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UNITED STATES AIR FORCE

ELECTRICAL CONDUCTANCE, DENSITY, AND VISCOSITY MEASUREMENTS OF AQUEOUS SOLUTIONS OF HYDROXYLAMINE HYDROCHLORIDE AT 25°C

BY

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Henry S. Nizko, B.S. Captain USAF

GAW/Mech 62-15

SCHOOL OF ENGINEERING

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THESIS

Presented to the Faculty of the School of Engineering of

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Preface

This investigation was conducted for the purpose of contributing knowledge on the properties of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$). In this aim the electrical conductance, density, and viscosity of hydroxylamine hydrochloride were measured. Additionally, the interionic attraction theory of conductance of aqueous solutions of electrolytes, from which evolves the Onsager equation (Ref. 18:449), was applied to data obtained.

While working with the Onsager equation a possible complex trimer ion of hydroxylamine hydrochloride may have been found. Several methods of carrying out further investigations on this trimer are listed in the recommendations.

This report has been prepared in a manner which enables a person with a limited chemistry background to comprehend its contents. No detailed theory has been included, but the bibliography contains many of the books and periodicals related to the field of electrical conductance of electrolytes.

We would like at this time to acknowledge our indebtedness to Dr. Kelso Morris, who recommended this topic, for his very helpful advice via several letters over the past few months. We would wish to acknowledge our indebtedness to Captain George P. Bowman, our thesis advisor, for his patience and help. He postulated the possible complex trimer ion of hydroxylamine hydrochloride. Dr. J. T. DuBois, Chemistry Research Branch, Aeronautical Research Laboratory, Wright-Patterson

Air Force Base, Ohio, and Dr. Larry A. Harrah, Physics Laboratory, Materials Section, Wright-Patterson Air Force Base, Ohio, were consulted on this trimer ion and made several recommendations for further investigation. We would also like to thank William W. Baker for his assistance in obtaining, assembling, and operating laboratory equipment. We would also like to thank our wives for their kind understanding and patience with us during these hectic days.

Jimmie J. Nelson

Henry S. Nizko

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Abstract

This is an investigation that determined the electrical conductance, density and viscosity of aqueous solutions of hydroxylamine hydrochloride at 25°C. A comparison of the experimental results with those obtained by using a theoretical equation developed by Onsager was made. The electrical conductance measurements were obtained by the use of a Leeds-Northrup Wheatstone Bridge and a Jones Conductance Cell in a constant-temperature bath. Cannon-Fenske-Oswald viscometers in the constant-temperature bath were used to obtain the kinematic viscosities. An approximately 25 ml calibrated pycnometer was used to measure densities. The electrical conductance measurements for $NH_2OH \cdot HCl$ indicated that $\Lambda_o = 153.15$ and the slope of the Λ vs. $(C)^{\frac{1}{2}}$ curve in the dilute range (slope = 260.5) was approximately equal to the calculated theoretical value for a 3-1 electrolyte. The density varied linearly with concentration from 0.99707 gm/ml for pure water to 1.0921 gm/ml for a 3.507 molar solution of $NH_2OH \cdot HCl$. The viscosity varied as an approximately straight line with concentration. Corrected values of viscosity ranged from 0.8963 centistokes for pure water to 1.050 centistokes for the 3.507 molar solution. It was recommended that freezing point depression measurements be made on known concentrations of $NH_2OH \cdot HCl$ to verify the possible existence of a cyclic trimer of the hydroxylamine (NH_3OH^+) ion. Tests should be run to determine whether the platinum electrodes were reacting with the NH_3OH^+ ion to form complexes that caused resistance to change with time when a constant potential was applied.

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ELECTRICAL CONDUCTANCE, DENSITY, AND VISCOSITY MEASUREMENTS OF AQUEOUS SOLUTIONS OF HYDROXYLAMINE HYDROCHLORIDE AT 25°C

I. Introduction

Purpose

The primary purpose of this investigation was to determine the electrical conductance, density, and viscosity of aqueous solutions of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) at 25°C. The secondary objective in the study was the application of the Onsager equation (Ref. 18:457) to compare the experimental results for agreement with the theoretical values.

Hydroxylamine hydrochloride was chosen for the study because no data were available on its conductance, density, or viscosity as determined from an extensive literature survey. This also indicated that there was no experimental confirmation of the Onsager equation for solutions of hydroxylamine. The exact ionization of hydroxylamine in aqueous solutions was not known but could be speculated upon by use of the Onsager equation. Another reason for choosing hydroxylamine hydrochloride was that it is a salt of hydroxylamine (NH_2OH), which becomes explosive in nature at higher temperatures. The nature of this explosive instability can be shown by an analogy between hydroxylamine, hydrazine, and hydrogen peroxide, all highly unstable compounds. This analogy is that if hydrazine (NH_2NH_2) is looked upon as a nitrogen analogue of hydrogen peroxide (H_2O_2), then the intermediate aquo-ammonia compound is hydroxylamine (NH_2OH). Other reasons for choosing hydroxylamine hydrochloride were that it is very soluble in water and readily available.

Hydroxylamine hydrochloride is a colorless, crystalline, hygroscopic solid with a melting point of 151°C. It is a strong electrolyte in aqueous solutions. The solubility of $NH_2OH \cdot HCl$ is 830 grams/liter or 12 mol/liter in cold water (17°C).

