SPECTRA, SOLUBILITIES AND CONDUCTANCES OF THE ALKALI METALS IN ETHYLENEDIAMINE AND KINETICS OF THE REACTION BETWEEN SOLVATED ELECTRONS AND WATER IN ETHYLENEDIAMINE

> Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Robert R. Dewald 1963

THESIS





MICHIGAN STATE UNIVERSITY

EAST LANSING, MICHIGAN

MICHIGAN STATE UNIVERSITY.



.

.

ABSTRACT

SPECTRA, SOLUBILITIES AND CONDUCTANCES OF THE ALKALI METALS IN ETHYLENEDIAMINE

AND

KINETICS OF THE REACTION BETWEEN SOLVATED ELECTRONS AND WATER IN ETHYLENEDIAMINE

by Robert R. Dewald

The absorption spectra, conductances and solubilities of the alkali metals in ethylenediamine were studied. The kinetics of the reaction between solvated electrons and water in ethylenediamine was also studied.

The absorption spectra for sodium-ethylenediamine solutions showed only one maximum at 660 m μ . Dilute solutions of potassium in ethylenediamine exhibited absorption maxima at 660 m μ and 1280 m μ , while more concentrated solutions showed maxima at 845 m μ and 1280 m μ with a shoulder at 660 m μ . Lithium solutions showed absorption maxima at 660 m μ and 1280 m μ . Rubidium solutions showed a strong absorption peak at 890 m μ and another peak at 1280 m μ . When rubidium ions from the decomposition were present in excess, a shoulder was also observed in the vicinity of 660 m μ . Dilute cesium solutions showed only a 1280 m μ absorption peak, while more concentrated solutions showed a maximum at 1030 m μ which strongly overlapped with the 1280 m μ absorption.

The 660 m μ absorption bands for lithium, sodium, and potassium and the 1280 m μ absorption for lithium, potassium, rubidium and

2

cesium were found to be independent of metal in shape and position. The conversion of the 660 m μ absorption into the infrared 1280 m μ absorption was shown to be a slow process.

The kinetics of decomposition of these solutions was studied both spectrophotometrically and by electrical conductivity. While specific rates of decomposition varied from one experiment to another, the decomposition was found to be essentially first-order.

The equivalent conductance \underline{vs} . the square root of the concentration for solutions of cesium, potassium and rubidium followed the same general form while that for sodium solutions exhibited a marked difference in behavior. The apparent limiting values of the equivalent conductances of cesium, potassium and rubidium solutions were evaluated using the Shedlovsky conductance function. The different alkali metals yielded very different values for these apparent limiting equivalent conductances with cesium having the largest value.

The properties of metal-amine solutions cannot be explained by existing models. A new model postulating the presence of three species is presented. The infrared peak (1280 m μ) is assigned to solvated electrons and ionic aggregates involving solvated electrons and solvated metal ions. The specie responsible for the 660 m μ absorption band is postulated to contain a core consisting of a solvated diatomic molecule-ion, M_2^+ . The optical electron is trapped by the potential of the ionic core in such a manner that its optical properties are essentially independent of the metal. Species of the third type, for which the absorption depends upon the metal, are thought to be diatomic molecules, M_2 , similar to those existing in the gaseous state.

The kinetics of the reaction between solvated electrons in ethylenediamine and water in ethylenediamine was studied using the stopped-flow technique. The rate constant of the elementary step: $e^{-}(en) + H_2O \longrightarrow$ intermediates or products was found to be 24.7 \pm 1.5 liter mole⁻¹ sec.⁻¹ at room temperature. An intermediate, which absorbs in the visible region, was formed following the elementary step, but its properties were not investigated.

SPECTRA, SOLUBILITIES AND CONDUCTANCES OF THE ALKALI METALS IN ETHYLENEDIAMINE

AND

KINETICS OF THE REACTION BETWEEN SOLVATED ELECTRONS AND WATER IN ETHYLENEDIAMINE

By

Robert R. Dewald

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

2 - 1 1/4 Y

ACKNOWLEDGMENT

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.

The author is indebted to Dr. Manfred Eigen of the Max-Planck-Institut für physikalische Chemie, Göttingen, Deutschland, where this work was performed. The author wishes to thank Dr. Eigen for his assistance and suggestions throughout the course of the work. He would also like to acknowledge and thank Dr. Leo DeMaeyer for his generous help during the course of this work.

TABLE OF CONTENTS

Page

		-
I.	INTRODUCTION	1
п.	HISTORICAL	3
III.	THE FLOW APPARATUS	15
IV.	EXPERIMENTAL	19
	A. General Laboratory Technique	19
	1. Glassware cleaning	19
	2. Vacuum technique	19
	B. Metal Purification	20
	C. Ethylenediamine Purification	2.2
	D Nitrogen Purification	25
	E Absorption Spectra Measurements	25
	Apparatus	25
	$\begin{array}{c} \mathbf{A} \mathbf{p} \mathbf{p} \mathbf{a} \mathbf{a} \mathbf{u} \mathbf{s} \mathbf{s} \mathbf{s} \mathbf{s} \mathbf{s} \mathbf{s} \mathbf{s} s$	25
	2. Solution make-up	20
	5. Mixed metal and salt experiments	28
	F. Conductivity Measurements	28
	1. Apparatus	28
	2. Solution make-up \ldots \ldots \ldots \ldots	28
	3. Conductivity readings	31
	4. Lithium conductivity	31
	G. Concentration Determination by Gas Analysis	32
	H. Procedure for Kinetic Studies	34
	l. Water ampoule make-up	34
	2. Water-ethylenediamine solution make-up	36
	3. Metal solution make-up	38
	4. Flow apparatus: reactant delivery assembly	
	and procedure	40
v.	RESULTS	43
	A. Solubility	43
	B. Absorption Spectra	45
	C. Mixture Spectra.	55

•

TABLE OF CONTENTS - Continued

D. Kinetics of Decomposition During Absorbance
Measurements
E. Conductance
F. Kinetics of the Reaction of Solvated Electrons with
Water
VI. DISCUSSION
A. Comparison of Spectra
B. Conductance
1. Comparison of conductance curves
2. The limiting values of equivalent conductances . 107
C. Comparison with the Work of Other Investigators 112
D. Nature of the Alkali Metal-Ethylenediamine
Solutions
The models for metal-ammonia solutions
2 A new model
E Vinction of the Departies of Colorts d Electrone with
L. Minetics of the Reaction of Solvated Electrons with
Water
F. Future Work
REFERENCED

LIST OF TABLES

TABLE	F	Page
Ι.	Absorption Maxima of Metals in Amine Solvents	10
11.	Paramagnetic Resonance Absorption of Metal-Amine Solutions	12
III.	Absorption Maxima of Some Metal-Ether Systems	14
IV.	Solubilities of the Alkali Metals in Ethylenediamine at Room Temperature	44
v.	Location of Absorption Maxima in Ethylenediamine	46
VI.	Conductance-Concentration Data for Solutions of Alkali Metals in Ethylenediamine	76
VII.	Conductance-Concentration Data for Decomposed Solutions of Sodium, Potassium, Rubidium and Cesium in Ethylenediamine	83
VIII.	Kinetic ExperimentsSummary of Results from Runs l and 3	92
IX.	Kinetic ExperimentsSummary of Results from Run No. 2	99
x.	Comparison of Limiting Equivalent Conductances	111

LIST OF FIGURES

FIGURE	Page
1. Mixing chamber and syringe assembly of the flow apparatus	, 16
2. Schematic diagram of the flow apparatus	, 18
3. Metal make-up vessel	, 21
4. Ethylenediamine purification train	, 24
5. Assembly for absorption spectrum measurements	, 27
6. Assembly for conductance measurements	, 29
7. Gas analysis assembly	, 33
8. Water degassing and water ampoule make-up train	, 35
9. Water-ethylenediamine solution make-up vessels	, 37
10. Metal solution make-up assembly for kinetic experi- ments	. 39
11. Flow apparatus: reactant delivery assembly	. 41
12. A/A _{max} . <u>vs</u> . wavelength for the 660 mµ absorption band of lithium in ethylenediamine	. 48
13. Absorption spectra of lithium in ethylenediamine	, 49
14. A/A max. vs. wavelength for the 1280 mµ absorption band of lithium in ethylenediamine	. 50
15. Absorption spectra of sodium in ethylenediamine	. 51
16. Absorption spectra of potassium in ethylenediamine	, 52

LIST OF FIGURES - Continued

FIGURE	Page
17. Absorption spectra of rubidium in ethylenediamine	54
18. Absorption spectra of cesium in ethylenediamine using a 0.1 mm. cell	56
19. A/A _{max} , <u>vs</u> . wavelength for the 1280 mµ peak of cesium in ethylenediamine	57
20. Absorption spectra of lithium metal solution mixed with rubidium metal solution	59
21. Absorption spectra of rubidium metal solution plus decomposed lithium solution	60
22. Absorption spectra of lithium metal solution plus decomposed rubidium solution	61
23. Absorption spectra of rubidium metal solution plus lithium iodide solution	62
24. Absorption spectra of rubidium metal solution plus decomposed sodium solution	63
25. Absorption spectra of cesium metal solution added separately to lithium chloride and to decomposed lithium solution	64
26. Spectral decomposition of sodium-ethylenediamine solutions	66
27. Spectral decomposition of potassium-ethylenediamine solutions	67
28. Spectral decomposition of rubidium-ethylenediamine solutions	69
29. Spectral decomposition of cesium-ethylenediamine solutions	70

LIST OF FIGURES - Continued

FIGURE	Page
30. Spectral decomposition of a lithium-ethylenediamine solution	71
31. Conversion of the 660 m μ peak into the 1280 m μ peak of lithium in ethylenediamine	72
32. Equivalent conductance vs. $C^{\frac{1}{2}}$ for sodium, potassium, rubidium and cesium in ethylenediamine	74
33. Log-log plot of specific conductance vs. concentration for sodium, potassium, rubidium and cesium in ethylenediamine	75
34. Semi-log plot of specific conductance vs. time for sodium, potassium, rubidium and cesium in ethylene-diamine.	78
35. Typical log of specific conductance vs. time plots used for decomposition corrections in conductance determinations.	79
36. Log of specific conductance <u>vs</u> . time for lithium in ethylenediamine	80
37. Equivalent conductances <u>vs</u> . $C^{\frac{1}{2}}$ for the decomposed solutions of sodium, potassium and cesium in ethylene-diamine.	82
38. Typical pictures from kinetic runs 1 and 2	85
39. Typical pictures from kinetic run no. 3	86
40. Log (Abs.) <u>vs</u> . time; pictures no. 2, run no. 3	87
41. Log (Abs.) vs. time; pictures 7 and 9, run no. 3	88
42. Log (Abs.) vs. time; pictures 11 and 12, run no. 3	89
43. Log (Abs.) vs. time; pictures from run no. 1	90

LIST OF FIGURES - Continued

FIGURE Pag	e
44. Log (Abs.) <u>vs</u> . time; picture no. 5, run no. 3 94	4
45. Absorbance vs. time; picture no. 5, run no. 3 9	5
46. Absorbance vs. time; picture no. 4, run no. 3 9	6
47. Absorbance vs. time; picture no. 6, run no. 3 9	7
48. Log (Abs.) vs. time; pictures from run no. 2 9	8
49. Log (Abs.) and absorbance vs. time; sodium-ethylene- diamine added to water-ethylenediamine solutions 10	1
50. Comparison of the 660 m μ absorption band of lithium, sodium and potassium in ethylenediamine 10	3
51. Comparison of the 1280 m μ absorption band of lithium, potassium, rubidium and cesium in ethylenediamine 10	4
52. Comparison of the conductance curves for metal- amine systems	6
53. Shedlovsky analysis plots for cesium, potassium and rubidium in ethylenediamine	9

I. INTRODUCTION

The nature of the radicals produced in the radiation of water and aqueous solutions is a subject of considerable current interest. Allen (1) has recently summarized the experimental evidence for the existence of two transient reducing species in the radiation chemistry of aqueous solutions. One possible pair of reducing species considered was the solvated electron, e_{aq} , and the H atom, and the other pair was the H atom and the H_2^+ ion (1-6). Recently kinetic salt effects (7,8) demonstrated that the reducing radical produced in water radiolysis has a unit negative charge and may be identified as the solvated electron. Hart and Boag (9) have recently observed a transient absorption band which peaks at 700 m μ when deaerated water is irradiated with a pulse of 1.8 Mev. electrons. They attributed this absorption to the solvated electron.

The solvated electron might be pictured as an electron bound by polarization of the dielectric medium (4, 10). The electron solvated according to this model (termed a polaron) is delocalized and its charge distribution is distributed over several solvent molecules.

The conversion of the solvated electron to H atoms by H_2O , i.e.

 $e_{aq}^- + H_2O \longrightarrow H + OH^-$

is a problem of primary interest to radiation chemists (11, 12) since the applicability of the specie, e_{aq}^- , in radiation chemistry mechanisms depends on the half-time of the above reaction. Recently several investigators (8, 11, 12) have pointed out that the reaction must be relatively slow in order to be consistent with many experimental results of radiation chemistry.

The existence of solvated electrons in solutions of alkali metals in liquid ammonia, methylamine and ethylenediamine has been recognized for many years. Dr. Eigen proposed that information about the rate at which an electron reacts with water could perhaps be obtained by making kinetic studies of the reaction of alkali metal-amine solutions with solutions of water in the amine.

The only technique for studying fast reactions in solution applicable to such an investigation is the flow method pioneered by Hartridge and Roughton (69). The alkali metal-liquid ammonia system has the experimental disadvantage that all operations must be carried out either under pressure or at temperatures below -33° C. On the other hand, ethylenediamine, which also dissolves the alkali metals, is a liquid from 8°C to 117°C and thus would eliminate the cooling problem. This consideration lead us to choose the alkali metal-ethylenediamine system for the kinetic studies. When this work commenced, the only studies (13) reported on alkali metal ethylenediamine solutions were the absorption spectra up to 1000 m_{μ}, and electron paramagnetic resonance measurements on solutions of sodium and potassium. It was clear from studies in other amine systems that solutions of different alkali metals had different physical properties. Therefore, it was necessary to make extensive studies of the metal-ethylenediamine solutions in order to characterize the nature of these solutions. The spectral studies were extended to other metals, more concentrated solutions and wavelengths up to 1900 $m\mu$. The electrical conductivities of the metals dissolved in ethylenediamine were also investigated in order to make a correlation with spectral data. In the course of this work several new experimental techniques were developed, especially modification of standard flow methods to allow studies of these reactive systems.

II. HISTORICAL

The dissolution of alkali metals in liquid ammonia, amines and ethers is indeed one of the most fascinating phenomena in chemistry. Since the early work of Weyl (14), the unusual physical and chemical properties of these solutions have aroused the interest of many investigators and more than a thousand articles have appeared in the literature on this and related subjects (15). When metals dissolve in these solvents, a metastable blue solution is formed with no net reaction. Concentrated solutions of these metals in ammonia are metallic in appearance. Due to the metastable nature of these solutions, traces of impurities such as water, carbon dioxide, oxides, hydroxides, and metals catalyze the reaction between the solvent and the dissolved metal. The stability is also temperature dependent.

