SPECTROPHOTOMETRIC MEASUREMENTS OF SOLUTIONS OF SODIUM METAL IN ETHYLENEDIAMINE

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ABSTRACT

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by Myron Stafford

Qualitative spectra obtained for solutions of sodium in ethylenediamine indicated the existence of a single peak at 657 mμ. In order to substantiate the theoretical explanation of this peak with quantitative experimental data, and to obtain a value for the molar absorptivity of such solutions, spectrophotometric measurements were carried out on solutions of sodium in ethylenediamine.

The Beckman DK-2 spectrophotometer was used in all the measurements along with specially constructed apparatus for transferring and handling the reactive solutions. From the first step in the purification of the ethylenediamine to the final step before actual measurements were taken, extreme care was exercised to avoid the admission of any impurities to any system involved. Out of such precautions has developed a valuable technique which may be extended to further work upon other alkali metal-ethylenediamine solutions.

The results of the quantitative studies upon sodium-ethylenediamine solutions indicate that the molar absorptivity value lies between 2.5×10^4 and 4.0×10^4 and

that the oscillator strength is about 0.5. This result is in accord with the model of Dye and Dewald which postulates a solvated molecule-ion, Na_2^+, and a de-localized "optical" electron.

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By

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Finally, the author wishes to recognize the sacrefices realized by his immediate family during these educational years.

And not least of all, the author will always be able to recall those "friendly comments" and "destructive threats" so eloquently delivered by "The Boys in Romm 109" while the writer attempted to teach them an appreciation for ethylenediamine vapors.

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INTRODUCTION

Many papers have been authored dealing with the chemical and physical properties of solutions of alkali metals in liquid ammonia and more recently these studies have been extended to include the solutions of alkali metals in amines and ethers. Such an extension is the reason for this thesis.

The data obtained from the liquid ammonia-alkali metal solutions are in the main presently interpreted on the basis of two models: the cavity model and the Becker, Lindquist, and Alder model (1). The name of the former model epitomizes the theory that supports it; namely, that in a sodium-ammonia solution, solvated electrons are present and the solvated electron is considered to be trapped in a spherical cavity surrounded by ammonia molecules. In the B. L. A. model, the two main structural concepts introduced which are different from the cavity model are the existence of the solvated monomer $\left[M^{+}(am) + e^{-}(am) = M(am) \right]$ and the dimer $\left[2\, M(am) = M_2(am) \right]$.

However, the data obtained from solutions with amines and ethers as solvents even qualitatively manifest such differences that these models alone are not sufficient to interpret the results. For a discussion of the various species proposed according to the above models as well as the proposal of a third and new model which takes into consideration the new data obtained from solutions of al-

kali metals in amines, the reader is directed to the doctoral thesis of R. R. Dewald (2).

In consulting the latter work, it will become evident that one of the difficult areas in these investigations using amines concerned the peak obtained at 657 mμ when absorbance data from the solutions of lithium, sodium, potassium, and rubidium in ethylenediamine were examined. The characteristic most important to the present work was that among these solutions sodium shows only the 657 peak. This fact plus the desire to determine the nature of the species responsible for this peak logically indicated that the first quantitative studies be done using sodium solutions.

The species believed to be responsible for the 657 peak in sodium-ethylenediamine solutions according to the new model is the solvated diatomic molecule-ion, Na_2^-, with a delocalized optical electron "smeared out" over the region outside the solvated ion. Therefore, it was proposed that examination of the oscillator strengths obtained from the spectrophotometric data would indicate whether only one out of two electrons absorbed radiation and thus whether the molecule-ion with one non-absorbing and one "optical" electron were valid as an explanation for the observed 657 peak. The development of an experimental technique for spectral studies would also permit study of the other alkali metal-ethylenediamine solutions so that one might explain these peaks as well.

EXPERIMENTAL

Any and all reliable experimental data obtained from solutions of alkali metals in ammonia and amines depend upon the recognition of the great sensitivity of such solutions to the presence of impurities. Therefore, the dependability of any quantitative results obtained from this work centered around the actual process involved in the purification of the solvent, ethylenediamine; in the purification of the sodium metal and all the alkali metals used in the purification train for the solvent; and in the handling and cleaning of all glassware involved.

I Purification of Ethylenediamine

To avoid any possible decomposition due to atmospheric oxidation, the initial three purification steps were carried out under a constant flow of pre-purified nitrogen while the final three stages were under vacuum (see diagram of apparatus in Figures 1 and 2). Reagent grade anhydrous ethylenediamine of approximately 98% purity was placed in the first flask which contained BaO and KOH and refluxed under a constant flow of pre-purified nitrogen for approximately 48 hours. When the heat was first applied to this system, the ethylenediamine deepened in color from clear to yellow to a dark brown. Transferral of the liquid to the second flask which contained sodium wire was accomplished by discontinuing the water flow through the reflux conden-

ser and allowing the solvent to distil directly into flask II where it remained for approximately 48-72 hours under atmospheric pressure of nitrogen. (The ethylenediamine may or may not have a blue coloration at this point. However, if it does, it subsequently fades into a reddish-brown color with blue streamers radiating out from the sodium wire proper.)

Since no nitrogen had been allowed to enter flask III (Figure 2), the next transferral merely involved allowing the solvent to flow directly from one flask to another where once again the liquid was refluxed over BaO and KOH for approximately 48 hours in a stream of pre-purified nitrogen.

Through the use of the attached fractionating column packed with short lengths of 5 mm glass-tubing, the bulk of the liquid was distilled over at constant temperature into flask IV; the first fraction being contained in the 500-ml waste vessel and discarded. Since flask IV again contained sodium wire, the solution turned blue immediately and remained blue for a rather extended period of time. From this point on all remaining purifications were carried out under vacuum. After standing over the sodium wire for several hours, lithium metal was added from the small bent side-arm or "thumb" by rotating it into an upright position. Immediately a deep blue coloration ensued which remained permanently. The solution was allowed to stand for several hours during which time any hydrogen formed was

pumped off through a cold trap to the vacuum line.