Background

The "classical" theory of conductance as proposed by Arrhenius stated that the decrease of the equivalent conductance (Λ) of an electrolyte with increasing concentration was considered to be due to a decrease in the relative number of ions, the proposition being given by the ratio

$$\alpha = \frac{\Lambda}{\Lambda_o} \qquad (1)$$

in which α is the "degree of dissociation", and Λ_o is the equivalent conductance at infinite dilution. It was also shown that the tacit assumption involved in the above equation is that the mobilities of the ions do not change with concentration. With the Debye-Huckel theory, it has been shown that the thermodynamic properties of aqueous solutions of strong electrolytes may be more readily accounted for if it is assumed that such electrolytes are substantially completely dissociated in solution. Since strong electrolytes are assumed to be completely dissociated for thermodynamic properties then, obviously, incomplete dissociation assumptions cannot be used to explain conductance. (Ref. 17:322)

Since it is not possible to account for the decrease of the equivalent conductance of strong electrolytes with increasing concentration by postulating a change in the number of ions carrying current, that decrease must be looked for in a diminution of the mobilities of the ions.

According to Debye and Huckel interionic attractions and repulsions lead to two "effects" both of which result in the lowering of ionic mobilities with increasing ion concentrations. These retarding effects are the relaxation of the ionic atmosphere due to an applied potential, and the electrophoretic effect. Their mathematical treatment was subsequently extended by Onsager to include not only the relaxation and electrophoretic effects, but also the natural Brownian movement of the ions. Onsager's equation for the equivalent conductance (Λ) of a solution containing C equivalents of solute per liter is

$$\Lambda = \Lambda_o - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} w\Lambda_o + \frac{(28.94)(z_+ + z_-)}{\eta(DT)^{\frac{1}{2}}}\right]\left[(z_+ + z_-) \quad C\right]^{\frac{1}{2}} \qquad (2)$$

in which z_+ and z_- represent respectively the valence of the positive and negative ions. D and η are the dielectric constant and the viscosity of the solvent, respectively, and T is the absolute temperature. Also

$$w = z_+ z_- \frac{2q}{1+(q)^{\frac{1}{2}}} \qquad (3)$$

$$q = \frac{z_+ z_- \left[1^o_+ + 1^o_-\right]}{(z_+ + z_-)(z_+ 1^o_- + z_+ 1^o_+)} \qquad (4)$$

in which 1^o_+ and 1^o_- are the equivalent ionic conductances at infinite dilution of the cation and anion, respectively. The first term in the brackets in equation (2) accounts for the relaxation effect and the second

for the electrophoretic effect. This equation is the mathematical expression for the Debye-Huckel-Onsager interionic attraction theory of conductance, and is the theoretical equation used in this investigation.

Scope

The investigation involved only aqueous solutions from 0.0005 molar to approximately 3.6 molar. In carrying out the investigation it was necessary to prepare and standardize solutions of hydroxylamine hydrochloride, the procedure for which is outlined in Appendix C. The methods of measuring density and viscosity are outlined in Appendix B.

After obtaining sufficient data on conductance, density, and viscosity to add to the literature, the Onsager equation was compared to experimental results. Measured and known values of conductance, density, and viscosity were applied to the Onsager equation to determine if experimental results were in agreement with values obtained by the theoretical equation.

II. Discussion and Results

Preparation of Hydroxylamine Hydrochloride Solution

Conductance Water. Conductance water was used in preparation of all solutions used in this investigation. This water was prepared by passage of distilled water through a Bantam demineralizer equipped with an ion exchange cartridge (see Fig. 1). All water used had a minimum measured resistance of 7.7×10^6 ohm in a conductance cell with cell constant ($K_c = 1.0753\ cm^{-1}$). Polyethylene tubing carried the water from the demineralizer to the solution, to prevent any contamination. The water was processed immediately prior to preparation of solution to prevent any contamination by standing. Every precaution was taken to minimize the entry of foreign material into the water or solution.

Preparation of Master Solution. Master solutions were used to prepare the individual solutions for the experiment. Two master solutions selected were approximately 0.1 molar and 3.5 molar. These master solutions were prepared by weighing the approximate amount of $NH_2OH \cdot HCl$ on a Type S "Right-A-Weigh" balance to the nearest 0.0001 gram. Sufficient conductance water was added to dissolve the crystalline salt and the contents emptied into a Kimax volumetric flask. The original container was rinsed several times and contents added to the volumetric flask. The flask was then filled to the etched mark. The flask was inverted several times to assure thorough mixing and then the solution was poured into a clean dry polyethylene bottle and stored in a dark cabinet to minimize deterioration from sunlight.

