METAL-AMINE AND SOLVATED ELECTRON SPECTRA AND REACTIONS. EVIDENCE FOR THE EXISTENCE OF M*

> Thests for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Marc G. DeBacker 1970



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presented by

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By

Marc G. DeBacker

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ABSTRACT

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By

Marc G. DeBacker

The nature of the absorbing species in metal-ethylenediamine solutions was investigated. The reactions and equilibria of these species were also studied. The following results were obtained:

(1) The molar absorptivity and the oscillator strength of the 660 nm band of sodium (V-band) were used to determine the nature of the V-species. The molar absorptivity was measured by using the reaction

 $Na^+ + e^-(IR-band) \longrightarrow V-band$

A molar absorptivity $\epsilon = 8.2 \pm 0.3 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ and an oscillator strength f = 1.9 \pm 0.2 was obtained. It was concluded that Na was responsible for the sodium V-band.

The rate of formation of the V-band was studied by using pulse radiolysis techniques. It was noted that both the growth of the V-band and the decay of the IR-band followed second order kinetics with respect to the concentration of solvated electrons. The rate constant obtained did not

depend upon tration ran of ion-pair was obtaine By using the ity of the ' reaction to it was possi electron in the oscillat The eff Water in eth was detected with respect ^{to} water. N A shift of t ^{by the} addit (2) The^{in eth}ylened ^{850 nm} (R-ba ^{librium} cons

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depend upon the concentration of sodium ions in the concentration range 0.0033 to 0.5 M. This was interpreted in terms of ion-pair formation. The value $k = 1.6 \times 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$ was obtained by using the expression $\frac{d[e^-]}{dt} = -2k [e^-]^2$. By using the pulse radiolysis results and the molar absorptivity of the V-band, and by assuming the stoichiometry of the reaction to be

 $2e^- + Na^+ \longrightarrow Na^-$

it was possible to calculate the molar absorptivity of the electron in ethylenediamine $\epsilon = 2.0 \pm 0.3 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ and the oscillator strength f = 0.88 ± 0.12.

The effect of hydroxide ion on the reaction of Na⁻ with water in ethylenediamine was studied. No hydroxide effect was detected. It was found that the reaction was first order with respect to sodium and close to third order with respect to water. No simple mechanism could account for this. A shift of the equilibrium Na⁻ \longrightarrow Na⁺ + 2e⁻ to the right by the addition of water was suggested.

(2) The addition of potassium ions to a cesium solution in ethylenediamine resulted in the formation of a band at 850 nm (R-band) attributed to K⁻. The evaluations of equilibrium constants were complicated by the presence of ionpairing equilibria and by ionic strength effect.

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(3) The spectrum of the solvated electron in waterammonia and water-ethylenediamine mixtures was observed by using pulse radiolysis. The spectrum in a given mixture consisted of a single absorption band whose position was intermediate between those of the pure solvents. The band shape was studied, and found to be of the same form for all of the mixtures. The oscillator strength of the solvated electron in each of the pure solvents was found to be close to 0.9. Assuming that this was also true for solvent mixtures, the molar absorptivities of the solvated electron in solvent mixtures were calculated.

(4) It was observed that a solution of dicyclohexyl-18-crown-6 in THF and in diethyl ether could dissolve potassium or cesium giving deep blue solutions. These solutions were found to contain paramagnetic species but their optical spectra showed only the R-band. The species M was considered to be the main absorbing species in these solutions.

METAL-AMINE AND SOLVATED ELECTRON SPECTRA AND REACTIONS: EVIDENCE FOR THE EXISTENCE OF M-

By

Marc G. DeBacker

To my Parence and Monique

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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linear accelerator for the pulse radiclysis studies and To my Parents and Monique Barl M. Hansen, S. Randall Minnich, and Vincent A. Nicely

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The author wishes to express his sincere appreciation to Professor James L. Dye for his guidance, assistance, and encouragement during the course of this investigation and the preparation of this thesis.

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Solutions of the alkali metals in ammonia have been studied for more than a century (1,2,3). Kraus (6) suggested that in dilute solutions, the metal dissociated into solvated electrons and solvated cations. The advent of pulse-radiolysis techniques and the discovery of the solvated electron in water (47), increased the interest in both stable and unstable solutions of solvated electrons. Solvated electrons produced by pulse radiolysis have only a transient existence in most solvents, but the life-times are long enough to permit some of their physical properties to be measured.

The nature of metal-ammonia solutions is still a subject of controversy. Nevertheless, there is general agreement that the optical absorption band can be attributed to the solvated electron. In order to explain other properties of these solutions however, it is also necessary to postulate the existence of loosely-bound aggregates.

The optical spectra of metal-amine solutions are more complicated than those of metal-ammonia solutions. Three bands have been observed, with maxima at 1300 nm (IR-band), at 660 nm (V-band), and at about 850-1050 nm (R-band) (44). The shapes and positions of the first two bands are

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independent of the metal. The IR-band has been attributed to solvated electrons by analogy with metal-ammonia solutions and in accord with the pulse radiolysis results of Dalton et al. (50).

Hurley et al. (54) demonstrated that the V-band was caused by the presence of sodium. Matalon et al. (55) attributed the V-band of sodium to the species Na^- by comparison of the spectrum of the V-species with the spectrum of I^- in solution. The R-band for the other metals was also attributed to the corresponding alkali anions.

The goal of the research described in this thesis was to establish the nature of the absorbing species in metalethylenediamine solutions, and to study the reactions and equilibria of these species. To attain this goal, the following studies were carried out:

(1) The nature of the V-band was studied by measuring its molar absorptivity and oscillator strength. The method involved the use of the reaction:

 $e^{-} + Na^{+} \longrightarrow V$ -band.

By such studies, it was possible to decide how many sodium ions per electron are involved in species responsible for the V-band. By using pulse radiolysis techniques the rate of this reaction was also studied.

The rea diamine has sodium hydro (2) The in metal-eth addition of followed by . spectrum. T they are fur by ionic stre (3) The water and in ^{using} pulse p ^{to an} equatio tained. This absorptivity ^{composition.} (4) Some ^{bilization} of ^{are n}ormally

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The reaction of sodium solutions with water in ethylenediamine has been further investigated with the role of sodium hydroxide being studied. FORICAL

(2) The equilibria existing between the absorbing species in metal-ethylenediamine solutions have been studied by the addition of various amounts of salt to metal solutions, followed by a measurement of the change in the optical spectrum. These equilibria are themselves fairly complex and they are further complicated by ion-pairing equilibria and by ionic strength effects.

(3) The spectrum of the solvated electron in ammoniawater and in ethylenediamine-water mixtures was measured by using pulse radiolysis techniques. The band shape was fitted to an equation whose form applies to all of the spectra obtained. This permitted estimates to be made of the molar absorptivity of the solvated electron as a function of solvent composition.

(4) Some preliminary experiments relating to the solubilization of the alkali metals in solvents in which they are normally insoluble were reported.

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II. HISTORICAL

2.1. Metal-Ammonia Chemistry

Alkali and alkaline earth metals can be dissolved freely in liquid ammonia without chemical reaction. The resulting solutions have been regarded both as scientific curiosities and as subjects for serious scientific investigation for most of the century since their discovery (1). They exhibit a blue or bronze color and sometimes a phase separation, depending upon concentration and temperature. The dilute blue solutions are electrolytic while the concentrated solutions behave as liquid metals. The intermediate region exhibits a metal-non-metal transition. The properties of these solutions were reviewed extensively during the "Colloque Weyl" I and II (2,3) and in several review articles (4,5). It is our purpose to discuss here only the properties of dilute solutions.

2.1.1. <u>Properties of Dilute Solutions</u> $(< 10^{-1} M)$.

Kraus (6) proposed that metals dissolved reversibly in ammonia to give atoms and ions in equilibrium according to:

tion in the d M \longrightarrow M⁺ + e⁻ we show a studies (1)
The reaction M is thermody by taking p catalyze th shown to be (7,8). Com as the conc species occ Inan of dilute s a) <u>Nu</u> an re Th ba or st er te as so tio and

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The reaction of the metal with the solvent:

$$M + NH_3 \longrightarrow MNH_2 + 1/2 H_2$$
 (2)

is thermodynamically favorable, but it can be made very slow by taking pains to avoid any trace of certain materials which catalyze the reaction with solvent. This reaction has been shown to be reversible under high pressures of hydrogen (7,8). Complete dissociation requires very dilute solutions; as the concentration increases, association to aggregate species occurs.

In a recent review, Dye (9) classifies the properties of dilute solutions in four categories.

a) <u>Null results</u>: properties independent of the metal and of the concentration. The most important null result is provided by the optical spectrum (10,11,12). The spectrum consists of a single broad absorption band whose position is independent of the metal and only slightly concentration dependent. The band is strongly asymmetric with a long tail on the high energy side. This shape is independent of metal, temperature, and concentration.

Some other properties must also be classified as "null results." The partial molar volume of the solute (13,14,15) is nearly independent of concentration in the dilute region. Solvent NMR studies (16) and line width of the EPR absorption (17,18,19) show

that electron relaxation is independent of concentration in this concentration range.

b) <u>Cation-electron interaction</u>: Conductance (20,21) and transference number (22) measurements show a concentration dependence of the cation conductance. The behavior of the conductance of dilute metalammonia solutions is similar to that of salts in liquid ammonia. The conductance decrease is explained in terms of ion pair formation.

Cation NMR studies (23,24,25) also show the effect of cation-electron interactions. The chemical shifts are both concentration- and temperaturedependent.

- c) <u>Electron-electron interaction</u>: The magnetic susceptibility (26,27,28) decreases markedly as the concentration increases. It also decreases as the temperature is decreased. This has been attributed to the formation of diamagnetic species.
- d) <u>Non-specific concentration effects</u>: These properties depend upon concentration but relate to the average properties of the solute species rather than to specific interactions. These properties cannot be used to develop a model for the solutions but are appropriate to test it.

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Activity coefficients (29) in dilute solutions give an indication of the extent of reactions involving the solvated electron.

The enthalpy of solution is strongly concentration and temperature dependent (30,14) and seems to correlate with susceptibility.

Transport numbers (22) indicate that most of the current is carried by negatively charged species and that the fraction carried by such species increases with concentration.

2.1.2. Models for Metal-Ammonia Solutions

Any model proposed for these solutions should explain all of the properties without too much reliance upon accidental cancellation of effects.

Two kinds of models can be considered; those based on a physical picture on one hand, and those based only on a py stoichiometry on the other.

2.1.2.1. Physical Models

The model proposed by Kraus (equation (1)) for the solution of metals, combined with the significant volume expansion accompanying the dissolution of metals led to the cavity model for the solvated electron.

 <u>Cavity Model</u>: This model postulates that in the case of infinitely dilute solutions, the electron is

removed from the metal cation and is located in a cavity in the liquid. The volume expansion data suggest that the electron creates a hole in the solvent. This model has been extensively used to interpret the optical spectrum.

Ogg (31) used this model to explain the optical spectrum. He considered the electron to be trapped in a "spherical box" surrounded by an infinite potential barrier. He calculated values for the solvation energy and position of the absorption maximum. His results gave a value of the position of the absorption maximum of 3,000 cm⁻¹ compared to the experimental value of 6,300 cm⁻¹.

A more quantitative formulation of the cavity model was carried out by Jortner (32). He supposed the electron to move in a cavity of radius R = 3.2 to 3.4 Å. The solvent around the cavity is polarized by the electron, producing, a potential, V(r), given by:

$$\begin{split} \mathbb{V}(\mathbf{r}) &= -\frac{e^2}{R} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{0}} \right) & \mathbf{r} < R \\ \mathbb{V}(\mathbf{r}) &= -\frac{e^2}{r} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{0}} \right) & \mathbf{r} > R \end{split}$$

where ϵ_{∞} is the high frequency, and ϵ_{o} the low frequency dielectric constant.

Jortner showed that a transition from the lowest s to the lowest p level in the potential well of the cavity could account for the optical absorption.

The value of the cavity radius required to fit the observed optical band position is 3.4 Å. This value also accounts for the volume expansion. Jortner, Rice and Wilson (33) attempted to improve this model with some SCF calculations but the agreement between calculated and experimental values worsened. This model is useful only in the limiting case of very dilute solutions.

b) Cluster model: This model was first introduced by Coulter (34) and later expanded by Becker, Lindquist, and Alder (35). This model considers that in dilute solution, the electron is removed from the vicinity of the cation. The electron polarizes the dipoles of the ammonia molecules so that they are oriented with their positive extremities preferentially turned towards the electron. The metal ion is also solvated in a similar way. The effect of the polarization of the ammonia molecules by the cation is to make the hydrogen extremities more positive, thereby increasing the affinity of these protons for the electron. Such a unit, consisting of a metal cation solvated by ammonia molecules upon which the electron is delocalized, is called a monomer. Becker, Lindquist and Alder further postulated that the diamagnetism resulted from the formation of dimers, M2.

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2.1.2.2. Models based on stoichiometry

In order to describe the concentration dependence of the properties of metal-ammonia solutions, some association of species and equilibria between these species must be introduced. Douthit and Dye (10) introduced the ion pair M_{am}^{+} , e_{am}^{-} to explain the optical spectrum of metal-ammonia solutions. In such pairing, the electron would stay surrounded by the same solvation sheath and the optical spectrum would stay unchanged when the concentration is increased.

Dye, Sankuer and Smith (22) used two equilibria (which had the same stoichiometry as the model of Becker, Lindquist and Alder) to account for their transference number results.

$$M^+ + e^- \longrightarrow M^+ \cdot e^-$$
 (3)

$$2M^{\dagger} \cdot e^{-} \longrightarrow M_2$$
 (4)

The presence of a species M_2 is difficult to reconcile with the null results provided by the optical spectrum. The optical spectrum follows Beer's law and this implies that M_2 is an absorbing species; but the spectral shape does not change with concentration and therefore M_2 must have the same spectral shape as e⁻ but twice the molar absorptivity. Gold, Jolly and Pitzer (36) proposed that (4) should be replaced by

$$2M^{+} \cdot e^{-} \longrightarrow (M^{+} \cdot e^{-})_{2}$$
 (5)

where $(M^+ \cdot e^-)_2$ is a quadrupolar aggregate in which each component retains its solvation shell.

These models give reasonable agreement for a few properties at a time, but cannot be used to explain all of the properties of metal-ammonia solutions. In particular if we try to get equilibrium constants from conductivity measurements and also from magnetic susceptibility measurements, serious discrepancies between these constants appear.

To resolve these discrepancies, Arnold and Patterson (37) assumed the existence of two diamagnetic species. They chose a species M⁻ consisting of an electron trapped in the field of an M center. The prime requirement on this M⁻ is that it is diamagnetic and negatively charged. The following equilibria were used:

$$M^+ + e^- \xrightarrow{K_{\theta}} M$$
 (6)

$$2M \xrightarrow{K_7} M_2$$
 (7)

$$M + e^{-} \xrightarrow{K_B} M^{-}$$
 (8)

The values of the three equilibrium constants were obtained by fitting conductance, transference data and paramagnetic susceptibilities. A remarkable fit of the experimental data was obtained.

Golden, Guttman and Tuttle (38) used a very similar model. The main difference was that they replaced the M_2 species by the ion-pair ($M^+ \cdot M^-$) and the "monomer" M by ($M^+ \cdot S^-$) (where S^- is a solvent anion or the solvated electron). Introducing a species A^- to represent either S^- or M⁻, they were able to reduce the number of equilibria to two, given by

$$M^+ + 2S^- \xrightarrow{K_B} M^- + 2S$$
 (9)

$$M' + A' \xrightarrow{K_{10}} M' \cdot A' \qquad (10)$$

The originality of this model arose from the fact that K_{10} was evaluated using Fuoss' theory of ion-pair dissociation. The constant K_9 was then used as the only adjustable parameter. Good agreement was obtained for vapor pressures, Knight shifts, conductances and optical spectra.