From this point on one must be careful not to overheat the ethylenediamine and so produce further decomposition. Therefore, a warm water bath was used to vaporize the liquid to distil it into flask V which was simultaneously cooled with an ice-water bath. Since potassium metal had previously been distilled into flask V through the use of an attached side-arm which was subsequently sealed off after the metal distillation, the entire flask contained a silvery mirror and the blue coloration appeared immediately when the solvent condensed in the cooled flask. The blue color remained permanently.

Finally using another warm water bath, the last transferral was made to flask VI by distilling the liquid over carefully and slowly avoiding too much heating. Here the pure colorless liquid was contained and covered with purified nitrogen so that it could be withdrawn into the second make-up vessel.

II Second Make-up Vessel

The second smaller two-vessel system (Figure 3) was constructed so that the ethylenediamine would be in contact with sodium metal for the last drying before its use in the spectrophotometric measurements. This system was evacuated and heated carefully with a flame to de-gas the glass surfaces and through the use of the attached side-arm, sodium metal was distilled into the first vessel

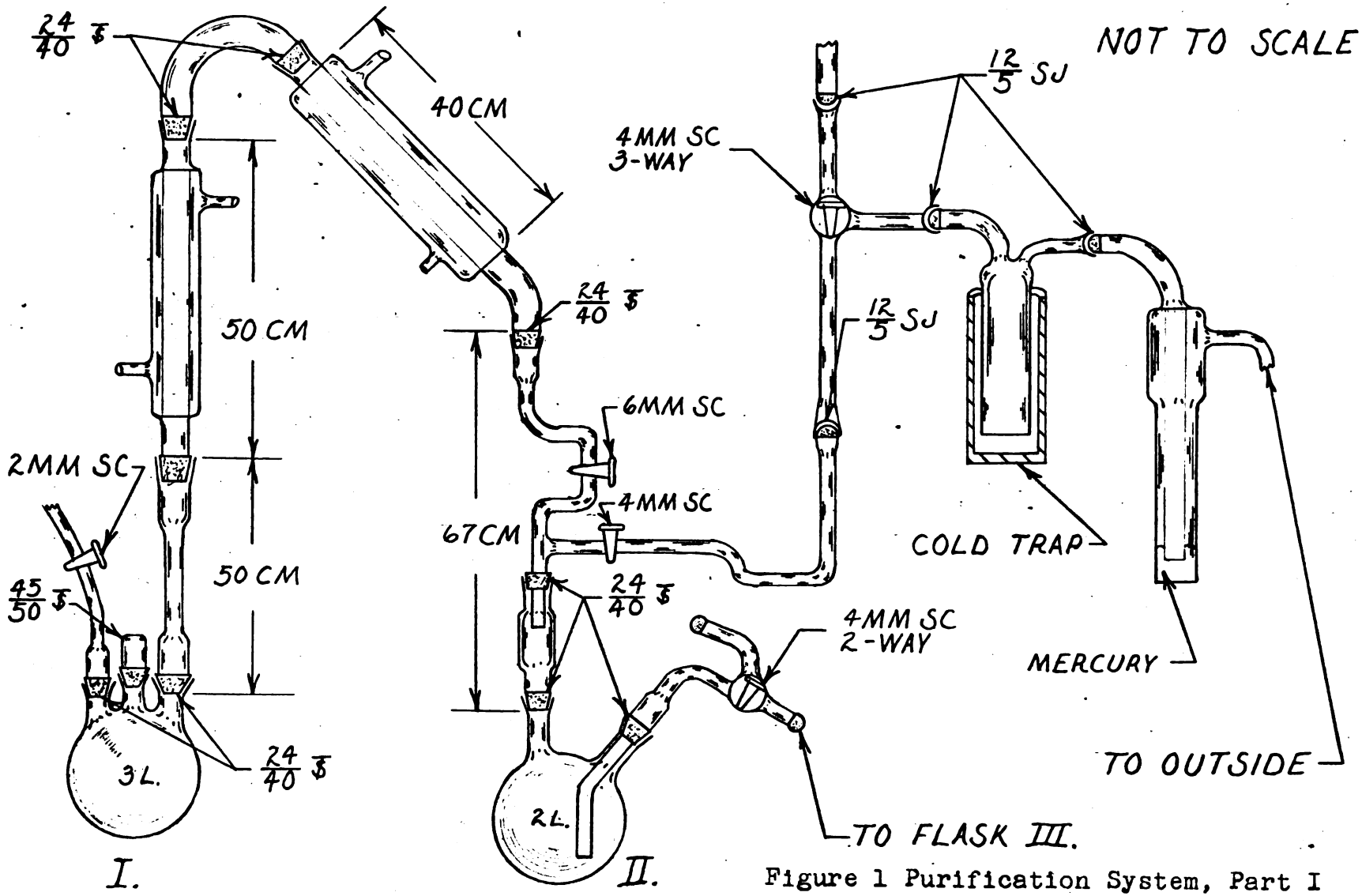


Figure 1 Purification System, Part I

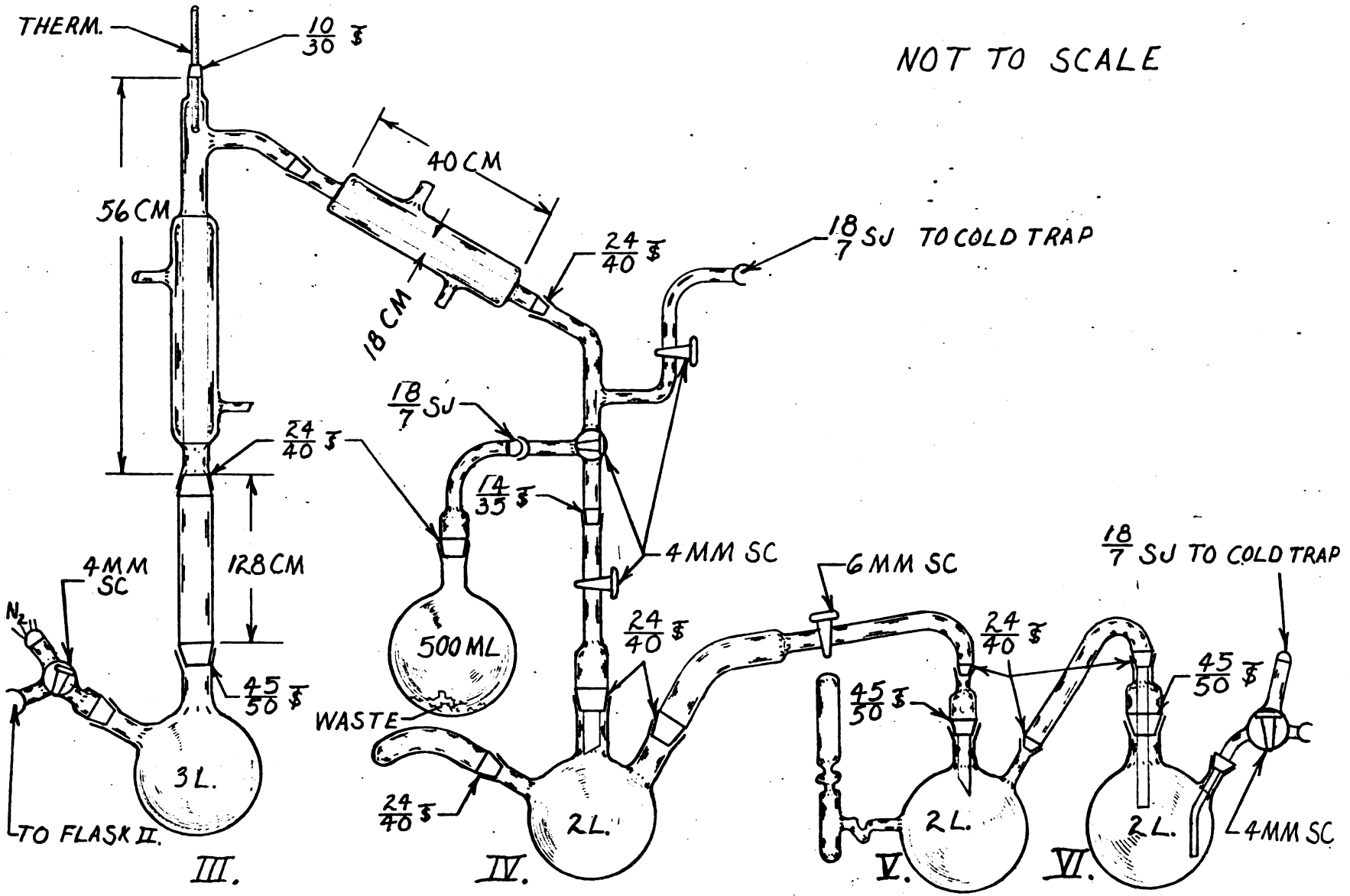


Figure 2 Purification System, Part II

which would receive the liquid from flask VI and the side-arm was sealed off under vacuum. The two-way stopcock on flask VI was then opened allowing approximately 300 ml of ethylenediamine to flow into the silvery-mirrored vessel and it immediately turned blue. The stopcock was closed and re-opened to the high vacuum line through a liquid-air trap.

Then with the use of a trichloroethylene-dry ice bath, the blue liquid was frozen and all of the free solvent droplets were distilled into the cooled portion. This was followed by removal of the bath allowing the frozen ethylene-diamine to melt. After several hours, the dry ice bath was placed on the empty remaining vessel and the ethylene-diamine was allowed to distil over very slowly. This distillation was aided by pumping off the hydrogen which was formed periodically. Also warm air flowing across the first vessel aided distillation, but care had to be exercised here so that the blue sodium solution was not carried over directly through the trap to the clear liquid.

The pure liquid was now stored in this second vessel and covered with purified helium in preparation for its transferral to the third set-up of apparatus which held the cell used in the actual spectrophotometric measurements.

III Make-up Vessel with Spectral Cell

By examining the photographs in Figure 4, one may locate the following main parts of the complicated-looking

