Bachelor's Thesis in Chemistry

ELECTRON SPIN RESONANCE STUDIES OF CONCENTRATED ALKALI METAL-AMMONIA SOLUTIONS

by

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ABSTRACT

Electron spin resonance spectra are obtained for sodium and cesium metal-ammonia solutions in the concentration range 1.0 molal to saturation. The asymmetric spectra are interpreted on the basis of existing theories for magnetic resonance in metallic conductors. The transverse relaxation time T_2 decreases with increasing concentration until it reaches a limiting value close to that observed for the pure metal.

Electron spin resonance spectra are obtained for concentrated sodium metal-ammonia solutions containing dissolved cesium halide salts. T_2 and g decrease with sodium metal concentration and are anion independent. The addition of the cesium cation causes a decrease in T_2 which is independent of cesium concentration above 0.10 molal salt. These results are taken as evidence for the formation of a lattice structure in concentrated solutions.

INTRODUCTION

Alkali metal-ammonia solutions have been a subject of intensive study because of their many interesting physical properties. The dilute solutions are blue and have the properties of highly conducting ionic solutions. The concentrated solutions are golden bronze in color and exhibit the characteristics of liquid metals.

A number of models[1] have been proposed to explain the behavior of these solutions. The one which has gained the most acceptance in recent years is the unified model[1], which combines the best features of two older models, the cavity[2] and cluster models[3]. The unified model assumes that when the metal atoms are dissolved in ammonia, they dissociate and produce metal ions and electrons. At low concentrations (less than 0.1 molal), the electrons are captured in spherical cavities surrounded by ammonia molecules. At intermediate concentrations (0.1 molal to 1.0 molal), the electrons are trapped by the potential produced by the metal ion and the oriented ammonia molecules around the ion. Such a unit is called a monomer. At high concentrations the solution structure has not been completely explained. Magnetic susceptibility studies[4] have shown that there is extensive electron spin pairing. Knight shift

studies[5] have indicated that the electron is closely associated with the metal nucleus. It is not known, however, whether the concentrated solution is made up of monomers and dimers*, or whether a larger lattice of metal nuclei, ammonia molecules, and delocalized electrons is formed.

The purpose of this research is to investigate the electronic environment of concentrated alkali metal-ammonia solutions by means of electron spin resonance. The strength of the spin-orbit coupling interaction between the electron and the metal nucleus is determined by measuring the relaxation time T_2 of cesium-ammonia and sodium-ammonia solutions. The extent of lattice formation is determined by studying the effect of the addition of cesium salts on the T_2 of sodium-ammonia solutions.

EXPERIMENTAL

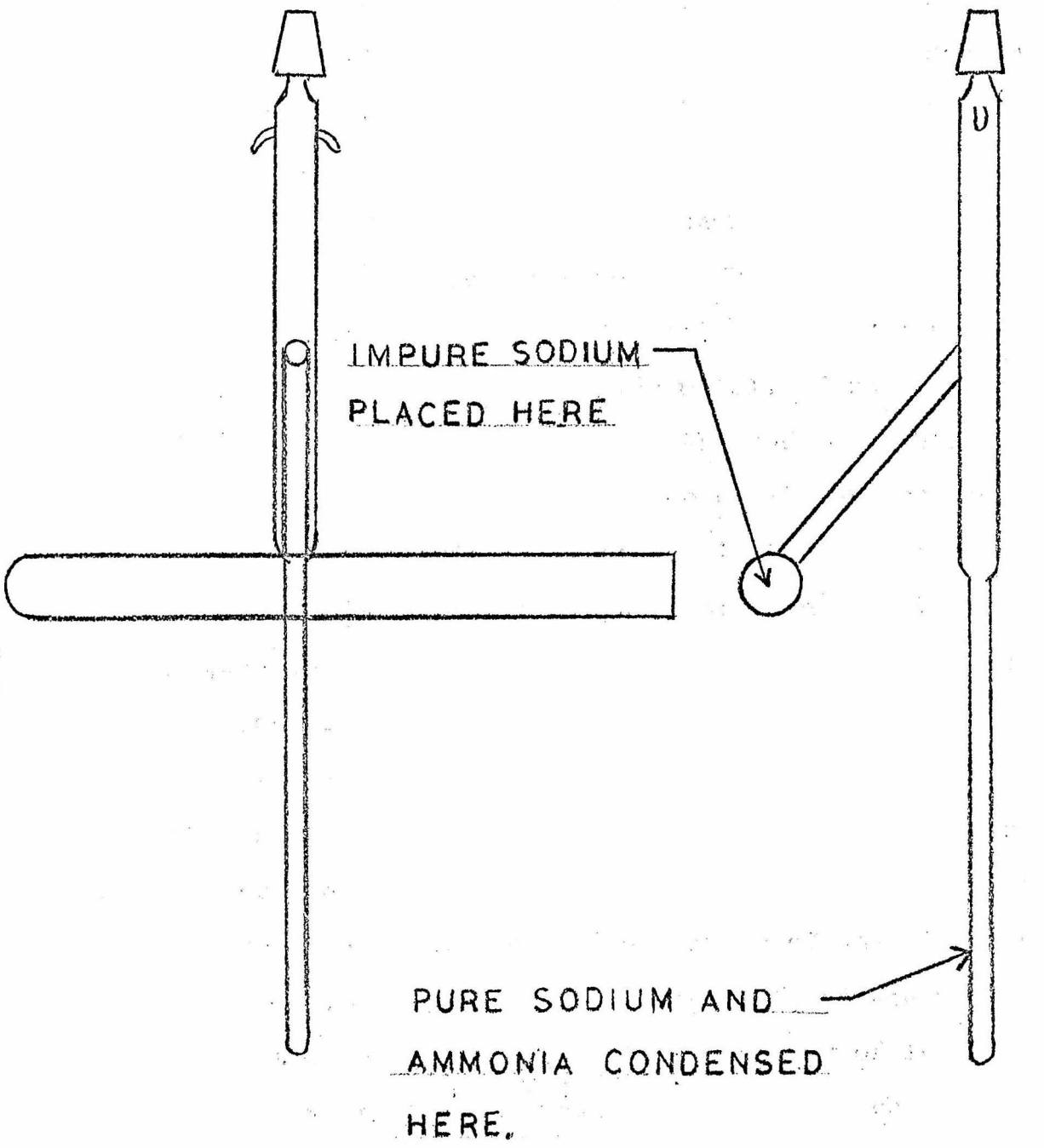
The concentrated sodium-ammonia solutions were prepared in the sample preparation vessel shown in Figure 1. The reaction chamber is originally open at one end. Approximately 10 grams of sodium metal are placed in the chamber and the open end is sealed. The vessel is placed on a vacuum system and evacuated to 10^{-3} mm Hg with the forepump. After about 6 hours, an oil diffusion pump is turned on and after and additional 18 hours of pumping a pressure of 10^{-5} mm Hg is achieved.

