules.

$$2Na^+ + 2e^-_{am} = Na_2 \qquad (2)$$

Freed and Sugarman[5] and Ogg[6] have proposed that the ammoniated electrons combine to form ammoniated electron pairs.

$$2e^-_{am} = e_2{}^{2-}{}_{am} \qquad (3)$$

Becker, Lindquist, and Alder[7] proposed that both the equilibrium proposed by Kraus[3] and that proposed by Huster[4] are important.

$$M^+ + e^-_{am} = M \qquad (1)$$

$$2M = M_2 \qquad (4)$$

This proposal is widely accepted inasmuch as a variety of physical measurements (conductance, transport, activity, and magnetic susceptibility) yield reasonably concordant equilibrium constants for reactions 1 and 4.[8]

We assumed that each of the species ($e^-_{am}$, M, and $M_2$) would have a unique absorption spectrum; therefore, we quantitatively studied absorption spectra as a function of concentration with the hope of using our data to evaluate the equilibrium constants. Douthit and Dye[9] have measured the absorption spectra of solutions up to 0.004 *M* for sodium and up to 0.01 *M* for potassium. With somewhat greater accuracy we have measured the spectra of lithium, sodium, potassium, and cesium up to 0.03 *M* at the absorption maximum and up to 0.2 *M* at other wave lengths. The spectra of calcium solutions were measured up to 0.02 *M*.

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[1] Taken from the Ph.D. Thesis of M. Gold, University of California, Berkeley, 1962.

[2] W. L. Jolly, *Progr. Inorg. Chem.*, **1**, 235 (1959).

[3] C. A. Kraus, *J. Am. Chem. Soc.*, **30**, 1323 (1908).

[4] E. Huster, *Ann. Physik*, **33**, 477 (1938).

[5] S. Freed and N. Sugarman, *J. Chem. Phys.*, **11**, 354 (1943).

[6] R. A. Ogg, *J. Am. Chem. Soc.*, **68**, 155 (1946); *J. Chem. Phys.*, **14**, 114, 295 (1946).

[7] E. Becker, R. H. Lindquist, and B. J. Alder, *ibid.*, **25**, 971 (1956).

[8] E. C. Evers, *J. Chem. Educ.*, **38**, 590 (1961).

[9] R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, **82**, 4472 (1960).

## Experimental[10]

We have designed and used two types of apparatus for measuring the absorption spectra of these solutions. Since such apparatus are of potential value for studying kinetics and equilibria in solutions of metals and other colored species in liquid ammonia (and conceivably for similar studies in other low-boiling solvents), we describe here the apparatus and certain unique aspects of their operation.

The following two facts were of particular concern in the design of the apparatus. (1) Metal–ammonia solutions have very large exinction coefficients in the infrared. Therefore a very short light path is necessary if one wishes to investigate any but the very dilute solutions. A short light path necessarily introduces a problem of mixing, and a procedure must be used which ensures homogeneity of the sample. (2) An alkali metal reacts slowly with ammonia to form the corresponding alkali metal amide and hydrogen. This reaction is catalyzed by certain materials such as heavy metals and rust. Because the rate of the 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.

**Apparatus I.**—This relatively simple apparatus (see Fig. 1) was made entirely of Pyrex glass except for a wooden support which was cemented with plaster of Paris to the bottom. The support was shaped to fit between the two metal rods in a Cary Model 14 spectrophotometer sample compartment. The optical cell had a light path of about 0.5 mm. and was useful mainly for dilute solutions. The cell was situated in an evacuated chamber for insulation. Two rotating side arms were attached to the upper part of the apparatus with standard taper joints. A length of 6 mm. tubing, closed at the bottom, dipped into the solution and served as a well for a copper–constantan thermocouple. The outlet near the top was for evacuation of the apparatus.

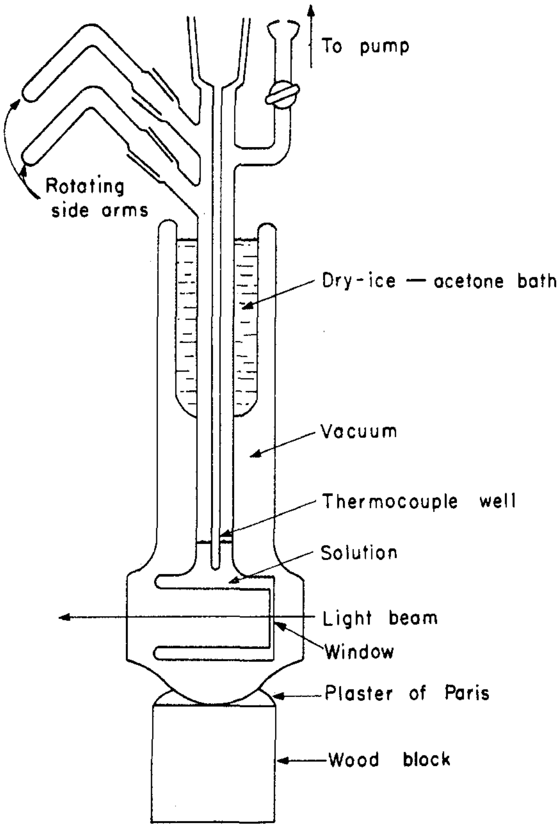

Fig. 1.—Apparatus I for measuring spectra of extremely dilute solutions.

**Operation of Apparatus I.**—Excess ammonium chloride (relative to sodium) was placed in one side arm. A small piece of sodium was cut under oil, rinsed in benzene, and quickly placed in the other side arm. The whole apparatus then was evacuated. The annular space between the vacuum jacket and central tube was filled with Dry Ice and acetone; then about 40 ml. of ammonia, previously dried over sodium, was distilled into the apparatus. The ammonia ran down the walls, cooling and filling the optical cell. The refluxing ammonia in the cell reached a steady-state temperature of −70°. The apparatus was placed in the sample compartment of the spectrophotometer and the spectrum of the solvent recorded. During the recording, a black cloth was used to cover the apparatus so that no outside light could reach the optics. The sodium then was added by rotating the appropriate side arm. Dissolution and mixing took place rapidly because the solvent was refluxing. When the optical density reached a constant value at a given wave length (about 5 min.), the solution was presumed to be homogeneous and its spectrum was recorded.