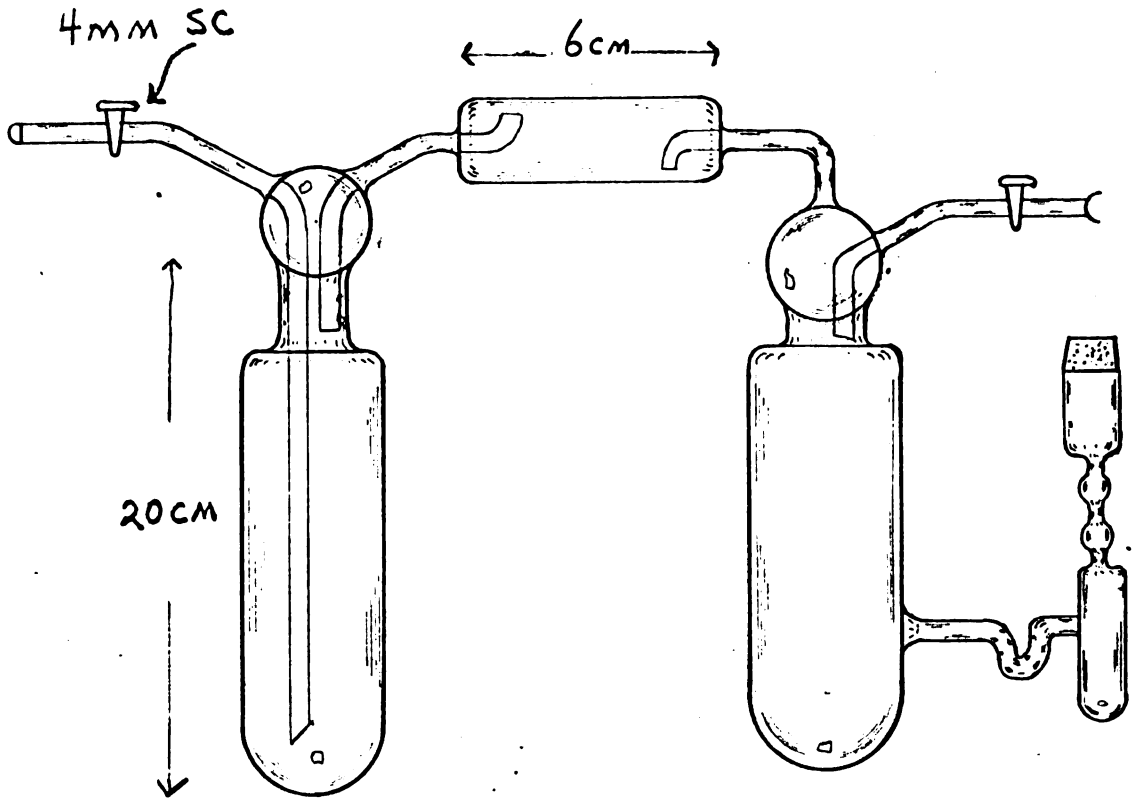


Figure 3 Diagram of Two-Vessel System

make-up vessel with its spectral cell: waste vessel (near cell); reservoir for pure ethylenediamine; reservoir for sodium and ethylenediamine solution; measuring cylinder. With these names and the apparatus actually in hand, the following outline of steps may be carried out.

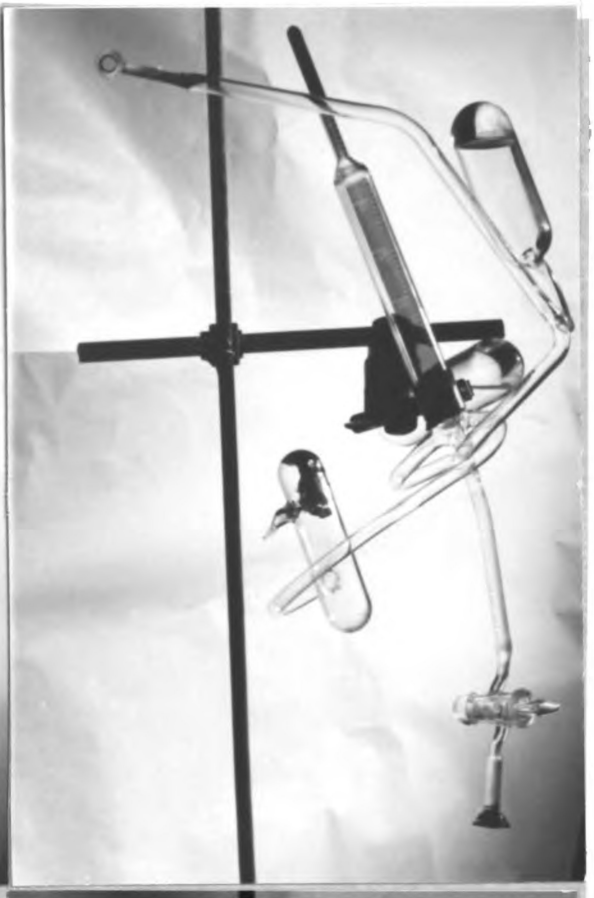
A) Preparation for measurement of the saturated solution

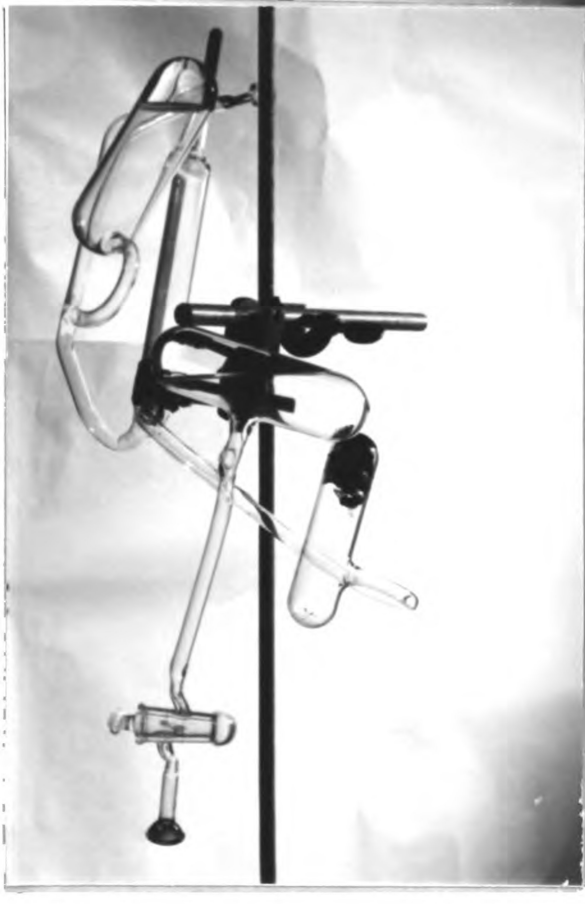
1) A small amount of ethylenediamine is poured from the ethylenediamine reservoir (which is approximately two-thirds full) into the measuring cylinder.