The sodium metal is vaporized in the reaction chamber with a hand torch. The vapor is allowed to condense in the chamber stem. The metal in the chamber stem is then vaporized and allowed to condense higher on the chamber stem or in the main stem. By a series of vaporizations and condensations the metal is moved along to the bottom of the main stem, from which it flows into the sample tube.

* Two associated metal nuclei

FIGURE 1

SAMPLE PREPARATION VESSEL



Considerable practice is required to keep the torch flame hot enough so that it vaporizes the metal, yet cool enough so that it does not cause the glass to become viscous. Considerable experience is also required to heat the metal and the glass in such a manner that the condensing metal moves in the desired direction.

Tank ammonia is purified by condensing it with sodium metal in a dry ice-acetone trap. Any impurities in the ammonia react with the sodium. The resulting sodium-ammonia admixture is blue in regions of dilute sodium-ammonia ammonia solutions and golden in regions of concentrated solutions. The dry ice-acetone Dewar is removed from the trap and the ammonia is allowed to condense into a second trap containing sodium metal. Here any remaining impurities in the ammonia react with the sodium. This process is repeated a third time to insure the purity of the ammonia.

The purified ammonia is condensed in the sample tube with the pure metal. The condensation is accomplished in several minutes by slowly moving a liquid nitrogen filled Dewar up the length of the sample tube. The tubes are then sealed. Experience is required to make a seal which is safe at room temperature.

The cesium-ammonia solutions are prepared by a slightly different procedure. Cesium chloride and chips of calcium metal are mixed together in the reaction chamber of the sample preparation vessel. The chamber is sealed off and the vessel is attached to the vacuum system. After a vacuum of 10^{-5} mm Hg is achieved, the mixture is heated, and the cesium chloride reacts with the calcium:

$$2\,CsCl + Ca \longrightarrow 2\,Cs + CaCl_2$$

When a suitable amount of cesium metal has been formed, it is vaporized and driven into the sample tube by the same process as was used for sodium metal.

The samples containing alkali halide salts are prepared by dropping a precisely weighed amount of the salt to the tip of the sample tube before placing the sample preparation vessel on the vacuum system. In all other respects, the procedure for preparing these samples is identical to that described above for plain sodium-ammonia samples.

The sealed sample tubes are allowed to remain at room temperature for several hours to test the seal and to insure that they won't explode inside the cavity of the spectrometer. They are stored in a dry ice-acetone Dewar.