The metastability of these solutions requires that studies be carried out in closed systems. Extreme precautions must be used to guarantee the cleanliness and purity of the materials involved. The problem of maintaining stable solutions is more troublesome in the amine and ether solvents. This is probably the reason for the limited number of investigations that have been reported in this area (16).

The pioneering studies of C. A. Kraus and co-workers (17) on the solutions of alkali metals in liquid ammonia originated most of the theoretical speculations concerning the structure of metal-ammonia solutions. These studies, which commenced over fifty years ago, included vapor pressures, densities, apparent molecular weight, conductivities, phase studies and relative transport numbers of the conducting species. Since Kraus' contribution and chiefly during the past two decades, the physical properties of the ammonia solutions

have been studied by the methods of paramagnetic resonance, nuclear magnetic resonance, conductivity, electromotive force and transference number measurements, x-ray diffraction, photo-electric effects, the thermo-electric effect and by absorption spectroscopy. The literature connected with these contributions is extensive and the reader is referred to several recent review articles for a more complete survey of the field (15, 16, 18-20).

As would be expected in the gradual development of a field, various theoretical models have periodically been suggested but have not stood the test of further experimentation or else were modified to explain new experimental facts. A few of the physical properties of metal-ammonia solutions which must be explained by any theoretical model are listed below:

- The nature of the blue coloration in dilute solutions and the change which occurs in the absorbing species when light is absorbed.
- 2. The volume expansion that occurs when the alkali metals dissolve in ammonia (21).
- 3. Concentrated solutions exhibit high electrical conductances characteristic of metals while more dilute solutions show electrolylic conductance (22).
- 4. The negative species carries approximately 85 per cent of the current in dilute solutions and exceeds 99 per cent in more concentrated solutions (23, 24, 25).
- 5. The absorption spectra of the different alkali metals are practically identical and follow Beer's law from 350 m μ to 1800 m μ for all concentrations investigated up to 0.02 molar (26).
- 6. Nuclear magnetic resonance experiments on sodium-ammonia solutions have shown a chemical shift for nitrogen and sodium

nuclei (usually called a Knight shift for metals) as well as an appreciable chemical shift for the protons (27-29).

 The results of both static and electron paramagnetic resonance measurements show that the molar susceptibility is larger at low concentrations than at high concentrations (30-32).

Of the several models that have been proposed to fit the experimental data two have gained prominence and will be reviewed below. Each of the models is capable of explaining some of the experimental data better than the other but neither can explain all of the observed facts.

Models

<u>The cavity model</u>. The early model by Kraus (33) assumed the presence of undissociated sodium atoms, sodium ions and solvated electrons according to the equations

$$Na = Na^{\dagger} + e^{-}$$
(1)

$$e^{-} + (NH_3)_{x} = (NH_3)_{x} e^{-}$$
 (2)

Ogg (34) extended Kraus' idea of solvated electrons and proposed that the solvated electron could be considered as being trapped in a spherical cavity surrounded by ammonia molecules. According to this model the electrons in the cavities are in equilibrium with respect to the following reaction:

$$2 e^{-}(am) = \frac{1}{2} e_{2}^{-}(am)$$

where $e_2^{=}$ (am) represents two electrons in one cavity with antiparallel spins, the $e_2^{=}$ (am) centers being energetically stable with respect to e^{-} (am) centers.

Ogg estimated the ammoniation energy of the electron by considering the energy of an electron confined to a spherical box assuming that the wall of the cavity represents an infinite potential barrier and a node in the wave function. Using this simple model, Ogg calculated values for the solvation energy and cavity radius which were in rather poor agreement with the experimental values.

Lipscomb (35) refined Ogg's approximate calculations by introducing energy contributions arising from electrostriction effects, electronic polarization of the molecules at the surface of the cavity and surface tension effects.

Further refinements were presented by Stairs (36) and Kaplan and Kittel (37). Stairs improved upon Lipscomb's calculation by using a graphical integration procedure to allow a better calculation of the wave function. This improved wave function enabled him to obtain a better estimate of other contributions to the electronic energy than the surface tension effect. Kaplan and Kittel employed a model in which the solvated electrons exist in delocalized molecular orbitals on all of the solvent protons surrounding the cavities which the electrons create in the solvent.

The polaron model is an extension and refinement of the simple cavity model. In the polaron model, the electron is considered to polarize the surrounding ammonia molecules in such a way as to provide a trapping potential for itself. The potential is derived from the laws of electrostatics adopted to a quantum mechanical description of the electron density in terms of the electronic wave function. In the polaron model, no assumption is made <u>a priori</u> as in the cavity model where the localization of the electron is described by some cavity whose boundaries act as limiting points for the electronic wave functions. The physical picture, however, is the same in the end result.

The polaron model of metal-ammonia solutions is similar to the corresponding model for trapped electrons in ionic crystals first introduced by Landau (38). The polaron model was first applied to metal-ammonia solutions by Dawydow (39) and later by Deigen (40) and by Jortner (41). In essense, Deigen considered a model consisting of three types of local centers; namely, polarons, F_1 centers and F_2 centers. The F_1 centers are considered analogous to those found in alkali halide lattices when excess alkali atoms are added to the lattice. The F_2 centers are anion vacancies with two bound electrons. The F_2 centers are diamagnetic while the polaron and F_1 centers are paramagnetic. The interaction of polarons with the alkali metal ions and the relative number of F_1 and F_2 centers at any concentration is used to explain the various observed properties of the solution. This picture results, however, in the same stoichiometry as the cluster model so that equilibrium constants do not reveal the nature of the species involved.

<u>The cluster model</u>. This model was first proposed by Coulter (42) and later expanded by Becker, Lindquist and Alder (43). It is also referred to as the expanded metal model or the B.L.A. model. Blumberg and Das (44) recently refined the calculation of the wave function for this model.

The cluster model postulates the ionization of the metal in very dilute solution to give a solvated metal ion, $M^+(am)$ and an electron. The solvated metal ion is assumed to have between four and six oriented ammonia molecules depending on the metal. With increasing concentration there is association to monomer units M(am) which can be represented by the following equilibrium

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

In the monomer the electron is assumed to be trapped by the potential

produced by the metal ion and the oriented solvent molecules around the ion. At higher concentrations, two monomers dimerize to the diamagnetic species, $M_2(am)$,

$$2M(am) = M_2(am)$$
 (2)

and the dimer is held together by a pair of electrons in a bonding molecular orbital located principally between the two ions.

Recently the exact nature of the monomer and dimer species of the cluster model has been questioned. Douthit and Dye (45) and Evers (20) have pointed out that the constancy of the absorption spectra in the dilute range could be explained if the monomer were simply an ion-pair consisting of an ammoniated metal ion and an ammoniated electron. Gold, Jolly and Pitzer (46) have recently postulated that the $M_2(am)$ species could be pictured as a quadrupolar ionic assembly of 2e⁻(am) and 2M⁺(am) in which there is little distortion of either the ammoniated electrons or ammoniated metal ions. The electrons and ions are presumed to be held in a square or rhombic configuration. These authors also pointed out that recent experimental results of absorption spectra (26) and molar volume (47) are understandable if the cavity retains its size through ion pair and quadruplet formation.

<u>Amine solvents</u>. The initial spectroscopic investigations of many of the alkali metal-ammonia and methylamine solutions were carried out by Gibson and Argo (48). Blades and Hodgins (49) reported spectral peaks for solutions of alkali metals in ammonia, methylamine and ethylamine. Hohlstein and Wannagat (50) contributed to the spectra of alkali metals in pure methylamine, pure ethylamine and mixtures of methylamine and ethylamine with ammonia. Fowles <u>et al</u>. (13), Shatz (51), Eding (52), and Douthit (53) did further work on the

absorption spectra of alkali metals in amine solvents. Recently Windwer and Sundheim (54) reported the absorption spectra of solutions of alkali metals in ethylenediamine. The results of these investigations are summarized in Table I. This summary points out also the many conflicts in the results reported by different investigators.

Examination of the spectroscopic data for the solutions in amine solvents as well as for the mixed solvents shows the presence of one to three very intense absorption bands. One of these is in the visible region (\sim 650-700 mµ), one in the near infrared region (800-1000 mµ), and the other in the infrared region (\sim 1200-1500). Symons (13) suggested that the visible band is characteristic of paired solvated electrons and the infrared band is characteristic of unpaired solvated electrons. Symons was unable to account for the absorption band at 850 m μ which is present in relatively concentrated solutions of potassium in methylamine and proplenediamine. He concluded that since this band is reproducible and occurs in two solvents, it is unlikely to be caused by impurities in the metal. Blades and Hodgins (49) attributed the visible and infrared bands to the variation in physical arrangement of the solvent molecules around the periphery of the cavities containing single electrons. They proposed that with the amines there are amine and aliphatic traps containing single electrons which give rise to the visible and infrared bands. They postulated that a mixed-type of trap might explain their reported 820 mµ peak for potassium in methylamine. Hohlstein and Wannagat (50) concluded that the methylamine and ethylamine are contaminated by the presence of minute amounts of ammonia and that all of the phenomena thus far observed were due solely to traces of ammonia in the amine solvents. Eding (52) suggested that his 820 m μ band for potassium might be due to a reaction product of potassium metal with Pyrex glass. Windwer and Sundhein (54) suggested that the peaks

Solvent	Metal	Range Investigated Mµ	Temper- ature °C	Absorption Max.	Refer- ence
CH ₃ NH ₃	Li	400-2000	-60	1300	49
5 5	\mathbf{Li}	400-1600		710,1500	50
	${f Li}$	400-750	-75	690	51
	\mathbf{Li}	visible	-70	650	48
	Li	320-1200	-70	680, IR [*]	52
	Na	400-2000	- 30	655	49
	Na	visible	-70	650	48,55
	Na	400-1600	· 	690	50
	Na	320-1200	-70	650	52
	к	400-2000	-60	654,820	49
	к	320-1200	-70	650, 820, IR*	52
	К	visible	-70	650	48
	Rb	none reported			
	Cs	visible	-70	650	48
		400-2000	-60	1000	53
	Ca	visible	-60	650	48
		400-2000	-60	1300	49
CH ₃ CH ₂ NH ₃	\mathbf{Li}	400-2000	-40	1420	49
	\mathbf{Li}	400-1600		600	50
	К	400-1600	-60	655	49
	Na	400-1600		680	50
$(CH_2 \cdot NH_3)_2$	Li	300-1700	ŖT	650-670	54
	Na	400-1000	RT	670	13
	Na	300-1700	RT	650-670	54
	к	400-1000	RT	670	13
	К	300-1700	RT	650-670**	54
	Rb	300-1700	RT	700,900	54
NH ₂ -CHM _e ·	- Na	400-1000	RT	660	13
CH ₂ -NH ₂	к	400-1000	RT	670	13
				shoulder at 820	

Table I. Absorption Maxima of Metals in Amine Solvents

*Strong absorption in the IR region. *Shoulder at 820 m μ -found in certain potassium solutions but not in others.

in the 800-1000 region which they observed for both rubidium and potassium in ethylenediamine might be due to a dimer and the two peaks might be thought of as associated with the same species. They did not, however, describe the nature of this dimer.

Vos (56) has recently studied the electron paramagnetic resonance absorption of metals in amine systems. His results as well as the results of other investigators are summarized in Table II.

Conductance data in amines are rather limited. Gibson and Phipps (58) contributed the only early work dealing with the electrical properties of metals in amine solvents. However, the reliability of their data has been questioned (24) because of the probable presence of impurities which tended to decompose their solutions. Only lithium in methylamine has been carefully studied. Evers, Young and Panson (24) reported a study of the conductance of lithium in methylamine at high concentrations. In 1960 Evers and Berns (59) extended this work to cover the dilute-solution range. Berns and Evers have successfully reproduced their experimental data with a conductance function that was earlier derived by Evers and Frank (60). This conductance function uses the mass action concept of Becker et al. (43) with a modified form of the Shedlovsky conductance function. Evers and Frank have also used this conductance function to explain the data of Kraus (22) for solutions of sodium in ammonia. Windwer and Sundheim (54) have recently reported conductance measurements of potassium in ethylenediamine, but their values can only be considered qualitative in nature due to the experimental procedure used and the instability of their solutions.

Metal-ether systems and oxygen-containing solvents. Wothorn and Fernelius (61) observed that both sodium and potassium appeared to form transitorily blue solutions with water and alcohol. Jortner and Stein (62) reported that potassium dissolves in deoxygenated water to

		Magnitude of	
Solvent N	letal	Absorption	Reference
CH ₃ -NH ₂	Li	strong	13
J	\mathbf{Li}	strong	56
	Li	strong	57
	Na	weak	56
	К	weak	13
	К	strong	56
	Cs	strong	56*
	Rb	strong	56*
$(CH_2NH_2)_2$	$\mathbf{L}\mathbf{i}$	detectable	57
	$\mathbf{L}\mathbf{i}$	strong	56
	Na	nil	13
	Na	detectable	54
	Na	strong	56
	К	very weak	13
	К	strong	54
	К	strong	56
	Rb	positive	54
	Rb	strong	56
	Cs	strong	56
NH ₂ -CHMe-CH ₂ -	Na	nil	13
NH ₂	К	nil	13

 Table II. Paramagnetic Resonance Absorption of Metal-amine Solutions

*Rubidium and cesium in methylamine show nuclear hyperfine splitting.

give a very unstable blue solution. Downs, Lewis, Moore and Wilkinson (63) reported that blue solutions of potassium were obtained in tetrahydrofuran and the cyclic tetramer of propylene oxide, as well as the dimethyl ether of ethylene glycol. Recently Downs, et al. (64) have listed some fifteen ethers and one aminoether which form moderately stable blue solutions with potassium or sodium-potassium alloy.

Cafasso and Sundheim (65) have found that potassium, rubidium and cesium dissolve in 1,2-dimethoxyethane and some of its homologs to give blue and electrically conducting solutions. They investigated the absorption spectra, electron paramagnetic resonance and conductivity in order to characterize the metal-ether system. Recently Dainton (66) reported the absorption spectra for potassium in dimethoxyethane and tetrahydrofuran. The spectral results for three ether systems are given in Table III. Dainton, et al. (66) report an infrared band at 1000 m μ in addition to a 700 m μ band for solutions of potassium in ethers, while Cafasso and Sundheim (65) only reported a 700 m μ band for the same system. Both investigators reported no electron spin resonance signal for potassium in dimethoxyethane whereas Tuttle and Weissman (67) reported a weak spin resonance absorption for this system.

At this point it is not possible to draw any conclusions about the blue solutions formed in the metal-ether systems until more quantitative and reproducible data has been accumulated in these systems.