**Apparatus II.**—The optical cell had a light path of about 0.02 mm. and was used for solutions of relatively high concentration. Because efficient mixing is hard to achieve in a cell with such a short light path, the solution was prepared in a make-up cell and then transferred to the optical cell. Two rotating side arms were attached with standard taper joints to the top of the vessel (see Fig. 2). Except for the quartz optical cell, the vessel was made of Pyrex.

An insulated cold box and cooling arrangement made up the rest of the apparatus. The cold box consisted of an inner box and an outer box, separated by "Styrofoam" insulation. The outer box was designed to fit the sample compartment of the Cary spectrophotometer. The lengths, widths, and heights of the inner and outer boxes were $5^1/_8 \times 2^1/_2 \times 5^1/_8$ and $8^1/_2 \times 5 \times 7^3/_8$ in., respectively. Part of the front wall of the sample compartment was removed and a slot was cut from the bottom of the box so that the box rested on the cylindrical rods in the compartment. 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 pointing at the optical cell and one at the make-up cell of the vessel. One tube

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[10] For more detailed experimental data, the reader is referred to the Ph.D. Thesis of Marvin Gold, UCRL 10062, 1962.

served as an entry for cold nitrogen, the other as an exit. Several pieces of Styrofoam, placed around a square piece of cork cemented to the vessel, formed an insulating cover for the box.

Dry H.P. nitrogen was passed through a copper coil immersed in a large dewar flask containing Dry Ice and acetone. The nitrogen flow was adjusted with the aid of a flow meter to maintain temperatures of −45, −55, or −65° in the cold box. Temperature was measured with a Rubicon portable potentiometer using a copper-constantan thermocouple taped to the side of the optical cell.

**Operation of Apparatus II.**—The vessel was connected to the vacuum line in a horizontal position. A pellet of ammonium chloride was placed in side arm (A) and a piece of alkali metal was placed in the long tube extending from the make-up cell. (When desired, other materials were added to the solution from the side arm (B).) The tube was sealed off near the end and the vessel evacuated and flamed below the cork. The sodium then was distilled to point (C) and the tube sealed off at (D). Since lithium and calcium cannot be distilled in glassware, clean pieces of these metals were placed directly in the make-up cell. The make-up cell was immersed in liquid nitrogen and about 3 ml. of dry ammonia was distilled in. The liquid nitrogen then was replaced by a Dry Ice–acetone bath and the ammonia allowed to melt. The sodium was dissolved by shaking ammonia into the tube containing the sodium. The vessel then was put in the cold box with the make-up cell still pointing down and the cover pieces were put into place. The cold nitrogen was directed at the make-up cell and the box was cooled to about −60°. The flow then was directed at the optical cell for 10–15 sec. so that it would not be much warmer than the make-up cell. 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 spectrophotometer sample compartment (see Fig. 3). The flow again was 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 was maintained until the optical density remained constant at a given wave length. The spectrum then was recorded and a similar procedure was followed 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.

By using a fogged photographic plate as a filter in the reference beam, it was possible to measure optical densities as high as 3.4. This permitted observation of the absorption peak for sodium solutions as concentrated as 0.035 *M*.

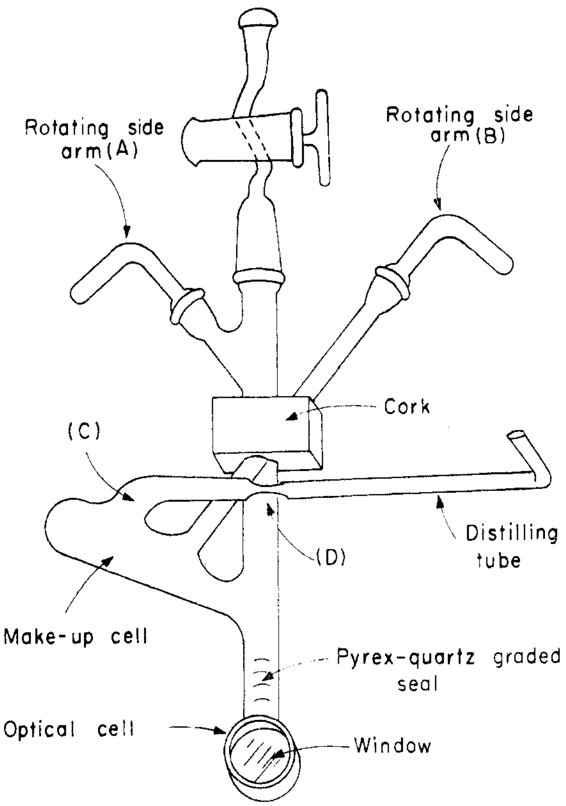

Fig. 2.—Apparatus II for measuring spectra of relatively concentrated metal solutions.

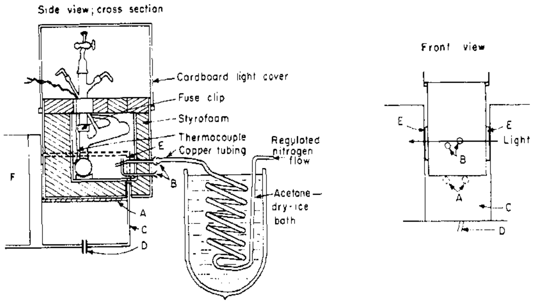

Fig. 3.—Apparatus associated with Apparatus II. The insulated cold box and its position in the spectrophotometer cell compartment are shown.

**Concentration Determination.**—Identical procedures were used for both apparatus; however, after the spectra were recorded with Apparatus II, the vessel was removed from the cold box and the optical cell immediately immersed in a Dry Ice–acetone bath. The amount of sodium that had reacted with ammonia during the run was determined by pumping off the hydrogen with a Toepler pump and measuring its pressure in a calibrated gas buret. Addition of ammonium chloride resulted in the reaction

$$NH_4^+ + Na \longrightarrow NH_3 + Na^+ + {}^1/_2H_2$$

The total hydrogen evolved was pumped into the gas buret and its pressure measured. Two liquid nitrogen traps between the solution and Toepler pump prevented ammonia from reaching the gas buret. The ammonia then was absorbed in a flask containing 80% sulfuric acid, the flask being weighed before and after the absorption of ammonia.