Recent conductance measurements by Dewald (21) showed that the previous conductance values at very low concentrations were in error. This new set of results showed that the conductance data could be explained by the standard electrolyte theory with only one ion-pairing equilibrium.

The main difficulty in finding a correct set of equilibria for the metal-ammonia solutions comes from the fact that magnetic and conductimetric data do not give the same equilibrium constants. At least five species are needed to explain the properties of these solutions: e⁻, the solvated electron; M⁺, the metal ion; M, the metal atom, monomer or ion-pair; M⁻, the metal anion or ion triple; and M₂ the metal dimer or ion quadrupole. Currently, these species are generally regarded as aggregates of solvated electrons and metal-ions, each species keeping its own solvation layer and therefore

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not being strongly perturbed by what is happening outside its layer. This approach helps to explain the invariance of the optical spectrum and the other null results. Dye (9) has attempted to fit all of the available data to a set of stoichiometric equations. In order to reconcile magnetic and conductimetric data, he postulated that magnetic interactions leading to a singlet state occurred, on the average over long distances such that deviations from normal ionic interactions caused by the spin pairing process are relatively small.

features. The band occurring at wavelengths around 650

2.2. Metal-Amine Chemistry

Alkali metals are less soluble in the aliphatic amines than in ammonia. While solutions of metallic character can be formed in ammonia, with concentrations of the order of several moles per liter, solubilities in amines are of the order of 10^{-3} M even in the most favorable cases.

2.2.1. Properties of Metal-Amine Solutions

The first studies of these solutions were done with methylamine by Gibson and Argo (39) who recorded the optical spectrum only in the visible region. One peak was observed with all of the metals and it was concluded by these authors that solutions in methylamine were similar to those in ammonia, with the difference that the peak was shifted to higher energies.

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The complete optical spectrum of alkali metals in methylamine was first recorded by Blades and Hodgins (40). Instead of a single peak as in ammonia, several bands were observed. Since then, a number of workers have studied the spectra of metal-amine solutions. Characteristic positions of the absorption maxima for metal solutions in several amines are summarized in Table I. From this table it can be seen that there are in general three bands depending upon the metal used, and that all of the amines present the same features. The band occurring at wavelengths around 650 nm is independent of the metal used and has been called the V-band. The band at about 1300 nm is also metal-independent and is called the IR-band. The position of the intermediate band is metal-dependent, this band is called the R-band.

The nature of the species responsible for these different bands has been a subject of controversy for a long time. The discovery of hyperfine splitting by the metal nucleus in methylamine and ethylamine solutions (45,46) demonstrates the presence of species of stoichiometry M involving a metal nucleus.

2.2.2. Models for Metal-Amine Solutions

a) <u>Infrared band</u>: This absorption band is independent of the metal used and its position and shape is very similar to the band observed with metal-ammonia solution. Furthermore, only the solutions exhibiting

Summary of the Position of the Absorption Bands of Metal-Amine Solutions Table I.

anIR-band are paramagnetic. The IR-band is attributed to the same types of species as those which exist in metal-ammonia solutions; that is the absorption is caused by solvated electrons which may, however exist in aggregate species. Further strengthening of this assignment comes from the pulse radiolysis studies (50). From the time of the first spectroscopic evidence for the formation of hydrated electrons (47), it has been assumed that solvated electrons produced by the radiolysis of water and other solvents are analogous to those formed when alkali metals are dissolved in liquid ammonia and amines. Compton and co-workers (48) showed that the spectrum obtained by pulse radiolysis of anhydrous ammonia was similar to that of metal solutions. On the other hand Anbar and Hart (49) reported an absorption maximum at 920 nm for the transient obtained in ethylenediamine. Dalton et al. (50) showed that this result was an instrumental artifact and that the shape of the absorption curve they obtained was close to that of the IR-band for solution of metals in ethylenediamine. The lack of fast infrared detectors at the time prevented a study of the spectrum up to the wavelength of the maximum.

b) <u>Visible (V) and red (R) bands</u>: These two bands are not observed in metal-ammonia solutions and a number

of interpretations have been proposed for them.

Blades and Hodgins (40) attributed the different bands to electrons trapped in different sites. In their model, the IR-band was due to an electron trapped into an ammonia-like cavity, i.e., an electron surrounded by the amino groups of the amine, and the V-band was due to aliphatic traps, i.e., cavities in which the amino groups have been replaced by methyl groups. The R-band was assigned to a third kind of trapping site which was presumed to be a mixture of the two preceding ones.

Fowles, McGregor and Symons (51) based their model upon magnetic considerations. Since the V-band was diamagnetic and seemed fairly independent of the metal, the diamagnetic species e_2^{-} was proposed for the V-band.

One very puzzling feature, observed by most investigators, was that in solutions exhibiting both V- and R-bands, the relative intensities of these two bands were absolutely irreproducible. Studies of the decay of the V- and R-bands in different laboratories gave different answers. Ottolenghi <u>et al</u>. (52) observed that the R-band decayed by a first order mechanism at a rate equal to twice the decay rate of the V-band and that the decay of the EPR signal due to monomers matched the decay of the

V-band. The V-band was therefore attributed to monomeric species and the R-band to dimeric species. On the other hand, Dve, and Dewald (53) observed a oneto-one decay of the V- and R-bands and observed some slow band interconversions for solutions of lithium in ethylenediamine. The R-band, being metal dependent, was attributed to the covalent dimer analogous to that observed in the gas phase. The peak position gave a good correlation with the transition ${}^{1}\Sigma_{u} \leftarrow {}^{1}\Sigma_{a}$ for dimers in the gas phase. These transitions occur at 860 nm for K2 and at 940 nm for Cs₂ (54). The species responsible for the V-band had to be metal-independent and be able to convert slowly to another species. This ruled out the possibility of using ion-paired species for which the equilibria would undoubtedly be fast. A species involving an electron trapped in the field of a molecular ion M2⁺ was proposed.

A major breakthrough occurred in 1968, when Hurley, Golden and Tuttle (55) reported that solutions of potassium in ethylamine prepared in a quartz apparatus did not show any V-band. Solutions of potassium previously prepared in Pyrex always showed a V-band. Flame analysis of the residue after solvent evaporation showed a correlation between the presence of the V-band and the presence of sodium. From this

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it seemed certain that the V-band was due to sodium contamination from the Pyrex glass. This explained part of the discrepancies in the measurements of optical spectra.

Recently, Matalon <u>et al</u>. (56) attributed the V-band to the species Na⁻. This assignment was based on properties of the spectrum of the V-band that paralleled those of I⁻ in solution. The spectrum of I⁻ in solution has an absorption band in the ultraviolet (≈ 250 nm) that does not correspond to any of the bands in the gas phase. It has been postulated that this band is caused by a chargetransfer-to-solvent (ctts) transition. Let us review briefly some of the characteristic properties of a ctts band.

The position (in energy units) of the absorption peak shifts linearly with the temperature to higher energies.

The positions of the peaks for two anions in a variety of solvents are in a linear relation to one another.

Matalon <u>et al</u>.(55) used solutions of sodium in ethylamine and ethylamine-ammonia mixtures to verify that the above relations also applied to metal-amine absorption bands.

The theory of ctts absorption was introduced by Frank and Platzman (57). Symons and co-workers (58). and Stein and Treinin (59) made further refinements. The calculations predict that the position of the maximum of absorption is given by the relation:

$$hv_{max} = I_{p} - I_{x} + \frac{e^{2}}{r_{o}} \left(\frac{1}{2} + \frac{1}{2D_{op}} - \frac{1}{D_{s}}\right)$$
$$- \frac{e^{2}}{2R_{e}} \left(1 - \frac{1}{D_{op}}\right) - \frac{\pi^{2}me^{4}}{2h^{2}} \left(\frac{1}{D_{op}} - \frac{1}{D_{s}}\right)^{2}$$

in which

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I_p = electron affinity of the ion. \overline{R}_{p} = radius of the excited state. D_S = static dielectric constant. D_{op} = optical dielectric constant. L_x = heat of solvation of the ion. r_0 = radius of the cavity.

ro can be related to the crystallographic radius by a multiplicative factor. For most of the anions in solution, a plot of hv max - I versus 1/r cryst gives a straight line.

Matalon et al. calculated the radii of the alkali anions using Slater's formula (60) r_M- = $2r_{M} - r_{M+}$. They used electron affinities obtained from molecular beam experiments. The plot of $hv_{max} - I_{p}$ versus $1/r_{M}$ - gave a straight line.

They concluded that both the V- and the R-bands were due to ctts transitions of alkali anions M^- , this anion being in equilibrium with solvated electrons. The presence of a V-band then implies the existence of Na⁻ in solution.

The results of the past few years simplify the picture of metal-amine solutions a great deal, since only two types of absorption bands are involved instead of three. The V-band is simply the sodium R-band.

The species, existing in metal-amine solution, responsible for the IR-band are probably similar to the species in metalammonia solutions. It seems that the main difference resides in the fact that in amines associated species tend to be more stable than in ammonia. It is also to be remembered that most of these species exist as ion pairs; even more so than in ammonia. Hansen (67) in order to explain the rate of reaction of solvated electrons with water in ethylenediamine postulated that electrons paired to form diamagnetic species in a manner similar to the pairing in ammonia.

2.3. Metal-Ether Solutions

Blue solutions of alkali metals in ether solvents were first reported in 1957 (61). These solutions are paramagnetic and have been compared to solutions in ethylamine. Cafasso and Sundheim (62) reported the positions of the optical

absorption bands, which corresponded to the V- and R-bands in amines.

Glarum and Marshall (63) recently described some photolysis experiments of solution in dimethoxyethane. In these studies they monitored the EPR signal of the solvated electron as a function of the wavelength of the irradiating light. The curve giving the intensity of the EPR signal as a function of the wavelength of the incident light resembles closely the absorption spectrum of these solutions. This suggests that the absorption of light is coincident with, or followed by, electron ejection.

2.4. Rationale for Thesis Research

The assignment of a species of stoichiometry M^- to the V- and R-bands is based only on some similarities with ctts bands and the observation that the species responsible for these bands gives no ESR signal. The optical studies were done by comparing the position of the I⁻ and M⁻ band in a very limited set of solvents (ethylamine-ammonia mixtures).

This work deals with studies of stoichiometry and kinetics of the reaction

m Na⁺ + ne⁻ \rightarrow V-band.

For this we needed to determine the molar absorptivities of the V-band and the solvated electron. The nature of the solvated electron was investigated by studying spectral shapes

b S Ģ K Π aÌ 11 t? Ŀ, t) Ţ i, ġį of the solvated electron band in the solvent mixtures waterammonia and water-ethylenediamine. From these data we hoped to be able to determine the species responsible for each band with more certainty than before.

We also studied the equilibria existing in solution when several bands are present. The particular reaction investigated was equally a subscription in the second state of the second st

(e⁻)_{solv} + $\kappa^+ \rightarrow R$ -band

K⁺ was chosen because its R-band is well separated from the IR-band. Avogadro's surber.

Throughout this study we were interested in band shapes, absorptivities and oscillator strengths. Because of the interpretations made on the basis of oscillator strength, the definition and nature of this function are considered here in some detail.

2.5. Theoretical Background: Oscillator Strength

A quantity of interest when studying optical spectra is the integrated molar absorptivity.

$$\mathbf{A} = \int_{\nu_{a}}^{\nu_{b}} \epsilon(\nu) d(\nu)$$
(1)

The amount of energy in the frequency range v_a to v_b which is absorbed by the sample per unit volume per unit time is given by



$$I.C.A. = I.C. \int_{v_{a}}^{v_{b}} \epsilon(v) dv$$
 (2)

where

C = concentration

I = intensity of light.

The energy absorbed per unit volume per unit time due to a certain frequency $v_{k\ell}$ associated with the transition $k \rightarrow \ell$ is given by the expression:

$$B_{k \to \ell} \rho(v_{k\ell}) \quad h v_{k\ell} \quad \frac{C N_0}{1000} \quad (3)$$

where $N_0 = Avogadro's$ number.

 hv_{kl} = energy absorbed per molecule undergoing a transition $k \rightarrow l$.

 $B_{k \rightarrow l} =$ Einstein transition-probability coefficient of absorption.

$$\rho(v_{k\ell}) = radiation$$
 density due to radiation of frequency $v_{k\ell}$.

If we assume that the absorption occurs over a narrow range of frequencies, $v_{k\ell}$ can be identified with the maximum of the absorption curve. We then equate (2) and (3) and solve for A to obtain

$$\mathbf{A} = \frac{\mathbf{B}_{\mathbf{k} \to \boldsymbol{\ell}} \quad \rho(\mathbf{v}_{\mathbf{k} \boldsymbol{\ell}}) \quad \mathbf{N}_{\mathbf{0}} \quad \mathbf{h} \mathbf{v}_{\mathbf{k} \boldsymbol{\ell}}}{1000 \text{ I}}$$
(4)

By definition

 $B_{k \to \ell} = \frac{2\pi}{3\hbar^2} | \overset{\mu}{\to} k_{\ell} |^{\beta}$ I (v) = cp(v)



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where $|\mu_{k\ell}|$ is the transition moment and c is the speed of light. We then obtain:

$$\mathbf{A}_{\text{theor}} = \frac{2\pi \left| \frac{\mu}{\sim k\ell} \right|^2 h N_0}{3000 \text{ h}^2 \text{ c}} v_{k\ell}$$
(5)

If the transition moment can be calculated one can predict the integrated absorption coefficient once v_{kl} is known.

Let us first consider the case of an heteronuclear molecule. In the approximation of the harmonic oscillator its dipole moment can be written, for displacement X as

$$\mu(\mathbf{x}) = \mu_0 + \left(\frac{\partial \mathbf{x}}{\partial \mathbf{x}}\right)_{\mathbf{x}=0} \mathbf{x}.$$

For transitions from the level v=0 to v=1 we have

$$\left| \underbrace{\mu_{01}}_{\text{Ho1}} \right| = \left\langle \psi_{1} \right| \mu_{0} + \left(\frac{\partial \mu}{\partial \mathbf{x}} \right)_{\mathbf{x}=\mathbf{0}} \mathbf{x} \right| \psi_{0} \right\rangle$$
(6)

where ψ_0 and ψ_1 are wave functions for the two states of the harmonic oscillator.

$$\left| \begin{array}{c} \mu \\ \sim \mathbf{0} 1 \end{array} \right|^{2} = \frac{\pi}{4\pi\mu_{m}} \frac{\eta}{\nu_{01}} \left(\frac{\partial\mu}{\partial\mathbf{x}} \right)^{2}_{\mathbf{x}=0}$$
(7)

Combining (7) with (5) we get:

$$\mathbf{A} = \frac{\pi \mathbf{N}_{0}}{3000 \ \mu_{m} \mathbf{c}} \left(\frac{\partial \mu}{\partial \mathbf{x}}\right)^{2}_{\mathbf{x}=0} \tag{8}$$

The classical theory of interaction of light with bound electrons considers that the electron is bound to the nuclear framework by a Hooke's law type of force. We will therefore apply the results obtained for the harmonic oscillator to the

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$$\mathbf{A} = \frac{\pi \mathbf{N}_{\mathbf{0}}}{3000 \ \mu_{\mathbf{m}} \ \mathbf{c}} \left[\left(\frac{\partial \mu}{\partial \mathbf{x}} \right)_{\mathbf{x}=0}^{2} + \left(\frac{\partial \mu}{\partial \mathbf{y}} \right)_{\mathbf{y}=0}^{2} + \left(\frac{\partial \mu}{\partial \mathbf{z}} \right)_{\mathbf{z}=0}^{2} \right]$$
(9)

As a reasonable approximation we replace the reduced mass μ_m by m the mass of the electron. As a further approximation we set

$$\left(\frac{\partial \mathbf{x}}{\partial \mathbf{\mu}}\right)_{\mathbf{z}}^{\mathbf{x}=\mathbf{0}} = \left(\frac{\partial \mathbf{x}}{\partial \mathbf{\mu}}\right)_{\mathbf{z}}^{\mathbf{\lambda}=\mathbf{0}} = \left(\frac{\partial \mathbf{z}}{\partial \mathbf{\mu}}\right)_{\mathbf{z}}^{\mathbf{z}=\mathbf{0}} = \mathbf{e}_{\mathbf{z}}$$

e = charge of the electron.
The integrated coefficient now becomes:

$$\mathbf{A}_{\text{model}} = \frac{\pi}{1000} \frac{\mathbf{N}_0}{\mathbf{m}_c} \frac{\mathbf{e}^2}{\mathbf{m}_c} \tag{10}$$

The ratio of the experimental integrated absorption coefficient to the intensity expected from an equivalent harmonic oscillator is called the oscillator strength and is defined by

$$f_{exp} = \frac{A_{exp}}{A_{model}} = 4.33 \times 10^{-9} \int \epsilon(\overline{\nu}) d\overline{\nu}$$
(11)

where $\overline{\nu}$ is in wavenumbers.