	Range Investigated	Absorption Max.		
Metal	(mµ)	(mµ)	Reference	
Solvent-Dime	thoxyethane			
Na-K alloy	300-2500	715	65	
Na-K alloy	600-2200	700	64	
K	600-1000	900,715	68	
К	300-2000	715	65	
К	400-2500	715,>1000	66	
Rb	300-2500	910	65	
Св 300-2500		715	65	
Solvent-Tetra	hydrofuran			
K 400-2500 700.>1000		66		
К	600-1000	900, 700	68	
Solvent-Bis[2	-(2 methoxy))ethoxy]	ethyl ether		
К	300-2500	690	65	
Rb	300-2500	890	65	
Cs	300-2500	690,1000	65	

Table III. Absorption Maxima of Some Metal-Ether Systems

.

III. THE FLOW APPARATUS

In 1923 Hartridge and Roughton (69) introduced a method for studying reactions with half-lives of a few milliseconds. In the many applications of this method, two reactants are forced into a special mixing chamber and the composition of the mixture is determined either (a) at various distances from the mixing chamber during flow; or (b) after sudden stoppage of the fluid. The method is too wellknown to justify a detailed description here, but reference is made to a few of the many papers and review articles on this subject (70-75).

Since contact with air rapidly decomposes metal-amine solutions, the stopped-flow apparatus used in this research was so designed that all operations connected with the reacting solutions could be performed in a closed system after evacuation. To force the liquids into the mixing chamber, glass syringes of 20 ml. capacity were used. Selected syringes of the interchangeable type could be evacuated to 1×10^{-4} torr when heavily lubricated with Dow-Corning silicone grease. The mounting of the syringes and the mixing chamber is shown in Figure 1. The pushing syringes were connected to the mixing chamber and fluid reservoirs with a two-way stopcock via standard tapers and ball joints. The stopping syringe was connected to the mixing chamber via standard tapers by a T-joint containing a stopcock which facilitated discharge of reacted solution. The entire assembly was mounted on a framework of properly cut aluminum plates which were bolted together and to a sturdy metal table. The following were also mounted on the table: a lever mechanism for pushing the syringes, the light source, the monochromator and lens, and the photomultiplier. The handle ends of the syringe plungers were fitted snugly into an aluminum block which was connected to a mechanism which kept the plungers parallel.



Figure 1. Mixing chamber and syringe assembly of the flow apparatus.

Rapid discharge of the syringes was accomplished by pushing manually on the lever mechanism. This forced the two solutions rapidly into the mixing chamber and thence upward through the observation tube. After leaving the observation tube, the mixed reactants forced the plunger of syringe C upward until it reached its seating. This caused the flow of the liquid to stop suddenly and tripped the microswitch which triggered the Tektronix oscilloscope.

The mixing chamber was constructed from Plexiglass. Four 0.5 mm I.D. jets were arranged so that they delivered tangentially into the bore of the observation tube which was 1 mm. I.D. A standard glass taper was sealed to the end of the observation tube using an epoxy resin, and glass-T's with standard tapers were also sealed to the jets as shown in Figure 1.

The reactions were followed by measuring changes in light absorption. Light from a tungsten lamp was passed through the monochromator (Carl Leiss-Berlin) and was focused on the center of the observation tube, Figure 2. After passing through the solution under observation, the light was focused onto a photomultiplier tube (Valvo No. 150 CVP). The response of the photomultiplier was amplified and displayed on the screen of a Tektronix oscilloscope. The trace on the scope was then photographed.





IV. EXPERIMENTAL

A. General Laboratory Technique

<u>l. Glassware cleaning</u>. For most of the spectral determinations, the glassware was cleaned with hot chromic acid cleaner followed by a hydrofluoric acid cleaner. The hydrofluoric acid cleaner was prepared by volume according to the following formula:

> 2% acid soluble detergent 33% concentrated reagent grade nitric acid 5% hydrofluoric acid 60% distilled water

During the course of the spectral determinations, it was observed that stability of the blue solutions increased greatly if the chromic acid cleaning was eliminated. After this observation, all glassware was cleaned first with hydrofluoric acid cleaner and then with boiling aqua regia. After the aqua regia treatment the glassware was rinsed approximately ten times with distilled water and then rinsed approximately twenty times with doubly-distilled conductance water. Next, the glassware was soaked in doubly-distilled conductance water for approximately four hours. The water was frequently changed during the soaking. Finally, the glassware was dried in an oven operating at 140° C. It should also be emphasized that ordinary tap water was not used at any time during the cleaning process. Furthermore, only reagent grade acids were used in preparation of the acid cleaners.

2. Vacuum technique. An oil diffusion pump permitted evacuation to better than 10⁻⁵ torr as read on a MacLeod gauge. All stopcocks on the vacuum line were lubricated with Apiezon "N" vacuum grease. In this work, all standard taper joints and ball joints were sealed with Apiezon "W" wax. Stopcocks, through which liquids were passed,

were lubricated with Dow Corning high-vacuum silicone grease. Direct contact of mercury vapor with the systems was avoided by using traps.

B. Metal Purification

Reagent grade sodium and potassium were obtained from E. Merck, A. G. Both metals were in rod form and stored under petroleum hydrocarbons. The petroleum hydrocarbons were first washed from the metal with dry toluene. The metal was then dried by evacuation via a liquid air trap using a mechanical roughing pump. After drying, the metal was cut from the center of a large piece with a stainless steel knife and forceps. Next, the metal was transferred into chamber A of the metal make-up vessel, Figure 3, which was connected to the high vacuum line. The metal make-up vessel was then evacuated. After the pressure stabilized to less than 10^{-5} torr, the metal was gently heated until it melted and ran down through the constrictions into chamber B, leaving the oxide at the constrictions. Chamber A was then removed from chamber B by sealing off under vacuum. Then, the molten metal was heated at intervals until all dissolved gases escaped. After the pressure had stabilized at less than 10^{-5} torr, the metal was distilled into the sample tubes. The sample tubes were then removed by sealing under vacuum.

Rubidium and cesium were obtained from Fluka, A. G., Buchs, S. G., Switzerland. Both metals were of the highest purity commercially available and came in sealed ampoules. The ampoules were first cooled with dry-ice, broken, and transferred immediately to the metal make-up vessel which was then immediately evacuated. It was necessary to cool the samples in order to avoid excessive oxidation of the metals during transfer. The rubidium and cesium metal makeup then proceeded as described above for sodium and potassium.



Figure 3. Metal make-up vessel.
The metal samples were then subdivided following essentially the same procedure as described above. In this case, however, the sample tubes were glass tubes and capillaries of known diameter. A glass tube containing the metal from the first purification steps described above was broken and introduced into chamber A of the metal make-up vessel. The metal was then melted, degassed, and distilled into the tubes and capillaries. By knowing the diameter of the tube or capillary and the length of the metal column, the amount of metal contained could be estimated and used to make a solution of an approximate desired concentration.

Lithium was obtained from E. Merck, A. G., stored under mineral oil. Lithium used for solvent purification was only washed with dry toluene and dried, since lithium cannot be heated in glass. In preparing lithium solutions for spectra and conductivity determinations, pieces of lithium were cut with a stainless steel knife and forceps from the center of a large piece under toluene. The toluene had previously been dried with sodium wire and lithium pieces. Prior to cutting the metal, the dissolved gases in the toluene were swept out with argon. The metal was transferred to the sample makeup vessel while the vessel was being swept out with argon.

For the spectral determinations, fragile glass ampoules of metals purified by vacuum distillation were used. These ampoules could readily be broken under vacuum by a magnet sealed in glass. The metal ampoules were prepared as described by Dye, Sankuer and Smith (25).

C. Ethylenediamine Purification

Reagent grade anhydrous ethylenediamine (>99% purity) was obtained from Buchs, A.G., Switzerland. It was first stored for several days over KOH and then refluxed over a mixture of BaO and

KOH in a stream of N_2 for two days (flask no. 1, Figure 4). After refluxing, it was then distilled in a stream of N_2 onto sodium wire and lithium pieces. The blue lithium solution formed immediately and was stored for one day (flask no. 2, Figure 4). The ethylenediamine was then poured into a second distillation flask (flask no. 3, Figure 4) and the fractionating column was evacuated via stopcock (A), Figure 4, and a liquid air trap by a mechanical roughing pump. The system was then filled with nitrogen and the ethylenediamine refluxed in a stream of N_2 for two days. It should be noted that the system was so designed that from this point on, no air came in contact with the ethylenediamine. The solvent was then distilled through a one meter insulated fractionating column packed with short lengths of 5 mm. glass tubing. The distillation was performed in a stream of N_2 and the first part of the distillate was discarded by running it into flask A, Figure 2. The bulk of the ethylenediamine, boiling at constant temperature, was then distilled into a two-liter flask containing Na wire and lithium pieces, flask no. 4. This flask had been previously evacuated and filled with purified nitrogen. The blue lithium solution formed readily upon solvent contact with lithium whereas the Na wire did not readily dissolve. The blue solution was allowed to stand for one day, during which time the hydrogen formed by reaction with dissolved O_2 and H_2O and by decomposition of the solvent, was occasionally pumped off by a mechanical roughing pump via stopcock (A) and a liquid air trap.

The next flask (flask no. 5, Figure 4) in the distillation line had a side-arm sealed to it which facilitated potassium metal distillation. After breaking and introducing a tube of purified potassium into this side-arm, flasks nos. 5 and 6 were evacuated and flamed until the pressure stabilized at less than 10^{-5} torr. Next, the potassium metal was distilled in vacuo to form a mirror in flask no. 5. After this



Figure 4. Ethylenediamine purification train.

distillation, the side-arm was sealed off and the ethylenediamine was vacuum-distilled. During this distillation, flask no. 4 was warmed to $40-50^{\circ}$ C with a water bath and the receiver flask was cooled with an ice-salt bath. The potassium dissolved immediately in the ethylenediamine forming a deep blue coloration which lasted for several weeks in the presence of excess potassium metal. Portions of this blue solution as needed were then vacuum-distilled into flask no. 6 and covered with purified N₂. From flask no. 6, the purified solvent could be drawn into a solution make-up vessel as needed. From this point on, flask no. 6 will be referred to as the solvent-reservoir flask.

D. Nitrogen Purification

Nitrogen used during the ethylenediamine refluxing and distillation was purified by passing it over Cu and CuO at 400° C, then through drying towers containing "Ascarite," MgClO₄ and BaO. The nitrogen used as a covering gas received the same treatment as described above, but was further purified by passing it through a trap containing activated silica gel at liquid air temperatures. It was stored on the vacuum line in two-liter Pyrex flasks.

E. Absorption Spectra Measurements

<u>1. Apparatus</u>. Pyrex absorption cells were purchased from the American Instrument Company and had nominal path lengths of 0.1 and 1.0 mm. The absorption cell was sealed to a solution makeup vessel and a waste vessel was attached to the apparatus <u>via</u> a 19/8 ball joint, Figure 5. The entire apparatus was so constructed that solution could be tipped into the absorption cell and then into the waste vessel. This allowed rinsing the cell with solution. The spectra

were measured with a Beckman DK-2 spectrophotometer at room temperature. Reference cells were filled with pure anhydrous ethylenediamine. A special cell holder was constructed for the DK-2 spectrophotometer.

2. Solution make-up. The solutions were made-up by essentially two different methods of solvent addition. In the first method, the absorption cell apparatus, with a metal ampoule and a magnet sealed in glass in chamber A, was connected directly to the solvent reservoir flask. After evacuation and flaming, the ampoule was broken with the magnet sealed in glass and the solvent was introduced through the stopcocks. In the second method, more often the case, the apparatus was connected to a 500 ml. distillation flask also shown in Figure 5. Before attachment, lithium metal was introduced into the distillation flask. The complete assembly was then evacuated and flamed until the pressure stabilized at less than 10^{-5} torr. Stopcock no. 1 was then closed and ethylenediamine introduced into the distillation flask. The blue lithium solution which formed immediately was allowed to stand for several hours. Finally after breaking the metal ampoule, the solvent was vacuum-distilled into the solution make-up chamber which was kept at dry-ice temperatures. Upon melting the frozen ethylenediamine, a blue solution readily formed with the metal. It was usually possible to melt a small amount of the solvent away from the metal and transfer it to the optical cell. In this way, a small amount of the metal solution could be added to a given solution whose maximum absorbance was less than two. The absorbance of the saturated solution was too high to permit its measurement directly. Alternatively, a small amount of the solution could be left in the cell and ethylenediamine distilled in to effect a dilution. Finally, in some cases the saturated solution was transferred into the cell and allowed to decompose until the traces were on scale.



Figure 5. Assembly for absorption spectrum measurements.

3. Mixed spectra and salt addition. The spectra apparatus was modified by attaching a secondary solution make-up vessel, chamber B, Figure 5. In this secondary solution make-up chamber, metal or lithium chloride solutions were made-up. These solutions were then mixed in the delivery tube to the absorption cell with metal solutions which were made-up in chamber A.

F. Conductivity Measurements

<u>1. Apparatus</u>. A conductance cell with small platinum ball electrodes was constructed of soft glass. The cell was sealed <u>via</u> a graded seal to a Pyrex storage vessel and <u>via</u> a ball joint to a waste vessel, Figure 6. The entire apparatus was so constructed that solution could be tipped into the conductivity cell and then into the waste vessel. This allowed rinsing the cell with solution if desired. The cell constant was measured by a series of standard KCl solutions. Conductivity was determined with a Siemens Wheatstone bridge at 100,000 cps.

2. Solution make-up. The solution make-up flask with a side-arm for metal distillation is shown in Figure 6. The flask was connected to the solvent-reservoir flask, decomposition vessel and vacuum line. The decomposition vessel was connected to the gas analysis assembly as shown in Figure 7. The conductivity cell apparatus was connected to the decomposition vessel as shown in Figure 6.

A glass tube or capillary of purified metal was broken and introduced into the side-arm of the solution make-up vessel. The complete assembly was then evacuated and flamed until the pressure stabilized at less than 10^{-5} torr. Next, the metal was melted so that it ran through the constriction and the side-arm was sealed off under vacuum. The metal was then vacuum-distilled into the bottom of the 500 ml. make-up flask. Next, stopcocks 1, 2 and 3, Figure 6, were closed and the





ethylenediamine was introduced into the make-up flask <u>via</u> the stopcock of the solvent-reservoir flask. The blue solution, which formed immediately, was then pumped on by the high vacuum system through a liquid air trap and stirred constantly with a magnet sealed in glass for about 10 minutes after all the metal had dissolved.

In preparing saturated solutions of the metals, a large excess of metal was distilled into the make-up flask. The solution was left in contact with the excess metal for two hours with continuous pumping and stirring before transfer. Using this technique, consistent concentration values were obtained for the saturated solutions of the metal investigated.

For preparation of unsaturated solutions, the amount of metal needed to prepare a solution of an approximate desired concentration was estimated by calculating the volume and hence the weight of metal in a given capillary. This metal was again distilled into the bottom of the make-up flask and all of the metal was allowed to dissolve before transfer of the blue solution. It was necessary to have all of the metal dissolved before transfer in order to insure that a uniform solution was transferred.