The density of pure liquid ammonia[11] at −65° was used to calculate the volumes of the solutions. The measured absorbancies at −55 and −45° then were cor-

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[11] C. S. Cragoe and D. R. Harper, Natl. Bur. Std. Sci. Paper No. 420, Government Printing Office, Washington, D. C., 1921 p. 287.

rected for the density differences between these temperatures and −65°.

The concentration of sodium was calculated on the basis of the hydrogen evolved upon addition of ammonium chloride. Any hydrogen found in the cell prior to the addition of ammonium chloride was excluded from the calculation. This hydrogen usually amounted to less than 2% of the total hydrogen and was attributed to decomposition during the make-up and transfer of the solution.

During the process of dissolving metals that had been distilled, some solution occasionally was trapped in the tip of the sealed distilling tube (D in Fig. 2) and did not run into the absorption cell. However, this ammonia could not be excluded from the ammonia analysis, and therefore, its estimated volume (usually less than 3% of the total ammonia volume) was subtracted from the total measured volume.

**Miscellany.**—The optical cell was made in the glass shop of this Laboratory. During its construction a piece of 1 mil copper foil was used to separate the two quartz windows which were fused to the cylindrical walls of the cell. The fact that the windows were not exactly parallel and that a portion of the light beam was scattered by the sides of the cell caused the effective light path to vary with concentration. Therefore, we calibrated the cell at several concentrations with alkaline potassium chromate solutions. When optical densities of the 3700 Å. peak were plotted as a function of concentration, the curve showed a negative deviation from Beer's law. The effective light path was found to change by 20% on going from the lowest to the highest observed optical densities. Since chromate ion is known to obey Beer's law, a correction was calculated for each observed optical density and these corrections were applied to the metal–ammonia solution spectra. The infrared source was used for the calibration because the ultraviolet and visible sources do not illuminate the same area of the cell as does the infrared source.

The optical cell was cleaned with hot aqua regia. Rinsing 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.

All mercury in the vacuum line was closed off from the cell while the ammonia was being distilled. To further ensure that no mercury contaminated the solution, some gold foil was placed in the tubing just above the stopcock of the vessel.

Addition of the room-temperature ammonium chloride pellet caused sodium to be splattered onto the walls above the solution. In order to avoid this splattering, the pellet was cooled to the solution temperature with a cold bath immediately before its addition.

Because of 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 persistent shaking. However, when these 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 sign of two phases, did show numerous small dark particles which were barely detectable in the dark blue solution. This phenomenon was not investigated further but its occurrence makes the accuracy of the calcium data subject to some doubt.

Since the absorption peaks are very broad, it was necessary to locate the wave lengths of the maxima by a standardized procedure. Several horizontal lines cutting both sides of the band were drawn at various absorbancies. The midpoints of these lines formed a straight line which was presumed to intersect the absorption curve at the maximum.

The absorption bands of ammonia at 15,300; 19,900; and 22,400 Å. did not seriously interfere with the spectra. In apparatus II, even the most intense of these bands (at 19,900 Å.) contributed less than 0.3 absorbancy unit.

## Results

**Concentration Dependence.**—Apparatus I was used for measuring the spectra of sodium solutions from 3500 Å. to as high a wave length as possible for concentrations 0.002 to 0.08 *M*. In Fig. 4, the absorbancy at 4500 Å. is plotted against the concentration on a log–log plot. The straight line through the points has been drawn with a slope of unity and corresponds to an average extinction coefficient of 634 l. $\text{mole}^{-1}$ $\text{cm.}^{-1}$. The values calculated from the individual measurements deviate from the mean by an average of ±1.8%. Apparatus I could not be used for measuring spectra in the region of the absorption peak (~15,000 Å.) except for extremely dilute solutions. Consequently, most of our spectra were obtained using Apparatus II, with an appreciable loss in precision.

Values of the absorbancies and extinction coefficients at selected wave lengths obtained with Apparatus II at −65, −55, and −45° are presented in Tables I, II, and III, respectively. Plots of absorbancy *vs.* concentration at −65° are presented in Fig. 5, 6, and 7. It will be noted that, from 6000 to about 18,000 Å., sodium obeys Beer's law at all concentrations investigated with an average experimental deviation of ±5%. The other alkali metals closely follow the behavior of sodium although the average deviation from the average sodium value at a given wave length is about ±10%. Our results for potassium are in marked disagreement with those of Douthit and Dye,[9] who found that the extinction coefficient for potassium decreased with increasing concentration. Our results indicate that the spectra of all the alkali metals are practically identical. On the long wave length side of the absorption band the alkali metals show a positive deviation from

Beer's law, as shown in Fig. 7. Unfortunately, the absorption peak could not be observed at concentrations greater than about 0.03 *M* and one cannot know whether or not this deviation is accompanied by a large shift in the wave length of the peak. The spectra show no sign of a new band or shoulder which might be responsible for the increase in the extinction coefficients in this region.

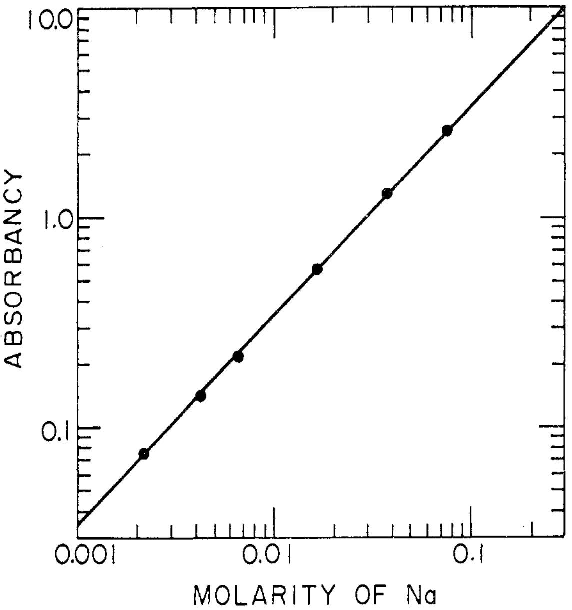

Fig. 4.—Log–log plot of absorbancy at 4500 Å. *vs.* concentration for sodium solutions at −70°.