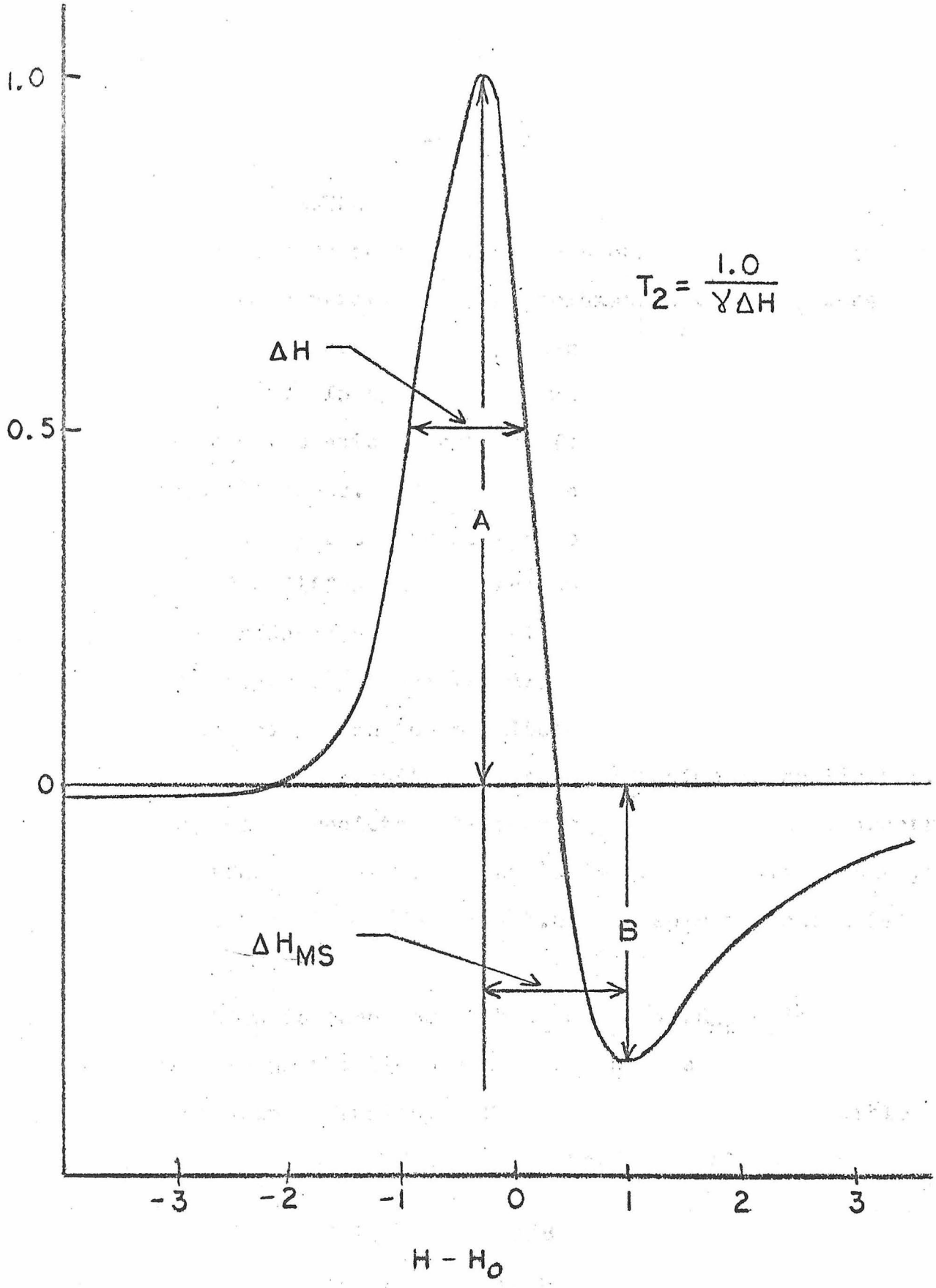
The resonance spectra were obtained with a Varian Model V-4500 EPR X-Band Spectrometer at a resonant frequency of 9.3 kmc. The line widths were measured against the 13.0 gauss splitting in Fremy's Salt (peroxylamine disulfonate), which was used as an internal standard. The asymmetry parameter A/B was measured at a constant phase setting for all samples.

The alkali metal content was determined as metal hydroxide by titration with standard HCl. A sample to be analyzed is first weighed and then submerged in liquid nitrogen. It is then broken in two and submerged in a beaker containing reagent grade methanol. The metal reacts to form methoxide:

$$M + CH_3OH \rightarrow MOCH_3 + \tfrac{1}{2} H_2$$

a reaction much less violent than the addition of the alkali metal to water. The solution is boiled to remove dissolved ammonia and

FIGURE 2



then ca. 100 cc distilled water is added. The solution is titrated with standard HCl to the phenolphthalein end point. Amounts of metal down to 10 mg were determined. The amount of ammonia was determined from the weight of the sample less the weight of the glass and the alkali metal.

INTERPRETATION OF SPECTRA

Asymmetric spectra such as the one shown in Figure 2 were recorded at all concentrations. The relaxation times T_2 were extracted from the spectra using Dyson's theory[6] for electron spin resonance in metals. In Dyson's treatment, the asymmetric line shape arises from the skin effect and from the spin diffusion of the conduction electrons. In the skin effect, the phase and amplitude of the microwave field is altered by the conduction electrons in the metal. The diffusion of electron spins with different phase memories produces an additional phase shift. Dyson calculates that the asymmetry parameter A/B should vary over the range 2.7 to 19.0 depending upon the magnitude of the spin diffusion effect. The value 2.7 results when spin diffusion is negligible. Dyson's theory also predicts a broadening of the resonance spectra due to spin diffusion. Feher and Kip[7] have treated this problem, with the result that $T_2 = f/\gamma\Delta H$ ($f = 1.0$ when spin diffusion is negligible).