After the blue solution was degassed, previously purified nitrogen or argon gas was introduced <u>via</u> stopcock no. 1. The gas pressure forced the blue solution through the frit such that the solution filled the delivery tube up to stopcock no. 2. The first fraction of the solution was then transferred into the waste flask (A) of the conductivity apparatus, Figure 6, <u>via</u> stopcocks 2 and 3. Then, the next fraction of the solution was transferred into the decomposition vessel, Figure 7. Finally, the remainder of the blue solution was transferred into the storage vessel of the conductivity cell apparatus. The time of transfer was recorded. The total time required to make the complete solution transfer was normally less than 15 seconds.

3. Conductivity readings. Immediately after solution transfer, the conductivity cell was disconnected and the electrodes of the cell were rinsed a few times with the blue solution. When the solution used for the conductivity measurement was tipped into the cell, the time was recorded. Next, conductivity readings were recorded as a function of time for about one and one-half hours. After this time, another sample was tipped into the cell and measurements were taken on a second sample as a function of time. Symons, et al. (13), and Windwer and Sundheim (54) reported that platinum acts catalytically on the alkali metal-ethylenediamine solutions accelerating the decomposition. This was also observed in this work but we also observed that during vigorous shaking the conductance of the solution increased. This suggests that the solution in the vicinity of the electrodes differs in nature from the solution in the bulk due to decomposition. Before and during each conductivity reading, therefore, the cell was shaken vigorously in order to insure a uniform solution between the electrons. The measurements were performed at room temperature.

For lithium, sodium and potassium, saturated solutions were also prepared directly in the storage vessel of the conductivity cell. The procedure for solution make-up in this case was the same as that described for spectral measurements. This procedure gave results for the conductivity of the saturated solutions identical to those obtained using the transfer method.

4. Lithium conductivity. Since lithium cannot be melted in glass, a bent side-arm was attached to the solution make-up flask by a standard taper joint so that it could be rotated into an upright position to tip the lithium metal into the previously evacuated and flamed flask. The lithium metal solution was stirred and pumped on for 20 minutes before transfer. Only the conductance of the saturated solution was studied because of the instability of the lithium solutions.

31 ·

G. Concentration Determination by Gas Analysis

The alkali metal concentration was determined by decomposing the solutions with NH₄Br and then measuring the amount of hydrogen gas envolved. The amount of metal could be determined from the stoichiometry of the reaction:

$$NH_4Br + M \longrightarrow \frac{1}{2}H_2 + NH_3 + MBr$$

The apparatus consisted of a decomposition vessel, liquid air traps, leveling bulb with mercury and a gas burette. The assembly is shown in Figure 7. The decomposition vessel was calibrated to 0.02 ml. Two gas burettes were also calibrated. A 25 ml. burette for measuring large amounts of gas was calibrated to 0.01 ml. and a 1 ml. burette to 0.001 ml.

The volume of the solution which was transferred into the calibrated decomposition vessel was noted. NH_4Br was then tipped, <u>via</u> a side-arm, into the blue solution, Figure 7. The blue solution decomposed immediately. The evolved H_2 gas was then pumped through two liquid air traps using the mercury bulb and collected in the gas burette where the volume of the gas was measured at a known pressure. The liquid in the decomposition vessel was then frozen slowly with pumping to insure that all of the hydrogen was removed from the decomposed solution. This freezing and pumping process was repeated until the gas reading became constant. Usually after the first freezing, no more hydrogen could be pumped off by repeated freezing, melting and pumping.

In some potassium conductivity runs, including a saturated solution run, the blue solution was decomposed with H_2O instead of NH₄Br. In this case, distilled water was introduced into the bent side-arm shown in Figure 7. The water was degassed by evacuation



Figure 7. Gas analysis assembly.

with a mechanical roughing pump and frozen slowly during this evacuation. Next, the water was melted and the same degassing procedure was performed on the high vacuum line. Finally, the bent side-arm containing the degassed water was attached to the decomposition vessel <u>via</u> a standard taper. To decompose the blue solution, the side-arm was first rotated into an upright position. The stopcock was then opened allowing the water to drain into the blue solution.

H. Procedure for Kinetic Studies

1. Water ampoule make-up. Doubly-distilled conductance water was placed into vessel A, Figure 8. The water was then degassed by pumping on it with a mechanical roughing pump via stopcock no. 1 and a dry-ice trap. During the evacuation, the water was slowly frozen with a dry-ice bath. Next, the ice in vessel A was cooled to liquid air temperature. The remainder of the train, with stopcock no. 1 closed and stopcocks 2 and 3 open, was evacuated on the high-vacuum line and flamed until the pressure stabilized at less than 10^{-5} torr. The water was then vacuum-distilled into vessel B which was cooled by a dry-ice bath. Next with stopcocks 2 and 3 closed, vessel C containing the fragile ampoules was again evacuated and flamed until the pressure was stabilized at less the 10^{-5} torr. Finally the water was vacuumdistilled into vessel C until the tips of the ampoule stems were covered with water. The water was then forced by argon pressure into the fragile glass bulbs. Next, the seal-off was made and vessel C filled to above atmospheric pressure with argon gas which had been previously purified and stored in 2-liter flasks on the vacuum line. Finally, vessel C was removed from the vacuum line and the capillary stems were sealed off from the bulbs. During the seal-off operation, vessel C was swept with argon to protect the water in the ampoules from contamination. The weight of the water in the ampoules was determined





from the initial weight of the bulb with its attached capillary stem and the final weight of the bulb and water plus the sealed-off capillary stem.

<u>2. Water-ethylenediamine solution make-up</u>. To prepare solutions of low water concentration, a fragile water ampoule prepared as described above was placed into the flask shown in Figure 9. The flask, containing the ampoule and a magnet sealed in glass, was first weighed and then connected to the solvent reservoir flask and the high vacuum, Figure 9. The solution make-up flask was then evacuated and flamed until the pressure stabilized at less than 10^{-5} torr. Next, stopcock no. 2, Figure 9, was closed and the water ampoule broken with the magnet. Finally, the ethylenediamine was introduced into the make-up vessel from the solvent reservoir flask. Then the water-ethylenediamine solution was covered with purified N₂ via stopcock no. 2. After disconnecting, the make-up vessel was again weighed in order to determine the amount of ethylenediamine which had been introduced.

For large water concentrations, the make-up vessel in Figure 9 was first weighed and then connected to the water degassing train in place of vessel C shown in Figure 8. Finally, the water was vacuumdistilled into the make-up vessel after treating the water as described previously. The make-up vessel was disconnected from the degassing train and weighed to determine the amount of water which had been introduced. The vessel was then connected to the solvent reservoir flask and high-vacuum line. After evacuation of the delivery tubes, ethylenediamine was introduced, filling the vessel to the volume mark which had been previously calibrated to give the volume within ± 0.5 ml. Finally, the solution was covered with purified N₂.



Figure 9. Water-ethylenediamine solution make-up vessels.

3. Metal solution make-up. A 500 ml. flask with a side-arm for metal distillation was connected to the solvent-reservoir flask and the decomposition vessel. A magnet sealed in glass was placed into the solution make-up vessel and the side-arm on the decomposition vessel contained NH₄Br. The decomposition vessel was connected to the high-vacuum line, Figure 10. The 2-way stopcock on the solventreservoir flask was also connected to the high-vacuum line via a liquid air trap. This facilitated the evacuation of the entire assembly, Figure 10. A cesium metal capillary containing the desired amount of metal was first cooled to dry-ice temperatures, broken and introduced into the side-arm of the solution make-up flask. The system was then immediately evacuated and flamed until the pressure stabilized at less than 10^{-5} torr. Next, the cesium metal was warmed gently until it melted and ran down through the constriction into chamber B. Chamber A was then removed by sealing-off under vacuum. By warming the top half of the 500 ml make-up flask, the cesium was distilled into the bottom half of the flask. After the make-up flask had cooled to room temperature, stopcocks no. 3, 4 and 5 were closed and the ethylenediamine was introduced. The blue solution was then pumped on by the high-vacuum system via stopcocks no. 1 and 2, Figure 10. During the pumping, the solution was stirred constantly with the magnet sealed in glass for about 10 minutes after all of the metal had dissolved.

Nitrogen gas, which had been previously purified and stored in 2 liter flasks on the vacuum line, was introduced <u>via</u> stopcocks no. 1 and 2. The gas pressure forced the solution up the delivery tube to stopcock no. 3. The first fraction of the solution was then transferred into the waste vessel or the spectral cell apparatus which, of course, had been previously connected, evacuated and flamed following the usual procedure. Then sufficient solution was transferred into the decomposition vessel to permit a volume reading to be made.





Finally, all stopcocks were closed and the decomposition vessel was removed and set aside for gas analysis. The metal make-up vessel was then removed and the delivery tube washed thoroughly with doublydistilled water. The procedure then continued as described below.

4. Flow apparatus: reactant delivery assembly and procedure.

After the syringes on the flow apparatus had been heavily lubricated with Dow Corning high-vacuum silicone grease, the syringes and mixing chamber were cleaned by rinsing with doubly-distilled water. The dilution mixing vessel (containing a magnet sealed in glass), the calibrated burette, waste vessel, and connecting tubes were then assembled as shown in Figure 11. The syringes and mixing chamber were then dried by evacuation with a mechanical roughing pump <u>via</u> stopcock no. 4. The water solution make-up flasks were connected as shown in Figure 11 (using flask no. 2 as an example). Next, the system was connected to the high vacuum line and tested for vacuum tightness. The syringes could be evacuated to 1×10^{-4} torr, but unfortunately they were not capable of holding this vacuum for extended periods of time.

Finally the preparation of the cesium solution commenced as described above. After the cesium solution was prepared, the solution make-up flask was connected immediately to the flow apparatus as shown in Figure 11 (flask no. 7). All necessary delivery tubes were then evacuated with the high-vacuum system. Then the vacuum of the complete assembly was tested. During the evacuation of the delivery tubes, time was available (15 minutes) to obtain an absorption spectrum of the cesium solution used in the flow run. This was done for flow run no. 3.

Finally, the flow experiment commenced. The reactant was run into the dilution mixing vessel; stopcock no. 6 was opened and the delivery tube was filled with reactant to stopcock no. 1, Figure 11.





Next, stopcock no. 7 was opened and the delivery tube was filled with blue solution to stopcock no. 2. Then stopcocks no. 1 and 2 were opened to the delivery tubes and the push syringes A and B were filled with the two reactants. Stopcocks no. 1 and 2 were then opened to the mixing chamber and the two reactants were degassed by pumping on them with the high-vacuum line <u>via</u> stopcock no. 3. Next, stopcock no. 3 was closed and the reactants were forced through the mixing chamber, completely filling stop-syringe C. Immediately after the picture of the trace was taken, stopcock no. 3 was opened. The reacted solution drained into the waste vessel and syringe C was forced to its original position by atmospheric pressure. The procedure was then repeated using another reactant. In most cases, two pictures were obtained for each water concentration.

Dilutions were accurately made by the dilution system shown in Figure 11. The 25 ml burette was calibrated to ± 0.02 ml. Measured amounts of a reactant and pure solvent were introduced into the dilution mixing vessel and mixed with a magnet sealed in glass.

After the flow experiment was completed, the decomposition vessel was connected to the high-vacuum line and gas analysis assembly as shown in Figure 7. The system, except the part of the decomposition vessel containing the blue solution, was evacuated until the pressure stabilized at less than 10^{-5} torr. The concentration of the metal solution was then determined by following the procedure described in the section entitled "Concentration Determination by Gas Analysis."

V. RESULTS

A. Solubility

In early attempts to study solubility using sodium and potassium, the metal was cut from the center of a large piece and introduced into the make-up flask <u>via</u> a side-arm. After evacuation, the metal was melted, allowing it to flow through the constrictions in the sidearm into the solution make-up flask. Using this procedure, the metal looked clean and lustrous since the oxide coating originally on the metal was left behind in the constrictions. In some cases, however, the blue solution did not form immediately when the solvent came in contact with the metal. The results obtained using this method were not reproducible from one determination to another.

Finally the procedure described in the experimental section was adopted. It was noted that when metal which had been previously double-distilled was distilled into the solution make-up flask, dark blue solutions formed immediately when the purified ethylenediamine came in contact with the metal mirror. Excess sodium, potassium and rubidium had no noticeable effect on the stability of the blue solution while excess cesium metal catalyzed the decomposition reaction to a noticeable extent.

The gas analysis method used for the determination of the metal concentration is a direct measure of the metal present in the zero oxidation state. This method has the advantage that metal present as decomposition products can be distinguished from the metal present in the zero oxidation state.

The solubilities of all of the alkali metals in ethylenediamine are given in Table IV.

Metal	Run Number	Solubility moles/liter	Average Solubility moles/liter
Lithium	1	0.283	
	2	0.264	$0.287 \pm .015^{*}$
	3	0.314	
Sodium	1	2.37 x 10^{-3}	
	2	2.35 x 10^{-3}	$2.39 \pm .04 \times 10^{-3}$
	3	2.45×10^{-3}	
Potassium	1	1.02×10^{-2}	
	2	1.03×10^{-2}	$1.04 \pm .02 \times 10^{-2}$
	3	1.05×10^{-2}	
	4	1.07×10^{-2}	
Rubidium	1	1.29×10^{-2}	$1.31 \pm .02 \times 10^{-2}$
	2	1.33×10^{-2}	
Cesium	1	5.43 x 10^{-2}	5.4 x 10^{-2}

Table IV.	Solubilities of the Alkali Metals in Ethylenediamine at
	Room Temperature

*Average deviation.

B. Absorption Spectra

The absorption data in many cases are plotted as wavelength versus A/A_{max} , where A is the absorbance at any wavelength and A_{max}, is the absorbance at the peak. Since this type of graph has a maximum value of unity, it is useful for examining the effect of concentration on line-shape and the reproducibility of independent runs. The data plotted in this manner were corrected, where necessary, for decomposition. This correction was possible because in all cases the decomposition was a smooth function of time. The decay of the absorbance as function of time was followed by allowing the Beckman DK-2 Spectrophotometer to re-cycle as the solutions decomposed in the spectral cell. Semi-log plots of the absorbance at a given wavelength vs. time resulted in a smooth curve. This allowed correction of the absorbances at different wavelengths to a common time, thus giving the complete spectrum independent of time. These corrections were normally small and did not alter the shape or peak position significantly. The absolute zero absorbance line, taken to be the trace of the decomposed solution, was also subtracted from the absorbance reading. The absorbance of the decomposed solutions was essentially zero at longer wavelengths. At shorter wavelengths, 400-550 mµ, the absorbance of the decomposed solution was appreciable due to the decomposition products. Therefore, the relative amount of decomposition product for all of the metals could be estimated from its absorbance, which began at about 400-550 m_{μ} and increased continually into the ultraviolet region. The range of the spectrum examined and the various absorption maxima are recorded in Table V. All results are qualitative with respect to various peak heights since analyses were not made.

Metal	Absorption Maxima (mµ)
Lithium	660
	1280
Sodium	660
Potassium	660
	845
	1280
Rubidium	660 shoulder
	890
	1280
Cesium	1030
	1280

Table V. Location of Absorption Maxima in Ethylenediamine*

*The range from 400 to 1800 m μ was scanned for all metals.