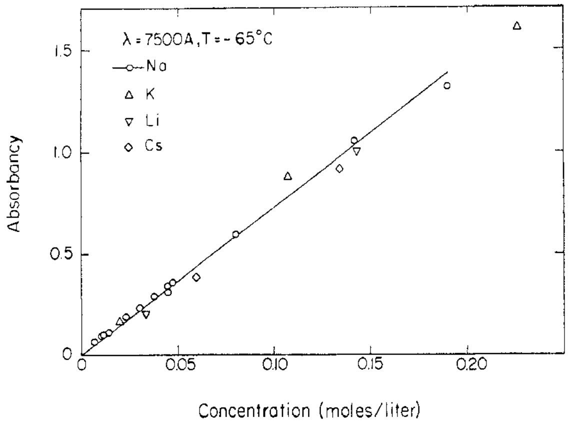

Fig. 5.—Absorbancy at 7500 Å. *vs.* concentration for alkali metals at −65°.

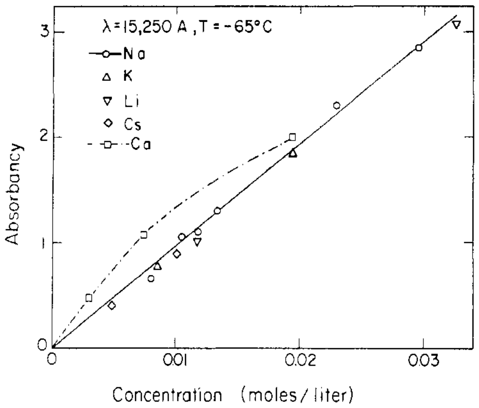

Fig. 6.—Absorbancy at 15,250 Å. *vs.* concentration for alkali metals and calcium at −65°.

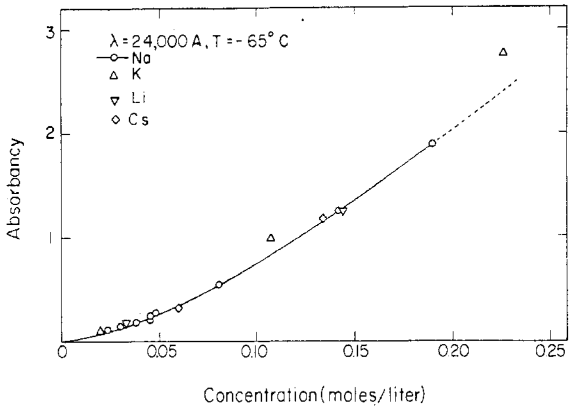

Fig. 7—Absorbancy at 24,000 Å. *vs.* concentration for alkali metals at −65°.

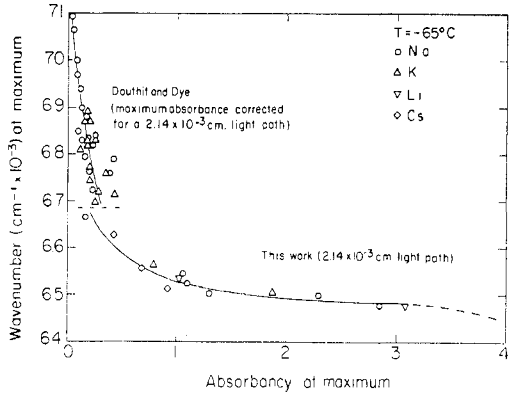

Fig. 8.—Wave number at maximum *vs.* absorbancy at maximum for alkali metals at −65°.

The shift of the peak wave length is very small in the concentration range 0.005–0.03 *M*. These wave length data are given in Table IV. A plot of $\nu_{\max}$ *vs.* $A_{\max}$ is shown in Fig. 8 in which we have included the data of Douthit and Dye for more dilute solutions. It is seen that below about 0.005 *M*, the shift is much more pronounced than it is for higher concentrations and that the two sets of data are in reasonable agreement where they overlap. Because the shift is so small for the solutions studied here, Fig. 6 is changed insignificantly if absorbancy at the maximum is plotted instead of absorbancy at 15,250 Å.