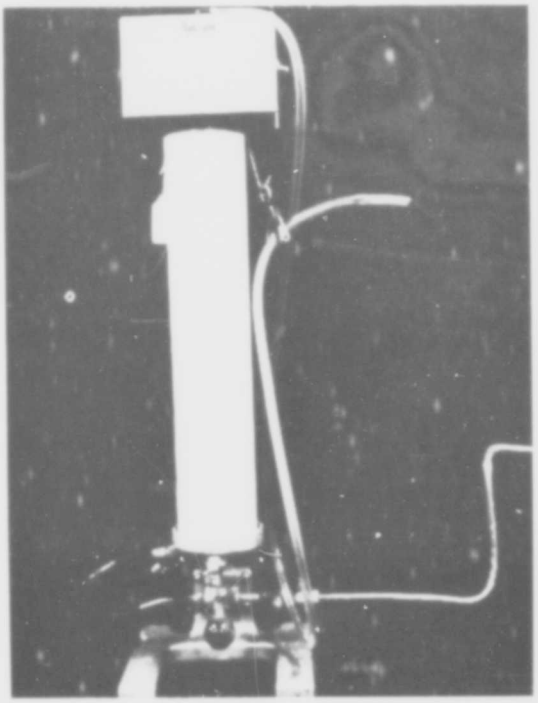

Fig. 1 Bantam Demineralizer

Individual Solution Preparation. Each desired concentration of solution was prepared by combining a specific amount of the master solution with conductance water. A simple ratio calculation was used to establish amount of master solution to use. A Kimax pipette was used to measure the amount of master solution and this was drained into a Kimax volumetric flask (most solutions were prepared in the 1000 ml flasks). The flask was filled to the proper mark with conductance water and the contents poured into polyethylene bottles with tight caps for storage. These solutions were prepared as close as possible to the time of their standardization and use.

Standardization of Hydroxylamine Hydrochloride Solution

The standardization procedure used for $NH_2OH \cdot HCl$ was the method outlined by Bray (Ref. 2:1363). This method uses standardized $KMnO_4$ as the titration measuring medium and is covered in detail in Appendix C. The sample preparation consists of adding an excess of ferric sulfate solution and concentrated sulfuric acid to the sample to be standardized and then boiling this mixture for a minimum of ten minutes. Bray (Ref. 2:1363) indicates that five minutes are sufficient, however, it was noted that samples boiled vigorously for at least ten minutes gave much more consistent results. Conductance water was added to the solution prior to boiling to prevent evaporation to dryness.

Another problem that was encountered was that of not adding a large enough excess of ferric sulfate ($Fe_2(SO_4)_3$). According to Treadwell (Ref. 24) if only slightly more than the theoretical amount of ferric ion is added, the oxidation of the hydroxylamine does not take place entirely

by the equation

$$2NH_2OH + 4\ Fe^{+++} \rightleftharpoons 4Fe^{++} + N_2O + 4H^{+} + H_2O$$

but part of the substance is oxidized to nitric oxide (NO) as indicated in the following equation

$$2NH_2OH + 6\ Fe^{+++} \rightleftharpoons 6Fe^{++} + 2NO + 6H^{+}$$

The occurrence of both reactions makes it impossible to obtain exact results.

The ferric salt concentration problem and the size of the Machlett burette (see Fig. 14) required that the size of the $NH_2OH \cdot HCl$ sample had to vary for the different concentration ranges. This size variation was achieved by either the use of a different size pipette or by dilution techniques. The dilution technique was only required for solutions of concentrations of 1.0 molar or greater. The accuracy of the dilution technique was not comparable to the use of pipette measurements, but was within acceptable limits. The higher concentrations were not as quantitatively important for this investigation as the dilute concentrations which were obtained in total by use of the pipette measurement technique.

Conductance Measurements

Conductance was determined by taking resistance measurements of a $NH_2OH \cdot HCl$ solution contained in a Jones Conductance Cell. The cell was immersed in an aquarium-type thermostat bath with a precision controlled temperature of 25°C. Resistance readings were made by balancing a Wheatstone Bridge, one leg of which contained the Jones Conductance Cell. Specific conductance (L_s) was calculated by use of the equation

$$L_s = \frac{K_c}{R} \tag{5}$$

where K_c is the cell constant. Equivalent conductance (Λ) was obtained by the equation

$$\Lambda = \frac{1000\ Ls}{C} \tag{6}$$

where C is the concentration in equivalents/liter.

A phenomenon of an irreversible reaction takes place when an a-c current is applied to aqueous solutions of $NH_2OH \cdot HCl$, which causes a destruction of the salt and an increase in the number of available ions, thereby decreasing resistance with time (see Fig. 2). The destruction of the 0.1 molar $NH_2OH \cdot HCl$ solution was observed when the concentration of the solution was found to have decreased by 4 percent after being subjected to a 5 volt potential for 25 hours. The technique used to obtain the conductance for zero time or before any change took place in the solution was to obtain equilibrium temperature and then to apply potential and take balanced Wheatstone Bridge readings of resistance at