This equation is compared with $T_2 = 1.27/\gamma\Delta H_{ms}$ which comes from the solution of the Bloch equations for the skin effect[8] in the absence of spin diffusion. If spin diffusion is negligible, the parameters A/B and $\Delta H_{ms}/\Delta H$ should have the values

$$\Delta H_{ms}/\Delta H = 1.27 \qquad A/B = 2.7$$

Since these parameters were found to have constant values in this

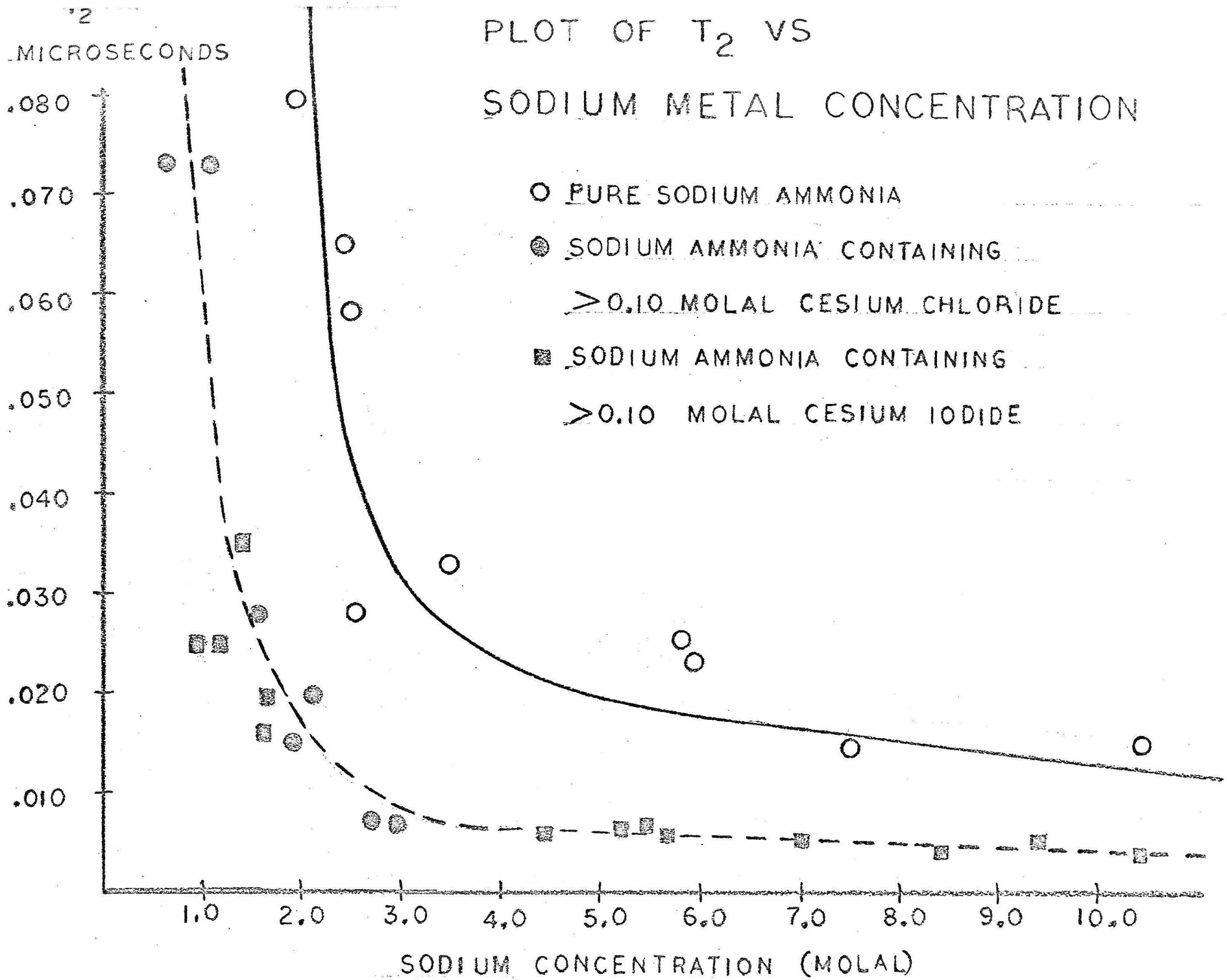

PLOT OF T_2 VS
SODIUM METAL CONCENTRATION
T_2
MICROSECONDS
.080
.070
.060
.050
.040
.030
.020
.010
PURE SODIUM AMMONIA
SODIUM AMMONIA CONTAINING
>0.10 MOLAL CESIUM CHLORIDE
SODIUM AMMONIA CONTAINING
>0.10 MOLAL CESIUM IODIDE
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
SODIUM CONCENTRATION (MOLAL)

FIGURE 4.