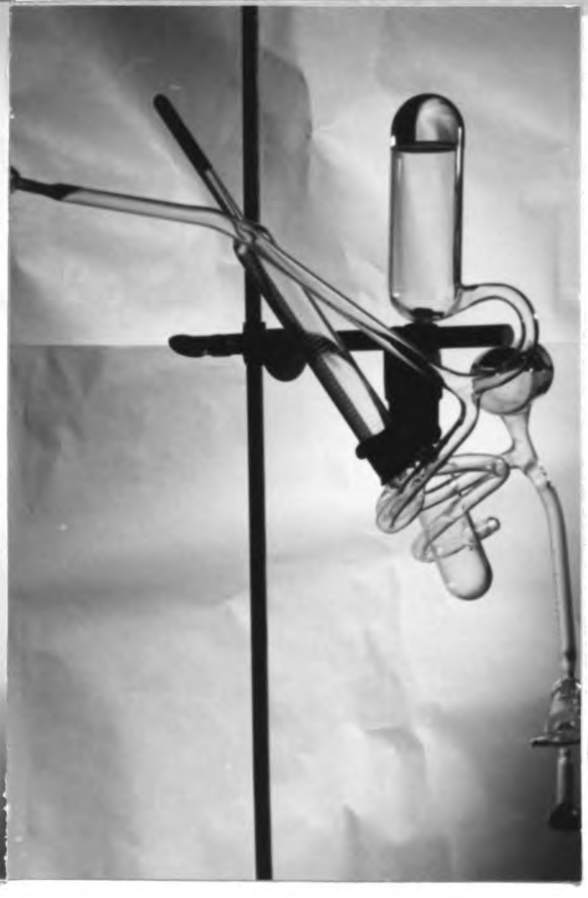
2) From the measuring cylinder it is poured (from a different direction) into the silvery-mirrored reservoir. (Sodium metal has previously been distilled from a side-arm attachment into the sodium-ethylenediamine solution reservoir and sealed off under vacuum). In order to obtain a saturated solution, it is allowed to stand on the metal for approximately one hour or more. To obtain a uniform mixture the blue solution is poured back and forth between the (ethylenediamine-sodium) solution reservoir and the measuring cylinder. This operation is carried out several times. (Avoid allowing the solution to come in contact with the sealed off area as much as possible).

3) Finally, only a small portion of the saturated solution is poured into the measuring cylinder, and by pouring in a different direction, enough solution to cover the cell is transferred. Then by tilting the

Figure 4 Photographs of Make-up Vessel with Spectral Cell







entire apparatus backward so that all the solution may leave the cell, several rinsings of the cell are made by pouring the same solution back and forth between the cell and the "crook" in the cell arm. Finally this solution is poured into the waste vessel.

4) Once again one returns to the measuring cylinder and removes a second sample which is large enough in volume to cover the cell. This may also be rinsed back and forth in the same manner as above.

5) The cell is now lowered into the spectrophotometer and positioned on a V-block especially built for this purpose. The rest of the apparatus proper is supported on a rod which is held by a fitting attached to the cover also especially made for this set-up.

B) Preparation for measurement of a dilute solution

1) Follow steps one and two in part A above.

2) A given amount of saturated solution is transferred from the solution reservoir into the measuring cylinder and the volume recorded. (Care should be taken to allow all the solution adhering to the sides of the glass to run down before making any readings). The measuring cylinder was calibrated with a 5 cc Luer-Lok syringe containing water. The results were: 1 cc of water gave a reading of 1.17; 2 cc of water gave a reading of 0.12; and 6 cc of water gave a reading of 6.8.

3) A given amount of clear solvent is transferred from the solvent reservoir onto the blue saturated solution in the

measuring cylinder. This final volume is recorded.

4) The apparatus is now tilted in such a way as if one were emptying the cell. This should not be done at too sharp of an angle or loss of material from other reservoirs will result. Then the solution is poured back again into the measuring cylinder by tilting it upright. This mixing is done several times until a uniform solution is obtained.

5) Now enough solution to cover the cell is removed and the cell is rinsed as directed in number 3-A above.

6) Follow step 5-A above.

IV Calibration of the Instrument

All measurements in this work were made on the Model DK-2 spectrophotometer in the near infra-red and visible ranges. In order to check the accuracy of the instrument, solutions of neodymium chloride were prepared by dissolving a definite weight of Nd_2O_3 in concentrated HCl in a 5 ml volumetric flask. (The final weight of the Nd_2O_3 was taken after it had been heated to 950° C). The molar absorptivities were calculated using Beer's Law and compared to values for such solutions in the literature. The results revealed the instrument to be in a proper working order. (6)

V Procedure for De-gassing the Make-up Vessel and Cell

To de-gas the spectral cell and make-up vessel, it was suspended on a rack near the high vacuum line, con-

nected to the line, and evacuated. Around this suspended system, a cylindrical furnace of asbestos paper and aluminum foil was built. With the use of a heating element the temperature of the system was brought to 260-280° C for de-gassing and pumped on for 24-36 hours at less than 10^{-5} torr.

VI Purification of Metals

Sodium and potassium were purified by double vacuum distillation of the best metals available commercially. The first distillation was made by distilling the metal into evacuated glass tubes which were sealed off under vacuum. These tubes were then broken and inserted into the side-arms provided on the apparatus. The metal was melted through the constrictions and distilled after sealing off the melt-down tube.

Lithium metal was cut under benzene (through which argon was bubbled) and quickly transferred to the attached side-arm which was then evacuated.

VII Cleaning of Glassware

1) Cleaning of the Six-Vessel Distillation System

Many of the parts of this system were annealed in an oven overnight, but if this were not possible, each vessel was rinsed first with a dilute solution of HF cleaner which had the following composition: 2% detergent, 5% HF, 33% HNO_3, and 60% water. The HF cleaner was followed by very thorough multiple rinsings of

every part with hot aqua regia. This was then followed by very thorough rinsing of every part with distilled water, and finally rinsing several times with de-ionized water.

2) Cleaning of Two-Vessel System

The entire assembly was cleaned with the HF cleaner which, after rinsing with water, was followed by thorough cleaning with hot aqua regia. The rinsings with water were the same as given above.