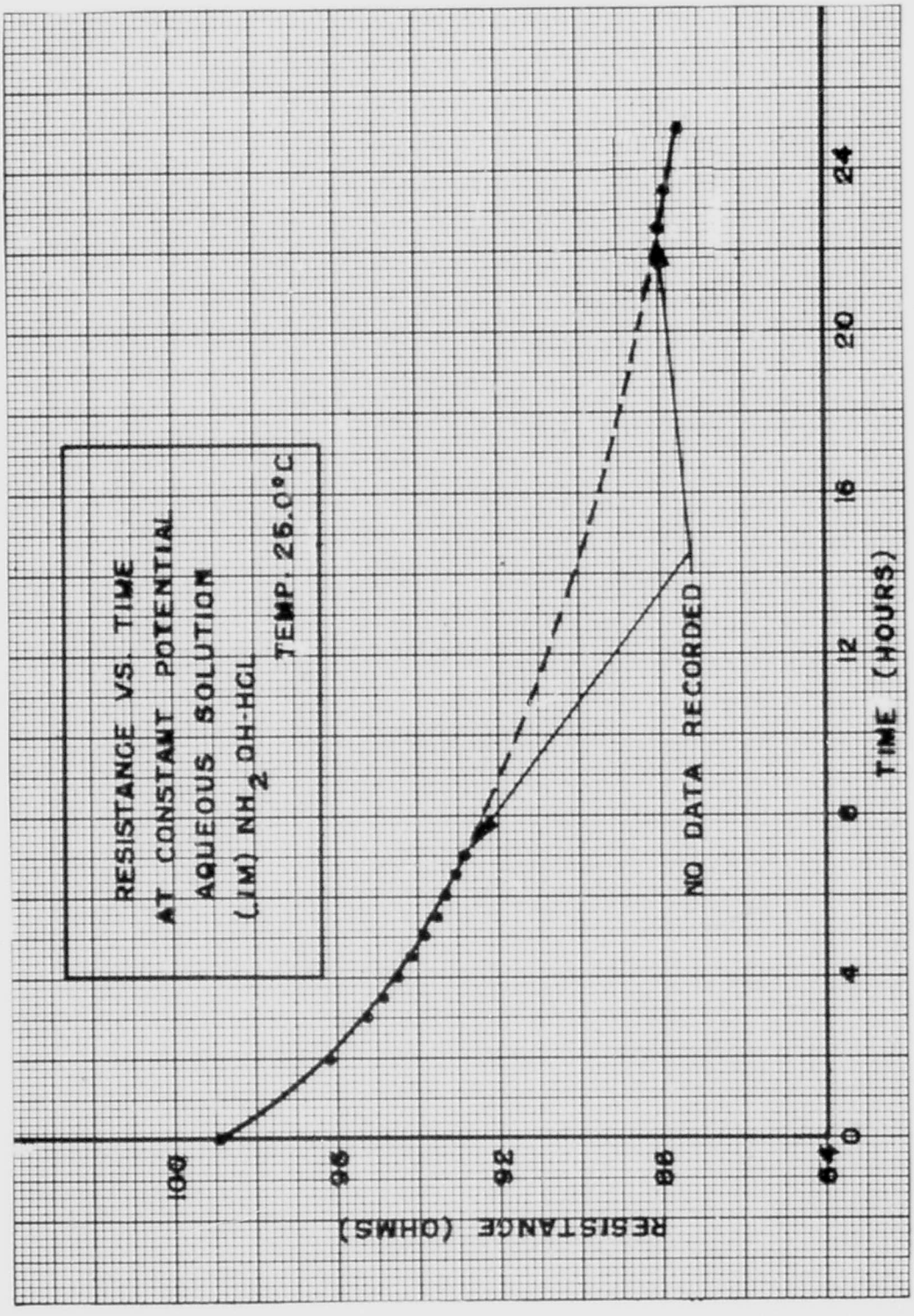

Fig. 2 Resistance vs Time at Constant Potential
0.1 molar NH_2OH·HCl Solution

30 seconds, 1 minute, and 2 minutes. These readings were extrapolated back to zero time to obtain the resistance or conductance at zero time. As can be seen in Fig. 2 the rate of change in resistance for a time interval of a few minutes is linear, this fact permitted the linear extrapolation mentioned above. Several determinations at frequencies of 500, 1000, and 2000 cps were made and indicated no differences in rate of change of resistance due to polarization. The potential was varied from 0.3 to 10 v, but no halt or reversal of the decomposing reaction was observed. A possible explanation for this decomposition is the complexation tendencies of $NH_2OH \cdot HCl$ with the platinum electrodes. Several suggestions are made in the recommendations for future investigations of this possible complexing tendency.

Curves of equivalent conductance of $NH_2OH \cdot HCl$ for concentrations varying from 0 to 3.57 molar are shown in Fig. 3. Curves of equivalent conductance for the dilute range of $NH_2OH \cdot HCl$ and KCl are shown in Fig. 4. The curve for KCl was obtained from Maron (Ref. 18:449), but this same data appears in numerous other publications. The equivalent conductance at infinite dilution (Λ_o) was found by extending the straight line curve for the dilute range until it intercepted the vertical axis. This value was found to be 153.15 mho/cm-equiv; that for KCl is 149.9 mho/cm-equiv. The slope for the dilute range of $NH_2OH \cdot HCl$ is 260.5 for KCl it is 93.84. The slope and intercept for $NH_2OH \cdot HCl$ was calculated by the least-squares method (see Appendix F). There is a definite break in the curves at approximately $(C)^{\frac{1}{2}}$ equal to 0.15. Though not pronounced a break can be observed on the KCl curve. This break is the dividing point for dilute