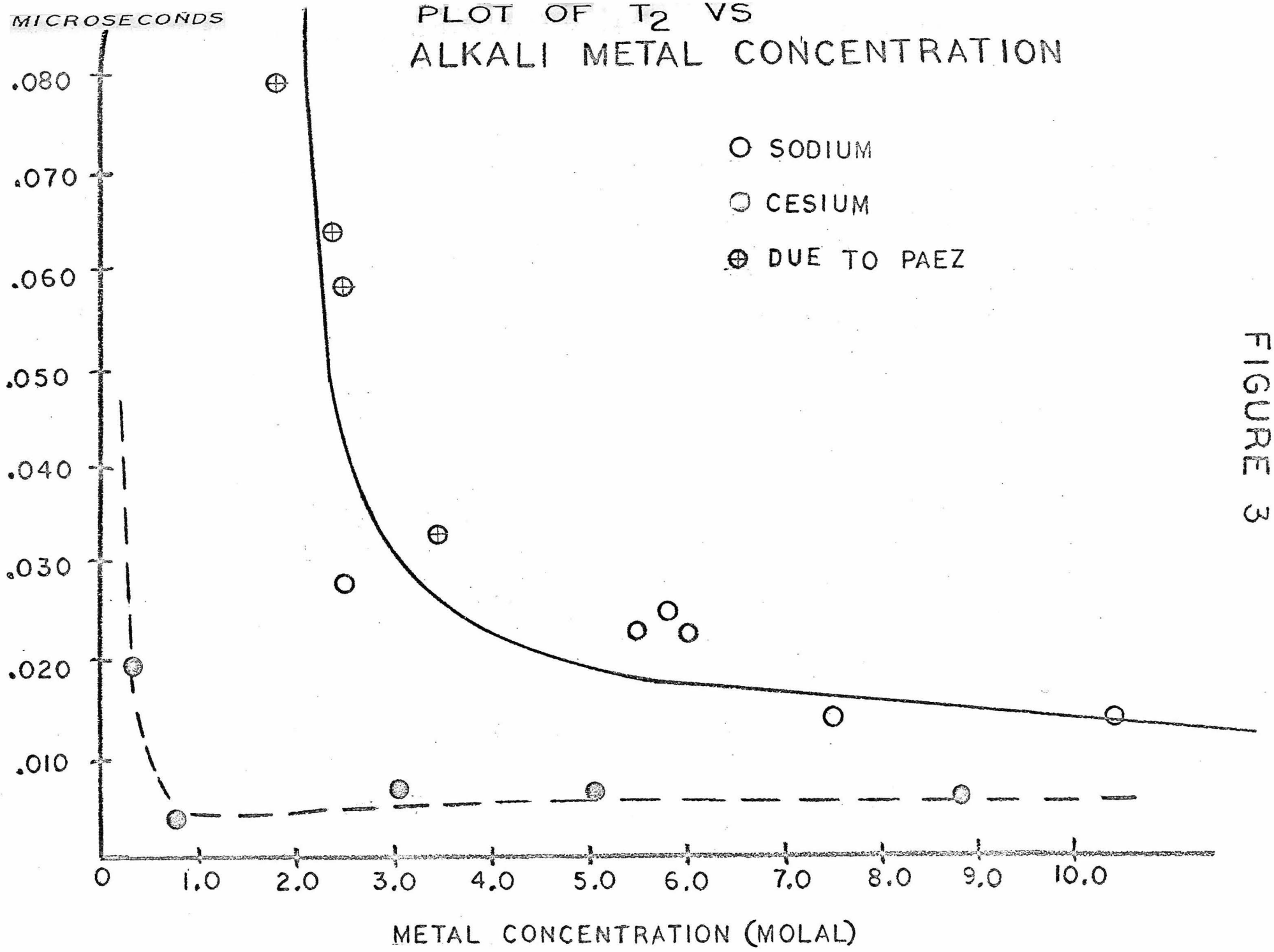

PLOT OF T_2 VS
ALKALI METAL CONCENTRATION
MICROSECONDS
.080
.070
.060
.050
.040
.030
.020
.010
SODIUM
CESIUM
DUE TO PAEZ
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
METAL CONCENTRATION (MOLAL)