A purely theoretical value can be obtained for the oscillator strength if the experimental value A_{exp} is replaced by A_{theor} given by (5)

$$f_{\text{theor}} = \frac{8\pi^2 \text{ mc}}{3 \text{ he}^2} v_{k\ell} \left| \begin{pmatrix} \mu \\ \sim k\ell \end{pmatrix} \right|^2$$
(12)

The oscillator strength of a transition is a measure of the intensity of that transition. For intense transition, and

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for one electron systems, f is usually of the order of unity. Kuhn and Thomas (82) have shown that

$$\sum_{n} f_{mn} = N$$
(13)

where f_{mn} is the oscillator strength for a transition from the state m to the state n. The sum is taken over all final states n; N is the total number of electrons in the system. This is known as the f-sum rule or the Kuhn-Thomas sum rule. It can be shown (64) that transitions to upper states have positive f_{mn} 's; those to lower states have negative f's.

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III. EXPERIMENTAL

3.1. General Techniques

3.1.1. Glassware Cleaning

All glassware was cleaned in two steps. The first involved the use of an HF cleaner $(33\% \text{ HNO}_3, 5\% \text{ HF}, 2\%$ acid soluble detergent, 60% water) followed by a thorough rinsing with conductance water. The second step was a washing with aqua regia prepared <u>in situ</u>. The glassware was then rinsed at least ten times with boiling conductance water and dried in an oven.

All parts of the stopped-flow apparatus were cleaned in the same way before assembling the system. Between each run, the flow system was washed by flowing freshly prepared aqua regia through it. This was followed by rinsing. The system was dried by evacuation.

The vessels destined to contain ethylenediamine were rinsed several times with anhydrous liquid ammonia.

3.1.2. Vacuum Techniques

All of our work was done using standard high vacuum techniques. The Pyrex vacuum lines were evacuated using

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dual-stage mechanical pumps and two-stage oil diffusion pumps. The use of Dow Corning 704 diffusion pump fluid allowed us to reach pressures as low as 10⁻⁶ torr without liquid nitrogen traps. Liquid nitrogen cooled traps were used whenever ethylenediamine or ammonia were in the vacuum line. The pressure measurements were made with a Veeco RG75P glass ionization gauge tube and a RGLL6 control circuit. Glass stopcocks were of the high vacuum type; they were greased with "Dow Corning High Vacuum" silicone grease. Teflon needle-valve stopcocks were also extensively used (Fisher-Porter, Delmar-Urry).

3.2. Metal Purification

Metals of the highest purity available were used. They were always distilled several times prior to use.

Na: J. T. Baker, Co. (99.99%)
Rb: Fairmount Chemical Co.
K: J. T. Baker, Co. (99.99%)
Cs: A gift from the Dow Chemical Co.

3.2.1. <u>Storage of Small Quantities of</u> <u>Alkali Metals</u>

Sodium and Potassium: Small pieces of metal were cut from the center of a larger piece and covered with nhexane. These pieces were introduced into a 40 mm OD vessel containing some lengths of 4 mm OD tubing which had been sealed at one end (Figure 1). The system was evacuated and





Figure 1. Apparatus for the preparation of storage tubes for sodium or potassium.

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the metal was melted. When all gas-evolution stopped, a slight pressure of helium was applied over the molten metal to force it into the small tubing. In this way, small samples of metal free of oxides could be obtained by cutting a small piece of glass tubing.

<u>Cesium and Rubidium</u>: Cesium and rubidium burn very easily in air. These metals were originally contained in glass ampoules of 30 to 40 grams of metal each. These large ampoules were first divided into smaller ones containing only a few grams by the method described by Dewald (66). To get even smaller samples of metal, the apparatus shown in Figure 2 was used. The ampoule containing the metal was scored with a glass-cutting knife and the metal was cooled by immersing the ampoule in liquid nitrogen. The ampoule was then broken and introduced into A. Tube A was quickly sealed and pumped. The metal was then melted and distilled into B under high vacuum. Constrictions C and D were then sealed off. The metals could then be melted into the long tube and the quantity needed taken by sealing a length of tubing.

3.2.2. Breakable Metal Ampoules

It was found very convenient for the preparation of metal solutions, to have the pure metals enclosed in an ampoule equipped with a breakseal. In this way the solvent could be degassed without being in contact with the metal. The procedure used to distillmetal into this ampoule was the

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same as that described previously. The apparatus is shown
in Figure 2(b).

3.2.3. Analysis of the Alkali Metals

The alkali metals, sodium and potassium were analyzed by both emission and absorption flame photometry. These studies were made by using a Beckman DB Flame Photometer and/or a Jarrell-Ash Atomic Absorption Flame Photometer. The alkali metals were analyzed after they had been introduced into a dilute aqueous solution of hydrochloric acid. Standard solutions for potassium and sodium were prepared. A stock solution containing 1g/l equivalent of potassium or sodium was prepared. All the other more dilute standard solutions were prepared by volumetric dilution from the stock solution, never by successive dilutions. The concentration of the unknown was determined by interpolation between two standard solutions.

The potassium was analyzed for the presence of sodium in this way. The potassium coming from the manufacturer did not show any detectable trace of sodium. After distillation of potassium metal in Pyrex with a flame containing no oxygen, no sodium was detected. Distillation of potassium with an oxy-gas flame produced a measurable amount of sodium in the distillate. In a typical experiment the molar ratio Na/K was 0.30.

3.3. Solvent Purification

Ethylenediamine of 99% stated purity was obtained as a gift from the Dow Chemical Co. The solvent was first put under vacuum in a 5 liter: vessel over barium oxide for a few days. A magnetic stirrer was used to insure good mixing of the liquid and the solid. Ethylenediamine was then transferred into an evacuated freeze purification vessel through a medium porosity glass frit. The freeze purification vessel is shown in Figure 3. The solvent was slowly frozen in a refrigerator whose temperature was kept near 0°C. During the freezing process, a low voltage was applied to the central heater to establish stirring by convection. The freezing process required from two to three days under those conditions. After freezing, the central core was melted and discarded.

After 5 cycles it was found that this ethylenediamine could be distilled onto a potassium film to form stable blue solutions. However ethylenediamine prepared in this way could not be mixed with a dilute metal solution without decomposition. One more step was added to the purification of the solvent. It involved the formation of a blue solution with Na-K alloy, followed by a distillation from this solution. Solvent prepared in this way usually gave very stable solutions.



Figure 3. Freeze-purification apparatus.

3.4. Solution Preparation

A typical vessel for the preparation of solutions is shown in Figure 4.

3.4.1. Metal Solutions

The metal was introduced into a side arm of the vessel in an ampoule equipped with a breakseal. Ethylenediamine was distilled into the vessel under vacuum by using a dry ice-isopropanol bath. The solvent was then degassed by successive freeze-pump-thaw cycles until no detectable change in pressure occurred. The freezing was done with a dry iceisopropanol bath rather than with liquid nitrogen, because there is a phase transition in solid ethylenediamine below -80°C which causes the solid to expand and to break the vessel. After degassing, the solvent was again frozen, the breakseal broken with the magnet, and the metal distilled. A pressure of about 100 torr of purified helium was applied and the vessel was separated from the vacuum line. The frozen ethylenediamine was then thawed with warm water and a blue solution formed immediately.

3.4.2. Salt Solutions

Analytical reagent grade salts were used. Quantities larger than 100 mg were weighed; smaller quantities were obtained by measuring the volume of a water solution which contained a known concentration of these salts. The salts



Figure 4. Solution make-up vessel.

were dried by pumping at 10⁻⁸ torr for a few days. After evacuation, anhydrous ammonia was condensed onto the salt and distilled away several times to complete the drying process.

3.5. Absorption Spectra

3.5.1. Spectrophotometer

The principal component of the spectrophotometer shown schematically in Figure 5, is a Perkin-Elmer Model 108 Rapid-Scan Monochromator. This and the associated electronics have been described by Dye and Feldman (65). We will review briefly the different components. The monochromatic light beam leaving the monochromator is divided by a beam splitter and focused on the sample and reference cells. The two light beams are received on two RCA 7102 or 6199 photomultipliers. The anode currents of the photomultipliers are sent to a transducer circuit (Philbrick-Nexus PL1P) which takes the logarithm of the ratio of the two intensity values. Operational amplifiers (Philbrick-Nexus P25A and P65AU) are used to produce an output voltage of about one volt per absorbance unit. The absorbance signal is recorded in analog form on a 4 channel: Ampex SP300 FM Tape Recorder. One channel is used to record the scan synchronization signal from the monochromator. The spectrophotometer can be assembled either on a stopped flow appratus or with a thermostated cell



Figure 5. Block diagram of the spectrophotometer.

compartment. The cell holders accept either square optical cells or round ESR tubes.

3.5.2. Variable Path Length Cell

A cell whose path length could be varied under vacuum was built. It is shown in Figure 6. It consisted of a 1 cm path length quartz cell with a square cross-section connected to a 16 mm cylindrical quartz or Pyrex tubing. In this cell, a quartz insert could be raised or lowered with an external magnet. This insert was built with three steps so that by raising or lowering the cell in the light beam or by completely removing the insert, four path lengths were obtained: 10.0, 1.0, 0.3 and 0.1 mm. Various side arms were fixed onto the quartz or Pyrex part so that dilutions could be made by distillation. This did not work well because the vapor pressure of ethylenediamine is too low to permit fast distillations, and the smallest trace of hydrogen from decomposition stops this distillation completely.

3.5.3. Stopped-flow System

The stopped-flow system used in this work is similar to those described by Dewald (66), Feldman (67), and Hansen (68). Only one concentration of metal could be used per run but a variety of solutes could be used, and dilutions could be made. The system down to the waste vessel was equipped with Teflon stopcocks and Fischer-Porter "Solv-Seal" joints. Only the minimum number of joints was used in order to



Figure 6. Variable path length cell for optical spectra.

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prevent leaks. A schematic view of this system is shown in Figure 7. The syringes were equipped with Teflon plungers on which lips had been machined to give a vacuum-tight liquid seal. The syringes used first were "gas tight" syringes from Hamilton. In the course of this work, however, it became necessary to have special syringes constructed. These syringes were made of precision bore tubing (Trubore 8700-60, Ace Glass Inc.). Teflon plungers were machined to fit these new syringes.

As shown in Figure 8, in order to eliminate air leakage from the syringes, a back-pumping of the seal was installed. (This modification was suggested by Dr. V. A. Nicely.) A side arm was sealed at the mid-point of the syringe, taking care not to distort the barrel, and the Teflon plunger was equipped with two pairs of seals, above and below the connection, so that this section could be constantly evacuated during the motion of the plungers.

The mixing cell was a quartz four-jet: mixing cell. This type of cell gives a mixing time of the order of 2 milliseconds. Details of the construction are given by Hansen (68).



Figure 7. Schematic of the stopped-flow system.



Figure 8. Detailed view of a syringe used in the flow system.

3.6. Data Analysis

3.6.1. Calibrations

a) <u>Wavelength calibration</u>: The sweep of the optical frequencies by the monochromator is nearly a sinusoidal function of time. Electronic circuitry which was designed to give a display linear in wavelength was supplied with the instrument, but this proved to be unreliable. Therefore a slotted disc was constructed which permitted light to reach a photodiode once each cycle. In this way a synchronization pulse was produced at the beginning of each scan. The wavelength calibration was done with respect to this reference pulse.

The wavelength calibration could be done in either of two ways:

- (i) The monochromator is equipped with two micrometers that permit reproducible adjustments of the position of the center of scan and of the scan width. These settings can be calibrated with respect to absorption lines of glass filters. The knowledge of these values and of the rotation speed of the mirror is sufficient to calibrate the wavelength scale.
- (ii) The second method (which was actually used in this work) involved the recording of a known

spectrum under the same conditions as the unknown. In this way, the unknown spectrum could be calibrated by comparison. A computer program, described in the next section, was written to do this calculation.

b) <u>Absorbance calibration</u>: The path length of the optical cell was measured by comparing the absorbance of a solution of potassium permanganate measured with our system, and with a UNICAM SP800 in a standardized cell. The absorbance signal which we measured appeared as an output voltage. To obtain the absolute absorbance, the signal obtained by using standard neutral density filters (Oriel Optics Inc.) was recorded and used for calibration.

3.6.2. Data Analysis with a CAT

Most of the data consisted of spectra that did not change over long periods of time. The main purpose of the analysis was to obtain spectral shape and absorbances. Data stored on magnetic tape were analyzed and put into digital form by using a time averaging computer (CAT) Varian C 1024. Figure 9 shows a block diagram of the circuit used for analysis.

Description of the Analysis.

The signal from a blank channel of the tape recorder and the signal carrying the spectrum were fed to a





differential amplifier in order that the noise from the tape recorder could be minimized. The output of the differential amplifier was sent to the input of the CAT and to an oscilloscope. The synchronization signal triggered the time base of the oscilloscope. The gate signal from the oscilloscope triggered the CAT and a time delay circuit. The delayed pulse triggered a waveform generator (Wavetek, Co.) which gave from 1 to 256 periods of a square wave. Each period of the square wave was then used to advance the channels of the CAT. Each period of the square wave advanced one channel. By changing the time delay, the frequency of the square wave and the number of periods, it was possible to analyze any part of the spectrum.

The data stored in the CAT memory were then plotted on an X-Y recorder or punched directly on cards.

It is to be noted that the oscilloscope was used only for monitoring purposes. All of the measurements were made from the output of the CAT.

3.6.3. <u>Typical Measurements Made During</u> <u>a Run</u>

- 1. The amplifiers of the tape recorder were calibrated to give a known amplification ratio (usually 1:1).
- 2. The base line was recorded.
- 3. The spectra of the neutral density filters were measured.

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- 4. The spectrum of a didymium or holmium glass filter was recorded to give the wavelength information.
- 5. The metal solution was introduced into the system and its absorbance was measured.
- 6. The metal solution was mixed with solvent. If the mixture was stable the run could be continued. Steps 2 through 4 were repeated several times during the run.

3.7 Computer Treatment of the Spectra

3.7.1. Linearization of the Energy Scale

If we assume that the dispersion of the prism of the spectrophotometer is linear over the region of interest and that the rotating mirror turns at a constant angular velocity, then we can write

 $P = A \sin [\pi(wt + \gamma' + 0.5)] + B$

with

P = wavenumber at the point in question. A = width of the scan in cm^{-1} . B = center of the scan in cm^{-1} . w = angular velocity of the mirror. t = time of rotation from arbitrary zero. Υ = phase factor.

To obtain the values of the above parameters, it was convenient to fit this equation to a calibration spectrum. The spectrum (both the forward and the reverse scan) of the didymium glass filter was recorded. The following quantities were then measured from an X-Y recording of the calibration spectrum.

- P (I) = wavenumber of the Ith calibration point.
- X (I) = fraction of total scan at the Ith point.

The values of w and \forall were obtained by using the relation: X = w.t + \forall . The values of A and B were calculated by fitting with a least-square method P and t to the equation giving P. After the calibration was completed, the wavenumber corresponding to any channel number could be calculated.