TABLE I

ABSORBANCIES ($A$) AND EXTINCTION COEFFICIENTS ($\epsilon$) AT −65°

| Concn. (moles/l.) | λ = 7560 Å. |  | λ = 10,000 Å. |  | λ = 13,000 Å. |  | λ = 15,250 Å. |  | λ = 18,000 Å. |  | λ = 21,000 Å. |  | λ = 24,000 Å. |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ |
| Sodium |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0.00800 | 0.065 | 3800 | 0.160 | 9350 | 0.50 | 29200 | 0.67 | 39100 | 0.41 | 24000 | 0.110 | 6430 | 0.020 | 1170 |
| .0105 | .085 | 3780 | .240 | 10700 | .76 | 33800 | 1.05 | 46700 | .66 | 29400 | .185 | 8240 | .035 | 1560 |
| .0118 | .090 | 3560 | .250 | 9920 | .78 | 30900 | 1.09 | 43100 | .69 | 27300 | .190 | 7520 | .040 | 1580 |
| .0133 | .105 | 3690 | .280 | 9850 | .91 | 32000 | 1.30 | 45700 | .84 | 29500 | .230 | 8070 | .045 | 1580 |
| .0229 | .185 | 3770 | .55 | 11200 | 1.58 | 32200 | 2.29 | 46700 | 1.50 | 30600 | .455 | 9280 | .115 | 2350 |
| .0295 | .230 | 3640 | .67 | 10600 | 1.88 | 29800 | 2.84 | 45000 | 1.82 | 28800 | .57 | 9010 | .145 | 2300 |
| .0379 | .285 | 3510 | .85 | 10500 | 2.41 | 29700 |  |  | 2.36 | 29100 | .69 | 8500 | .180 | 2200 |
| .0452 | .315 | 3250 | .96 | 9930 | 2.70 | 27900 |  |  | 2.57 | 26600 | .81 | 8370 | .200 | 2070 |
| .0454 | .335 | 3450 | 1.04 | 10700 | 3.07 | 31600 |  |  | 2.86 | 29400 | .91 | 9360 | .245 | 2520 |
| .0476 | .355 | 3480 | 1.09 | 10700 | 3.41 | 33400 |  |  | 3.24 | 31800 | .98 | 9610 | .260 | 2550 |
| .0805 | .59 | 3420 | 1.83 | 10600 |  |  |  |  |  |  | 1.66 | 9640 | .54 | 3130 |
| .142 | 1.05 | 3450 | 3.52 | 11600 |  |  |  |  |  |  | 3.90 | 12800 | 1.25 | 4110 |
| .190 | 1.32 | 3240 |  |  |  |  |  |  |  |  |  |  | 1.89 | 4650 |
| Potassium |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0.00846 | 0.080 | 4410 | 0.195 | 10800 | 0.58 | 32000 | 0.78 | 43100 | 0.49 | 27000 | 0.140 | 7740 | 0.030 | 1660 |
| .0194 | .165 | 3970 | .455 | 11000 | 1.35 | 32500 | 1.86 | 44800 | 1.26 | 30400 | .37 | 8910 | .095 | 2280 |
| .107 | .88 | 3840 | 2.72 | 11900 |  |  |  |  |  |  | 2.79 | 12200 | .99 | 4320 |
| .226 | 1.60 | 3310 |  |  |  |  |  |  |  |  |  |  | 2.76 | 5700 |
| Lithium |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0.0117 | 0.070 | 2790 | 0.230 | 9180 | 0.73 | 29100 | 1.02 | 40700 | 0.66 | 26300 | 0.195 | 7790 | 0.050 | 2000 |
| .0325 | .210 | 3020 | .68 | 9780 | 2.05 | 29500 | 3.07 | 44100 | 2.02 | 29000 | .63 | 9050 | .160 | 2300 |
| .143 | 1.01 | 3300 | 3.51 | 11500 |  |  |  |  |  |  | 4.1–4.2 | 13500 | 1.25 | 4080 |
| Cesium |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0.00483 | 0.030 | 2900 | 0.100 | 9670 | 0.33 | 31900 | 0.420 | 40600 | 0.245 | 23500 | 0.070 | 6770 | 0.020 | 1940 |
| .0101 | .070 | 3230 | .20 | 9260 | .66 | 30500 | .92 | 42600 | .60 | 27700 | .170 | 7860 | .045 | 2080 |
| .0599 | .385 | 3000 | 1.26 | 9830 |  |  |  |  |  |  | 1.25 | 9750 | .330 | 2570 |
| .134 | .92 | 3210 | 2.95 | 10300 |  |  |  |  |  |  |  |  | 1.17 | 4080 |
| Calcium |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0.00298 | 0.04 | 6300 | 0.12 | 18800 | .37 | 58000 | 0.475 | 74500 | 0.26 | 40800 | 0.075 | 11700 | 0.0030 | 4700 |
| .00739 | .09 | 5700 | .27 | 17000 | .80 | 50500 | 1.06 | 67100 | .62 | 39200 | .200 | 12600 | .075 | 4740 |
| .0194 | .19 | 4600 | .57 | 13700 | 1.56 | 37600 | 2.00 | 48100 | 1.25 | 30100 | .460 | 11100 | .195 | 4700 |

**Temperature Dependence.**—An increase in temperature broadens the band and shifts the peak to longer wave lengths with an increase in the maximum absorbancy. The temperature dependence of the spectrum is illustrated in Fig. 9 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 cm.$^{-1}$ deg.$^{-1}$ from −65 to −55° and −11.3 cm.$^{-1}$ deg.$^{-1}$ from −55 to −45°.

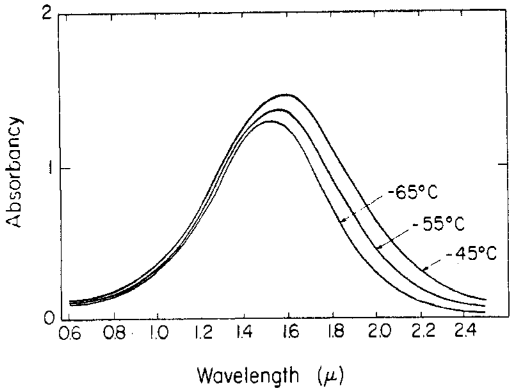

Fig. 9.—Absorption curves for alkali metals at −65, −55, and −45°.

**Addition of Sodium Iodide.**—Because Clark, *et al.*,[12] reported the appearance of shoulders at 6700 and 8000 Å. in the absorption spectra of ammonia solutions of sodium and sodium iodide, we repeated these measurements using higher concentrations of sodium iodide. With the exception of solution 3 (Table V), sodium solutions containing sodium iodide did not show any excessive decomposition during the several hours required for a run. In the case of solutions 1 and 4, some hydrogen was evolved shortly after the solutions were prepared, presumably due to residual water in the sodium iodide. However, this hydrogen was pumped off before taking the spectrum and should be of no consequence.

The addition of excess sodium ions causes the entire absorption band to shift to shorter wave lengths with a corresponding increase in the maximum absorbancy. This is illustrated in Fig. 10 for one of the two runs in which the peak could be observed. The spectrum of the 0.0203 $M$ sodium solution was calculated from data in Table I. There was no indication of shoulders on the absorption band.

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[12] H. C. Clark, A. Horsfield, and M. C. R. Symons, *J. Chem. Soc.*, 2478 (1959).