Lithium. Two absorption maxima were found for lithium in ethylenediamine; one at 660 m μ and the other at 1280 m μ . The 1280 mu absorption band tails strongly into the visible. In some cases, the 1280 m_{μ} band was initially much greater than the 660 m_{μ} band but in all cases the infrared band decayed more rapidly leaving a large 660 m μ absorption. The rate of decomposition of both bands varied from one determination to another. Since the 1280 $m\mu$ band decayed leaving the 660 m μ peak, it was possible to determine the line-shape of the 660 m $_{\mu}$ absorption band. Figure 12 shows $A/A_{max.}$ vs. wavelength for the 660 m μ peak for three independent runs. The absorption bands could then be separated. To make this separation, the traces were first made independent of time by following the scheme previously described. The contribution of the 660 m μ absorption band was then substracted from the total absorbance to give the 1280 m_{μ} band. Figure 13 shows the absorption spectra with the two peaks and the separated 1280 m μ absorption band. A/A_{max}, vs. wavelength is given in Figure 14 for 1280 m μ peak for lithium in ethylenediamine.

Sodium. Three separate preparations of sodium gave spectra showing only a single peak at 660 m μ which are shown in Figure 15. Sodium exhibits a very small infrared absorption, but this was almost negligible in comparison with the 660 m μ band. For example in one case where the absorbance at 660 m μ was larger than two, the absorbance in the infrared was less than 0.03.

<u>Potassium</u>. Potassium solutions in a 0.1 mm. cell show a broad maximum peaking at 845 m μ with shoulders in the vicinity of 650 m μ and 1300 m μ . In a 1 mm. cell (less concentrated) the main absorption was at 660 m μ with a shoulder at 840 m μ . Typical traces of these spectra are given in Figure 16. Repeated runs using a 0.1 mm. cell always resulted in the broad 845 m μ absorption band.







Figure 13. Absorption spectra of lithium in ethylenediamine.









Figure 16. Absorption spectra of potassium in ethylenediamine.

During decomposition in the spectral cell, the 845 peak in all cases disappeared more rapidly than did the 1280 and 660 m μ absorption bands. Also, in the 0.1 mm. cell, the amount of 660 m μ absorption seemed to be a function of the concentration of decomposition product and varied from one run to another.

Using the 1 mm. cell, for which the maximum occurred at 660 m μ , the amount of 840 m μ shoulder varied from one separate determination to another. In some runs, the 840 m μ shoulder was rather pronounced, while in others it was negligible. In all cases initial 840 m μ shoulders, regardless of initial intensity, rapidly disappeared while the well-defined peaks at 660 m μ and 1280 m μ decayed more slowly.

The peak at 1280 m μ was always present regardless of the cell path used. The intensity of the 1280 peak varied from one run to another but in all cases the 1280 m μ absorption was smaller than either the 840 or 660 m μ absorption.

<u>Rubidium</u>. Rubidium solutions showed a strong absorption peak at 890 m μ with considerable absorption in the infrared. Under some conditions, a shoulder was also present in the vicinity of 650 to 700 m μ . Typical traces showing these two cases are presented in Figure 17. Freshly prepared solutions of rubidium in ethylenediamine had no apparent shoulder in the visible. When new samples were poured into the cell from the vicinity of the excess metal, the shoulder tended to appear. In these cases, considerable decomposition product had built-up so that an excess of Rb[†] ions was present. The relative amount of decomposition product could be estimated from its absorbance as previously mentioned.





<u>Cesium</u>. Cesium solutions of fairly high concentration, run in the 0.1 mm. cell, showed a maximum at 1030 mµ as shown in Figure 18. This absorption band decayed extremely fast (\sim 10 minutes) leaving an absorption peak at 12**8**0 mµ.

When more dilute solutions were studied using a 1 mm. cell, only an infrared peak at 1280 m μ was present and no other peaks or shoulders were evident. The absorption spectrum of the 1280 m μ band is given in Figure 19. It should be noted in reference to Figure 19, that the absorption band resulting after decomposition of the 1030 m μ band in the 0.1 mm. cell was identical to the 1280 m μ band observed in runs using a 1 mm. cell.

C. Mixture Spectra

The spectral data showed that rubidium had only a 660 mµ shoulder and that this shoulder became more pronounced as the Rb^+ ion concentration increased due to decomposition. On the other hand cesium had only the 1280 mµ peak at low concentrations and no 660 peak or shoulder at high concentrations. These facts suggested that an alkali ion is involved in the 660 mµ absorbing specie and that the light alkali metals are preferred. A simple test for this idea involves addition of either Li or Na salts to cesium or rubidium solutions to see if the 660 mµ peak forms. Generally, the addition of salts like LiCl and LiI markedly increased the rate of decomposition. This is attributed to traces of impurities in the salts. Another source of Na⁺ or Li⁺ ions is the decomposed solution of the metal. Solutions of rubidium and cesium were mixed with solutions containing Na⁺ or Li⁺ ions either from their halide salts or from decomposed solutions of the metal.








As was previously mentioned, lithium solutions have peaks at 600 and 1280 m μ while rubidium solutions have the 1280 m μ peak, only a shoulder at 660 m μ and another peak at 890 m μ . When rubidium and lithium metal solutions were mixed, all three peaks were obtained, as expected, Figure 20. When rubidium metal solution was added to the decomposition product of lithium, the three were again obtained, Figure 21. The spectrum for a solution containing the mixture of lithium metal solution plus the decomposed solution of rubidium is given in Figure 22. Again the three peaks were obtained. A solution of lithium iodide mixed with a solution of rubidium in ethylenediamine had again the three peaks. The spectrum obtained is recorded in Figure 23.

A solution of rubidium metal mixed with a decomposed sodium solution is recorded in Figure 24. In this case, the 660 mµ absorption was the main absorbing band indicating that the sodium 660 mµ absorbing specie is favored at the expense of the others. This is consistent with the spectra of sodium metal solutions.

Cesium metal solutions when mixed with either a lithium chloride solution or a decomposed lithium solution gave spectra having the 660 $m\mu$ peak. This is shown in Figure 25.

D. Kinetics of the Decomposition During Absorbance Meäsurements

The rate of decomposition of the metal-ethylenediamine solutions was studied by following the absorbance as a function of time. This was accomplished by allowing the Beckman DK-2 spectrophotometer to re-cycle as the solutions decomposed in the spectral cell. It was important that the solutions under study decompose uniformly in the cell proper. This could be determined spectrophotometrically or visually. In some cases it was observed that the absorbance in different















Absorbance



solution.

Absorbance



Absorbance

regions of the optical cell decayed at different specific rates and that there were streaks in the solution between the cell windows. This behavior was considered due to traces of impurities on the cell walls that catalyzed the decomposition reaction. When this occurred, the cell was rinsed with blue solution. The rinsing was an effective method of further cleaning the cell. This procedure resulted in uniform decomposition which was then recorded. The decomposition reaction, according to

$$M + H_2NCH_2CH_2NH_2 \longrightarrow M^+ + H_2NCH_2CH_2NH^- + \frac{1}{2}H_2$$

is believed to be heterogeneous and surface catalyzed, since the decomposition rate decreased markedly upon rinsing the cell and decomposition occurred more rapidly in the cell with its large surfaceto-volume ratio than in the waste vessel or solution make-up vessel.

The spectral decomposition of three independently prepared sodium solutions is shown in Figure 26. For a given run, the specific rates of decomposition at different wavelengths are the same, indicating that only one specie is involved. The decay in two independent studies was strictly first-order as shown in Figure 26. In another run, the decay deviated slightly from first-order kinetics and this was attributed to the fact that in this case there was considerable salt present from previous decomposition.

The spectral decomposition of potassium showed that the absorption at different wavelengths did not decay at the same specific rate. This is shown in Figure 27. Since the absorption bands strongly overlap one another and decay at different specific rates, it is difficult to make any conclusions about the kinetics of the disappearance of any single peak. Studies in the 1 mm. cell, which showed only two peaks, fitted a first-order decay law best, Figure 27.



Figure 26. Spectral decomposition of sodium-ethylenediamine solutions (log(abs.) vs. time)

Absorbance



Figure 27. Spectral decomposition of potassium-ethylenediamine solutions (semi-log plot of absorbance vs. time).

The optical absorption for rubidium solutions decayed essentially first-order with time. Again the absorbance at three different wavelengths decayed at different specific rates indicating the presence of more than one species. Figure 28.

The decay of the 1280 m μ peak for cesium fitted first-order kinetics best, Figure 29. The absorption at different wavelengths decayed at the same specific rate indicating that the 1280 m μ absorption band is due to a single specie.

Lithium solutions generally decomposed more rapidly than solutions of the other alkali metals. Also when lithium solutions decomposed, precipitation of the decomposition product usually occurred which further aided the decomposition. The absorption at 660 m μ and at 1280 mµ decayed at quite different rates proving the presence of two species. In one case, the infrared peak decomposed almost completely while the visible 660 m μ peak remained essentially constant. After the infrared absorption was nearly gone, then the 660 m_{μ} peak decomposed essentially first-order, Figure 30. This phenomenon indicates that the 1280 mµ absorbing specie may act as a buffering agent for the 660 m μ specie. In another spectral study, blue solution was tipped into the cell from the solution make-up vessel in which a considerable amount of precipitate had been present. The spectrum initially showed only the 660 $m\mu$ visible peak but as the 660 m μ peak decomposed the infrared 1280 m μ peak built-up and finally both peaks decayed, Figure 31. This shows that the 660 mµ peak decomposes giving the 1280 mµ peak and the conversion of the 660 m_{μ} peak into the infrared peak is relatively slow $(t_1 \sim 1-3 min.).$

оригранса

(



Figure 28. Spectral decomposition of rubidium-ethylenediamine

Absorbance (

(

0.

0.02



Figure 29. Spectral decomposition of cesium-ethylenediamine solutions (Semi-log plot of absorbance \underline{vs} . time).

Absorbance



Figure 30. Spectral decomposition of a lithium-ethylenediamine solution (semi-log plot of absorbance <u>vs</u>. time).





E. Conductance

Since the spectra were different for the different alkali metalethylenediamine solutions, conductivity studies were undertaken in order to make a correlation between conductivity and spectra. The conductances were determined at room temperature without precise temperature control since the main source of error was considered to result from decomposition. Symons, et al. (13), and Windwer and Sundheim (54) reported that platinum wire acts catalytically on the alkali metal-ethylenediamine solutions, accelerating the decomposition. In the present work, solutions also decomposed more rapidly with platinum present than without. However, the method employed in this work allowed correction for the decomposition. Usually this correction amounted to less than 2% of the initial conductivity reading and normally the conductivity decreased between 5 and 20% in the first hour.

The values of \bigwedge , \mathcal{K} , \mathbb{C} and $\mathbb{C}^{\frac{1}{2}}$ are given in Table VI. The equivalent conductances, \bigwedge , are expressed in Kohlrausch units. The specific conductances, \mathcal{K} , are expressed in ohms⁻¹ cm⁻¹, and the concentrations, \mathbb{C} , in moles per liter. The values of \bigwedge for sodium, potassium, rubidium and cesium are plotted <u>vs</u>. $\mathbb{C}^{\frac{1}{2}}$ in Figure 32. A log-log plot of the specific conductance <u>vs</u>. concentration for these same metals is given in Figure 33. The reproducibility of these conductance measurements is satisfactory as shown by both Figures 32 and 22. It is to be emphasized that each point represents an independent solution make-up.

Figure 33 shows that the specific conductivity for the concentrations investigated can be expressed by the following function:

$$\log \mathcal{K} = a \log c + b \tag{1}$$



Figure 32. Equivalent conductance <u>vs.</u> $C^{\frac{1}{2}}$ for sodium, potassium, rubidium and cesium in ethylenediamine.



Concentration (moles/liter) x 10^4

Figure 33. Log-log plot of specific conductance vs. concentration for sodium, potassium, rubidium and cesium in ethylenediamine.

Spreetite Provide Active Structure S Number News

Run		Concentration	Specific	Equivalent	-1	
Number	Metal	$(moles/liter)xl0^3$	Conductance x 10°	Conductance	$C^{2} \times 10^{2}$	
Cs-1	Cesium	54.3	1420	26.2	23.4	
Cs-2		48.9	1350	27.7	22.1	
Cs-5		20.8	742	35.6	14.5	
Cs-6		7.65	342	44.8	8.75	
Cs-3		3.55	193	54.4	5.96	
Cs-7		1.68	113	67.3	4,11	
Cs-4		.960	78.6	81.8	3.10	
Na-2	Sodium	2.45	62.5	25.5	4.96	
Na-l		2.35	60.0	25.5	4.86	
Na-4		1.04	27.0	25.9	3.23	
Na-3		. 242	6.36	26.3	1.56	
K-3	Potassium	10.7	301	28.1	10.4	
K-2		10.5	297	28.2	10.3	
K-1		10.3	299	29.0	10.2	
K- 10		6.02	201	33.4	7.78	
K-6		3.68	139	37.8	6.08	
K-8		3.66	135	36.9	6.06	
K-4		2.43	103	42.5	4.84	
К-9		2.37	99.0	42.7	4.49	
K-5		2.10	92.6	44.1	4.59	
K-7		2.04	90.8	44.5	4.54	
K- 11		0.416	29.7	71.3	2.03	
K-12		0.135	12.1	89.7	1.16	
Rb-1	Rubidium	13.3	321	24.2	11.6	
Rb-7		6.94	199	28.7	8.34	
Rb-2		2.85	102	35.8	5.35	
Rb-6		2.78	98.6	35.5	5.28	
Rb-3		1.78	70.0	39.5	4.22	
Rb-5		0.696	35.0	50.3	2.63	
Rb-4		0.525	30.6	58.3	2.29	
Li-1	$\mathbf{Lithium}^{*}$	3.14	15300	48		
Li-2		2.87 ^{**}	14000	49		
* Lithium	results are qui	alitative only. ** T	he average solubility	y value.		

Ш

Spectral data showed that solutions decayed essentially first-order so that

$$\log C = -kt + d \tag{2}$$

If the decomposition in the conductance cell is first-order, we have:

$$\log \mathcal{K} = -\frac{k}{a}t + (d-b)$$
(3)

In the above three equations, a, b, d are constants, \mathcal{K} is the specific conductivity, t is time and C is concentration.

A semi-log plot of the specific conductance <u>vs</u>. time is shown in Figure 34 for saturated solutions of sodium, potassium and rubidium. This plot again shows the first-order decay of the decomposition. The deviations from straight lines can probably be attributed to the effects of the decomposition products, temperature fluctuations and the catalytic nature of the decomposition reaction itself. Figure 35 shows two typical semi-log plots of the specific conductance <u>vs</u>. time that illustrate the extrapolation method used to obtain the specific conductance values.

Lithium conductivity. Lithium solutions were very unstable in the conductance cell compared to the other metals. The conductivity of saturated lithium solutions, however, was qualitatively examined. A plot of the logarithm of the specific conductance <u>vs</u>. time is shown in Figure 36. In one case, the initial points obtained when four different samples were tipped into the cell fall on a straight line which allowed extrapolation to zero time in order to obtain the estimated specific conductance value. This plot also shows the difference in the decomposition rate of samples in contact with the platinum electrodes as compared with the decomposition rate of solution in the make-up vessel of the conductivity apparatus. When lithium solutions decompose,



Figure 34. Semi-log plot of specific conductance vs. time for sodium, potassium, rubidium and cesium in ethylenediamine.