All of the spectra studied in a given run were analyzed under exactly the same conditions as the calibration spectrum and punched on cards.

3.7.2 <u>Calibration of Absorbance</u>

The absorbance curves obtained with the neutral density filters were analyzed at the same time as the spectra of metal solutions. For each channel number, a power series was calculated which related the true absorbance to the number of counts from the CAT. In this way the spectrum could be transformed to real absorbances.

3.7.3. Band-Shape Analysis

In order to analyze a spectrum consisting of V-, R-, and IR-bands together it was necessary to know the positions and band shapes of these bands and, if possible, to assign equations which describe these bands. All of the bands are asymmetric with a long absorption tail towards the high energy side. A combination of a Gaussian band shape and a Lorentzian band shape was used. The procedure used involved fitting the data to the following equations:

for
$$\overline{\nu} < \overline{\nu}_{max}$$

$$\mathbf{A} \ (\overline{\nu}) = \mathbf{A} \ (\overline{\nu}_{max}) \cdot \exp \left[-0.69315 \ \left(\frac{\overline{\nu} - \overline{\nu}_{max}}{\Delta \overline{\nu}_{1}} \right)^{2} \right]$$

for
$$\overline{\nu} \ge \overline{\nu}_{max}$$

$$A(\overline{\nu}) = \frac{A(\overline{\nu}_{max})}{1 + \left(\frac{\overline{\nu} - \overline{\nu}_{max}}{\Delta \overline{\nu}_{1}}\right)^{2}}$$

with

A
$$(\overline{\nu})$$
 = absorbance at the wavenumber
 $\overline{\nu}_{max}$ = wavenumber at the maximum.
 $\Delta \overline{\nu}_{\frac{1}{2}}^{G}$ = half-width at half-height for the Gaussian
side.
 $\Delta \overline{\nu}_{\frac{1}{2}}^{L}$ = half-width at half-height for the Lorentzian
side.

A non linear least-square program was used to fit these equations to the data (69). This program adjusted four parameters

$$A(\overline{\nu}_{max}), \overline{\nu}_{max}, \Delta \overline{\nu}_{\frac{1}{2}}$$
 and $\Delta \overline{\nu}_{\frac{1}{2}}$.

The results of this fit are shown in Figures 10 and 11 for cesium in ethylenediamine and sodium in ethylenediamine.

It is not possible to obtain only the R-band of potassium so we had to assume that the R-band followed the same form of equation as did the V- and IR-bands.

With one equation for each of the bands, a program was written (Program SPFIT) that fitted any composite spectrum to a sum of V-, R- and IR-bandsby least-squares. It is to be noted that the program SPFIT did not adjust the band-widths. These were obtained from spectra of the pure components. The fits obtained with this program will be given in the Results section.

3.8. Pulse Radiolysis Experiments

Two kinds of experiments were performed, spectral determinations and kinetic studies. Neither of these required precise dosimetry.

3.8.1. The Accelerator

These experiments (70) were performed at the Ohio State University with a Varian V-7715A linear electron accelerator. Electrons were generated with energies of 3-4 MeV, with a pulse current of about 350 mA. The pulse width was varied from 0.1 to 1.2 μ sec. The average dose of radiation received by the solution was about 6 x 10⁶ eV/g for a 0.1 μ sec pulse.









3.8.2. Optical System

A block diagram of the optical detection system is shown in Figure 12. The light beam from a 500 W-Osram Xenon lamp, type XBO450W, was split, after passing through the cell, by a partially silvered mirror. The two light beams entered two grating monochromators (Bausch and Lomb, Type 33-86-25, f/3.5). This set-up allowed two wavelengths to be monitored simultaneously. The detectors used in this work were of two kinds depending on the type of studies.

(i) For the spectral studies a liquid-nitrogen cooled indium-antimonide detector, type A10X (Barnes Engineering, Inc.) was used. An RCA 7102 photo – multiplier was used in the other beam as a reference wavelength monitor in point-by-point spectral scanning.

For effective use of the indium antimonide detector it was found desirable to pulse the lamp to obtain a higher output. In the high intensity pulsed mode a current pulse of 150 A is added to the normal continuous current of 20 A. The resulting increase in intensity is about 25-40 times that of the steady state operation depending on the wavelength. The duration of the light flash is several milliseconds, with a usable constant intensity portion of 0.15 msec synchronized with the electron pulse.





(ii) For the kinetics studies two wavelengths were monitored: 600 nm with a 1P25 photomultiplier and 1020 nm with an RCA 7102 photomultiplier. The output of both detectors were displayed on a dual beam oscilloscope and pictures of the traces were taken.

3.8.3. Reaction Cells

The optical-irradiation cells were made of high-purity silica. They were connected to a sample handling device in which samples of material to be added to the solvent were contained in sealed, evacuated glass bulbs which could be successively broken <u>in situ</u> to change the composition of the system. This sample system is shown in Figure 13.

This technique was very useful since all solute: additions were made to the same sample of solvent.



Figure 13. Cell used for pulse radiolysis studies.
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IV. RESULTS

In this section the band at 660 nm will be referred to as the V-band, the band at 850 nm as the R-band and the band at 1300 nm as the IR-band.

4.1. Sodium Solutions

4.1.1. Influence of Sodium Ions Upon the V-band

Hurley, Golden and Tuttle (55) concluded that the V-band observed in potassium amine solutions resulted from the exchange of potassium ions with sodium from Pyrex glass. A series of experiments was done here to test these conclusions. We established in section III that distillation of potassium through Pyrex did not cause contamination of the distillate by sodium provided that a cool flame was used.

When a Pyrex cell was filled with anhydrous ethylenediamine, allowed to stand for several hours, and then emptied by distillation, no sodium could be detected in an aqueous leach. When an identical cell was filled with a solution of potassium in ethylenediamine, with no excess metal present, allowed to stand for one hour, and then emptied by distillation, the molar ratio of Na/K was 0.13 (it should be noted,



however that only 1.7×10^{-6} gram atoms of potassium were used). By using a quartz optical cell of path length 1.0 cm attached to a Pyrex apparatus, it was found that distillation of the metal through Pyrex, and contact of the solution with Pyrex gave essentially only the V-band. Analysis of the solution gave an Na/K ratio of 0.5, with enough total sodium to account for the V-band.

A solution prepared in an all quartz apparatus showed only the R-band. Analysis of the solution showed no detectable sodium. In another experiment, when a solution prepared in quartz and containing only the R-band, came in contact with Pyrex, a V-band developed immediately.

The difficulties involved in the production of stable dilute solutions prevented us from getting reliable values of the concentrations of species responsible for each of the absorption bands. Concentrations of alkali-metals as low as those we were using could only be determined by flame photometry and even then only the total concentration of the particular metal could be measured.

It was also noted in these experiments that a solution of cesium could be prepared in a Pyrex vessel without giving any trace of a V-band. This agrees with previous observations in this laboratory (66,68).

4.1.2. <u>Molar Absorptivity of Sodium</u>-Ethylelediamine Solutions

The instability of metal-amine solutions has prevented

the determination of the concentration of active metals by the usual analytical techniques. None of the techniques which involve analysis for the alkali metal permit distinction between the metal present as decomposition product, and as active metal. Direct determination of the concentration of metal solutions can be done by reacting the solutions with an acid (H_{20} or NH_4^+) and measuring the volume of hydrogen evolved (66).

 $e^{-}(or M) + H_2O \longrightarrow OH^{-} + 1/2 H_2 (+ M^{+})$

This method requires large volumes of solution and/or relatively high concentrations in order to obtain a volume of hydrogen large enough to permit accurate measurement.

The optical spectrum of a sodium solution in ethylenediamine consists of a single band centered at 660 nm (15,200 cm^{-1}) with little or no absorption in the infrared region. This indicates that the equilibrium

V-band ____ IR-band

lies very far to the left. The results described later also indicate that the reaction

 $e^{-}(IR-band) + Na^{+} \longrightarrow V-band$

occurs very rapidly.

The reaction of sodium ions with a source of solvated electrons, such as a cesium solution, proceeds quantitatively

to give the V-band presumably by the reaction

m Na⁺·X⁻ + n Cs⁺e⁻
$$\longrightarrow$$
 V-band (IR-band)

By keeping the initial concentration of the solvated electrons greater than that of sodium ions, the dependence of the absorbance of the V-band upon the concentration of sodium ions added could be determined.

Some typical spectra are shown in Figure 14 in which we have shown the effects of various amounts of sodium ion. It is to be noted that the IR-band does not follow the variations of the V-band. This is because of the decomposition of the cesium solution. The data were analyzed by using the program SPFIT to separate the absorbance due to the V-band from the absorbance due to the remaining IR-band. A typical fit of the data is shown in Figure 15. The results are shown in Table II. The absorbances have been corrected to a pathlength of 1 mm. A plot of the absorbance of the V-band versus the concentration of sodium ions added is shown in Figure 16. These data can be fitted by least squares to a straight line of slope $8.2 \pm 0.3 \times 10^3 \text{ M}^{-1}$. This yields a molar absorptivity of 8.2 \pm 0.3 x 10⁴ M⁻¹ cm⁻¹ based upon added sodium. The data obtained when sodium ions were in excess have not been included. In this case, the absorbance is proportional to the concentration of the cesium solution at the time of the experiment. This concentration can vary









| [Na ⁺] M x 10 ⁵ | A | Standard deviation |
|---|-------|-----------------------|
| 2.15 | 0.23 | 0.02 |
| 2.50 | 0.195 | 0.02 |
| 3.15 | 0.22 | 0.02 |
| 4.30 | 0.41 | 0.04 |
| 6.30 | 0.356 | 0.07 |
| 9.45 | 0.85 | 0.07 |
| 10.75 | 0.94 | 0.07 |
| 12.60 | 0.89 | 0.03 |
| 14.60 | 1.25 | 0.08 |
| 18.90 | 1.82 | 0.10 |
| 18.90 | 2.11 | 0.05 |
| 22.00 | 1.79 | 0.12 |
| 37.85 | 2.65 | 0.15 |
| 44.00 | 3.86 | 0.40 |
| | | |

Table II. Absorbance of the V-band Produced by Addition of Sodium Ions to a Cesium Solution



Figure 16. Absorbance of the V-band as a function of the concentration of sodium ions.

because of decomposition. Therefore the amount of V-band obtained in such experiments is not reproducible. It was just such non-reproducibility of metal solution concentrations which led us to use the present method in the first place.

4.1.3. <u>Reaction of the V-band Species</u> with Anthracene

From the results of pulse radiolysis of solutions of aromatic compounds in alcohols, it was known that the electron transfer reaction to give the negative radical ions was very fast (70). It was thought that the reaction of the V-band species with anthracene would also be very fast. Previous observations indicated that anthracenide ion was very stable in ethylenediamine, and did not even react with water (68). Furthermore, these observations showed that the radical anion was very rapidly formed when cesium solutions were mixed with solutions of anthracene.

When a sodium solution, of concentration 2.5×10^{-4} M, was allowed to contact a crystal of anthracene, the solution turned to a bright yellow color very rapidly. The optical spectrum of this solution in a 1 mm cell did not show any spectrum characteristic of the anthracenide but, rather, exhibited a new band at 437 nm. A small peak of anthracenide was observed when the pathlength was increased to 1.0 cm. After a few hours it was noted that the solution gradually became greener. An optical spectrum recorded 24 hours later

showed the characteristic spectrum of anthracenide as well as the peak at 437 nm. At this time, both peaks were of the same magnitude. This spectrum did not change further with time. The spectrum is shown in Figure 17; the positions of the peaks of anthracenide in tetrahydrofuran (75) and their intensities have also been reported. The solvent was then distilled back over sodium to regenerate a blue sodium solution. This solution was put back into contact with antracene and anthracenide. The optical spectrum of the resulting solution was recorded as a function of time. A decay of the band at 437 nm was observed together with a growth of the anthracenide peak. An isosbestic at 530 nm was observed. Experimental difficulties prevented us from obtaining the beginning of the reaction. The spectra observed during the reaction are shown in Figure 18. Both the growth and the decay follow second order kinetics as shown in Figure 19.

4.1.4. <u>Kinetics of the Reaction of Sodium</u> <u>Ions with the Solvated Electrons</u>

The formation of the V-band by the reaction:

 $m e^{-} + n Na^{+} \longrightarrow V-band$

can be studied very conveniently by pulse radiolysis. Each pulse of electrons was used to obtain two sets of kinetic data: the growth of the V-band, monitored at 600 nm (16,600 cm^{-1}), and the simultaneous decay of the e⁻ band (IR-band)











Figure 19. Kinetics of growth of the anthracenide ion and of decay of the intermediate (yellow) band.

monitored at 1020 nm (9,800 cm⁻¹). A set of typical traces is shown in Figure 20. Both the growth of the V-band and the decay of the IR-band follow second order kinetics within experimental error. A typical pair of curves is shown in Figure 21, together with the fit of these curves to a second order mechanism using 3 parameters: A_0 and A_{∞} , absorbances at time zero and infinity; and k the rate constant. Each pair of curves gives us some informations about the relative absorbances of the two species. In Table III, we have listed the values of the initial absorbance of the IR-band and of the final absorbance of the V-band. It is to be noted that the ratio of these two absorbances is a constant whose value is 1.88 ± 0.28 .

In order to reduce the number of adjustable parameters needed to fit the data, each set of curves was fitted simultaneously to the same kinetic equation.

Analysis of Kinetic Results

For reasons of clarity we are going to assume here some of the results that will be established later. Namely, we Postulate that the stoichiometry of the reaction is:

 $Na^+ + 2e^- \longrightarrow Na^-$ (1)

and that the two absorbing species are e⁻(IR-band) and Na⁻ (V-band).









| Identification | Α _{Na} -(600,∞) | A _e -(1020,o) | $\frac{\dot{A}_{Na}}{A_{e}} = (1020, o)$ |
|----------------|--------------------------|--------------------------|--|
| | | | |
| 3.69.81 | 0.462 | 0.231 | 2.00 |
| 82 | 0.426 | 0.203 | 2.10 |
| 86 | 0.215 | 0.086 | 2.50 |
| 87 | 0.156 | 0.079 | 1.97 |
| 88 | 0.812 | 0.328 | 2.47 |
| 89 | 0.715 | 0.345 | 2.07 |
| 90 | 0.666 | 0.334 | 1.99 |
| 91 | 0.691 | 0.380 | 1.82 |
| 102 | 0.644 | 0.369 | 1.74 |
| 103 | 0.624 | 0.367 | 1.70 |
| 107 | 0.851 | 0.561 | 1.51 |
| 109 | 0.118 | 0.068 | 1.72 |
| 112 | 0.177 | 0.090 | 1.96 |
| 113 | 0.757 | 0.491 | 1.54 |
| 114 | 0.617 | 0.364 | 1.69 |
| 115 | 0.973 | 0.528 | 1.84 |
| 116 | 1.139 | 0.781 | 1.46 |
| 117 | 1.093 | 0.533 | 2.05 |
| 120 | 0.251 | 0.134 | 1.87 |
| 121 | 0.259 | 0.151 | 1.71 |

Table III. Reaction $e^- + Na^+ \longrightarrow V$ -band. Relation Between the Absorbance of the IR-band at the Beginning of the Reaction to that of V-band at the End The absorbance at any wavelength is given by:

$$\mathbf{A}(\lambda, \mathbf{t}) = \epsilon_{\mathbf{Na}^{-}}(\lambda) \cdot \mathbf{b} \cdot [\mathbf{Na}^{-}] + \epsilon_{\mathbf{e}^{-}}(\lambda) \cdot \mathbf{b} \cdot [\mathbf{e}^{-}]$$
(2)

in which $\epsilon_{Na}(\lambda)$ and $\epsilon_{e}(\lambda)$ are the molar absorptivities at the wavelength λ and b is the pathlength. Furthermore we assume that after a very long time the only absorbing species is Na⁻. In Table IV, we have listed the values of $A_{Na}(600, \infty)$ and $A_{e}(1020, \infty)$ and their ratio. This ratio does not change appreciably with hundred-fold change in the concentration of the sodium ion. This substantiates the assumption that:

$$\mathbf{A}(\lambda, \mathbf{\omega}) = \epsilon_{\mathbf{N}\mathbf{a}^{-}}(\lambda) \cdot [\mathbf{N}\mathbf{a}^{-}]_{\mathbf{\omega}}$$
(3)