3) Cleaning of Spectral Cell and Make-up Vessel

Every reservoir and arm of this apparatus was first rinsed with the dilute HF cleaner being very careful not to leave the cleaner in the cell for more than a few minutes. Next, the main reservoirs and the cell were partially filled with aqua regia, and the entire apparatus was suspended in a large glass cylindrical container and steamed for 24 hours. Then a new solution of aqua regia was added and the steaming procedure repeated. With most of the aqua regia removed, the apparatus was rinsed with de-ionized water several times. Then this water was added to the main reservoirs and cell, and the entire apparatus again was steamed for 24 hours. This step likewise was repeated. This was finally followed by several rinsings with de-ionized water and the apparatus dried thoroughly in an oven.

VIII Conductivity Measurements of Water in Ethylenediamine

Before the spectrophotometric measurements were carried out, a set of conductivity measurements were completed on solutions of water in ethylenediamine. The purpose of these conductance measurements was to examine the extent of the following reaction: $H_2O + en = enH^+ + OH^-$.

1) Conductivity Apparatus

The conductivity apparatus consisted of two main parts. The first part was made up with the male part of a standard taper. Extending straight down into this taper was the capillary end of a calibrated cylindrical vessel which was connected to the body proper of the calibrated vessel through a two-way stopcock. The other opening of this stopcock served to connect the capillary tip with an ordinary cylindrical glass vessel which was separate from the calibrated vessel and was filled with purified helium.

A small standard taper attached to the very upper side of the calibrated vessel accommodated an attached side-arm shaped like a thumb which could hold about 20 ml of water. By turning this to an upright position water entered the calibrated vessel. The opposite end of the calibrated vessel (beyond the thumb) was bent in a U-shape and connected to ordinary glass tubing which at its opposite end was sealed into the side of the head of the male taper. This connection was used to equilibrate gas pressure during transfer.

The second part of the apparatus consisted of an or-

dinary Erlenmeyer flask with the female portion of the standard taper and was equipped at the base with two disk-shaped platinum electrodes.

2) Experimental Procedure

After evacuating the entire system, the de-ionized water which had previously been added to the "thumb" was de-gassed by freezing with liquid air, pumping on the frozen water through a cold trap connected with the vacuum line, and then thawing. This was repeated several times.

After transferring about 100 ml of ethylenediamine (the exact weight of the liquid was obtained by weight difference) to the Erlenmeyer flask from flask VI of the purification train (Figure 2), the entire system was removed from the vacuum line. The thumb was turned upward and water entered the calibrated vessel. Purified helium was now released from the attached cylindrical glass vessel and used to push each desired amount of water through the capillary tip into the ethylenediamine. The volume of water added was read from the calibrated cylindrical vessel.

The conductance cell was now suspended in a constant temperature oil bath and the resistance of each solution was measured.

The cell constant was obtained from the measurement of the resistance of a standardized KCl solution.

RESULTS

I Results of Spectrophotometric Measurements

The data obtained from the spectrophotometric measurements were used first to calculate the molar absorptivity of the solution. For the shape of the curve, the reader is referred to the thesis of R. R. Dewald (2).

The first set of data treated involved a solution which was obtained by the dilution of 1.09 ml of saturated sodium-ethylenediamine solution with pure solvent to a final volume of 7.5 ml ($c = 3.49 \times 10^{-4}$ M).
The data obtained from this solution are listed in Table 1.

Table 1 Data Used to Calculate Molar Absorptivity Value I

Peak Number	Absorbance, A	Time, t(sec)	Δt(sec)
First Transfer	1.42	2365	0
1 (Sheet 2)	1.382	2545	180
2 (Sheet 2)	1.212	2645	280
3 (Sheet 2)	1.152	2762	397
4 (Sheet 2)	1.063	2883	518
Second Transfer	1.21	3650	0
1 (Sheet 3)	1.162	3740	90
2 (Sheet 3)	1.192	3880	230
3 (Sheet 3)	1.022	3985	335
4 (Sheet 3)	0.912	4125	475

Both sets of data in Table 1 were plotted on semi-log paper with the absorbance, A, as the ordinate and Δt as the abscissa. Extrapolation back to the respective transfer times then gave the absorbance values listed for the solution at the time of its transferral to the cell.

A molar absorptivity value of 5.2×10^4 liter-cm^{-1}-mole^{-1}

was obtained by plotting the absorbance, A, against time, t for the two transferral values and extrapolating to zero time to give an absorbance of 1.82 which represents the absorbance value of the original solution.

A second set of data was treated in the same manner for a solution that was prepared by diluting 0.93 ml of the saturated solution to a final volume of 6.4 ml (c equals 3.49×10^{-4} M). (This last concentration is the same as the first concentration for Table 1 only by circumstance). The data obtained from this solution are given in Table 2.

Table 2 Data Used to Calculate Molar Absorptivity Value II

Peak Number	Absorbance, A	Time, t(sec)	Δ t(sec)
First Transfer	1.80	965	0
1 (Sheet 4)	1.770	1190	225
2 (Sheet 4)	1.733	1310	345
3 (Sheet 4)	1.642	1470	505
4 (Sheet 4)	1.580	1665	700
5 (Sheet 4)	1.521	1895	930
6 (Sheet 4)	1.451	2150	1185
7 (Sheet 4)	1.410	2430	1465
8 (Sheet 5)	1.335	2655	1690
9 (Sheet 5)	1.300	2915	1950
10 (Sheet 5)	1.230	3205	2240
11 (Sheet 5)	1.150	3565	2600
12 (Sheet 5)	1.090	3745	2780

Table 2 Data Used to Calculate Molar Absorptivity Value II

Peak Number	Absorbance, A	Time, t(sec)	Δ t(sec)
Second Transfer	1.70	3925	0
1 (Sheet 6)	1.618	4520	595
2 (Sheet 6)	1.553	4770	845
3 (Sheet 6)	1.534	4890	965
4 (Sheet 6)	1.541	5180	1255
6 (Sheet 6)	1.512	5395	1470
7 (Sheet 6)	1.490	5660	1735
8 (Sheet 6)	1.458	5905	1980
9 (Sheet 7)	1.413	6085	2160
10 (Sheet 7)	1.365	6320	2395
11 (Sheet 7)	1.337	6625	2700
12 (Sheet 7)	1.331	6755	2830
13 (Sheet 7)	1.329	6870	2945
14 (Sheet 7)	1.273	7110	3185
15 (Sheet 7)	1.270	7225	3300

The plot of the two absorbance values for the solution at the time of transferral and extrapolation to zero time gave an absorbance value of 1.83. This resulted in a molar absorptivity of 5.2×10^4 liter-cm^{-1}-$mole^{-1}$.