Table II

Absorbancies ($A$) and Extinction Coefficients ($\epsilon$) at −55°

| Concn. (moles/l.) | λ = 15,500 Å. $A$ | $\epsilon$ | λ = 18,000 Å. $A$ | $\epsilon$ | λ = 21,000 Å. $A$ | $\epsilon$ | λ = 24,000 Å. $A$ | $\epsilon$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Sodium | | | | |
| 0.00800 | 0.75 | 43800 | 0.54 | 31500 | 0.190 | 11100 | 0.050 | 2920 |
| .0105 | 1.12 | 49900 | .80 | 35600 | .285 | 12700 | .080 | 3560 |
| .0118 | 1.20 | 47500 | .91 | 36000 | .310 | 12300 | .085 | 3360 |
| .0133 | 1.39 | 48800 | 1.05 | 36900 | .365 | 12800 | .100 | 3510 |
| .0229 | 2.45 | 50000 | 1.86 | 37900 | .73 | 14900 | .205 | 4180 |
| .0295 | 3.07 | 48600 | 2.30 | 36400 | .89 | 14100 | .270 | 4270 |
| .0379 | | | 2.95 | 36300 | 1.16 | 14300 | .365 | 4500 |
| .0452 | | | 3.37 | 34800 | 1.34 | 13800 | .420 | 4340 |
| .0454 | | | | | 1.40 | 14400 | .470 | 4830 |
| .0476 | | | | | 1.53 | 15000 | .525 | 5150 |
| .0805 | | | | | 2.41 | 14000 | .84 | 4870 |
| .142 | | | | | | | 1.98 | 6520 |
| .190 | | | | | | | 3.12 | 7670 |
| | | | | Potassium | | | | |
| 0.00846 | 0.85 | 47000 | 0.63 | 34800 | 0.225 | 12400 | 0.060 | 3310 |
| .0194 | 2.02 | 48600 | 1.57 | 37800 | .64 | 15400 | .205 | 4940 |
| .107 | | | | | | | 1.47 | 6410 |
| | | | | Lithium | | | | |
| 0.0117 | 1.09 | 43500 | 0.81 | 32300 | 0.290 | 11600 | 0.090 | 3590 |
| .0325 | 3.47 | 49900 | 2.55 | 36600 | 1.01 | 14500 | .300 | 4310 |
| .143 | | | | | | | 2.03 | 6630 |
| | | | | Cesium | | | | |
| 0.00483 | 0.445 | 43000 | 0.300 | 29200 | 0.110 | 10700 | 0.035 | 3380 |
| .0101 | 1.00 | 46200 | .75 | 34700 | .270 | 12500 | .085 | 3930 |
| .0599 | | | | | 1.93 | 15000 | .64 | 4990 |
| .134 | | | | | | | 1.88 | 6550 |
| | | | | Calcium | | | | |
| 0.00298 | 0.505 | 78900 | 0.33 | 51700 | 0.120 | 18800 | 0.040 | 6270 |
| .00739 | 1.14 | 72100 | 0.79 | 50000 | .285 | 18000 | .115 | 7280 |
| .0194 | 2.19 | 52700 | 1.55 | 37400 | .66 | 15900 | .230 | 5540 |

The volumes of the sodium–sodium iodide solutions were calculated using the density of sodium iodide solutions.[13]

## Discussion

**Concentration Dependence.**—The most striking result of the investigation is that the spectra undergo very little change with changing concentration. Over the concentration range 0.002–0.03 $M$, in which extensive aggregation and spin-pairing take place, the spectra are practically unchanged. It is clear that the species $e_{am}^-$, M, and $M_2$ have very similar spectra. However this conclusion would not have been anticipated from the description of the latter two species (the monomer and dimer) given by Becker, Lindquist, and Alder.[7] These authors describe the monomer as an ammoniated metal ion with an electron circulating on the protons of the coördinated ammonia molecules. They picture the dimer as two ammoniated metal ions held together by a pair of electrons in a molecular orbital located principally between the two ions. Only by a remarkable coincidence could species like

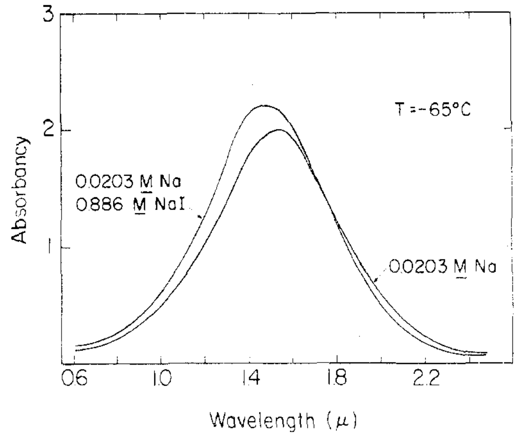

Fig. 10.—Absorption curves for 0.0203 $M$ sodium solution with and without added sodium iodide.

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[13] W. C. Johnson and R. I. Martens, *J. Am. Chem. Soc.*, **58**, 15 (1936).

TABLE III

ABSORBANCIES ($A$) AND EXTINCTION COEFFICIENTS ($\epsilon$) AT −45°

| Concn. (moles/l.) | λ = 15,750 Å. | | λ = 18,000 Å. | | λ = 21,000 Å. | | λ = 24,000 Å. | |
|---|---|---|---|---|---|---|---|---|
| | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ |
| Sodium | | | | | | | | |
| 0.00800 | 0.82 | 47900 | 0.66 | 38500 | 0.275 | 16100 | 0.090 | 5260 |
| .0105 | 1.21 | 53900 | .98 | 43600 | .430 | 19100 | .155 | 6900 |
| .0118 | 1.31 | 51900 | 1.11 | 44000 | .490 | 19400 | .170 | 6740 |
| .0133 | 1.50 | 52600 | 1.26 | 44300 | .495 | 17400 | .180 | 6320 |
| .0229 | 2.67 | 54500 | 2.17 | 44300 | 1.03 | 21000 | .350 | 7140 |
| .0295 | 3.41 | 54000 | 2.82 | 44600 | 1.29 | 20400 | .455 | 7200 |
| .0379 | | | 3.79 | 46700 | 1.59 | 19600 | .60 | 7400 |
| .0452 | | | | | | | .74 | 7640 |
| .0454 | | | | | 2.10 | 21600 | .78 | 8030 |
| .0476 | | | | | 2.12 | 20800 | .82 | 8040 |
| .0805 | | | | | 4.16 | 24200 | 1.34 | 7780 |
| .142 | | | | | | | 3.13 | 10300 |
| Potassium | | | | | | | | |
| 0.00846 | 0.94 | 51900 | 0.77 | 42500 | 0.325 | 17900 | 0.110 | 6080 |
| .0194 | 2.25 | 54200 | 1.92 | 46300 | .92 | 22100 | .315 | 7590 |
| .107 | | | | | | | 2.38 | 10400 |
| Lithium | | | | | | | | |
| 0.0117 | 1.18 | 47100 | 0.97 | 38700 | 0.425 | 17000 | 0.155 | 6190 |
| .0325 | | | 3.18 | 45600 | 1.46 | 21000 | .540 | 7760 |
| .143 | | | | | | | 3.35 | 10900 |
| Cesium | | | | | | | | |
| 0.00483 | 0.480 | 46400 | 0.36 | 34800 | 0.160 | 15500 | 0.055 | 5320 |
| .0101 | 1.11 | 51300 | .92 | 42600 | .420 | 19400 | .160 | 7400 |
| .0599 | | | | | 2.83 | 22100 | 1.08 | 8440 |
| .134 | | | | | | | 2.72 | 9490 |
| Calcium | | | | | | | | |
| 0.00298 | 0.564 | 88600 | 0.43 | 67500 | 0.180 | 28200 | 0.065 | 10200 |
| .00739 | 1.26 | 79700 | .99 | 62600 | .445 | 28100 | .180 | 11400 |
| .0194 | 2.60 | 62600 | 2.02 | 48600 | .97 | 23400 | .400 | 9630 |