The presumed stoichiometry of reaction (1) gives

$$[Na^{-}]_{\infty} = \frac{1}{2} [e^{-}]_{0}$$
 (4)

or

$$[Na^{-}] = \frac{1}{2} ([e^{-}]_{0} - [e^{-}])$$

The above relation is useful only if we can determine the initial time of the reaction. When basic ethylenediamine was subjected to pulse radiolysis, a growth of the electron band was observed for 5-10 microseconds after the end of the electron pulse, as shown in Figure 22. This growth prevented the determination of the exact initial time of the reaction with Na⁺. Therefore, the initial electron concentrations and the zero of time were used as parameters in the

| Table IV. Reaction | on e + Na - | → V-band. Comp | arison of the Abso | rbances at Infinite Time |
|--------------------------------------|-------------------------|---|---|--|
| Identification | [Na ⁺] M | A _{Na} -(600, ∞) | A _e -(1020, ∞) | $\frac{A_{e^{-}}(1020, \infty)}{A_{Na^{-}}(600, \infty)} \times 100$ |
| 3.25.81 82 | 0.00334 | 0.540 0.489 | 0.034 0.029 | 6.3 5.9 |
| 86 87 88 | | 0.248 0.179 0.886 | 0.023 0.010 0.037 | 9.3 5.6 4 .2 |
| 89 90 91 | | 0.853 0.808 0.831 | 0.036 0.039 0.050 | 4 .8 6.0 |
| 3.25.102 103 107 | 0.02198 | 0.715 0.714 0.972 | 0.026 0.019 0.031 | 3.6 3.2 |
| 1120 1120 114 05 4120 | | 0.141 0.208 0.725 0.653 1.007 | 0.009 0.008 0.026 0.023 0.023 | 6.4 3.8 3.5 7.5 |
| 3.25.116 117 121 | 0.2179 | 1.194 1.094 0.296 | 0.015 0.017 0.012 | 4.5 2.5 4 |
| 3.25.122 123 124 125 125 | 0.5424 | 0.447 0.312 0.229 0.594 | 0.032 0.055 0.002 0.015 | 7.1 17.6 0.8 2.6 |
| 128 128 1309 1309 | | 0.685 0.772 0.751 0.657 | 0.030 0.016 0.018 0.005 | 4.2 4.0 4.0 |
| 132 133 134 | | 0.828 1.051 0.982 | 0.032 0.032 0.023 | 3.8 3.0 2.3 |

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investigation of the kinetics of decay of the IR-band and growth of the V-band.

The growth of the V-band and the decay of the IR-band represent the kinetics of the same reaction. It was possible to fit each pair of data sets to the same kinetic equation. The parameters used are: A(1020,0), the initial absorbance of the IR-band; \overline{G} , the initial time at the presumed zero of time; $\frac{k}{\epsilon_{e^-}(1020) \cdot b}$, where k is the pseudo-second order rate constant; and $A(600, \infty)$, the final absorbance of the V-band. By using this method of analysis, it is possible to fit the data with four parameters instead of six used when each curve was fit individually.

The rate of the reaction (1) was found to follow the equation

$$\frac{d[e^{-}]}{dt} = -\frac{2d[Na^{-}]}{dt} = -2k[e^{-}]^{2}$$
[5]

in which k is the pseudo-second-order rate constant. By using the relations (2), (3), (4), and (5), it is possible to write equations in terms of absorbances and molar absorptivities.

$$A(600, t) = \frac{1}{2} = \frac{\epsilon_{Na}(600)}{\epsilon_{e}(1020)} \cdot A(1020, 0) +$$

$$\frac{\frac{\epsilon_{e^{-}}(600)}{\epsilon_{e^{-}}(1020)} - \frac{1}{2} \frac{\epsilon_{Na^{-}}(600)}{\epsilon_{e^{-}}(1020)}}{\frac{1}{A(1020, 0)} + \frac{2 k (t + 7)}{\epsilon_{e^{-}}(1020) .b}}$$

and

$$A(1020, t) = \frac{1}{2} \frac{\epsilon_{Na}(1020)}{\epsilon_{Na}(600)} \cdot \frac{\epsilon_{Na}(600)}{\epsilon_{e}(1020)} \cdot A(1020, o) +$$

$$\frac{1 - \frac{1}{2} \cdot \frac{\epsilon_{Na} - (1020)}{\epsilon_{Na} - (600)} \cdot \frac{\epsilon_{Na} - (600)}{\epsilon_{e} - (1020)}}{\frac{1}{A(1020, 0)} + \frac{2 k (t + \tau)}{\epsilon_{e} - (1020) \cdot b}}$$

Some of these ratios can be simplified, but they are written in this way so that the known quantities appear explicitly. The quantities $\frac{\epsilon_{Na}(1020)}{\epsilon_{Na}(600)}$ and $\frac{\epsilon_{e}(1020)}{\epsilon_{e}(600)}$ are obtained directly from spectra of sodium and cesium solutions in ethylenediamine, respectively. The quantity $\frac{\epsilon_{Na}(600)}{\epsilon_{e}(1020)}$ is obtained from Table III.

$$\frac{A(600, \infty)}{A(1020, 0)} = \frac{\epsilon_{Na}(600) \cdot b \cdot [Na]_{\infty}}{\epsilon_{e}(1020) \cdot b \cdot [e]_{0}}$$

From relation (4) we obtain:

$$\frac{\mathbf{A}(600, \infty)}{\mathbf{A}(1020, 0)} = \frac{1}{2} \frac{\epsilon_{\mathrm{Na}}^{-(600)}}{\epsilon_{\mathrm{a}}^{-(1020)}}$$

which yields:

$$\frac{\epsilon_{\text{Na}}^{-}(600)}{\epsilon_{a}^{-}(1020)} = 3.76 \pm 0.55$$

The results obtained by adjusting three parameters to each set of decay-growth curves are shown in Table V, in which we have listed the sodium ion concentration, the initial absorbance of the electron band and the value of the rate

| [Na ⁺] | A (1020,o) | k/∈(1020) | Standard Deviation |
|--------------------|-------------------|---|---|
| M | | cm.sec ⁻¹ x 10 ⁻⁴ | cm.sec ⁻¹ x 10 ⁻⁴ |
| 0.00334 | 0.297 | 8.12 | 0.22 |
| | 0.263 | 8.12 | 0.20 |
| | 0.123 | 8.08 | 0.29 |
| | 0.103 | 7.28 | 0.24 |
| | 0.497 | 8.16 | 0.32 |
| | 0.483 | 7.52 | 0.24 |
| | 0.448 | 7.32 | 0.22 |
| | 0.473 | 6.80 | 0.19 |
| 0.018* | 0.228 | 12.6 | 0.64 |
| | 0.211 | 8.72 | 0.98 |
| | 0.273 | 10.77 | 0.84 |
| | 0.297 | 12.3 | 0.43 |
| | 0.206 | 15.1 | 0.81 |
| | 0.306 | 12.6 | 0.68 |
| | 0.180 | 8.76 | 0.47 |
| | 0.228 | 12.6 | 0.64 |
| 0.022 | 0.403 | 10.8 | 0.21 |
| | 0.406 | 11.2 | 0.27 |
| | 0.562 | 9.7 | 0.10 |
| | 0.084 | 9.7 | 0.19 |
| 0.065* | 0.156 | 10.74 | 1.31 |
| | 0.215 | 10.14 | 2.00 |
| | 0.177 | 14.0 | 2.7 |
| | 0.260 | 10.6 | 1.66 |
| 0.086 | 0.127 | 14.16 | 0.37 |
| | 0.116 | 11.92 | 0.52 |
| | 0.411 | 10.84 | 0.37 |
| | 0.375 | 10.48 | 0.11 |
| | 0.564 | 10.24 | 0.16 |
| 0.1211* | 0.156 | 8.8 | 0.70 |
| | 0.234 | 7.88 | 1.34 |
| | 0.300 | 8.8 | 0.82 |
| | 0.213 | 8.7 | 0.96 |
| | 0.457 | 7.36 | 5.2 |

Table V. Kinetic Analysis of the Reaction Na⁺ + 2e⁻ \rightarrow Na⁻ $\frac{d[e^{-}]}{dt} = - 2k[e^{-}]^{2}$

continued

| [Na ⁺] | A(1020,o) | k/e(1020) | Standard Deviation |
|--------------------|---|---|--|
| M | | cm.sec ⁻¹ x 10 ⁻⁴ | cm.sec ⁻¹ x 10 ⁻⁴ |
| 0.2179 | 0.662 | 12.0 | 0.31 |
| | 0.602 | 10.6 | 0.28 |
| | 0.583 | 9.76 | 0.21 |
| | 0.165 | 10.56 | 0.65 |
| | 0.172 | 9.60 | 0.16 |
| 0.5424 | 0.256 0.183 0.137 0.343 0.338 0.411 0.474 0.455 0.420 0.506 0.648 0.611 0.734 0.691 0.541 | 12.44 10.24 10.76 9.76 9.24 9.28 8.84 9.56 8.72 9.24 10.12 8.72 9.40 10.00 8.92 | $\begin{array}{c} 0.30\\ 0.13\\ 0.14\\ 0.08\\ 0.10\\ 0.11\\ 0.18\\ 0.12\\ 0.14\\ 0.15\\ 0.29\\ 0.19\\ 0.24\\ 0.25\\ 0.13\end{array}$ |

Table V--continued

* = different run

constant with its standard deviation. The parameter $\frac{A(600,\infty)}{A(1020,0)}$ which appears in the ratio $\frac{\epsilon_{Na}^{-(600)}}{\epsilon_{e^{-}}(1020)}$ was not adjusted in our study. A typical fit of the data is shown in Figure 23. These results were used to obtain the averages given in Table VI. It can be seen that the pseudo-secondorder rate constant is independent of the concentration of sodium ions over the concentration range studied.

4.2. Equilibria in Metal-Ethylenediamine Solutions

4.2.1. Equilibrium, R-band _____ IR-band in Potassium Solutions

The absorption spectra of solutions of potassium in ethylenediamine showed two bands. One was characteristic of the solvated electron, and the other was metal dependent. By analogy with sodium solutions, and in accordance with the conclusions of Matalon <u>et al</u>. (56) and of Glarum and Marshall (63), we considered the metal-dependent band to be characteristic of the species K⁻. Since the two bands exist together, it is logical to postulate that we have an equilibrium that can be written

$$2e^{-} + K^{+} \xrightarrow{K^{-}} K^{-} (6) K_{6} = \frac{[K^{-}]}{[e^{-}]^{2} \cdot [K^{+}]} \cdot \frac{\gamma_{K^{-}}}{\gamma_{e^{-}} \cdot \gamma_{K^{+}}}$$

or

$$\mathbf{e}_{2}^{=} + \mathbf{K}^{+} \underbrace{\longrightarrow}_{\mathbf{K}^{-}} \mathbf{K}^{-} (7) \quad \mathbf{K}_{7} = \frac{[\mathbf{K}^{-}]}{[\mathbf{e}_{2}^{=}] \cdot [\mathbf{K}^{+}]} \quad \cdot \quad \frac{\gamma_{\mathbf{K}^{-}}}{\gamma_{\mathbf{e}_{2}^{=}} \cdot \gamma_{\mathbf{K}^{+}}}$$

where K₆ and K₇ are the equilibrium constants.

| Na ⁺ M | k/e cm.sec ⁻¹ | Standard deviation cm.sec ⁻¹ |
|----------------------|-----------------------------|--|
| 0.0033 | 7.68 x 10 ⁴ | 0.57 x 10 ⁴ |
| 0.0180 | 11.68 x 10 ⁴ | 0.82×10^4 |
| 0.0220 | 10.36 x 10 ⁴ | 0.45×10^4 |
| 0.0650 | 11.37 x 10^4 | 1.02×10^4 |
| 0.0860 | 11.52×10^4 | 0.80×10^4 |
| 0.1211 | 8.31 x 10^4 | 0.33×10^4 |
| 0.2179 | 10.52×10^4 | 0.47×10^4 |
| 0.5424 | 9.68 x 10^4 | 0.24×10^4 |

Table VI. Reaction Na⁺ + 2e⁻ \rightarrow Na⁻. Average Values of the Rate Constant





This equilibrium was investigated by using the same technique as in the study of sodium solutions. A cesium solution was used as the source of solvated electrons, and was mixed with a solution of a potassium salt of known concentration. This reaction is faster than the mixing time so that study of its kinetics by stopped-flow methods is not possible. Because the reactions (6) and (7) give an equilibrium position which is not too far to the right, it is possible to generate various amounts of the K⁻-band with the same starting cesium solution. The study of this reaction was made more difficult than the corresponding study of the sodium ion reaction by two effects:

- (i) Potassium solutions are much more reactive than sodium solutions.
- (ii) The amount of R-band generated could not be determined easily during a run and it was necessary to wait for the computer analysis of the spectrum to know if the results were valid.

The potassium solution was generated in a quartz mixing chamber so that sodium exchange after mixing was not an important factor. The spectra obtained after mixing were analyzed by the program SPFIT which gave the contribution of each band to the spectrum. A typical fit is shown in Figure 24.

The results for two different runs are shown in Table VII, which gives the absorbance of the starting cesium





| | | | r | | | | |
|---|----------------------------|--------------|--|--|---------------------------------------|--|--|
| Identification | K + M x 10 ² | AIR | AIR | AR | M ⁻¹ X 10 ⁻² | M ⁻¹ x 10 ⁻² | |
| | Run of Marc | :h 25, 1970 | | | | | |
| 6.5 6.6 6.7 | 0.0615 | 4.0 | 2.5 4 2.67 2.80 | 0.32 0.505 0.613 | 3.25 4.52 5.08 | 2.06 3.02 3.55 | |
| 19.6 19.7 19.8 | 0.102 | 4 • O | 1.69 1.65 2.11 | 0.545 0.736 0.934 | 7.48 10.64 8.16 | 3.16 4.40 4.30 | |
| 20.5 20.6 | 0.142 | 4 • O | 1.70 1.79 2.03 | 1.40 1.34 1.69 | 13.6 11.8 11.6 | 5.80 5.28 5.86 | |
| 4.2 4.3 22.6 22.6 22.9 8 | 0.205 | 4 • O | 2.22 2.31 2.51 2.51 2.15 2.15 2.15 | 1.93 2.06 2.06 2.02 2.02 2.02 | 7.48 8.44 12.12 8.48 8.48 | 4.15 4.45 4.56 4.56 4.56 4.53 | |
| 21.3 21.4 21.5 | 0.307 | 4 °O | 1.53 1.64 1.85 | 2.03 2.19 2.19 | 11.28 9.28 8.32 | 4.31 3.80 3.85 | |
| 3.2 4.2 | 0.462 | 4.0 | 2.05 2.70 2.44 | 2.37 2.45 2.69 | 4.88 2.91 3.91 | 2.50 1.96 2.38 | |
| 2.54 .85 .85 | 0.615 | 4.0 | 1.13 1.42 1.26 | 1.95 2.23 2.02 | 9.92 7.2 8.32 | 2.80 2.55 2.62 | |

Table VII. Equilibrium Studies IR-band + K⁺ ____ R-band

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continued

| Identification | \mathbf{K}^{+} M x 10 ² | A _{IR} ^o | AIR | Å _R | K' M-1 x 10 ⁻² | K" M-1 x 10 ⁻² |
|--|---|------------------------------|----------------------------------|----------------------------------|------------------------------|------------------------------|
| | Run of Dece | ember 2, 19 | 69 | | | |
| ດ ເຊິ່າ ເຊິ່າ | 0.0445 | 0.6 | 0.425 0.349 | 0.107 0.09 | 7.92 10.00 | 5.61 5.82 |
| 0 4 4 4 0 የ. 4. 4 0 የ. 4. ቢ | 0.089 | 0.6 | 0.237 0.237 0.244 0.272 | 0.130 0.130 0.114 0.125 | 10.00 15.57 12.87 | 6.05 6.15 5.23 6.45 |
| 3 2 3 2 3 2 3 2 3 2 3 2 3 2 3 2 | 0.445 | 0.6 | 0.153 0.197 | 0.234 0.234 0.285 | 11.46 13.46 9.85 | 3.23 3.23 |
| | | | | Average value: | 8.9 + 0.5 | 4.11 ± 0.22 |

Table VII--continued

solution: A_{IR}^{0} , the concentration of potassium ions: $[K^{+}]^{0}$, and the absorbances of the R-band and of the IR-band in the final solution: A_{R} , and A_{IR} respectively.