A third value for the molar absorptivity was estimated by examining the absorbance of the saturated solution of sodium in ethylenediamine. The absorbance of this solution at a wavelength of 493 mμ was 1.542. The value for A/A_{max} at this wavelength was found tobe 0.217 (see Table 6 below). Assuming the shape of the curve to be independent of concentration yields $A_{max} = 7.1$ for the saturated solution. Since the concentration of the saturated solution is 2.4×10^{-3} M (2), the molar absorptivity is 3.0×10^4 liter-cm^{-1}-$mole^{-1}$.

After allowing the make-up vessel and cell to stand

for more than one week, Dr. Dye made up five more solutions using the sodium that still remained and re-using the ethylenediamine that was now clear due to decomposition over this length of time. The first solution was made by diluting 1.88 ml of saturated solution to a final volume of 8.5 ml ($c = 5.31 \times 10^{-4}$ M). The data obtained from this solution are given in Table 3.

Table 3 Data Used to Calculate Molar Absorptivity Value IV

Peak Number	Absorbance, A	Time, t(sec)	Δ t(sec)
First Transfer	1.217	225	0
6 (Sheet 1)	1.139	400	175
7 (Sheet 1)	1.071	570	345
8 (Sheet 1)	1.009	640	415
9 (Sheet 1)	0.468	1530	1305
Second Transfer	1.167	1830	0
10 (Sheet 2)	1.078	1960	130
11 (Sheet 2)	1.053	2115	285
12 (Sheet 2)	0.968	2295	465
13 (Sheet 2)	0.896	2523	693

The molar absorptivity of 2.4×10^4 was obtained after plotting and extrapolating to zero time the data from the two transferrals.

The second solution was prepared by diluting 1.24 ml of the saturated solution to a final volume of 9.6 ml ($c = 3.10 \times 10^{-4}$ M). The data obtained from this solution are given in Table 4.

Table 4 Data Used to Calculate Molar Absorptivity Value V

Peak Number	Absorbance, A	Time, t(sec)	Δ t(sec)
First Transfer	0.556	240	0
20 (Sheet 4)	0.420	455	215

Table 4 Data Used to Calculate Molar Absorptivity Value V

Peak Number	Absorbance,A	Time,t(sec)	Δt(sec)
21 (Sheet 4)	0.312	640	400
22 (Sheet 4)	0.271	827	587
23 (Sheet 4)	0.222	945	705
Second Transfer	0.275	1120	0
24 (Sheet 5)	0.256	1232	112
25 (Sheet 5)	0.229	1425	305
26 (Sheet 5)	0.200	1602	482

The molar absorptivity of 2.2×10^4 liter-cm^{-1}-$mole^{-1}$ was obtained from extrapolation of these data.

After diluting 1.40 ml of the saturated solution to 6.0 ml, a third solution of concentration, 5.60×10^{-4} M, was prepared. The data for this solution are given in Table 5.

Table 5 Data Used to Calculate Molar Absorptivity Value VI

Peak Number	Absorbance,A	Time,t(sec)	Δt(sec)
First Transfer	1.551	260	0
29 (Sheet 6)	1.489	407	147
30 (Sheet 6)	1.439	530	270
31 (Sheet 6)	1.385	672	412
32 (Sheet 6)	1.360	812	552
33 (Sheet 6)	1.281	1050	790
Second Transfer	1.150	1305	0
34 (Sheet 7)	1.132	1431	126
35 (Sheet 7)	1.104	1553	248
36 (Sheet 7)	1.021	1695	390
37 (Sheet 7)	1.011	2055	750
38 (Sheet 7)	0.924	2820	1515

A molar absorptivity of 3.0×10^4 liter-cm^{-1}-$mole^{-1}$ was obtained from extrapolation of these data.

The data for the last two molar absorptivities were obtained at even a later date than those given in Tables 3-5 above. For a solution of concentration 5.97×10^{-4} M which was treated in the same way as those above, a molar absorptivity of 3.3×10^{4} liter-cm^{-1}-mole^{-1} was obtained. For the last solution of concentration 4.63×10^{-4} M, the value for the molar absorptivity was 3.1×10^{4} liter-cm^{-1}-mole^{-1}.

In order to aid in the interpretation of these results, the oscillator strength was next calculated using the following data and the equation (3)

$$f_i = 4.319 \times 10^{-9} \left[\frac{9\, n_o}{(n_o^2 + 2)^2} \right] \int a_i \, d\bar{\nu}$$

$$\text{or} \quad f_i = (4.319 \times 10^{-9})\,(0.773)\; a_{max} \int A/A_{max} \, d\bar{\nu}$$

where $n_o = 1.454$ (4).

The integral in this equation was evaluated by plotting A/A_{max} against wave number and finding the area under the curve. The values used for this curve are given in Table 6. The area was found to be 5311 cm^{-1}. Using this area and the value obtained from the refractive index substitution, the data in Table 7 were obtained.