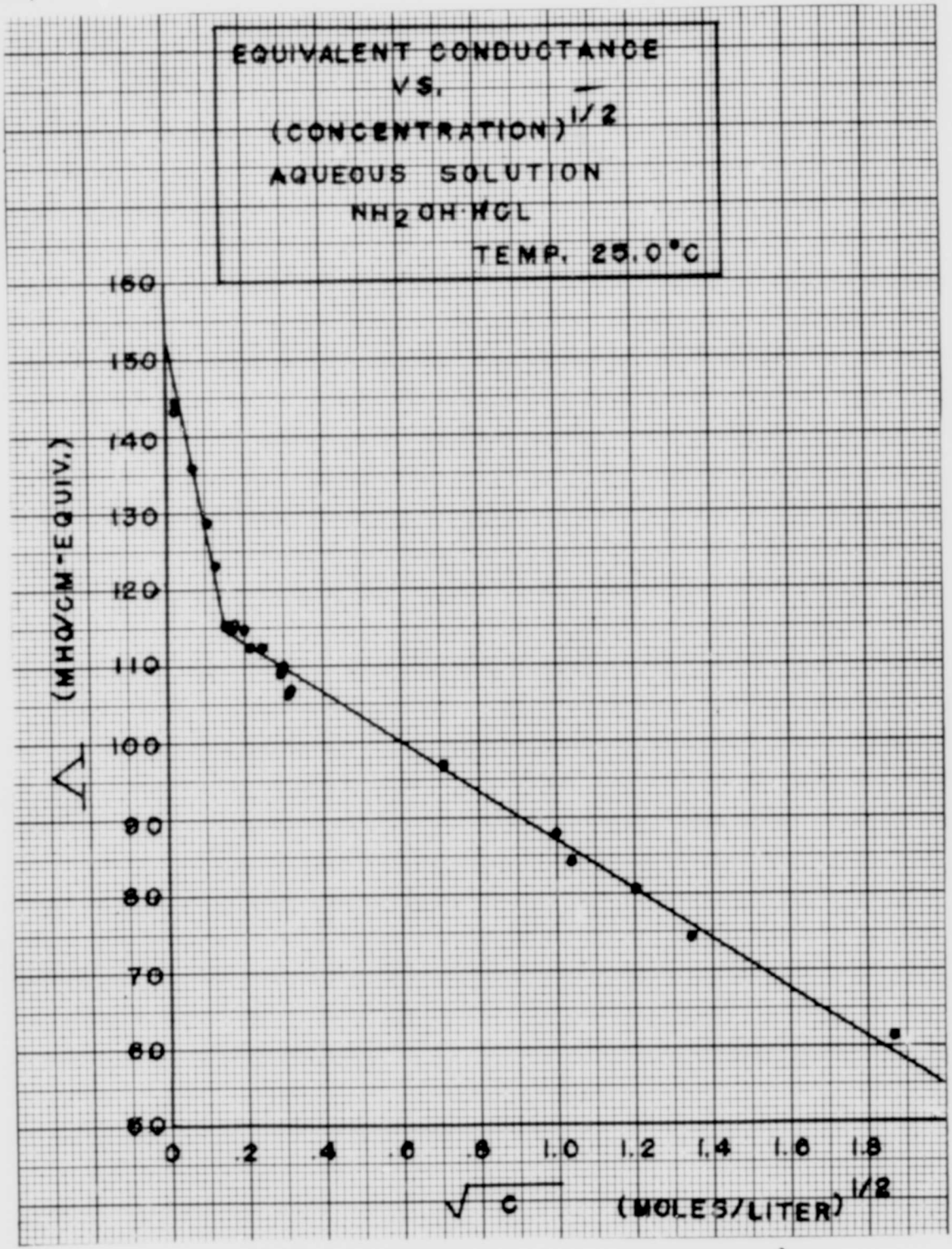

Fig. 3 Equivalent Conductance vs (Concentration)$^{\frac{1}{2}}$
Aqueous Solutions $NH_2OH.HCl$