The value K' is taken as

$$K' = \frac{A_R}{(A_{IR})^2} \cdot \frac{A_{IR}^0}{[K^+]^0}$$

and K" as

$$K'' = \frac{A_R}{A_{IR} \cdot [K^+]^\circ}$$

The reasons for the calculations of these pseudo-equilibrium constants will be explained in the Discussion section. It is to be noted that the values of K' and K" are fairly constant for both runs.

A control experiment was performed in which the blue cesium solution used for the run was analyzed for total cesium content by flame photometry. The effect of adding a cesium salt solution to the solution of potassium salt, before mixing it with the cesium metal solution, was studied. This run was characterized by very poor stability of the solution after mixing with a solution of either the potassium salt or of the cesium salt although the cesium solution was stable by itself.

The absorbance of the cesium solution used in this run was about 0.6 at the maximum, which, with a molar absorptivity of 2 x $10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ (defined in the next section), implied a concentration of cesium of 3 x 10^{-4} M. However, the analysis of the cesium residue yielded a concentration of about 2 x 10^{-3} M in cesium ions. Upon analysis of the data, it was noted that the absorbance of the R-band was only of the order of 0.05 absorbance units. Given the very poor stability of these solutions, these values are unreliable and, no useful information concerning the equilibrium constants could be obtained.

4.2.2. Attempt to Study the Reaction $e^- + K^+ \rightarrow R$ -band by pulse Radiolysis

This study was attempted in the same way as the study of the reaction of sodium ions with electrons. The solutions were prepared similarly but no growth of a band in the region of 850 nm was observed upon irradiation. The spectrum obtained was mapped at different times during the decay. These spectra, shown in Figure 25, do not show any variation of the band shape with time. Therefore, no kinetic studies of this reaction were possible.

4.2.3. Equilibrium V-band + $K^+ \rightarrow R$ -band

The purpose of this study was to see whether the equilibrium

or

V-band +
$$K^+$$
 $\xrightarrow{}$ R-band + Na⁺

could be shifted to the right. We added a massive excess of


Figure 25. Spectrum obtained by pulse radiolysis in an attempt to study the reaction $e^- + K^-$.

potassium iodide to a solution of sodium in ethylenediamine. No drastic changes in the spectrum occurred during the reaction. In particular, no band in the neighborhood of the R-band appeared by the reaction

$$V-band + K^+ \longrightarrow R-band + Na^+$$

We show, in Figure 26, the spectra obtained with and without addition of potassium salt. Both spectra have been normalized to the maximum of absorbance of the V-band.

The effect of the addition of potassium solution whose concentration was 1000 times greater than that of the sodium solution was a slight change in the absorbance towards the infrared. In order to verify that this was not an instrumental effect, some experiments were done in which the potassium salt solution was mixed with a concentrated sodium salt solution. As shown in Table VIII, for pushes of series 5 and 8, when sodium ion was present in excess, almost no absorption in the infrared was detected.

4.3. <u>Reaction of Sodium-ethylenediamine</u> Solutions with Water: Hydroxide Effect

This reaction was studied extensively by Feldman (67) and by Hansen (68). In this work, the effect of various concentrations of sodium hydroxide on the rate constant for this reaction was tested.







| Identifica- tion | [K ⁺] M | A _{.IR} | A _R | A _v |
|---------------------------------|-----------------------------------|---|---|---|
| 3.3 3.4 3.5 3.6 3.7 | 0.125 | 0.108 0.143 0.129 0.136 0.146 | 0.036 0.030 0.031 0.030 0.019 | 0.253 0.379 0.292 0.373 0.348 |
| 5.2 5.3 5.4 | 0,125 [Na ⁺] added | 0.0 0.0 0.012 | 0.020 0.013 0.010 | 0.297 0.334 0.324 |
| 6.3 6.4 6.5 | 0.1875 | 0.044 0.042 0.042 | 0.00 | 0.610 0.641 0.646 |
| 7.3 7.4 7.5 | 0.375 | 0.139 0.165 0.149 | 0.00 0.00 0.01 | 0.431 0.554 0.374 |
| 8.7 | 0,375 [Na ⁺] added | 0.026 | 0.00 | 0.481 |

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Table VIII. Equilibrium Studies $K^+ + V$ -band

As was the case for reactions with water in ethylenediamine, the reactions in the presence of sodium hydroxide follow first order kinetics with respect to the V-band. The decay curves of absorbance as a function of time can be fit to the equation

$$A = A_0 e^{-kt} + A_{00}$$

where A_0 = absorbance at the beginning A_{∞} = absorbance at infinite time.

Three parameters were used to fit the curves: A_0 , A_{00} and k the pseudo-first-order rate constant. A typical fit is shown in Figure 27. In all of the cases studied, A_{00} was of the order of 0.01 A_0 .

The pseudo-first-order rate constants, k_{ps} , are listed in Table IX, together with the water and sodium hydroxide concentrations. In Figure 28 log k_{ps} is plotted <u>versus</u> log [H₂O], the slope of the straight line has been obtained by least-squares and is 3.2 ± 0.15.

4.4. <u>Optical Spectrum of the Solvated Electron</u> <u>in Water-Ammonia Mixtures and in</u> Water-Ethylenediamine Mixtures

The spectra of the solvated electron in water-ammonia mixtures and in water-ethylenediamine mixtures were obtained by pulse radiolysis. As shown in Figures 29 and 30, the spectra obtained in pure ammonia and ethylenediamine by pulse





| Identifi- cation | [H ₂ O] M | [NaOH] M | k ps sec ⁻¹ | Standard Deviation sec ⁻¹ |
|--------------------------------------|-------------------------|-------------------------|---|--|
| 18.3 18.4 18.5 18.6 18.7 | 1.90 | 3.5 x 10 ⁻³ | 0.574 0.625 0.519 0.507 0.557 | 0.010 0.008 0.008 0.004 0.006 |
| 17.3 17.4 17.6 17.7 17.8 | 2.16 | 1.75 x 10 ⁻³ | 0.982 1.114 0.690 0.734 0.645 | 0.021 0.015 0.005 0.004 0.004 |
| 19.4 19.5 19.6 19.7 | 2.43 | 0.00 | 0.642 0.642 0.583 0.594 | 0.004 0.005 0.004 0.006 |
| 20.3 20.6 20.7 20.8 | 2.79 | 2.92 x 10 ⁻³ | 1.445 1.193 1.210 1.455 | 0.035 0.007 0.012 0.031 |
| 15.3 15.4 15.5 15.6 | 3.54 | 8.75 x 10- ³ | 6.71 5.07 6.50 5.35 | 0.20 0.05 0.18 0.05 |
| 12.4 12.5 12.6 12.7 | 4.01 | 5.5 x 10 ⁻³ | 8.95 10.68 10.21 9.84 | 0.15 0.09 0.07 0.11 |
| 11.5 11.6 11.7 | 4.20 | 4.38 x 10 ⁻³ | 13.67 14.77 13.59 | 0.07 0.09 0.11 |
| 14.4 14.5 14.6 14.8 | 4.41 | 2.92 x 10 ⁻³ | 9.77 9.56 10.01 9.18 | 0.08 0.08 0.26 0.05 |

Table IX. Reaction Na + H₂O; Hydroxide Effect

continued

Table IX--continued

| Identifi- cation | [H ₂ O] | [NaOH] | k ps | S tandard Deviation |
|---------------------|--------------------|----------------------|---------|-------------------------------|
| | M | M | sec-1 | sec-1 |
| 16.4 | 4.73 | 9.7×10^{-4} | 9.30 | 0.06 |
| 16.5 | | | 9.31 | 0.23 |
| 16.6 | | | 13.80 | 0.30 |
| 16.7 | | | 11.90 | 0.20 |
| 16.8 | | | 11.80 | 0.50 |
| 16.9 | | | 10.00 | 0.10 |
| 10.8 | 4.86 | 0.00 | 11.17 | 0.12 |
| 10.9 | | | 11.17 | 0.09 |
| | | | | |
| | | | | |



Figure 28. Plot of log (k) versus log $[H_2O]$ for the reaction of sodium with water in ethylenediamine.









radiolysis were the same as those obtained for solution of metals in these solvents. As we have shown in Section 3.7.3, these spectra can be fit by a combination of a Gaussian and Lorentzian band shape. As shown in Figure 31, as the concentration of water increases, the position of the maximum shifts to higher energies and the band broadens markedly. All of the spectra obtained have the Gaussian-Lorentzian line shape. In Figure 32 we have plotted on a normalized energy scale such a Gaussian-Lorentzian band shape, together with the experimental points obtained for a variety of ammonia mole fractions.

A method of treating the data was sought which would permit error estimates to be made for both peak positions and half-widths. The procedure chosen involved fitting the data with a shape function by using a damped non-linear least-squares program (69) which provided estimates of the standard deviations of the parameters. The function used was a combination of a Gaussian on the low energy side and a Lorentzian on the high energy side. This procedure yielded excellent representations of the spectra.

The peak position and half width for ammonia-water and ethylenediamine-water mixtures are given in Tables X and XI. Figures 33 and 34 show the variation of the position of the maximum and of the band-width with water concentration.





Figure 32. Solvated electron band-shape in ammonia-water mixtures.

| Mole Fraction of Water | Position of the Maximum | Standard Deviation | Width at Half- Height | Standard Deviation |
|------------------------------|-------------------------------|-----------------------|-----------------------------|-----------------------|
| | cm-1 | cm-1 | cm ⁻¹ | cm ⁻¹ |
| 0.0 | 6300 | | 3100 | |
| 0.144 | 6350 | 210 | 3410 | 710 |
| 0.213 | 6970 | 700 | 3700 | 200 |
| 0.358 | 7180 | 90 | 4470 | 360 |
| 0.367 | 7470 | 40 | 3710 | 60 |
| 0.421 | 7650 | 110 | 4000 | 160 |
| 0.421 | 7620 | 140 | 4200 | 200 |
| 0.489 | 8230 | 70 | 4930 | 100 |
| 0.496 | 8300 | 270 | 5550 | 420 |
| 0.533 | 8900 | 120 | 5800 | 400 |
| 0.594 | 9570 | 240 | 6520 | 440 |
| 0.594 | 9570 | 50 | 5850 | 100 |
| 0.717 | 11090 | 100 | 6580 | 210 |
| 0.752 | 11820 | 80 | 7230 | 130 |
| 0.759 | 12170 | 250 | 6530 | 600 |
| 0.841 | 12950 | 70 | 6780 | 80 |
| 0.862 | 12900 | 80 | 7120 | 170 |
| 0.929 | 13370 | 110 | 6930 | 130 |
| 0.949 | 13470 | 100 | 7100 | 200 |
| 1,000 | 13640 | 70 | 7210 | 110 |

-

| Table X. | Solvated Electron | n Absorption Bar | d Position | and Half- |
|----------|-------------------|------------------|------------|-----------|
| | width For Ammonia | a-Water Mixtures | 6 | |

| Mole Fraction of Water | Position of the Maximum | Standard Deviation | Width at Half- Height | Standard Deviation |
|------------------------------|-------------------------------|-----------------------|-----------------------------|-----------------------|
| | cm-1 | | cm-1 | Cm |
| 0.0 | 7360 | 145 | 7070 | 533 |
| 0.263 | 8860 | 140 | 7930 | 360 |
| 0.424 | 9340 | 210 | 7050 | 330 |
| 0.424 | 9390 | 200 | 7260 | 350 |
| 0.524 | 10160 | 250 | 6600 | 360 |
| 0.537 | 10170 | 70 | 7210 | 100 |
| 0.603 | 11000 | 100 | 7000 | 135 |
| 0.655 | 11400 | 100 | 6916 | 150 |
| 0.702 | 12460 | 150 | 6730 | 150 |
| 0.757 | 13020 | 170 | 6815 | 180 |
| 0.820 | 13840 | 230 | 7140 | 220 |
| 0.863 | 13700 | 160 | 7000 | 190 |
| 1.000 | 13640 | 70 | 7200 | 100 |

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Table XI.Solvated Electron Absorption Band Position andHalf Width for Ethylenediamine-Water Mixtures



Figure 33. Variation with solvent composition of the peak position and the half-width of the solvated electron spectrum in ammonia-water mixtures.



Figure 34. Variation with solvent composition of the peak position and the half-width of the solvated electron spectrum in ethylene-diamine-water mixtures.

4.5. <u>Preliminary Investigation of</u> Cyclohexyl-18-crown-6

It has been reported (72) that some cyclic polyethers are able to complex strongly the alkali-metal cations. The compound we used is: 2,3,11,12-dicyclohexyl, 1,4,7,10,13,16hexaoxacyclooctadecane, to which the trivial name cyclohexyl-18-crown-6 has been given (73). The structure of this compound is shown below. We will refer to this compound as "crown".



4.5.1. Ethylenediamine Solutions

We first established that a solution of "crown" did not react with a solution of solvated electron by mixing a cesium solution in ethylenediamine with a solution of "crown".

A solution consisting of a mixture of sodium ions with an excess of "crown", was mixed with a cesium solution. When this reaction was allowed to occur a short time after the solution of "crown" and sodium ions was prepared, the reaction with cesium proceeded as usual giving the V-band. The crownsodium ion solution was then allowed to stand for about ten minutes and then mixed with the cesium solution. It was noted that the V-band was much smaller than before. The same experiment was repeated at different times with the same crown-sodium ion solution. At longer times it was observed that the reaction with the cesium solution gave less V-band. The complexation reaction between sodium ions and "crown" therefore seemed to be slow. We attempted to see if this reaction could be followed by conductimetric methods.

A solution of sodium bromide in ethylenediamine (10^{-3} M) was prepared in a conductance cell. When the value of the conductance, measured with a Wayne-Kerr bridge, was constant, a weighed amount of "crown" was added to the solution to give equimolar concentration. The conductance was then measured as a function of time. A slight increase in conductance was observed during the solubilization of the "crown" (5 minutes) after which the conductance stayed stable. A large excess of "crown" was then added with the same result.

The same experiment was attempted with solutions of potassium iodide. A solution of "crown" (10^{-3} M) was prepared in a conductance cell. A weighed amount of potassium iodide was added to give a concentration of 10^{-3} M. The conductance rose sharply just after the addition and stayed stable thereafter. The same experiment was done with smaller concentrations of KI (10^{-4} M) with the same result.

The effect of "crown" upon a solution of sodium metal in ethylenediamine was studied. We were interested to see

if the complexing of the sodium ion by the "crown" would shift the equilibrium

V-band \rightarrow Na⁺ + IR-band

towards the formation of the IR-band. This study was done by pouring a solution of sodium over some solid "crown". The resulting spectrum was the same as the spectrum of pure sodium solution and showed no IR-band. After decomposition of the solution, the solvent containing dissolved "crown" was poured over metal. The spectrum of the resulting blue solution did not show any IR-band.