Table 7 Calculated Oscillator Strengths for Solutions of Sodium in Ethylenediamine

Molar Absorptivity, a_{max}	Solution Concentration	Oscillator Strengths
5.2×10^{4}	3.49×10^{-4}	0.926
5.2×10^{4}	3.49×10^{-4}	0.926
3.0×10^{4}	2.4×10^{-4}	0.525
2.4×10^{4}	5.31×10^{-4}	0.426

Table 6 Data Used to Calculate the Oscillator Strength

A/A_{max}	Wavelength (mμ)	Wavenumber (x 10^{-2}) (cm^{-1})
0.103	820	122.0
0.139	812	123.2
0.175	800	125.0
0.211	794	125.9
0.247	787	127.1
0.284	781	128.0
0.320	775	129.0
0.356	771	129.7
0.392	764	130.9
0.428	761	131.4
0.465	758	131.9
0.501	752	133.0
0.537	748	133.7
0.573	742	134.8
0.609	735	136.0
0.645	732	136.6
0.682	725	137.9
0.718	719	139.1
0.790	716	139.7
0.826	710	140.8
0.863	703	142.2
0.899	695	143.9
0.935	687	145.6
0.971	679	147.3
1.000	657	152.2
0.971	640	156.2
0.935	635	157.5
0.899	629	159.0
0.863	623	160.5
0.826	619	161.6
0.790	615	162.6
0.754	610	164.0
0.718	608	164.5
0.682	603	165.8
0.645	597	167.5
0.609	594	168.3
0.573	592	168.9
0.537	587	170.4
0.501	584	171.2
0.465	580	172.4
0.428	572	174.8
0.392	565	177.0
0.356	557	179.5
0.320	550	181.8
0.284	535	187.0
0.247	515	194.2
0.211	482	207.5

Table 7 Calculated Oscillator Strengths for Solutions of Sodium in Ethylenediamine (continued)

Molar Absorptivity, a_{max}	Solution Concentration	Oscillator Strengths
2.2×10^4	3.10×10^{-4}	0.390
3.0×10^4	5.60×10^{-4}	0.525
3.3×10^4	5.97×10^{-4}	0.585
3.1×10^4	4.63×10^{-4}	0.550

If the species present is the $Na_2^+ \cdot e^-$ dimer as postulated by Dye and Dewald, then only one electron would absorb to give the 657 peak in sodium-ethylenediamine solutions. An oscillator strength greater than 0.5 would not be expected. However, if for some reason, one mole of electron for each mole of sodium is involved in the absorbance, an oscillator strength near unity would be expected.

II Results of Conductance Measurements

Using the value for the cell constant of 0.2496 cm^{-1}, the data in Table 8 were obtained from the measured resistances of each solution (water in ethylenediamine).

Table 8 Data Obtained from Conductance Measurements of Solutions of Water in Ethylenediamine

Concentration of H_2O(M)	Conductance, L($cm^{-1}ohm^{-1}$)	Δ L
0	0.753×10^{-6}	0
0.139	0.796×10^{-6}	0.043×10^{-6}
0.390	0.858×10^{-6}	0.105×10^{-6}
0.878	1.016×10^{-6}	0.263×10^{-6}

Using the values from Table 8, $\Delta L \times 10^6$ was plotted against the concentration of water in ethylenediamine. Extrapolation to a 1 M solution concentration gave an approximate value of 0.28×10^{-6} $cm^{-1}ohm^{-1}$ for ΔL.

To determine the extent of the reaction,

$$H_2O + en = enH^+ + OH^-$$

the equilibrium constant for the reaction was calculated. Using an approximate value of 50 for the equivalent conductance of each ion in the reaction, the concentration could be obtained for each ion since,

$$\Lambda_i = \frac{1000\,\omega L}{c_i} \simeq 50$$

Since the weight of the ethylenediamine used was 97.3 grams (c = 15 M) and the concentration of the water was 1 M, the equilibrium constant is approximately 2×10^{-12}. This value indicates that water does not react with ethylenediamine to any appreciable extent.

III Mass Spectrometer Results: Nitrogen

After allowing the ethylenediamine to stand in the presence of the sodium metal for approximately three weeks under an atmosphere of helium, a test portion of the gas was collected and analyzed with the use of the mass spectrometer. The results showed peaks due to break down products of ethylenediamine as well as peaks which showed that there was 8.8% hydrogen and 0.6% nitrogen.

DISCUSSION

One of the main purposes of this work was to establish as closely as possible a value for the molar absorptivity of solutions of sodium in ethylenediamine. Directly related to this problem was an experimental test of the plausibility of the proposal that the species present which is responsible for the 657 peak obtained with sodium-ethylenediamine solutions is the ionic-covalent dimer, $Na_2^+ \cdot e^-$. Examination of the data listed in Table 7 reveals that the oscillator strength is probably closer to 0.5 rather than to unity. This would indicate that the species present could be the solvated molecule-ion with its "optical" electron so that only one out of the two electrons absorbs. The molar absorptivity for the sodium-ethylenediamine solution appears to lie between 2.5×10^4 and 4.0×10^4 liter-cm^{-1}-$mole^{-1}$.

It is well to indicate here that the two highest values of the molar absorptivity and oscillator strengths could be in error since they were obtained in the first runs and it was discovered later that much of the saturated solution adhered to the glass and ran into the volumetric vessel only slowly. This would result in a high value for the concentration of the solutions.

The data obtained from the analysis of the gas over the sodium-ethylenediamine solutions with the mass spectrometer indicates that the data reported by Windwer and Sundheim (5) to the effect that nitrogen and hydrogen are formed in a ratio of 2:1 may be incorrect.

REFERENCES

1. E. Becker, R. Lindquist and B. Alder, J. Chem. Phys., 25, 971 (1956).

2. R. Dewald, Ph. D. Dissertation, Michigan State University (1963).

3. L. Pauling and E. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Company, Inc., New York, N. Y.

4. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio (40th Edition).

5. S. Windwer and B. Sundheim, J. Phys. Chem., 66, 1254 (1962).

6. D. C. Stewart and D. Kato, Analytical Chemistry, 30, (1958).