Figure 35. Typical log of specific conductance vs. time plots used for decomposition corrections in conductance determinations.





(_{\$01} × 7) 807

precipitation occurs and the lithium spectral data show that the precipitate results in rapid disappearance of the infrared absorption. The behavior of the decomposition curves in Figure 36 is understandable if the solutions decompose normally until precipitation occurs. If precipitate is formed near the platinum electrodes, it could also speed the decomposition and hence the precipitation. The infrared specie is thus rapidly destroyed by the precipitate. Its rapid removal causes a sudden drop in the conductivity. This indicates that the infrared specie is the main contributor to the conductivity of this solution.

<u>Conductivity of decomposed solutions</u>. The resistances of the bleached solutions approached constant values. This conductivity is considered to be due to the metal ions and ethylenediamide ions which result from the decomposition reaction. The conductivity data for the decomposed solutions are given in Table VII. The equivalent conductance vs. $C^{\frac{1}{2}}$ for the decomposed solutions of sodium, potassium, rubidium and cesium in ethylenediamine is given in Figure 37. These data are of interest because they emphasize the low equivalent conductance values of the decomposition products. It is evident from these data that a small accumulation of decomposition products in any given metal-ethylenediamine solution would lead to no significant error in the conductivity attributed to the metal in the zero oxidation state.

F. Kinetics of the Reaction of Solvated Electrons With Water

Dilute cesium-ethylenediamine solutions which are thought to contain only solvated electrons and solvated metal ions as well as ion-pairs, etc. were reacted with water-ethylenediamine solutions. The over-all reaction is:



Metal	Concentration moles/liter $x 10^3$	Specific Conductivity x 10 ⁶	Equivalent Conductivity	$C^{\frac{1}{2}}x10^{2}$
Cesium	54.3	96.0	1.76	23.4
	48.9	87.4	1.78	22.1
	20.8	72.5	3.31	14.5
	1.68	11.4	6.80	4.11
Sodium	2.45	6.40	2.61	4.96
	2.35	5.88	2.50	4.86
	1.04	3.26	3.13	3.23
	0.242	1.06	4.38	1.56
Potassium	10.7	31.7	2.96	10.4
	10.5	27.3	2.60	10.3
	10.3	30.3	2.94	10.2
	2.82	12.7	4.67	5.30
	2,42	12.3	5.06	4.84
	2.10	10,1	4.82	4.59
	0.412	3,36	8.16	2.03
	0.138	2.12	15.4	1.18
Rubidium	13.3	38.7	2.91	11.6
	12.9	37.4	2.90	11.4
	6.92	22.8	3.29	8.34
	2.78	12.7	4.57	5.28
	0.497	4.89	9.85	2.24

Table VII. Conductance--Concentration Data for Decomposed Solutions of Sodium, Potassium, Rubidium and Cesium in Ethylenediamine

$$(e^{-})_{en:} + H_2O \longrightarrow \frac{1}{2}H_2 + OH^{-}$$

The progress of the reaction was followed by recording the rate of decrease of the absorbance of the solvated electrons as a function of time.

The pictures obtained from the flow apparatus give the intensity of light striking the photo-tube as a function of time. Some typical pictures are shown in Figures 38 and 39. The original intensity of incident light, I_0 , is directly proportional to the difference in distance on a trace between zero transmittance and maximum transmittance. The latter occurs when the solvated electrons are completely reacted. The intensity, I, at a given time is directly proportional to the distance between the zero transmittance line and the position of the trace at that time. In this way, the ratio I_0/I can be determined as a function of time from the picture. Since $\log I_0/I =$ absorbance, which is directly proportional to concentration, plots of apparent concentration <u>vs</u>. time can readily be constructed from these pictures.

The photomultiplier used in this work had its maximum sensitivity at 950 m μ and most of the pictures were made at this wavelength. Some traces for run no. 3 were taken at 740-780 m μ . The wavelength of observation for the one run using a sodium-ethylenediamine solution was 650 m μ .

When the log. of the absorbance is plotted against time, a straight line is obtained. Examples of these plots are given in Figures 40-44 for some of the pictures obtained in runs 1 and 3. Note that in all cases water was present in such large excess that its concentration can be considered to remain constant. The results shown in Figures 40-43 allow one to write the pseudo-first-order rate expression:

$$\frac{d[e^{-}]}{dt} = - \mathcal{K}[e^{-}]$$














$\Box \quad \text{Picture no. 11} - t_1 = 5.05 \text{ m sec.}$ O Picture no. 12 - $t_1 = 5.35 \text{ m sec.}$ 50 Ω $\lambda = 950 \text{ mu}$ -40 Time (millisec.) Point of flow stop 30 20 -0.5 -1.0 0.0

Figure 42. Log (Abs.) vs. time; pictures 11 and 12, run no. 3 (Cesium conc. = 5×10^{-4} moles/liter, water conc. = 5.1 moles/liter).

89

(.adA) gol





where κ is the pseudo-first-order rate constant, and depends on the water concentration. The value of κ for each water concentration was found from the half-life period of the reaction since this is given for first-order-reactions by:

$$t_{\frac{1}{2}} = \frac{\ln 2}{\mathcal{K}}$$

The half-life periods can readily be obtained from the graphs. This method for the evaluation of \mathcal{K} has the advantage that the concentration of the solvated electrons need not be known. The pseudo-first-order rate constant is related to the water concentration by the expression:

$$\mathcal{K} = k [H_2O]^n$$
or
$$\log \mathcal{K} = n \log [H_2O] + \log k$$

where n is the order of the over-all rate expression in water and is the rate constant. A plot of log \mathcal{K} vs. log [H₂O] gives a straight line with a slope of essentially unity. The order in water is therefore unity and the second-order rate constant is 24.7 \pm 1.5 liters mole⁻¹ sec⁻¹. These results are summarized in Table VIII.

Other observations obtained in these kinetic studies can best be presented by discussing the runs individually.

<u>Kinetic run no. 3</u>. Examination of the pictures given in Figure 39 shows a difference between observations made at 950 m μ and at 740-780 m μ . For example, pictures 2 and 5 show different results even though the cesium and water concentrations are the same for both pictures. Only the wavelength of observation is different. The data obtained from picture 5 will be used as an example of the evaluation of the traces observed at 740-780 m μ . When log (Abs.) vs. time is plotted for

Picture Number	Run Number	Cesium Conc. Moles/Liter	Water Conc. Moles/Liter	t ^t	አ	k (1/mole sec)
ŝ	l	∼1.5 x 10 ⁻³	5.42×10^{-2}	0.51 sec	1.36	26.0
ഹ	l	∼1.5 x 10 ⁻³	5.42×10^{-2}	0.59 sec	1.20	22.1
6	l	∼1.5 x 10 ⁻³	5.42 x 10^{-2}	0.67 sec	1.03	19.1
80	l	∿l.5 x 10 ⁻³	$6.2 \times 10^{-2^*}$	0.45 sec	l.54	24.8
2	ς	5 x 10 ⁻⁴	8.75×10^{-3}	3.05 sec	.227	26.0
4	ς	5 x 10 ⁻⁴	8.75×10^{-3}	3.1 sec	.224	25.6
ഹ	ŝ	5 x 10 ⁻⁴	8.75×10^{-3}	3.1 sec	.224	25.6
7	ŝ	5 x 10 ⁻⁴	5.25×10^{-2}	0.548 sec	1.27	24.1
6	ŝ	5 x 10-4	5.25×10^{-2}	0.543 sec	1.28	24.3
10	ŝ	5 x 10 ⁻⁴	5.25×10^{-2}	0.475 sec	1.46	27.8
11	ŝ	5 x 10 ⁻⁴	5.1	5.05 m sec	137	26.1
12	γ	5 x 10 ⁻⁴	5.1	5.35 m sec	130	25.4
		A	verage = 24.	7 土 1.5		-

Table VIII. Kinetic Experiments -- Summary of Results from Runs 1 and 3.

.

* KOH added

92

Ŧ,

picture no. 5 the initial slope of the curve obtained gives a half-life the same as that obtained from picture no. 2 (line "A" in Figure 44). This immediately suggests that the total absorbance in this case is the sum of the absorbances of two separate species. Since the decay rate of solvated electrons is known from a number of observations at longer wavelengths to be given by line "A," Figure 44, curve "B" can be obtained by subtracting "A" from the total absorbance. Curve "B" must then represent the build-up of an intermediate specie. The build-up and decay of this intermediate is also shown in Figure 45 in which absorbance <u>vs</u>. time is plotted. The results from picture no. 4 show the same behavior and are shown in Figure 46. Figure 47 shows the results obtained from picture no. 6 for which the water concentration was larger. These results indicate that the build-up of the intermediate depends on the water concentration.

From these few observations, no definite conclusions should be drawn concerning the kinetics of the intermediate. These preliminary results, however, indicate the build-up of the intermediate to be zero-order and its decay to be first-order. It should also be noted that a spectral analysis of the cesium solution used in run no. 3 showed only the presence of the 1280 m μ peak.

<u>Kinetic run no. 1</u>. The results obtained in run no. 1 agree with the results of run no. 3. The only essential difference between runs 1 and 3 is the difference in the metal concentration used in the experiments. It should be noted that the presence of KOH in picture no. 8 of run no. 1 appeared to have no effect on the rate of reaction.

<u>Kinetic run no. 2.</u> The results of this run again fitted a pseudofirst-order rate expression as is evident from the plot of log (Abs.) <u>vs.</u> time obtained from the various picture, Figure 48. In this case, however, an analysis of the rate expression seems to give a one-halforder dependence on water as summarized in Table IX. This result









ADSOTDADCE













able IX.	Kinetic	ExperimentsS	ummary of Re:	sults from I	Run No. 2. [Cs]	= 1.7 x 10 ⁻³	moles/liter.
icture umber	dr ^t	χ = k [H ₂ 0] ⁿ	[H2O]	log X	log[H2O]	[Н2О] ²	$k = \frac{\chi}{[H_2O]^{\frac{1}{2}}}$
4	1.7	.408	2.44×10^{-2}	382	-1.612	.157	2.6
Ŋ	2.1	. 330	2.44×10^{-2}	481	-1.612	.157	2.1
6	2.7	. 256	2.44×10^{-2}	592	-1.612	.157	1.6
7	0.72	.963	0.188	016	726	.435	2.2
8	0.76	.912	0.188	039	726	.435	2.1
6	1.3	.533	5.93×10^{-2}	272	-1.226	. 244	2.2
11	1.2	.577	5.93×10^{-2}	239	-1.226	.244	2.4
12	1.23	. 564	5.93 x 10 ⁻²	249	-1.226	.244	2.3

/lit
oles/
E E
-0
хJ
٢.
-
, S
Ű
•
Z
Rur
В
[ro]
ts 1
sul
Re
Ъ.
ry
ma
Ĩ
งี-
ts-
len
rin
pei
ă
tic
net
Ki
×.
еГ
abl

is not consistent with the results obtained in runs 1 and 3. It should be noted that the solution used in run no. 2 had an inherent stability about 4 times that of the solution used in run no. 1 and that the concentration of cesium was more than three times that used in run no. 3.

<u>Miscellaneous kinetic observations</u>. One kinetic observation was made on the reaction of a sodium-ethylenediamine solution with water in ethylenediamine. At 950 mµ, where the absorbance of sodium solutions is very small, no change was evident. The result of the trace observed at 650 mµ is shown in Figure 49. It should be pointed out that this slow reaction of solutions containing the 660 mµ specie was also observed visually in two independent preliminary observations.

Preliminary kinetic studies of the reaction of solvated electrons with NH_4^+ ions were attempted. In this case, dilute cesium ethylenediamine solutions were reacted with NH_4Br in ethylenediamine. The protons in solutions of NH_4Br in ethylenediamine are mainly transferred to ethylenediamine since a positive pressure build-up attributed to ammonia evolution was always observed upon preparing these solutions. The over-all reaction with electrons can be expressed as:

$$e^{-}(en) + en H^{+} \longrightarrow \frac{1}{2} H_{2} + en$$

This reaction was too fast for the concentrations used in our attempt. From the preliminary experiments, however, we conclude that the rate constant for this reaction is large, at least >> 10^6 M⁻¹ sec⁻¹.





Absorbance

VI. DISCUSSION

A. Comparison of Spectra

The 660 mµ peak for sodium, lithium and potassium can be compared by plotting $A/A_{max.}$ vs. wavelength. Figure 50 shows that the 660 mµ peaks are the same for these metals both in peak position and shape. Although the potassium spectrum in Figure 50 appears to be different in shape, this can be attributed to the contribution of its infrared absorption. The results of salt addition to cesium solutions showed that the metal is associated with the species responsible for the 660 mµ absorption band but, from the shape and position of the absorption, we conclude that once a basic metal core is present the optical transition responsible for the absorption is independent of metal.

The comparison of the 1280 mµ absorptions is difficult because of the contributions of the other peaks present in the spectra for the different metals. The long-wavelength tails of the infrared bands can, however, be compared by plotting A/A_{max} . in which A_{max} . is the absorbance at 1280 mµ and A is the absorbance at any given wavelength. Such a comparison plot is shown in Figure 51. Within experimental error, the metals cesium, potassium and rubidium give the same absorption spectra from 1300 to 1800 mµ. The tail of the lithium band in this region is slightly below the band for the other metals. This seems to be a true effect since it was observed in the spectra of three independently prepared lithium solutions.

The intermediate absorption bands (830-1050 m μ) observed for cesium, rubidium and potassium solutions have a close resemblance



Figure 50. Comparison of the 660 m μ absorption bands of lithium, sodium and potassium in ethylenediamine.



in shape but are displaced for each of the metals. We conclude, therefore, that the species involved in these absorption bands are similar in nature but depend on the metal as indicated by the shift in wavelength. That the metal atom is involved in this specie is shown by the fact that when lithium metal solution was added to the decomposition product of rubidium solutions (containing Rb^+ , but no Rb metal) the 660,890 and 1280 mµ peaks were all observed.

B. Conductance

1. Comparison of conductance curves. The general form of the conductance curves for potassium, rubidium and cesium in ethylenediamine is similar to that for alkali metals in methylamine but differs somewhat from that of sodium in liquid ammonia. A good way to compare the different systems is to plot the log of the product of the specific conductance and viscosity vs. the log of the concentration as shown in Figure 52. Figure 52 shows again the general trend that cesium-amine systems are better conductors than the other metal-amine systems. Figure 52 also shows the scatter in the data of Gibson and Phipps (58) which can therefore be considered only qualitative. The data of Berns (59) show a deviation from the usual straight-line log-log plot at about .02 molar and continuation at higher concentration with a straight line having the same slope as before. This anomalous behavior might be attributed to a systematic error introduced in the measurements of the high concentration region. However his results of a number of runs are consistent. One should note that the product of specific conductance and viscosity for cesium in ethylenediamine seems to approach that of the sodium-ammonia system at low concentrations.