4.5.2. Other Solvents

Noting that the stabilization of the cations should increase the solubility of metals (as suggested by Dr. V. A. Nicely), we studied the effect of adding "crown" to tetrahydrofuran (THF) and diethyl ether, in the presence of a mirror of potassium. Alkali metals alone are only very slightly soluble in THF and not soluble in diethyl ether. With both solvents, deep blue solutions were formed in the presence of "crown". Solutions of both potassium and cesium in THF formed readily at room temperatures and were stable for several hours even in the absence of excess metal. Solutions stored at -78° C for several days showed no visible signs of decomposition. In order to dissolve potassium and cesium in diethyl ether it was necessary to first cool the system (-78°C was the temperature used). Once formed, the blue solutions in this solvent were stable at room tempera-ture for five to ten minutes and for hours at -78°C.

The optical spectrum of each of these solutions was recorded at room temperature and is shown in Figure 35. No other absorption bands could be detected in the infrared as far as we could go before the cut-off of the solvent (1.5 μ for THF and 2.4 μ for diethyl ether in a 1.0 cm path length cell). The EPR signal of these solutions consists of a single line corresponding to the solvated electron line. In diethyl ether at $25^{\circ}C$, in addition to the single line $(C \simeq 10^{-7} M)$, a weak four-line pattern $(C \simeq 10^{-8} M)$, A = 11. G.) was observed for potassium solutions. No such fourline pattern was observed in THF solutions. The single line observed in THF could be observed down to the freezing point of the solvent. In contrast, in diethyl ether the single line disappeared below $0^{\circ}C$. In both solvents at low temperatures $(-60^{\circ}C \text{ and below})$, a weak seven line pattern was observed. The splitting values and relative intensities indicated that this absorption was probably due to the benzenide anion (74). This identification was strengthened by adding small amounts of benzene to a similar solution of potassium in THF in the presence of "crown". This resulted in an intensification of the seven-line pattern.





V. DISCUSSION

5.1. Oscillator Strengths and Molar Absorptivities

The main difficulty in the estimation of the oscillator strength, resides in the evaluation of the area under the absorption curve. We have shown in Section 3.7.3, that each of the absorption bands (V, R or IR) could be fit by an equation consisting of a Gaussian band shape for the low energy side and of a Lorentzian band for the high energy side.

The area under a Gaussian curve is given by

$$A^{G} = 2 \times 1.0643 \cdot \Delta v_{m}^{G} \cdot y_{m}$$
 (1)

and under a Lorentzian curve by

$$\mathbf{A}^{\mathbf{L}} = 2 \times 1.57 \cdot \Delta \mathbf{v}_{\mathbf{h}}^{\mathbf{L}} \cdot \mathbf{y}_{\mathbf{m}}$$
(2)

where $\Delta v^{\mathbf{G}}$ and $\Delta v^{\mathbf{L}}$ are the half-width at half-height for $\frac{1}{2}$ $\frac{1}{2}$ Gaussian and Lorentzian curves respectively and $y_{\mathbf{m}}$ is the maximum amplitude.

5.1.1. Solutions in Ethylenediamine

a) Sodium solutions

The method used to determine the molar absorptivity of sodium solutions by using the reaction

IR-band + X Na⁺
$$\longrightarrow$$
 V-band (3)

yields different values of the molar absorptivity of sodium depending upon the number of sodium ions involved in the formation of the V-band. The value of the molar absorptivity of sodium solutions is $8.2 \pm 0.3 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ assuming one sodium atom in the V-band.

Using $\Delta v_{\frac{1}{2}}^{G} = 1720 \text{ cm}^{-1}$ and $\Delta v_{\frac{1}{2}}^{L} = 2280 \text{ cm}^{-1}$ obtained from sodium spectra, an oscillator strength of 1.9 ± 0.2 is calculated. According to the f-sum rule, the sum of the oscillator strengths from a state m to all of the possible other states is equal to the number of electrons in the state m. An oscillator strength of about 2, obtained when we consider one sodium atom per V-species, indicates that two electrons are involved in the transition. Furthermore (64,75), it is known that the sum of the oscillator strengths for the oneelectron transitions of the sodium atom in vacuo is very close to unity, and the transition $3s \longrightarrow 3p$ accounts for 0.94 of this value. This indicates that the core electrons are not involved in the sodium spectrum to any significant extent. Therefore a species Na with two electrons in a 3s state is compatible with an oscillator strength of 2. A species Na is isoelectronic with the Mg atom. The reported value of the oscillator strength for the transition $3^{1}S \rightarrow 3^{2}P$ of the magnesium atom is 1.745 (76). If two sodium ions were involved in the formation of the V-band, the molar absorptivity would become twice what it was before, i.e., 1.6 x 10^5 $M^{-1} \cdot cm^{-1}$ and the oscillator strength would be nearly four.

In this case, according to the f-sum rule, four electrons are needed. There is no direct evidence that a species such as Na₂ can give an oscillator strength of four.

If the determination of molar absorptivity were to be done by dissolving sodium, and if decomposition effects could be ignored, a value of half that which we found should be expected since the solubilization reaction is

$$2Na \longrightarrow Na^+ + Na^-$$
 (4)

However, this method would not offer any way of deciding whether the V species is Na^{-} or Na_{2} .

b) Solvated electron in ethylenediamine

During the study by pulse radiolysis, of the reaction

$$2e^{-} + Na^{+} \longrightarrow Na^{-}$$
 (5)

we have determined the ratio

$$\frac{A_{Na}^{-}(600)}{A_{p}^{-}(1020)} = 1.88 \pm 0.28$$

where A_{Na} (600) refers to the final absorbance of the Na band at 600 nm and $A_{e^{-}}(1020)$ refers to the initial absorbance of the solvated electron at 1020 nm.

Using the stoichiometry of the above equation we get

$$\frac{A_{Na^{-}(600)}}{A_{e^{-}(1020)}} = \frac{\epsilon_{Na^{-}(600)}}{\epsilon_{e^{-}(1020)}} \cdot \frac{[Na^{-}]_{00}}{[e^{-}]_{0}} = \frac{1}{2} \frac{\epsilon_{Na^{-}(600)}}{\epsilon_{e^{-}(1020)}}$$

 ϵ_{Na} (600) can be obtained from the value of ϵ_{Na} (Max) and the shape of the V-band

$$\epsilon_{Na-}(600) = 5.95 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

so that

$$\epsilon_{e^{-}}(1020) = 1.58 \times 10^{4} M^{-1} \cdot cm^{-1}$$

By using the band shape of the solvated electron we can get the molar absorptivity at the maximum

$$\epsilon_{p-}(1360) = 2.0 \pm 0.3 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

By using the band parameters of cesium-ethylenediamine solutions $\Delta v_{\frac{1}{2}}^{G} = 2300 \text{ cm}^{-1}$ and $\Delta v_{\frac{1}{2}}^{L} = 4760 \text{ cm}^{-1}$ we find an oscillator strength

$$f = 0.88 \pm 0.12$$

If two sodium ions were involved in the V-band, the molar absorptivity of the solvated electron would have to be

$$\epsilon_{e^{-}} = 4.0 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

and the oscillator strength would be

$$f = 1.76$$

From the results of section 4.4 we know that the band shape of the spectrum of solvated electron in ethylelediamine-water mixtures does not change with water concentration. Therefore, we postulate that the oscillator strength does not vary appreciably with the concentration in solvent mixtures. Since the band-width does not change when we go from water to ethylenediamine, the integrated molar absorbance is a constant. Therefore the same molar absorptivity is expected for the electron in water and in ethylenediamine. The value of the molar absorptivity of the electron in water has been measured by Fielden and Hart (77) and has the value $\epsilon_{e^-}(H_2O) = 1.85 \pm 0.2 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$. This value is the same within experimental error as the value of $2.0 \pm 0.3 \times 10^4$ $\text{M}^{-1} \times \text{cm}^{-1}$ obtained for the solvated electron in ethylenediamine. The value of $4.0 \times 10^4 \text{ M}^{-1} \times \text{cm}^{-1}$ that would be obtained if two sodium ions were involved in forming the V-species is twice too large for this kind of comparison. This strengthens the assignment of Na⁻ as the species responsible for the V-band rather than, for example, a species of stoichiometry Na₂.

c) <u>Molar absorptivity of the R-band of potassium solu-</u> tions

Let us assume that the R-band observed for solutions of potassium in ethylenediamine is due to K⁻. Let us further assume that the oscillator strength of this band is the same as for Na⁻. This assumption permits an estimate of the molar absorptivity of K⁻ to be made. By using $\Delta v_{\frac{1}{2}}^{\text{G}} =$ 1720 cm⁻¹ and $\Delta v_{\frac{1}{2}}^{\text{L}} = 2530$ cm⁻¹ the molar absorptivity is 7.6 x 10⁴ M⁻¹ x cm⁻¹. This value is only an estimate so no standard deviation is given.

5.1.2. <u>Solvated Electron in Water-Ammonia</u> <u>Mixtures</u>

The oscillator strength of the solvated electron in water can be determined by using the spectrum reported by

Matheson (78) and the molar absorptivity of Fielden and Hart (77). The value obtained is f = 0.81. This value may have a large error attached to it because of possible errors in the peak shape. The area under the curve was obtained from the only published spectrum (78) in which $\frac{\epsilon(720)}{\epsilon(580)} = 1.45$, while more recent measurements yield a value of 1.7 for this ratio (77).

The oscillator strength and molar absorptivity of the solvated electron in liquid ammonia have been reported by a number of workers. The most recent results are those of Lagowski (12) for very dilute metal-solutions. The value obtained for the molar absorptivity is $4.8 \pm 0.2 \times 10^4$ $M^{-1} \cdot cm^{-1}$ which is in accord with the values published previously (10). The oscillator strength calculated by Lagowski is 0.64 ± 0.04 . This value is much lower than previously published values. However, this value was calculated using a formula (80) valid only for Gaussian absorption curves. As we have seen this is not the case for metal-ammonia solutions. Using $\Delta v_{\frac{1}{2}}^{\mathbf{G}} = 1275 \text{ cm}^{-1}$ and $\Delta v_{\frac{1}{2}}^{\mathbf{L}} = 1975 \text{ cm}^{-1}$ we obtain $f = 0.92 \pm 0.1$. We postulate that in water-ammonia mixture, the oscillator strength of the solvated electron will vary linearly from the value 0.81 in pure water to the value 0.92 in pure ammonia. We note furthermore that these values are actually equal within the limits of error. This assumption enables us to calculate the molar absorptivities of the solvated electron in solvent mixtures. The results are shown in Table XII and in Figure 36.

| ole Fraction f Water | Molar Absorptivity M ⁻¹ .cm ⁻¹ |
|-------------------------|--|
| 1.00 | 18,500 |
| 0.949 | 18,100 |
| 0.930 | 19,900 |
| 0.862 | 19,800 |
| 0.841 | 21,200 |
| 0.759 | 22,500 |
| 0.752 | 20,300 |
| 0.717 | 22,000 |
| 0.594 | 24,500 |
| 0.594 | 22,500 |
| 0.533 | 26,900 |
| 0.496 | 26,700 |
| 0.489 | 29,200 |
| 0.421 | 35,200 |
| 0.367 | 41,000 |
| 0.358 | 34,000 |
| 0.144 | 45,600 |

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5.1.3. Conclusions

Our results are summarized in Table XIII.

The oscillator strength of the solvated electron is close to unity in all of the solvent systems we have studied. This indicates that the absorbing species is a single electron. It also indicates that we should not expect another strong absorption band for the solvated electron. The value of two for the oscillator strength of the V-band and the value of $8.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the molar absorptivity are consistent with the assignment of Na⁻ as the species responsible for the V-band.

Our results do not give any indication as to the nature of the transition causing the V-band. They are not at variance with the interpretation of Matalon <u>et al</u>. (56) who consider this band to be caused by a charge-transfer-tosolvent.

5.2. Equilibria in Metal-Ethylenediamine Solutions

The optical spectrum of metal-ammonia solutions consists of a single band which follows Beer's law over a wide range of concentrations. However, it is known from conductance and magnetic susceptibility measurements (28) that even in the dilute region, a substantial fraction of the dissolved metal is present as ion pairs and diamagnetic aggregates which might be represented as $(e^-)_2$, $e^- \cdot M^+ \cdot e^-$, $(M^+ \cdot e^-)_2$ or higherorder aggregates.

| Species/Solvent | M-1.cm-1 | f |
|----------------------------------|---------------------------------|-------------|
| Na ⁻ /EDA | 8.2 \pm 0.3 x 10 ⁴ | 1.9 ± 0.2 |
| K /EDA* | 7.5 x 10 ⁴ | 1.9 |
| e /EDA | $2.0 \pm 0.3 \times 10^4$ | 0.88 ± 0.12 |
| e /NH3 | 4.8 \pm 0.2 x 10 ⁴ | 0.92 ± 0.1 |
| e ⁻ /H ₂ O | $1.85 \pm 0.2 \times 10^4$ | 0.81 |

f

Table XIII. Summary of Molar Absorptivities and Oscillator Strengths

*Estimated values.

EDA = ethylenediamine.
We have established that in metal-ethylenediamine solutions the species e and M are present. We also know that in a solvent of dielectric constant as low as ethylenediamine, extensive ion pairing must occur. In order to fit the kinetics of the reaction of cesium solutions with water, Hansen (68) had to postulate that in cesium solutions some equilibria of the type

paramagnetic \longrightarrow diamagnetic

also existed.

In the studies of decomposition of metal solutions, Dewald (66) noted that most of the decays were first-order but that different bands reacted at different rates. In particular, for potassium and rubidium solutions, the R-band reacted faster than the IR-band. This suggests strongly that the R-band consists of aggregated species.

5.2.1. Equilibrium IR-band + K⁺ = R-band

From the optical spectrum of potassium solutions in ethylenediamine it is known that we have equilibria of the type

$$\begin{array}{c} \mathbf{K}^{-} & \longrightarrow & 2\mathbf{e}^{-} + \mathbf{K}^{+} \\ (\mathbf{R}-\mathbf{band}) & & (\mathbf{IR}-\mathbf{band}) \end{array}$$
(7)

This is obviously an oversimplified view. To be more realistic, ion pairs have to be introduced and the equilibrium involved in the reaction of Cs solutions with KX may be written

$$2Cs^{+} \cdot e^{-} \longrightarrow Cs^{+} \cdot Cs^{-}$$
 (8)

$$Cs^{+} \cdot Cs^{-} + K^{+} \cdot X^{-} \rightleftharpoons Cs^{+} \cdot K^{-} + Cs^{+} \cdot X^{-}$$
(9)

$$Cs^{+} \cdot K^{-} + K^{+} \cdot X^{-} \xleftarrow{} K^{+} \cdot K^{-} + Cs^{+} \cdot X^{-}$$
(10)

All of these equilibria are probably important in determining the relative intensities of the R- and IR-bands. Unfortunately, this leaves us with too many unknowns. Therefore a few simplifying assumptions have to be made. Equilibrium (8) plays only a minor role and only at high concentrations. In fact in none of our experiments could the Cs⁻ spectrum be detected. Equilibrium (9) will be ignored since it is not detectable in the experiments unless $K^+ \cdot K^-$ has a different molar absorptivity than $Cs^+ \cdot K^-$, which is unlikely.

Relation (10) can be rewritten

$$2 \operatorname{Cs}^{+} \cdot \operatorname{e}^{-} + \operatorname{K}^{+} \cdot \operatorname{X}^{-} \longrightarrow \operatorname{Cs}^{+} \cdot \operatorname{K}^{-} + \operatorname{Cs}^{+} \cdot \operatorname{X}^{-}$$
(11)

which gives an equilibrium constant

$$K = \frac{[Cs^{+}.K^{-}] \cdot [Cs^{+}.X^{-}]}{[Cs^{+}.e^{-}]^{2} \cdot [K^{+}.X^{-}]} \cdot \frac{\gamma_{Cs}^{+}.K^{-} \cdot \gamma_{Cs}^{+}.X^{-}}{\gamma_{Cs}^{2}.e^{-} \cdot \gamma_{K}^{+}.X^{-}}$$
(12)

where γ_{A^+,B^-} are the activity coefficients of the ion-paired species A^+,B^- .