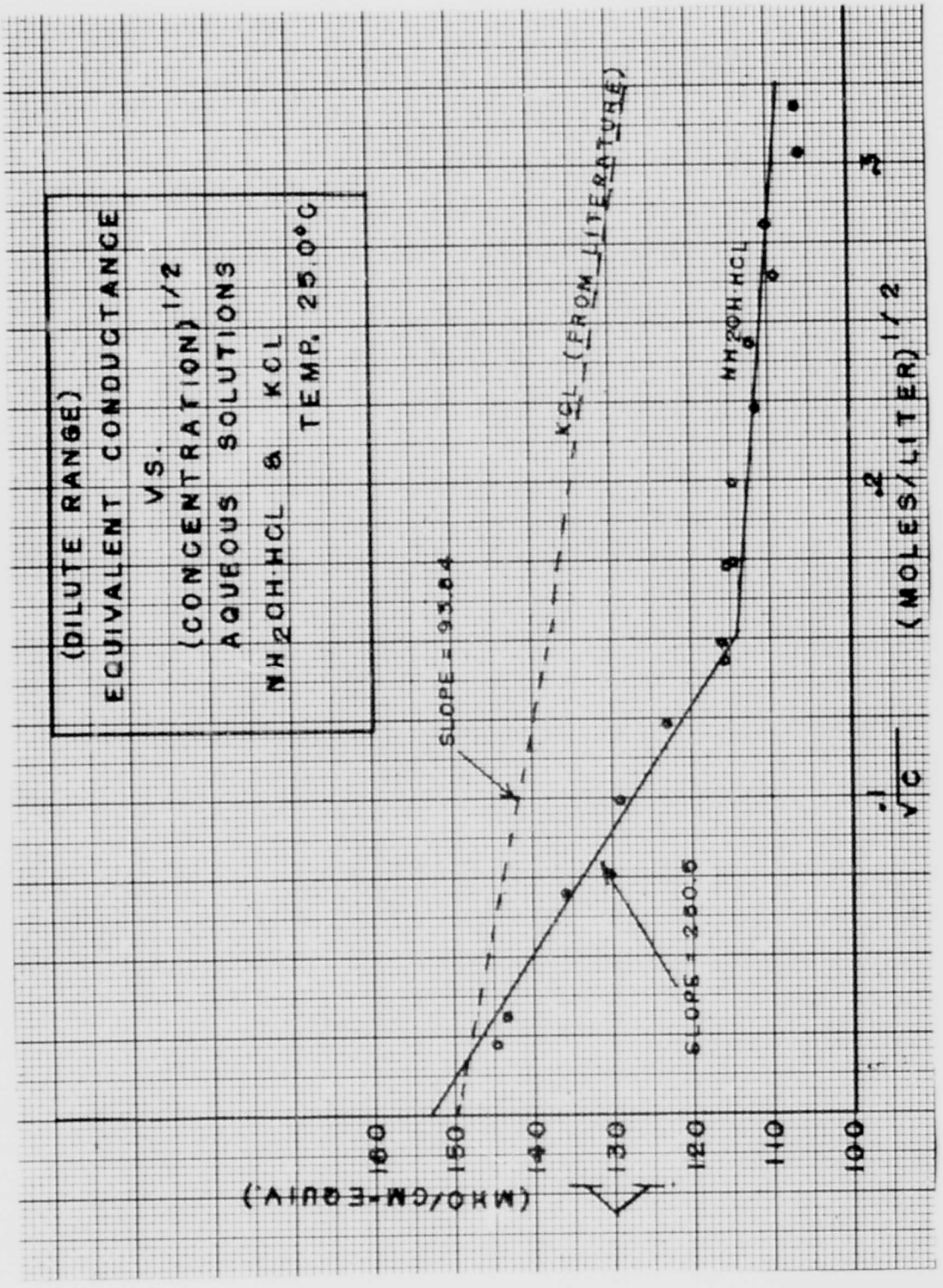

Fig. 4 Equivalent Conductance vs $(\text{Concentration})^{\frac{1}{2}}$
Aqueous Solution $NH_2OH \cdot HCl$ (Dilute Range)

and concentrated ranges of concentration. The Onsager equation is applicable only to the dilute range of strong electrolytes.

Using the experimentally obtained value of Λ_o, the Onsager equation was applied to different postulated theoretical electrolyte-type combinations for which values of slope were then calculated. The following listing shows type of electrolyte and slope based on the assumption that the Cl^- ion is the negative ion:

Type of Electrolyte	Slope	
1-1	94.7	
2-1	187.7	
2-2	367.2	
3-1	284.8	(See Appendix F)

According to the Onsager equation the 3-1 electrolyte most closely approximates the measured slope of 260.5. A relative error of 8.17 percent exists between the two values. An ionic structure which could possibly account for the presence of a 3-1 electrolyte is the complex cyclic trimer ion shown in Fig. 5.

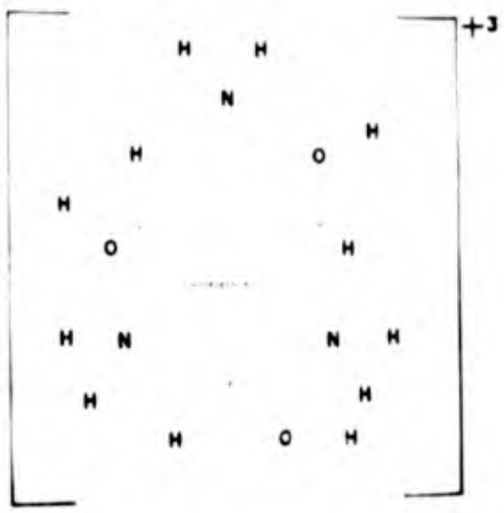

Fig. 5 (Possible) Cyclic Trimer NH_3OH^+ Ion

Density Measurements

The density measurements were made with a glass pycnometer (specific gravity bottle) of approximately 25 ml capacity (see Fig. 12). The pycnometer was calibrated as outlined in Appendix B. In making density measurements several samples of each solution were measured to assure reliable results. In order to avoid increase in weight of the pycnometer with successive weighings, due to adsorption of water on the glass surface, the following technique was adopted: The empty bottle was immersed in the aquarium type constant-temperature bath and allowed to come to equilibrium (about 15 minutes). The bottle was then removed from the bath, dried with a lintless towel and placed in a desiccator for five minutes. At the end of five minutes the empty pycnometer was weighed. The same procedure was used with the filled pycnometer and the volume was obtained by subtracting the empty weight from the full weight (see Appendix F for sample calculation).

The results as shown in Fig. 6 are tabulated in Appendix E. The density of the solution varied as a straight line function of concentration from the density of pure water (0.99707 gm/ml) to that of 1.0921 gm/ml for a solution concentration of 3.507 molar. The concentration accuracy of the more concentrated solutions (greater than 1 molar) due to the dilution technique required in preparation were not as reliable as the more dilute samples, therefore the curve is believed to be approximately as shown in Fig. 6. It should be noted that the very dilute solutions (less than 0.001 molar) were not tabulated as they were so close to the density of pure water than the variance between measured samples was greater than the variance from pure water and therefore were of no practical use.