FIGURE 3

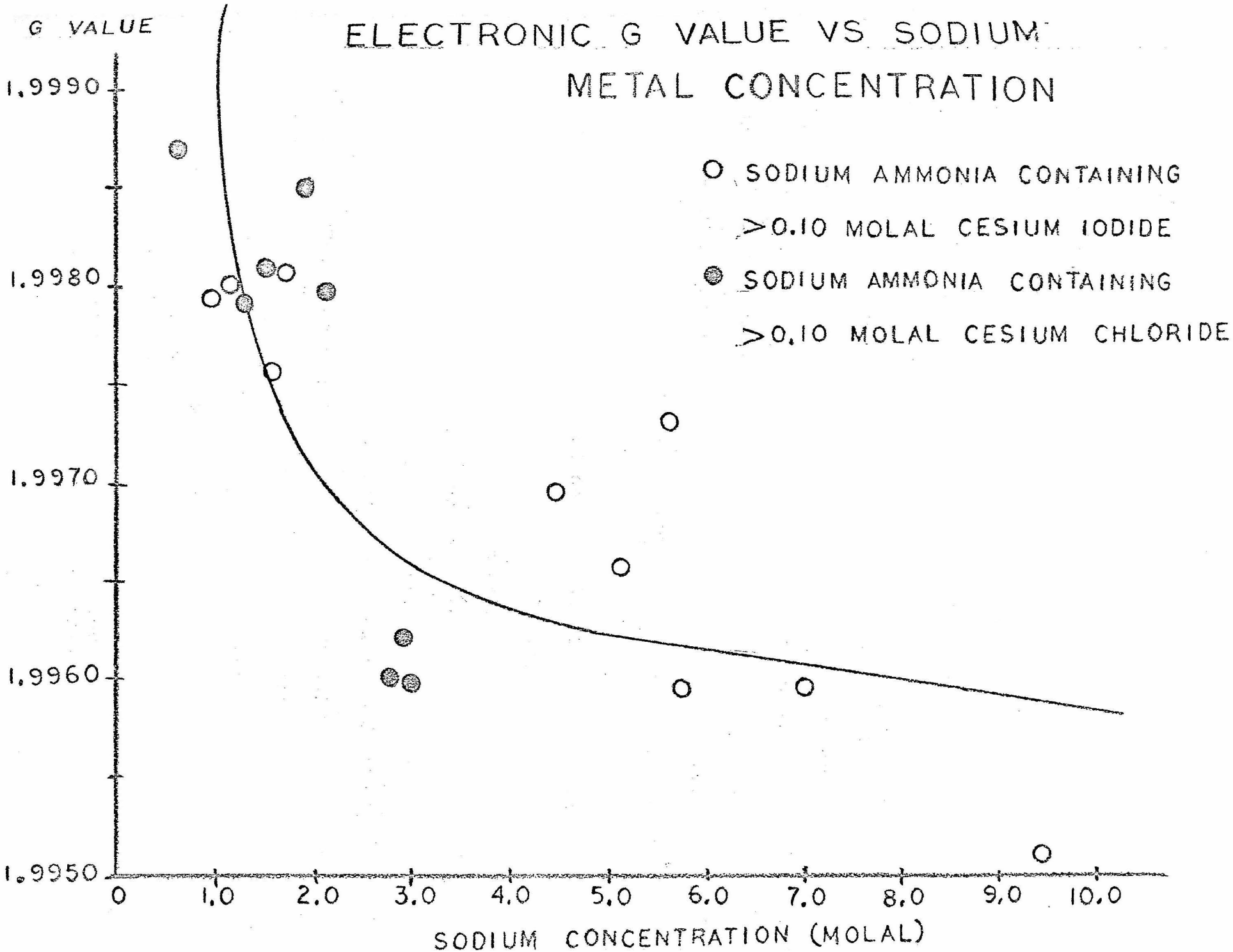

G VALUE
ELECTRONIC G VALUE VS SODIUM METAL CONCENTRATION
SODIUM AMMONIA CONTAINING >0.10 MOLAL CESIUM IODIDE
SODIUM AMMONIA CONTAINING >0.10 MOLAL CESIUM CHLORIDE
1.9990
1.9980
1.9970
1.9960
1.9950
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
SODIUM CONCENTRATION (MOLAL)

FIGURE 5

research

$$\Delta H_{ms}/\Delta H = 1.3 \pm 0.1 \qquad A/B = 3.0 \pm 0.5$$

it was assumed that spin diffusion was negligible. T_2 is therefore given by the equation:

$$T_2 = 1.27/\gamma \Delta H_{ms} = 1.0/\gamma \Delta H$$

RESULTS

Plots of T_2(at 30°C) vs. metal concentration for sodium-ammonia solutions* and cesium-ammonia solutions are shown in Figure 3. Cesium-ammonia solutions exhibit a smaller relaxation time because the spin-orbit coupling parameter of the cesium core is larger than that of sodium. For both metals T_2 decreases with concentration, approaching the limiting values 0.014 microseconds for sodium-ammonia and 0.007 microseconds for cesium-ammonia. These are very close to the values observed in the pure alkali metals at this temperature.

The effect of the addition of cesium salts to sodium-ammonia solutions is shown in Figure 4. The plot of T_2 vs. concentration is shifted downward by the addition of the cesium nucleus. At a given sodium metal concentration, the downward shift is independent of the cesium concentration in the range 0.10 molal salt to saturation. (It was impossible to make solutions more dilute than 0.10 molal cesium by the experimental procedure employed.) Above 3.0 molal sodium metal, the addition of 0.10 molal cesium salt causes T_2 to be completely characteristic of a concentrated cesium-ammonia solution. T_2 and g are independent of the type of halide anion (chloride or iodide) used in the cesium salt.

* Four data points taken from unpublished Master's Degree Thesis of Oscar Anthony Paez, University of California, Riverside

DISCUSSION

The data for pure alkali metal-ammonia solutions make it clear that the metal ion core plays an important role in the electronic environment. The decreasing relaxation times support the contention that the electron is closely associated with the metal nucleus in the form of a monomer, dimer, or larger species.