Equation (12) can be re-written

$$K = K' \frac{\gamma_{CB}^{+} K^{-}}{\gamma_{CS}^{2} + e^{-}}$$
(13)

where

$$K' = \frac{[Cs^+ \cdot K^-] \cdot [Cs^+ \cdot X^-]}{[Cs^+ \cdot e^-]^2 \cdot [K^+ \cdot X^-]}$$
(14)

K' will be referred to as the pseudo-equilibrium constant of reaction (11).

The concentrations in equation (14) can be obtained easily. From Beer's law:

$$[Cs^+.K^-] = \frac{A_{K^-}}{\epsilon_{K^-}}; \quad [Cs^+.e^-] = \frac{A_{e^-}}{\epsilon_{e^-}}$$

The other two concentrations can be obtained from the conservation equations:

$$[K^{+}]^{\circ} = [K^{+}.X^{-}] + [Cs^{+}.K^{-}]$$
 (15)

This can be approximated by

$$[K^{+}]^{\circ} = [K^{+} \cdot X^{-}]$$

since the concentration of potassium ion is much larger than the concentration of species present as K^- .

The conservation of the total cesium yields:

$$[Cs^{+}]^{\circ} = [Cs^{+}.e^{-}] + [Cs^{+}.K^{-}] + [Cs^{+}.X^{-}]$$

From the control experiment we know that the concentration of cesium ions is much larger than the concentration of solvated electrons $(Cs^+.e^-)$. The concentration of cesium salt present in the solution will be considered as constant for any particular run. The following approximation will be made

$$[Cs^{\dagger}]_{\text{total}} \alpha \quad \frac{A_{e}^{o}}{\epsilon_{e}^{-.b}}$$

That is the total concentration of cesium is proportional to the initial absorbance of the cesium solution. This introduces an unknown factor in the equilibrium constant.

The pseudo equilibrium constant is therefore:

$$K^{\dagger} \alpha = \frac{\frac{A_{K^{-}}}{\epsilon_{K^{-}} \cdot b} \cdot \frac{A_{e^{-}}^{\circ}}{\epsilon_{e^{-}} \cdot b}}{\frac{A_{e^{-}}}{(\epsilon_{e^{-}} \cdot b)^{2}} \cdot [K^{\dagger}]^{\circ}}$$
(16)

$$K' \alpha \frac{\epsilon_{e^-}}{\epsilon_{K^-}} \cdot \frac{A_{K^-} \cdot A_{e^-}^0}{A_{e^-}^2 \cdot [K^+]^0}$$
(16')

The second part of this ratio has been calculated in Section 4.2. This value is nearly constant showing that all of our assumptions are reasonable.

Let us now consider the possibility of having aggregates of high order than ion pairs. As shown at the beginning of this Section this certainly occurs in ethylenediamine. The problem becomes much more complicated. Let us try a very simple model

$$e_2^{=} + K^{+} \longleftrightarrow K^{-}$$
(17)

The equilibrium constant is written

$$K = \frac{[K^-]}{[K^+] \cdot [e\overline{2}]} \cdot \frac{\gamma_{K^-}}{\gamma_{K^+} \cdot \gamma_{e2}}$$
(18)

and the pseudo-equilibrium constant is

$$\mathbf{K}_{ps}^{"} = \frac{[\mathbf{K}]}{[\mathbf{e}\overline{z}] \cdot [\mathbf{K}]} = \frac{\epsilon_{\mathbf{e}\overline{z}}}{\epsilon_{\mathbf{K}}} \cdot \frac{\mathbf{A}_{\mathbf{K}}}{\mathbf{A}_{\mathbf{e}} \cdot [\mathbf{K}]_{0}} \quad (19)$$

The second part of this ratio has been calculated and called K" in section 4.2. For both runs this value is a constant.

At the present point there is no way of deciding which are the important equilibria. A realistic approach would involve taking all possible equilibria into account, but the complexity added by aggregates such as $e_2^{=}$ or M_2 makes this treatment impossible.

The average values obtained for the two pseudo-equilibrium constants are:

$$K' = 1.42 \times 10^2 \text{ M}^{-1}$$
$$K'' = 1.37 \times 10^2 \text{ M}^{-1}$$

The value of K" has been calculated by assuming $\epsilon_{e\overline{2}} = 2 \times \epsilon_{e^{-}}$. The similarity between the values of K' and K" is surprising but we must remember that K' as defined contains an unknown multiplicative factor and that therefore the similarity is probably fortuitous.

5.2.2. Effect of Potassium Salt Upon the Spectrum of Sodium Solutions

Sodium solutions do not show any appreciable absorption in the infrared region. This indicates that the concentration of solvated electrons is very low. However, by analogy with the solutions of other metals, it is postulated that there is an equilibrium:

$$Na^{-} \xrightarrow{} Na^{+} + 2e^{-}$$
 (20)

lying far to the left.

The addition of a potassium salt to such a solution might give the reaction

$$K^{\dagger} + Na^{-} \xrightarrow{} K^{-} + Na^{+}$$
 (21)

to give an R-band. However, this is not what is observed experimentally. The experimental results show an increase of the absorbance in the infrared when the potassium is mixed with a sodium solution. This increase disappears when a sodium salt is added to the potassium salt prior to the mixing with the sodium solution.

Several possibilities exist to explain these results.

(i) The addition of a massive excess of potassium ions and of its counter-ion bromide or iodide makes possible the equilibrium

$$Na^{+} Br^{-} = Na^{+} Br^{-} + 2e^{-}$$
 (22)

in which the bromide ion replaces two electrons. This is not in contradiction with the fact that in presence of sodium bromide no effect is observed, since then the massive excess of sodium ions would shift the equilibrium (20) to the left regenerating the V-band. However, if the reaction (22) were responsible for the observed effect, it is difficult to explain the absence of an R-band from K⁻.

(ii) The other possibility involves the change of the properties of the medium occurring when a large amount of salt is added to a solution. The equilibrium constant for reaction (20) is:

$$K = \frac{[Na^+] \cdot [e^-]^2}{[Na^-]} \cdot \frac{\gamma_{Na^+} \cdot \gamma_{e^-}^2}{\gamma_{Na^-}}$$

Assuming $\gamma_{Na^+} = \gamma_{Na^-} = \gamma_{e^-} = \gamma_{\pm}$ gives

$$K = \frac{[Na^{+}] \cdot [e^{-}]^{2}}{[Na^{-}]} \cdot \gamma_{\pm}^{2}$$

In solutions of sodium, this equilibrium is difficult to measure because there is almost no solvatedelectron-band. From measurements of the spectrum we can conclude that the absorbance of the IR-band does not exceed 5% of the absorbance of the V-band in pure sodium solution. When the potassium salt is added, the intensity of the IR-band becomes about 30% of that of the V-band. With these estimates let us try to evaluate what changes in activity coefficients could lead to the observed increase in the IR-band. In the case of a pure sodium solution of unit absorbance, the equilibrium constant satisfies the inequality

$$K \leq \frac{[Na^+] \cdot (\frac{0.05}{\epsilon_{e^-}})^2}{\frac{1.0}{\epsilon_{Na^-}}} \cdot \gamma_{\pm}^2 \cdot (23)$$

In the presence of an excess of potassium ions, if no new equilibria are involved $K \simeq \frac{[Na^+] \cdot (\frac{0.3}{\epsilon_e})^2}{(\frac{1.0}{\epsilon_N})} \cdot \gamma_{\pm}^{\prime 2} \cdot$

Assuming that [Na⁺] is the same in both cases, we get

$$0.09 \gamma_{\pm}^{*} \leq 0.0025 \gamma_{\pm}^{2}$$

or

 $\gamma_{\pm} \geq 6 \gamma_{\pm}'$.

The solutions we are dealing with are much too concentrated to evaluate γ_{\pm} theoretically. However, the observed change is in the expected direction, and if γ_{\pm} decreases by a factor greater than six when salt is added to the solution, the observed increase in the absorption in the infrared could result. It is to be noted that ionic strength effects would not be expected to influence reaction (21) significantly.

5.3. <u>Kinetics of the Reaction $M^+ + e^- \longrightarrow M^-$ </u>

5.3.1. Sodium Ion Reaction

The rate constants that we have obtained for the reac-

$$Na^{+} + 2e^{-} \longrightarrow Na^{-}$$
 (24)

do not appear to depend upon the sodium ion concentration in the concentration range 3 x 10^{-3} to 0.5 M, that we have studied (except possibly for the lowest concentration used). This is evidence that the mechanism does not correspond to the rate expression:

$$\frac{d[e]}{dt} = -2k[Na^{\dagger}] \cdot [e]^{2}$$

Several mechanisms can be proposed to explain the absence of sodium ion dependence. These mechanisms are based on the ion-pairing concepts we have developed in the preceding section.

a) We can consider a first slow step

$$e^- + e^- \xrightarrow{slow} e_2^-$$
 (25)

followed by the ionic reaction

$$e_2^{=} + Na^{+} \xrightarrow{fast} Na^{-}$$
(26)

Such a mechanism gives the correct featrues of our reaction: second order with respect to the electron concentration and no dependence on the concentration of sodium ions.

b) Alternately we can consider that the first step is a fast ion pairing equilibrium

$$Na^+ + e^- \xrightarrow{fast} Na^+ \cdot e^-$$
 (27)

$$K = \frac{[Na^+.e^-]}{[Na^+]\cdot[e^-]} \cdot \frac{\gamma_{Na}^+.e^-}{\gamma_{Na}^+\cdot\gamma_{e^-}}$$
(28)

followed by the rate determining step

$$2Na^+ \cdot e^- \xrightarrow{slow} Na^+ \cdot Na^-$$
 (29)

Since in our experiments the concentration of the sodium ion was at least 3 orders of magnitude greater than the electron concentration and was high enough to give nearly complete ion-pairing at equilibrium, most of the electrons would be present in the ion-pair Na⁺.e⁻ if reaction (27) is fast. Therefore, no dependence upon the sodium ion concentration would be expected.

These two mechanisms could be tested by lowering the concentration of sodium ions. If no change is observed, then the mechanism (a) is probable, in the other case mechanism (b) seems more appropriate. Preliminary testing of this effect are currently in progress at the Ohio State University. The use of lower concentrations of sodium introduces another difficulty, however: the equilibrium ratio of the V-band to the IR-band becomes smaller so that changes are difficult to detect.

Since no growth of an R-band was observed in the pulse radiolysis of solutions of KBr in ethylenediamine, it would be possible to add an excess of potassium salt to the solution to give

$$K^{+} + e^{-} \xrightarrow{K^{+} \cdot e^{-}}$$
(30)

 $Na^+ + e^- \longrightarrow Na^+ \cdot e^-$ (31)

The potassium salt being in excess with respect to the sodium salt, most of the electrons would be tied up as K^+ .e⁻ leaving most of the sodium ions paired with the counter ion X^- .

The sodium ions could then react by:

$$2 \text{ K}^{+}.\text{e}^{-} + \text{Na}^{+}.\text{X}^{-} \longrightarrow \text{K}^{+}.\text{Na}^{-} + \text{K}^{+}.\text{X}^{-} \cdot \qquad (32)$$

5.3.2. Potassium Ion Reaction

The reaction of electrons with potassium ions did not occur under the conditions of the pulse radiolysis experiment. In fact, we know from metal solution studies that we have an equilibrium

$$K^{+} + 2e^{-} \longleftarrow K^{-}$$
 (33)

we have evaluated a pseudo-equilibrium constant for the reaction

$$2Cs \cdot e^{-} + K \cdot X^{-} \xrightarrow{} K \cdot Cs^{+} + Cs \cdot X^{-}$$
(12)

and we postulate that it is similar to

$$2K^{+}.e^{-} + K^{+}.X^{-} \xrightarrow{} K^{+}.K^{-} + K^{+}.X^{-} \cdot \qquad (34)$$

The pseudo-equilibrium constant is

$$K' = \frac{[K^+ \cdot K^-]}{[K^+ \cdot e^-]^2} \approx 1.4 \times 10^2 M^{-1}$$

At equilibrium, the concentration of K is given by

$$[K^{-}] = K' \cdot [K^{+} \cdot e^{-}]^{2}$$
.

In most of the pulse radiolysis experiments the concentration of solvated electron was of the order of 10^{-5} to 10^{-6} M so that $[K^-] \approx 1.5 \times 10^2 \times 10^{-10} = 1.5 \times 10^{-8}$ M. At equilibrium then, the maximum absorbance of the R-band in a 4 cm cell would be

$$A_{R} = 4 \times 7.5 \times 10^{4} \times 1.5 \times 10^{-8} = 4.5 \times 10^{-3}$$

which is below the limits of detection. Therefore, the observation that no R-band was formed in the pulse radiolysis experiments is consistent with the studies of metal solutions.

5.4. <u>Reactions of Sodium Solutions with</u> <u>Water in Ethylenediamine</u>

Sodium solutions in ethylenediamine occupy a special place by reason of their stability. The reaction of water with sodium follows first order kinetics with respect to the sodium. Feldman [67] observed that the pseudo-first order rate constant did not change appreciably with water concentration below 1 M. Above 1 M and up to 6 M our data together with Hansen's data (68) indicate a dependence on at least the third power of the water concentration.

The present data also indicate that there is no effect of hydroxide concentration upon the reaction rate. This rules out the presence of equilibria of the type

 $Na^{+} H_{2}O \longrightarrow Na^{-}.H^{+} + OH^{-}$

in the rate-determining scheme.

No reasonable mechanism can be proposed that would account for a rate expression of the type

$$\frac{d [Na^-]}{dt} = -k [Na^-] \cdot [H_2O]^3$$

The apparent zero-order dependence upon water at low water concentrations and the sudden increase in rate above 1 M, suggest that these effects may be caused by a change in solvent properties. At low concentrations of water, the sodium anion is relatively stable and does not react with water in less than a few seconds. When enough water is added, the solvent properties might change such that Na⁻ becomes less stable and reacts with water via the intermediate formation of solvated electrons.

5.5 Studies of the "Crown" Compound

"Crown" appears to be an efficient complexing agent for the sodium ion according to

$$Na^+ + "Crown" \longrightarrow Complex$$
 (35)

does not proceed.

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Furthermore the reaction (35) seemed to require times of the order of ten minutes or longer to occur to a significant extent. However, the conductimetric results did not show any effect when "crown" was added to a solution of sodium or potassium ions in ethylenediamine. We cannot propose any reasonable explanation for these results. Either the complexation results in ethylenediamine are in error, or the conductivity of the complex is the same as the conductivity of the corresponding solvated cations. This problem could probably be elucidated by a study of sodium NMR in ethylenediamine with and without the addition of "crown".

The complexation of the metal cations by the "crown" is confirmed by the fact that in THF, potassium solutions containing "crown" do not show hyperfine splitting by the nucleus in contrast to solutions of potassium in THF in the absence of "crown". This indicates that the equilibrium

$$M \longrightarrow M^+ + e^-$$

is shifted to the right by the complexation equilibrium

$$M^+$$
 + "crown" \longrightarrow Complex .

The optical spectra of metals such as cesium and potassium in diethyl ether and in THF show only the R-band of these metals (81). Presumably the solubility equilibrium

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$$^{2M}(s) \xrightarrow{M^+ + M^-}$$

is shifted to the right by the addition of "crown". The metal cation is complexed, and the metal anion gives rise to the observed band.

The absence of effect of "crown" upon the spectrum of sodium in ethylenediamine indicates that the equilibrium

 M^{-} + "crown" \rightarrow complex + 2e⁻

lies far to the left in this solvent.

With the possibility that alkali metals can be dissolved in a variety of solvents in which they are normally insoluable, it should be possible to further test the validity of the assumption (56) that the observed transition is of the ctts type. The ability to use a wide variety of solvents should provide a better test than is obtained with ammoniaamine mixtures. REFERENCES

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