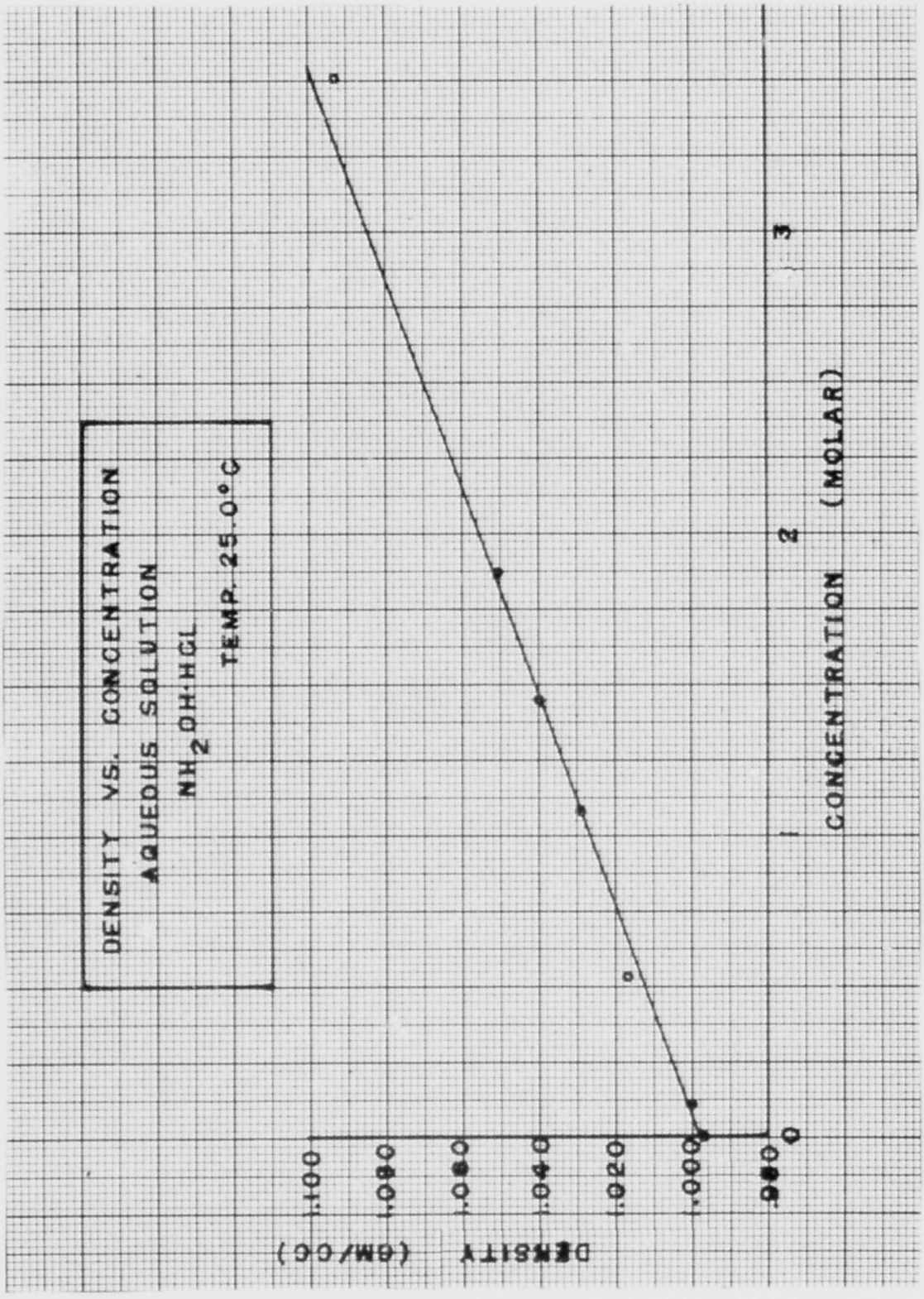

Fig. 6 Density vs Concentration
Aqueous Solution $NH_2OH \cdot HCl$

Viscosity Measurements

The viscosity measurements for the hydroxylamine hydrochloride solutions (see Fig. 7) were obtained by use of a certified calibrated Cannon-Fenske-Oswald type viscometer. The method that was used is outlined in Appendix B and sample calculations are listed in Appendix F. Table II of Appendix E gives the tabulated data.

A stop watch was used to record the efflux time for each sample and when the elapsed time did not agree within a few tenths of a second for the several runs, the solution was removed, the viscometer was cleaned thoroughly, a new solution of 5.0 ml was inserted into the viscometer from a pipette, and a redetermination was made.

It can be seen from Fig. 7 that the viscosity varied as approximately a straight line in the dilute region. The slope increased slightly in the more concentrated range, this was possibly due to an error in preparation by the dilution technique. The corrected values ranged from 0.8963 centistokes for pure water to 1.050 centistokes for the 3.507 molar solution.

The uncorrected curve as seen in Fig. 7 is the kinematic viscosity, as calculated in centistokes from the experimental data. The viscosity data had to be corrected because the conductance water that was used was distilled water that had had the ionic salts removed by the demineralizer shown in Fig. 1. This demineralizer (ionic exchange column) does not remove any bacteria or low boiling organic material from the water. The correction factor was obtained by measuring several samples of conductance water in both of the viscometers. The kinematic viscosity was calculated to be