Evidence for the formation of a lattice structure comes from the data for sodium-ammonia solutions containing dissolved cesium salts. The observation that a very small number of cesium ions is sufficient to give a relaxation time characteristic of cesium suggests that all or nearly all of the electrons in the solution have a finite probability of being at a cesium nucleus within the time interval defined by the relaxation time. A large lattice structure provides the only means by which all the electrons could interact with the cesium nucleus in the time span of 10^{-8} seconds. The delocalized electrons in such a lattice have a finite probability at all the nuclei in the lattice.

The alternative possibility for the concentrated solutions - that they exist as independent monomers and dimers - would not give a relaxation time characteristic of cesium. The sodium ion is much more strongly electron attracting than the cesium ion.* The equilibrium for the association of the electron with sodium monomer $M(Na^+)$ and cesium monomer $M(Cs^+)$

$$M(Na^+) + M(Cs) \underset{K}{\rightleftharpoons} M(Na) + M(Cs^+)$$

should heavily favor the sodium monomer: $\frac{M(Na)M(Cs^+)}{M(Na^+)M(Cs)} = K >> 1$

*Ionization Potentials: Na = 5.14 ev, Cs = 3.89 ev

The electron is almost completely associated with the sodium nucleus in the form M(Na) and the relaxation time T_2 is characteristic of sodium. Since this is not the case experimentally, we conclude that lattice formation must take place.

The region of Figure 4 where the sodium metal concentration is greater than 1.0 molal but less than 3.0 molal is interesting in that the relaxation times are intermediate between those observed for pure sodium-ammonia and pure cesium-ammonia solutions. These results can be explained by assuming that independent monomers and small lattice structures exist simultaneously. The electrons associated with the monomers give a resonance characteristic of sodium, while the delocalized electrons in the lattice structures give a resonance characteristic of cesium. The combination gives a relaxation time intermediate between the two cases.

These results complete the unified model for alkali metal-ammonia solutions. In dilute solutions, electron cavities are formed. As the concentration is increased, monomers and dimers are formed. Finally, in the region around 1.0 molal metal, lattice formation begins to take place. The transition to a lattice structure explains the change in color from blue to bronze observed at this concentration, and more generally, accounts for the metallic properties of the concentrated solutions.

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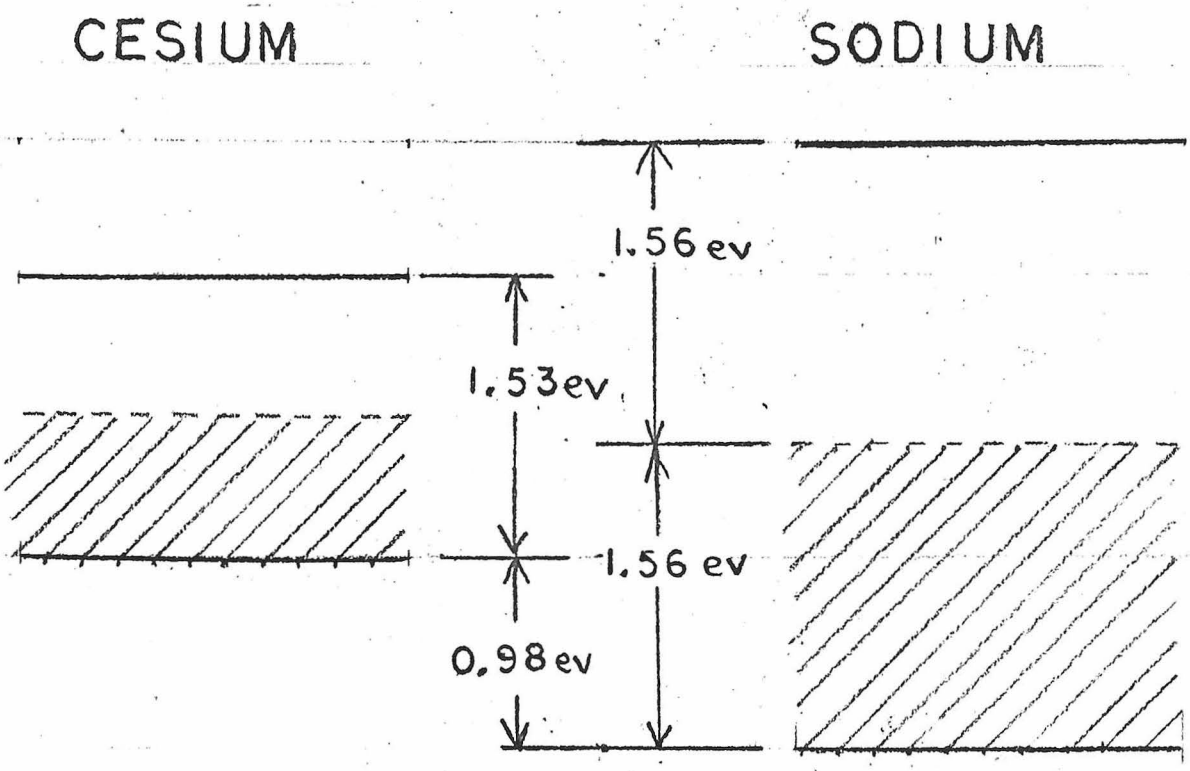
Evidence for the formation of a lattice structure comes from the data for sodium-ammonia solutions containing dissolved cesium salts. The observation that a very small number of cesium ions is sufficient to give a relaxation time characteristic of cesium suggests that all or nearly all of the unpaired electrons in the solution are closely associated with the cesium nuclei. A model which would predict this result is that of a large lattice of sodium and cesium nuclei, ammonia molecules, and delocalized electrons.