The conductance behavior of sodium in ethylenediamine (Figures 32 and 33) differs markedly from the other alkali metals in amines.



The equivalent conductance of sodium solutions is much lower than for the other alkali metals in ethylenediamine and is virtually independent of concentration over the ten-fold concentration range investigated. This indicates that the number of current carriers is proportional to the concentration and that the mobility is essentially independent of concentration. Such behavior would not be expected for conventional electrolytes in this medium since extensive ionpairing would cause the equivalent conductance to be strongly dependent upon concentration.

2. The limiting values of the equivalent conductances. The extension of the method of Fuoss (76) due to Shedlovsky (77) was used to evaluate the limiting equivalent conductance, Λ_0 , and also to approximate the pairing constant K_1 for potassium, rubidium and cesium metal-ethylenediamine systems. The values of Λ_0 obtained for the different metal-amine systems are given in Table X.

The method of Shedlovsky is based on the solution of the semiempirical equation

$$\bigwedge = \gamma \left[\bigwedge_{0} - \alpha \left(\frac{\Lambda}{\Lambda_{0}} \right) \sqrt{C \gamma} \right] \qquad (1)$$

in which \bigwedge is the equivalent conductance, γ is the degree of dissociation, \bigwedge_0 is the limiting equivalent conductance, **a** is the Onsager coefficient and C is the concentration in equivalents per liter. A new variable Z is introduced which is defined as

$$Z = \alpha \int_{0}^{-\frac{3}{2}} \sqrt{C \Lambda}$$
 (2)

Equation (1) may now be written as

whe

$$\gamma = \frac{\bigwedge S(Z)}{\bigwedge_{0}}$$
(3)
re $S(Z) = \left[\frac{Z}{2} + \sqrt{1 + (Z/2)^{2}}\right]^{2}$
or $S(Z) = 1 + Z + \frac{Z^{2}}{2} + \frac{Z^{3}}{8} + \dots$ (4)

A crude estimate of \bigwedge_0 , called \bigwedge_0 ', can be obtained by extrapolation of the \bigwedge vs. $C^{\frac{1}{2}}$ curve. \bigwedge_0 ' is then used to calculated Z for each concentration from equation (2) and S(Z) from equation (4). The activity coefficient at each concentration is then determined according to

$$-\log_{10} f^2 = 2\beta (C\gamma)^{\frac{1}{2}}$$
 (5)

where f is the mean ionic activity coefficient and β is a constant given below. The final plot of $\frac{1}{\sqrt{S(Z)}}$ vs. $Cf^2 S(Z) \wedge Should give a$ straight line with an intercept of $\frac{1}{\sqrt{0}}$ and a slope of $\frac{1}{K_1} \frac{1}{\sqrt{0}}$. If \bigwedge_0 differs from \bigwedge_0' the process is repeated using \bigwedge_0 for \bigwedge_0' until convergence is obtained. The constants in the above equations are

$$a = \frac{8.18 \times 10^5 \Lambda_0}{(DT)^{\frac{3}{2}}} + \frac{82}{\eta (DT)^{\frac{1}{2}}}$$

and

$$\beta = \frac{1.815 \times 10^6}{(\text{DT})^{\frac{3}{2}}}$$

where D is the dielectric constant of the solvent and η is the viscosity of the solvent in poises. Constants used for the Shedlovsky analysis of the data were $\eta = 1.54 \times 10^{-2}$ poises and D = 12.9. The results for potassium, rubidium and cesium are plotted in Figure 53. The intercepts and slopes were determined by the method of least squares. In order to have sufficient points in the dilute region for cesium, it was necessary to estimate three points. These points could be reliably estimated by extrapolation of the log of the specific conductance <u>vs</u>. log of the concentration plot, Figure 53. This is felt to be valid in view of the data obtained for potassium and rubidium.

Evers (60) has evaluated the limiting equivalent conductance and the pairing constant for the sodium-ammonia system and Berns (59)



Figure 53. Shedlovsky analysis plots for cesium, potassium and rubidium in ethylenediamine.

for the lithium-methylamine system. These values, as well as the values obtained in this work, are given in Table X. The value of Λ_0 for lithium in methylamine reported by Berns may be too high. When the five highest concentration points are eliminated, which fall in the anomalous region of the plot of log K <u>vs</u>. log C using Berns' data, one obtains a value of Λ_0 of about 180 rather than 228.

Table X shows that the Walden product, $\bigwedge_0 \eta$, for cesium in ethylenediamine is larger than for the sodium-ammonia system while the Walden products for the other metals in amines are considerably lower than this. The Walden product should be considered a qualitative comparison since Walden's rule holds only if Stoke's law is obeyed and the ions have the same size in different media.

Since the spectra of dilute cesium-ethylenediamine solutions exhibit only an infrared absorption band and the conductance behavior appears to be similar to that of the sodium-ammonia system, we conclude that the conductance processes for these two systems are essentially the same. The spectra of dilute solutions of potassium and rubidium in ethylenediamine show absorption bands other than the infrared absorption. If the contribution to the total conductivity of these species is small and essentially a constant fraction over the concentration range as observed for sodium, one concludes that the major contributor to the conductivity of these solutions is the infrared absorbing specie. This requires that the general form of the conductance curves be the same for rubidium, potassium and cesium in ethylenediamine. This is shown to be the case in Figures 32 and 33. The ion-pair dissociation constants given in Table X are essentially the same for these three metals and this further indicates the same conduction process. The dissociation constant for sodium in liquid ammonia is somewhat larger than for these metals in ethylenediamine. This, however, would be expected on the basis of the higher dielectric constant of ammonia.

Solvent	Metal	٨.	$\Lambda_0 \eta_0$	K1	Reference
Ethylenediamine	Cesium	204	3.14	1.44×10^{-4}	this work
	Potassium	139	2.14	1.54×10^{-4}	this work
	Rubidium	117	1.80	1.69×10^{-4}	this work
	Sodium	27*			this work
Methylamine	Lithium	228,3	2.07	5.5 x 10^{-5}	(59)
Ammonia	Sodium	1022	2.61	7.23 x 10 ⁻³	(60)
*	Δ	$c^{\frac{1}{2}}$			

٠,

Table X. Comparison of Limiting Equivalent Conductances

In our proposed model, we have assigned the infrared absorption band to solvated electrons and ion pairs between solvated electrons and solvated metal ions plus ion aggregates of higher order. These conductivity results indicate also that other species besides the infrared absorbing species which are present in the metal-ethylenediamine system do not tend to dissociate into solvated electrons and solvated metal ions at the dilutions studied. Otherwise the large difference in the apparent limiting equivalent conductance values could not be accounted for.

C. Comparison with the Work of Other Investigators

Fowles, McGregor and Symons (13) reported the absorption spectra of sodium and potassium in ethylenediamine up to 1000 m μ . They did not, however, make observations in the infrared region as in this work. Their results for the spectra in the visible region for dilute solutions of these metals are in general agreement with this work. More recently Windwer and Sundheim (54) reported that no absorption could be detected in the infrared region for solutions of lithium, potassium and rubidium. These observations are in direct conflict with the spectral results reported in this work.

Because of the difficulty of preparing reasonably stable solutions, the differences observed by various workers is not as surprising as it might at first appear. Small amounts of impurities can catalyze the decomposition and affect the results obtained. We have assigned the infrared absorption to the solvated electron and it is well-known that impurities such as O_2 and CO_2 (78) are good scavengers for electrons. Traces of these scavengers can deplete the electron concentration very rapidly (9,78). This work has shown, moreover, that the conversion of the 660 mµ absorbing specie into the infrared absorbing specie is a slow process. In the case of rather unstable solutions, one concludes that the observed properties might well be the properties of species that decompose rather slowly compared to the infrared absorbing specie. Windwer (79) reported a solid decomposition product which when analyzed after exposure to air was found to be potassium carbonate. In this work, however, no solid decomposition product has ever been observed in potassium solutions. It should also be noted that Windwer was unable to obtain cesium solutions that were stable enough for simple spectral studies. Since dilute cesium solutions exhibit only the infrared absorption band, this is additional evidence that his experimental techniques introduced impurities that rapidly catalyzed the decomposition of the infrared-absorbing species.

The absorption spectra for solutions of lithium (51) and potassium (52) in methylamine have been reported. A close analysis of these data shows that the absorption spectra for lithium and potassium in methylamine are essentially the same as reported in this work for the same two metals in ethylenediamine. This is to be expected since the small structural difference between these two solvents would certainly not lead to extreme differences in the optical properties of their alkali metal solutions. The stability of metal-methylamine solutions is greater under normal conditions due to temperature considerations alone. In methylamine, observations are normally made between -78 $^{\circ}C$ and -33°C while room temperature studies are reported for ethylenediamine. The lower temperature slows the decomposition process and results in increased stability for metal-methylamine solutions. The results reported in this work are in agreement with the observations reported in methylamine. This author concludes, therefore, that Windwer and Sundheim have reported only the optical properties of very unstable solutions rather than the true properties of relativity stable solutions as reported in this work.

Windwer and Sundheim (54) report the conductivity vs. apparent concentration for potassium in ethylenediamine. These results are not in agreement with the reproducible potassium conductivity data reported in this work. Windwer (79) apparently made only one experiment of this type in which he observed the conductivity and optical absorbance as a function of time during decomposition of the solution. From this observation he draws conclusions about the behavior of the conductivity as a function of the concentration. A close analysis of Windwer's data (79) leads one to conclude that he used an absorption cell with a 0.1 mm. path length. Our experience has been that it is impossible to pour or shake the solution from between the windows of a cell having a path length of only 0.1 mm. It is difficult to understand how Windwer's procedure afforded a method for determining an absorption spectrum-conductivity relationship which could then be converted to a concentration-conductivity relationship. He followed the decay of the 660 m μ absorption band in his measurements and then assumed that Beer's Law is obeyed in order to obtain his concentrationconductivity relationship. Since potassium-ethylenediamine solutions contain three interconvertible species, one certainly would not expect Beer's Law to hold for such a system. It seems reasonable that the experimental procedure used was not sufficient to enable him to obtain quantitative and reproducible results.

Windwer (79) has also reported that in all cases the optical absorption decreased linearly with time. This is again in direct conflict with this work. He also states that the absorbance in different regions of his optical cell decayed at different specific rates. These observations are by no means consistent with homogeneous decomposition but indicate that his absorption cells were not properly cleaned and traces of impurities decomposed the solution at different rates in different regions of his cell. Since Windwer had different

decomposition rates in different regions of his cell, there must have been diffusion of solute from one region of the cell to another and decomposition studies would not be expected to be very reliable.

D. Nature of the Alkali-metal Ethylenediamines Solutions

1. The models for metal-ammonia solutions. The cavity model does not account for metal dependence of any specie and treats the solutions of the different alkali metals as being essentially the same. This model describes the properties of these solutions in terms of the state of the electron. The spectra and conductivity of different metal-ethylenediamine solutions has been shown to differ greatly with metal and therefore this model cannot be a complete one for metal-amine solutions.

The cluster model or Becker, Lindquist, Alder (43) model cannot account for the slow conversion of the visible specie into the infrared species as found in this work. This model also cannot account for the metal dependence of the 845 m μ , 890 m μ and 1030 m μ peaks observed in solutions of potassium, rubidium and cesium in ethylenediamine respectively and also seen for potassium and cesium in methylamine. The cluster model postulates that the species involved are essentially independent of the metal but depend upon concentration. This model must also be discarded as a possible model for metalamine solutions.

2. A new model. We have proposed a new model for metal-amine solutions. Only the essence of this model will be presented here. A detailed discussion will be given in a separate publication. This model is based on available data from the literature as well as this work. It pictures three types of solute species which account for the physical and chemical properties of metal-amine solutions.

The infrared absorbing species. The infrared absorption band is broad in shape and has essentially the same form as the infrared band observed in metal-ammonia solutions. The conductivity of dilute cesium solutions which show only this infrared absorption band seems to approach that of sodium in ammonia when corrected for viscosity. The behavior of the conductivity of lithium in ethylenediamine can readily be explained if the infrared absorbing specie is considered an extremely good conductor. These arguments lead one to conclude that the species responsible for the infrared absorption in metalamine solutions are similar to the species that are present in metalammonia solutions. We assign the infrared absorption band to solvated electrons. Since ion pairing between solvated electrons and solvated metal ions apparently does not appreciably affect the optical properties of the solvated electrons in liquid ammonia (46), the species responsible for the infrared band in a low dielectric medium such as ethylenediamine can be pictured as solvated electrons, ion pairs between solvated electrons and solvated metal ions plus ion triples, quadrupoles, etc. We term these species collectively as polarons.

<u>The 660 mµ absorbing specie</u>. We have shown in this work that a metal core is required to form the specie absorbing at 660 mµ. The metal ions Li⁺, Na⁺, and K⁺ can form the necessary metal core readily while Rb⁺ ions seem to be less favorable and Cs⁺ ions are not satisfactory since cesium solutions do not exhibit the 660 mµ absorption band. It has also been shown in this work that the conversion of the 660 mµ absorbing specie into the infrared absorbing species is a slow process. This slow conversion suggests strongly that a covalent bond is broken. The spectral data of this work have also shown that the 660 mµ absorbing specie is independent of metal both in position and shape. Shatz (51) reported the absorption spectra as a function of

concentration for lithium-methylamine solutions. The results of his work indicate that the visible absorbing specie is dimeric.

We picture the metal core of the 660 mµ specie to be a oneelectron-bonded molecule-ion, M_2^+ . This conclusion is in agreement with the fact that the bond strengths of the molecule-ions Li_2^+ and Na_2^+ in the gas phase are greater than those of the molecules Li_2 and Na_2 by approximately 35% (80,81). The break-up of this molecule-ion can account for the slow conversion of the peak to the infrared absorption. We postulate that the optical electron is trapped by the potential of the solvated molecule-ion in such a manner that its optical properties are independent of the metal.

<u>The intermediate absorbing species</u>. The intermediate absorption peaks at 845, 890, and 1030 mµ for potassium, 'rubidium and cesium respectively correlate well with the positions of $\sum u \leftarrow \sum g$ transitions for the gaseous M₂ molecules (82). The species absorbing in the intermediate range are therefore postulated to be solvated metal dimers similar to the gas phase dimers. These dimers interact with the solvent through van der Waals-type forces so that the effect of the solvent upon the spectrum would not be expected to be large. Straightforward thermodynamic calculations based upon bond energies in the dimer and the solid metal show that no detectible dimer formation would be expected in solutions of lithium and sodium.

E. Kinetics of the Reaction of Solvated Electrons with Water

The principle result obtained in this work is the first-order dependence of both the electron and water concentration on the reaction rate. The simplest explanation of this result would be the assumption of a rate-limiting step $1 \longrightarrow 2$ in the scheme

$$e^{-} + H_2O \rightleftharpoons H + OH^{-} - - \rightarrow H_2$$

This scheme requires that the reaction $2 \rightarrow 3$ must occur fast enough so that there is no appreciable reverse reaction $2 \rightarrow 1$. The simplest reaction by which H atoms can disappear is recombination. The reaction might be as fast as diffusion controlled, i.e., $k_{23} = 10^9$ to 10^{10} l. mole⁻¹ sec⁻¹. Jortner (10) has reported a second-order rate constant of 6×10^5 l. mole⁻¹ sec⁻¹ for the reaction $2 \rightarrow 1$ in water. It is apparent that in neutral solutions the reaction $2 \rightarrow 1$ will not compete with $2 \rightarrow 3$.