these and the ammoniated electron described earlier have almost identical absorption spectra. Douthit and Dye[9] and Evers[8] have pointed out that if the monomer were simply an ion-pair in which the ammoniated electron retained its identity, the constancy of the spectra in the dilute range could be explained. Our results for more concentrated solutions lead us to a similar conclusion regarding the dimer. We picture the dimer as an ion quadrupole[14] in which two ammoniated metal ions and two ammoniated electrons are electrostatically held in a square or rhombic configuration. The wave functions for the two ammoniated electrons in the dimer will overlap significantly, and it is reasonable that the singlet state be lower in energy than the triplet state by more than $kT$.

The increase in extinction coefficient which occurs above 0.03 $M$ at high wave lengths corresponds to the formation of still higher ionic polymers in the solution. As a solution becomes more and more concentrated, this type of aggregation continues to the point where there are no longer sufficient ammonia molecules to properly coördinate the sodium ions and the electrons. (If we assume that the sodium ion and the electron each coördinate six ammonia molecules, this should occur at approximately 2.8 $M$.) The ammoniation energy of the sodium ion is much greater than that of the electron.[2,15] Hence at still higher concentrations, electrons will become unsolvated and free to conduct electricity. At 3 $M$, the conductance of sodium is increasing very rapidly with increasing concentration. The saturated solution, with almost metallic conduction, corresponds to a "molten metal" in which ammoniated sodium ions are held together by a sea of electrons.

It is interesting to compare the experimental equilibrium constants for reactions 1 and 4 with values estimated from electrostatic considerations. By assuming a radius of 3.7 Å. for the ammoniated electron, a radius of 2.7 Å. for the ammoniated sodium ion, and an effective dielectric

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(14) M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2264 (1962).

(15) W. L. Jolly, *J. Phys. Chem.*, **58**, 250 (1954).

TABLE IV

ABSORBANCY AT THE MAXIMUM ($A_{max}$) AND POSITION OF THE MAXIMUM ($\lambda_{max}$)

| Concn. (moles/l.) | −65° | | −55° | | −45° | |
|---|---|---|---|---|---|---|
| | $A_{max}$ | $\lambda_{max}$, Å. | $A_{max}$ | $\lambda_{max}$, Å. | $A_{max}$ | $\lambda_{max}$, Å. |
| | | | Sodium | | | |
| Unknown | 0.16 | 15,000 | ... | ... | ... | ... |
| 0.00800 | 0.67 | 15,250 | 0.75 | 15,590 | 0.82 | 15,820 |
| .0105 | 1.05 | 15,280 | ... | ... | 1.21 | 15,900 |
| .0118 | 1.09 | 15,320 | 1.20 | 15,620 | 1.32 | 15,920 |
| .0133 | 1.30 | 15,370 | 1.39 | 15,670 | 1.51 | 16,000 |
| .0229 | 2.29 | 15,380 | 2.47 | 15,780 | ... | ... |
| .0295 | 2.85 | 15,430 | 3.09 | 15,730 | 3.44 | 16,100 |
| .00591[a] | 0.66 | 15,000 | 0.71 | 15,300 | ... | ... |
| .0203[a] | 2.23 | 14,750 | 2.46 | 15,120 | ... | ... |
| | | | Potassium | | | |
| 0.00846 | 0.78 | 15,230 | 0.85 | 15,550 | 0.94 | 15,800 |
| .0194 | 1.86 | 15,370 | 2.03 | 15,800 | 2.22 | 16,090 |
| | | | Lithium | | | |
| 0.0117 | 1.02 | 15,300 | 1.09 | 15,630 | 1.18 | 15,910 |
| .0325 | 3.08 | 15,400 | 3.50 | 15,870 | ... | ... |
| | | | Cesium | | | |
| 0.00483 | 0.42 | 15,080 | 0.44 | 15,340 | 0.48 | 15,560 |
| .0101 | .92 | 15,350 | 1.00 | 15,690 | 1.11 | 15,970 |
| | | | Calcium | | | |
| 0.00298 | 0.48 | 14,930 | 0.50 | 15,250 | 0.56 | 15,630 |
| .00739 | 1.06 | 14,980 | 1.14 | 15,330 | 1.26 | 15,725 |
| .0194 | 2.01 | 14,990 | 2.19 | 15,410 | 2.60 | 15,750 |

[a] Sodium iodide added; see Table V for concentrations.