Consider Figure 6 which shows the relative energies of the Fermi distributions in sodium and cesium metal. In a lattice containing cesium and sodium atoms, most of the electrons will go into the lower regions of the sodium band and will be in a paired state. These electrons will have zero probability of turning over when a magnetic field is applied, because the opposite spin states are already occupied. Some of the electrons near the top of the sodium band, however, will be in an unpaired state, since the thermal energy at room temperature ($\sim$ 0.025ev) will promote them to higher states. These electrons have a chance to turn over in a magnetic field and will be the sole contributors to the electron spin resonance.

From Figure 6 it can be seen that the electron states near the top of the sodium band will have the same energy as the electron states of the cesium band. The states in this region ($\sim$ 0.98ev

FIGURE 6

FERMI DISTRIBUTION OF ELECTRONS IN SODIUM AND CESIUM METAL



to 1.56ev) will therefore be a mixture of the higher states of the sodium band and the states of the cesium band.

$$\Psi(e^-) = A\Psi_{Na}(e^-) + B\Psi_{Cs}(e^-)$$

We are interested in the interaction of these electrons with their orbital motion about the metal ion core, since the spin-orbit interaction is the predominant relaxation mechanism in concentrated solutions. We write $H_{L\cdot S} = \lambda \vec{L}\cdot\vec{S}$

$$\left(0\,-\tfrac{1}{2}\middle|\, H_{L\cdot S}\middle|\, 0\,\tfrac{1}{2}\right) = \sum_{l'',m''} \frac{\left(0\,-\tfrac{1}{2}\middle|\, H_{L\cdot S}\middle|\, l''m''\right)\left(l''m''\middle|\, H_{L\cdot S}\middle|\, 0\,\tfrac{1}{2}\right)}{E_o - E_{l''}}$$

where E_o is the energy of the electrons near the top of the Fermi Distribution ($\Psi(e^-)$), and $E_{l''}$ is the energy of the lower lying orbital angular momentum states of sodium and cesium. The 4p state of cesium is much closer to E_o than the 2p state of sodium:

$$E_o - E_{4p}^{Cs} \cong 0.5 \text{ ev}$$
$$E_o - E_{2s}^{Na} \cong 5.0 \text{ ev}$$

Therefore $\left(0\,-\tfrac{1}{2}\middle|\, H_{L\cdot S}\middle|\, 0\,\tfrac{1}{2}\right)$ should be much larger for cesium, and the spin-orbit coupling with the cesium ion core should be the principal determiner of the line width.

Of course, the presence of ammonia molecules in the lattice alters the levels of the Fermi distributions with respect to the case of the pure metals. Since Na^+ is smaller than Cs^+, we would expect that it is better solvated and that the 3s level of Na is made more stable relative to the 5s level of cesium. Then

$$E_o - E_{4p}^{Cs} \ll E_o - E_{2p}^{Na}$$

and the spin orbit coupling for the solvated Cs^+ is all the stronger

relative to the solvated Na^+. Cesium would be the principal determiner of the linewidth, and the relaxation properties of the mixed lattice would be the properties of the cesium relaxation.

The alternative possibility for concentrated solutions - that they exist as independent monomers and dimers - would not give a relaxation time characteristic of cesium at all cesium salt concentrations. At low salt concentrations (0.10 molal), most of the electrons would be associated with the sodium nucleus in the form of monomers (and/or dimers), and the relaxation time T_2 is characteristic of sodium. Since this is not the case experimentally, we conclude that lattice formation must take place.

The region of Figure 4 where the sodium metal concentration is greater than 1.0 molal but less than 3.0 molal is interesting in that the relaxation times are intermediate between those observed for pure sodium-ammonia and pure cesium-ammonia solutions. These results can be explained by assuming that independent monomers and small lattice networks exist simultaneously. The extent of formation of lattice networks is dependent on electron concentration. The electrons associated with the monomers give a resonance characteristic of sodium, while the conduction electrons in the small lattice structures give a resonance characteristic of cesium. The combination gives a relaxation time which is intermediate between the two cases and which is electron concentration dependent.

These results complete the unified model for alkali metal-ammonia solutions. In dilute solutions, electron cavities are formed. As the concentration is increased, monomers and dimers are formed. Finally, in the region around 1.0 molal metal, lattice structure explaines the change in color from blue to bronze ob-

served at this concentration, and more generally, accounts for the metallic properties of the concentrated solutions.