There must also be some hydrolysis according to:

$$EDA + H_2O = EDAH^+ + OH^-$$

The ion EDAH⁺ can react with the electron, and preliminary experiments showed that the rate constant of this reaction is large, at least >> 10^6 l. mole⁻¹ sec⁻¹. The maximum extent of this hydrolysis was estimated from conductance measurements (83). These results showed that

$$\frac{[EDA H^{+}][OH^{-}]}{[EDA][H_2O]} < 10^{-11}$$

This same constant in water as a solvent is much larger. Even if some hydrolysis takes place, the concentration of $EDAH^+$ seems to remain low enough to keep the rate $k[e^-][EDAH^+]$ negligibly small. If this were not the case, then the linear relationship with $[H_2O]$ up to a water concentration of 5 moles/liter certainly would not hold. It seems most probable that the extent of hydrolysis is too small to compete and reaction $1 \longrightarrow 2$ occurs instead.

If scheme (1) is complete and correct, then it would not be possible to observe the intermediate as was the case. Also in two preliminary experiments in which KOH was added to the water $(OH^- > 10^{-3} \text{ M})$ no effect on the rate was observed. Using Jortner's rate constant, one would expect some observable competition from the reaction $2 \longrightarrow 1$ if the concentration of hydrogen atoms exceeded about 10^{-6} M.

The first-order behavior observed over a range of water concentrations of 8.8 x 10^{-3} to 5 molar can only be consistent with the rate limiting process for the disappearance of the electron involving the direct reaction of the electron with the water. Also the value for the second-order rate constant (25 1. mole⁻¹ sec⁻¹) seems reasonable since extrapolation to pure H₂O gives $k = 1.4 \times 10^{-3} \text{ sec}^{-1}$ for the decay of the electron in pure water. Recently Czapski and Schwarz (8) reported $k < 10^4 \text{ sec}^{-1}$ from experiments on the radiolysis of water. These values are in good agreement.

Our observations are not extensive enough at the present time to allow one to determine the nature of the intermediate which forms when the electron reacts with water. It is clear, however, that in our system electrons and water molecules do not simply react to give products. In fact the rate of build-up of the intermediate suggests that even the intermediate is not formed directly. This suggests that the hydrogen atom might be associated with the intermediate.

The results of run no. 2 indicated the stoichiometry of the rate expression to be proportional to $[H_2O]^{\frac{1}{2}}[e^-]$. This result is not consistent with the results obtained in run no. 1 for which the conditions were nearly the same. The high cesium concentration and stability of the solution used in run no. 2 suggests that Cs₂ dimers were probably present in this solution. Therefore the rate dependence observed in this run may be due to the reaction of cesium dimers with water. This argument is consistent with the conclusion that the different species present in metal-ethylenediamine solutions react by different mechanisms and rates as indicated by the decomposition rate studies. For sodium solutions, the results obtained from kinetic and visual

observations showed the 660 m μ absorbing specie reacts much slower with water than does the solvated electron. Our kinetic data in the case of sodium solutions, however, are too limited to draw any valid conclusions about the kinetics of this reaction except to suggest that the disappearance of the 660 m μ specie is zero order in this specie.

F. Future Work

The slow conversion of the specie absorbing in the visible region is an important result that should be confirmed by further experimentation. Hohlstein and Wannagat (50) have shown that the visible peak of sodium in methylamine can be converted to the infrared absorption by the addition of ammonia. If one part of a solution of sodium in methylamine which contains only the 660 mµ absorption peak were mixed with ten parts of liquid ammonia, the 660 specie would then be converted to polarons. The polaron should form from a free electron in 10^{-11} sec. (84) so that the observable conversion will be the slow step connected with the break-up of the 660 mµ absorbing species.

The rate of formation of the 660 absorbing specie could also be studied by mixing sodium iodide solutions or decomposed sodium metal solutions with dilute cesium-ethylenediamine solutions. This rate should be within the range of flow techniques.

More information about the role played by the cation in forming the 660 m μ specie could be gained by addition of salts containing a wide variety of cations to these metal solutions.

The absorption spectra as a function of concentration for metalethylenediamine solutions would also be of interest. Such data would allow an estimation of the equilibrium constants for the species involved in these systems. This would allow one to make a better correlation of spectra and conductivity data.

The absorption spectra of cesium-methylamine and ethylamine solutions should be measured in order to determine whether these solutions have the same spectral properties as observed in this work for cesium in ethylenediamine.

The conductivity of sodium in methylamine is of interest since this information would help to clarify the anomalous conductivity behavior reported in this work for sodium in ethylenediamine. The conductivity of cesium in methylamine should be repeated since this solution should exhibit conductivity in the dilute region comparable to the metal-ammonia system.

The nature of the decomposition reaction of these solutions should be investigated more fully. Windwer (79) has reported that analysis of the gaseous decomposition products using a mass spectrometer showed the presence of hydrogen and nitrogen in the ratio of two to one. This observation should be repeated.

There are some interesting solubility experiments that could be performed. Since I_2 dissolves in a number of nonpolar solvents, the same forces that are responsible for its dissolution should also dissolve the highly polarizable Rb-Rb and Cs-Cs molecules. This would give added evidence for the existence of gas-like metal dimers in metalamine solutions.

There are a number of points in the kinetic studies of the reaction between the solvated electron and water that need further investigation. The nature and kinetics of the intermediate which was observed in this work should be studied. The effect of excess OH⁻ ions on this reaction as well as the rate of reaction with EDAH⁺ ions should be investigated. These same measurements should also be made using liquid ammonia solutions in order to determine the role of the solvent and temperature in this reaction.

Kinetic studies of the reaction between cesium solutions having the 1030 absorbing specie and water would help clear up the water dependence observed in one of the flow runs of this work. Since rubidium solutions in ethylenediamine show a large and very stable 890 m μ peak, this specie when reacted with water should give the same kinetic behavior as the 1030 m μ specie of cesium solutions if the two species are similar in nature. The kinetics of the reaction of sodium-ethylenediamine solutions with water would be interesting since this would give information about the kinetics of the reaction of the 660 m μ specie with water.

The kinetics of various electron attachment reactions should be investigated. Information about the rates of these reactions would be of interest since these reactions are essentially elementary kinetic steps. They should be fast, and simple to interpret, since mechanisms of elementary steps tend to be simple.

REFERENCES

- A. Allen, "The Radiation Chemistry of Water and Aqueous Systems," D. Van Nostrand Co., New York, N. Y., 1962.
- 2. N. Barr and A. Allen, J. Phys. Chem., 63, 938 (1959).
- 3. J. Rabani, J. Am. Chem. Soc., 84, 682 (1962).
- 4. J. Weiss, Nature, 186, 751 (1960).
- 5. J. Allan and G. Scholes, Nature, 187, 218 (1960).
- 6. E. Hayon and A. Allen, J. Phys. Chem., 65, 218 (1961).
- 7. E. Collinson, F. Dainton, D. Smith and S. Tazaki, Proc. Chem. Soc., 1962, 140.
- 8. G. Czapski and H. Schwarz, J. Phys. Chem., 66, 471 (1962).
- 9. E. Hurt and J. Boag, J. Am. Chem. Soc., 84, 4090 (1962).
- 10. J. Jortner and J. Rabani, J. Phys. Chem., 66, 2081 (1962).
- 11. J. Rabani and G. Stein, J. Chem. Phys., 37, 1865 (1962).
- 12. J. Jortner, M. Ottolenghi, J. Rabani and G. Stein, <u>J. Chem. Phys.</u>, <u>37</u>, 2488 (1962).
- 13. G. Fowles, W. McGregor and M. Symons, <u>J. Chem. Soc</u>., <u>1957</u>, 3329.
- 14. W. Weyl, Ann. Physik, 121, 601 (1864).
- 15. W. Jolly, "Progr. Inorg. Chem., "1, 235 (1959).
- 16. T. Das, "Advances in Chemical Physics," Interscience Publishers, New York, Vol. IV (1962).
- 17. C. Kraus, J. Am. Chem. Soc., 30, 1323 (1953).

- 18. C. Kraus, J. Chem. Education, 30, 83 (1953).
- 19. M. Symons, Quarterly Reviews, 8, 99 (1959).
- 20. C. Evers, J. Chem. Ed., 38, 590 (1961).
- 21. C. Kraus, E. Carney and W. Johnson, <u>J. Am. Chem. Soc.</u>, <u>49</u>, 2206 (1927).
- 22. C. Kraus, J. Am. Chem. Soc., 43, 749 (1921).
- 23. C. Kraus, J. Am. Chem. Soc., 36, 864 (1914).
- 24. C. Evers, A. Young and A. Panson, J. Am. Chem. Soc., 79, 5118 (1957).
- 25. J. Dye, R. Sankuer, and G. Smith, <u>J. Am. Chem. Soc.</u>, <u>82</u>, 4797 (1960).
- 26. M. Gold and W. Jolly, Inorg. Chem., 1, 818 (1962).
- 27. H. McConnell and C. Holm, J. Chem. Phys., 26, 1517 (1957).
- 28. J. Acrivos and K. Pitzer, J. Chem. Phys., 66, 1693 (1962).
- 29. T. Hughes, Jr., J. Chem. Phys., 38, 202 (1963).
- 30. C. Hutchison and R. Pastor, J. Chem. Phys., 21, 1959 (1953).
- 31. E. Huster, Ann. Physik, 33, 477 (1938).
- 32. D. O'Reilly, Ph. D. Dissertation, University of Chicago (1955).
- 33. C. Kraus, J. Am. Chem. Soc., 30, 1197 (1908).
- 34. R. A. Ogg, Phys. Rev., 69, 668 (1946).
- 35. W. Lipscomb, J. Chem. Phys., 21, 52 (1953).
- 36. R. Stairs, J. Chem. Phys., 27, 1431 (1957).
- 37. J. Kaplan and C. Kittel, J. Chem. Phys., 21, 1429 (1953).
- 38. L. Landau, Physik Z. Sowjetunion, 3, 664 (1953).
- 39. A. Dawydow, <u>J. Exptl. Theoret. Phys.</u>, <u>U.S.S.R.</u>, <u>18</u>, 918 (1948).
- 40. M. Deigen and Y. A. Tsvirko, Ukrain. Fiz. Zhur., 1, 245 (1956).
- 41. J. Jortner, J. Chem. Phys., 27, 823 (1957); 30, 839 (1959).
- 42. L. Coulter, J. Chem. Phys., 19, 1326 (1951).
- 43. E. Becker, R. Lindquist and B. Alder, <u>J. Chem. Phys.</u>, <u>25</u>, 971 (1956).
- 44. W. Blumberg and T. Das, J. Chem. Phys., 30, 251 (1959).
- 45. R. Douthit and J. Dye, J. Am. Chem. Soc., 82, 4472 (1962).
- 46. M. Gold, W. Jolly and K. Pitzer, <u>J. Am. Chem. Soc.</u>, <u>84</u>, 2264 (1962).
- 47. S. Gunn and L. Green, J. Chem. Phys., 36, 363 (1962).
- 48. G. Gibson and W. Argo, J. Am. Chem. Soc., 40, 1327 (1918).
- 49. H. Blades and J. Hodgins, Can. J. Chem., 33, 411 (1955).
- 50. G. Hohlstein and U. Wannagat, Z. Anorg. Chem., 288, 193 (1956).
- 51. M. Shatz, Ph. D. Dissertation, University of Penn. (1958).
- 52. H. Eding, Ph. D. Dissertation, Stanford University (1952).
- 53. R. Douthit, Ph. D. Dissertation, Michigan State University (1959).
- 54. S. Windwer and B. Sundheim, J. Phys. Chem. 66, 1254 (1962).
- 55. G. Gibson and W. Argo, Phys. Reviews, 7, 33 (1916).
- 56. K. Vos, Ph. D. Dissertation, Michigan State University, (1962).
- 57. E. Levinthal, E. Rogers, and R. Ogg, Phys. Rev., 83, 182 (1951).
- 58. G. Gibson and T. Phipps, J. Am. Chem. Soc., 48, 312 (1926).
- 59. D. Berns, E. Evers and P. Frank, <u>J. Am. Chem. Soc.</u>, <u>89</u>, 310 (1960).

- 60. E. Evers and P. Frank, J. Chem. Phys., 30, 61 (1959).
- 61. H. Wolthorn and W. Fernelius, J. Am. Chem. Soc., 56, 1551 (1934).
- 62. J. Jortner and G. Stein, Nature, 175, 893 (1955).
- 63. J. Down, J. Lewis, B. Moore and G. Wilkinson, Proc. Chem. Soc., 1958, 209.
- 64. J. Down, J. Lewis, B. Moore and G. Wilkinson, <u>J. Chem. Soc.</u>, <u>1959</u>, 3767.
- 65. F. Cafasso and B. Sundheim. J. Chem. Phys., 31, 809 (1959).
- 66. F. Dainton, D. Wiles, and N. Wright, J. Chem. Soc., 1960, 4283.
- 67. T. Tuttle and S. Weissman, J. Am. Chem. Soc., 80, 5342 (1958).
- 68. H. Lenschitz and J. Eloranta, Z. Electrochem., 64, 169 (1960).
- 69. H. Hartridge and F. Roughton, Proc. Roy. Soc. London, A104, 376 (1923).
- 70. R. Roughton and B. Chance, "Physical Methods of Organic Chemistry," ed. Weissberger, 1953, vol. 8, chap. 10.
- 71. B. Chance, J. Franklin Inst., 1940, 229, 455, 613, 737.
- 72. H. Millikan, Proc. Roy. Soc. A., 155, 277 (1936).
- 73. B. Chance and V. Legallais, <u>Discuss. Faraday Soc.</u>, <u>17</u>, 125 (1954).
- 74. Q. Gibson, Discuss. Faraday Soc., 17, 137 (1954).
- 75. B. Chance, Rev. Sci. Instruments, 22, 619 (1951).
- 76. R. Fuoss, J. Am. Chem. Soc., 57, 488 (1935).
- 77. T. Shedlovsky, J. Franklin Inst., 225, 739 (1935).
- 78. E. Hayon, <u>Nature</u>, <u>196</u>, 533 (1962).
- 79. S. Windwer, Ph. D. Dissertation, New York University (1960).

- 80. R. Barrow, N. Travis and C. Wright, Nature, 187, 141-2 (1960).
- 81. J. James, J. Chem. Phys. 3, 9 (1935).
- 82. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1962.
- 83. M. Stafford, unpublished work.
- 84. R. Platzman, "Basic Mechanisms in Radiobiology," U. S. Nat. Acad. Sci. Pub., No. 305, 1953, p. 34.

CHEMISTRY LIBRARY

.

.

.

`

,

٠