TABLE V[a]

ABSORBANCIES ($A$) AND EXTINCTION COEFFICIENTS ($\epsilon$) OF SODIUM–SODIUM IODIDE SOLUTIONS

| | Solution no. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | 4 | |
| λ, A. | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ | $A$ | $\epsilon$ |
| | | | | −65° | | | | |
| 7500 | 0.07 | 5500 | 0.20 | 4660 | 0.46 | 3950 | 0.57 ± 0.05 | 3570–4250 |
| 10000 | .17 | 13400 | .57 | 13100 | 1.46 | 12500 | 1.73 | 11900 |
| 13000 | .49 | 38700 | 1.73 | 39800 | ... | ... | ... | ... |
| 15250 | .65 | 51400 | 2.19 | 50400 | ... | ... | ... | ... |
| 18000 | .34 | 26900 | 1.16 | 26700 | 3.22 | 27600 | 3.47 | 23800 |
| 21000 | .08 | 6300 | 0.27 | 6210 | 0.89 | 7210 | 1.05 | 7210 |
| 24000 | .03 | 2400 | .07 | 1610 | .26 | 2230 | 0.40 | 2740 |
| | | | | −55° | | | | |
| 15500 | 0.70 | 55400 | 2.44 | 56100 | ... | ... | ... | ... |
| 18000 | .45 | 35600 | 1.52 | 35000 | ... | ... | ... | ... |
| 21000 | .14 | 11100 | 0.46 | 10600 | 1.27 | 10900 | ... | ... |
| 24000 | .05 | 3900 | .13 | 3000 | 0.42 | 3600 | ... | ... |
| | | | | −45° | | | | |
| 15750 | 0.75 | 59300 | ... | ... | ... | ... | ... | ... |
| 18000 | .54 | 42700 | ... | ... | ... | ... | ... | ... |
| 21000 | .19 | 15000 | ... | ... | 1.61 | 13800 | ... | ... |
| 24000 | .06 | 4700 | ... | ... | 0.52 | 4470 | ... | ... |

[a] Concentrations of solutions: (1) 0.00591 $M$ Na, 0.446 $M$ NaI; (2) 0.0203 $M$ Na, 0.886 $M$ NaI; (3) 0.0544 $M$ Na, 1.49 $M$ NaI; (4) 0.0681 $M$ Na, 0.923 $M$ NaI.

constant of 23 (the bulk dielectric constant of ammonia at −34°), we calculate $K = 115$ for reaction 1. For the radii we have chosen, a square configuration is the most stable for the quadrupole, and we calculate $K = 16$ for reaction 4. These values may be compared with the experimental values in Table VI. In view of the crudeness of our calculations, the agreement is quite satisfactory and lends credence to the postulate that the monomer and dimer are simply electrostatic assemblies of ammoniated metal ions and electrons.

TABLE VI

EXPERIMENTAL AND ESTIMATED EQUILIBRIUM CONSTANTS

| Method | $K_1 = \frac{(\mathrm{Na})}{(\mathrm{Na}^+)(\mathrm{e}^-_{\mathrm{am}})}$ | $K_4 = \frac{(\mathrm{Na}_2)}{(\mathrm{Na})^2}$ |
|---|---|---|
| Conductance[16] | 138 | 730 |
| Transport[17] | 109 | 342 |
| Activity[18] | 104 | 530 |
| Estimated | 115 | 16 |

**Temperature Dependence.**—Previous workers, who studied much more dilute solutions than we did, found a somewhat smaller temperature dependence of the peak wave length than we did. Blades and Hodgins[19] report a value of $-9.1$ cm.$^{-1}$ deg.$^{-1}$ for potassium in ammonia from $-42$ to $-78°$. Douthit and Dye[9] report $-9.7$ and $-11.5$ cm.$^{-1}$ deg.$^{-1}$ for sodium and potassium, respectively, from $-37$ to $-65°$. Our average value from $-45$ to $-65°$ is $-12.7$ cm.$^{-1}$ deg.$^{-1}$. Jortner[20] has given a reasonable explanation of this shift in terms of the temperature dependence of the dielectric constant and the cavity radius.

Douthit and Dye estimated the displacements on the sides of the band from $A/A_{\max}$ measurements rather than from measured absorbancies. Hence they mistakenly concluded that the entire absorption curve is shifted to lower energies as the temperature is increased. Actually, as can be seen from Fig. 9, the low wave length side of the band is displaced slightly toward shorter wave lengths.

**Effect of Sodium Iodide.**—No new features appeared in the absorption spectrum of sodium upon adding high concentrations of sodium iodide. The shift of the spectrum toward shorter wave lengths was not expected on the basis of equilibria 1 and 4 and the observed shift toward longer wave lengths upon concentrating metal solutions.

Possibly the effect is due to the formation of a new species such as $\mathrm{Na}_2^+$

$$\mathrm{Na}_2 + \mathrm{Na}^+ = \mathrm{Na}_2^+ + \mathrm{Na} \qquad (5)$$

Since reaction 5 corresponds to an increase in the concentration of unpaired electrons, it would be interesting to measure the paramagnetic susceptibility of sodium–sodium iodide solutions.

**Calcium Solutions.**—Our measured extinction coefficients for calcium are only 60–85% of the values expected on the basis of two ammoniated electrons per calcium atom. We have pointed out that there were experimental difficulties peculiar to our calcium runs, but any errors caused by these difficulties are such as to make our measured extinction coefficients too high.[21] Therefore we believe the abnormally low extinction coefficients for calcium are significant. It seems likely that the hypothesis which Yost and Russell[22] offered in order to explain the abnormally low magnetic susceptibility of calcium[5] is applicable here. It was proposed that an appreciable fraction of the calcium atoms ionize to give only one ammoniated electron and that the $\mathrm{Ca}^+$ ions dimerize to give $\mathrm{Ca}_2^{+2}$ ions. We propose that the latter ions are structurally analogous to $\mathrm{Hg}_2^{+2}$ ions and hence colorless. Significantly, Gibson and Argo[23] found that the visible absorption spectrum of calcium differed in type from that of the alkali metals. It is obvious that the alkaline earth–ammonia solutions require much further investigation.

**Acknowledgment.**—We wish to thank Professor K. S. Pitzer for helpful discussions. This work was supported by the U. S. Atomic Energy Commission.

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(16) E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, **30**, 61 (1959).

(17) J. L. Dye, R. F. Sankuer, and G. E. Smith, *J. Am. Chem. Soc.*, **82**, 4797 (1960).

(18) J. L. Dye, G. E. Smith, and R. F. Sankuer, *ibid.*, **82**, 4803 (1960).

(19) H. Blades and J. W. Hodgins, *Can. J. Chem.*, **33**, 411 (1955).

(20) J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

(21) The concentrated phase which clung to the walls of the make-up cell yielded its ammonia during analysis and caused our measured concentrations to be too low. The dark foreign particles which were observed in the cell caused the measured absorbancies to be too high.

(22) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1946, p. 148.

(23) G. E. Gibson and W. L. Argo, *J. Am. Chem. Soc.*, **40**, 1327 (1918).