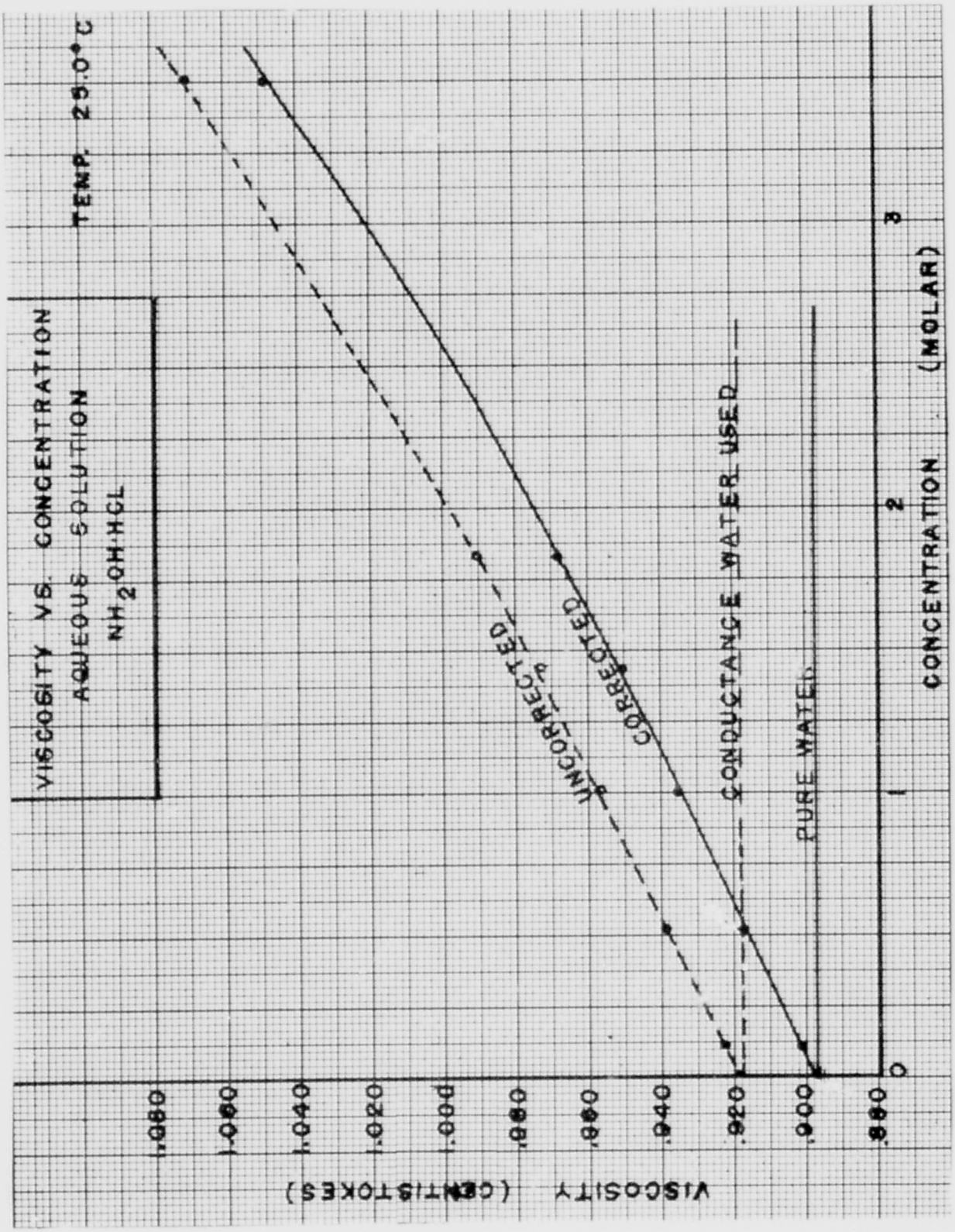

Fig. 7 Viscosity vs Concentration Aqueous Solution $NH_2OH \cdot HCl$

0.9174 centistokes versus the U.S. Bureau of Standards value of 0.8963 centistokes. The Bureau of Standards' value was subtracted from the calculated conductance water value and this difference was found to be 0.0211 centistokes. It was assumed that the conductance water caused a constant error of 0.0211 centistokes, therefore the error was subtracted from each calculated value to obtain the corrected curve shown in Fig. 7.

III. Conclusions and Recommendations

Electrical Conductance

Aqueous solutions of $NH_2OH \cdot HCl$ behave as a strong electrolyte. The equivalent conductance (Λ) is in the same order of magnitude as that of KCl. The slope of Λ versus $(C)^{\frac{1}{2}}$ curve for $NH_2OH \cdot HCl$ in the dilute range of concentrations is 260.5 as compared to 93.84 for KCl. This would indicate that some sort of complexation is occuring in $NH_2OH \cdot HCl$ solution. A theoretical calculation that used the assumption that $NH_2OH \cdot HCl$ was a 3-1 electrolyte and that the Cl^- ion constituted the anion indicated that the slope of this theoretical electrolyte was 284.8 or within 8.17 percent of the experimental value. The Λ_o for KCl is 149.9 and the experimental Λ_o for $NH_2OH \cdot HCl$ is 153.15. A marked difference between KCl and $NH_2OH \cdot HCl$ is that KCl solutions showed no changes in resistance with time with a constant potential applied. The $NH_2OH \cdot HCl$ showed a very definite change of resistance with time with a constant potential applied. Different frequencies and potentials applied to the solutions showed no variance in the resistance due to polarization, although the "resistance change with time" phenomenon still continued. At the end of 25 hours with an applied 5 volt potential on 0.1 molar solution of $NH_2OH \cdot HCl$ a 4 percent change in concentration was observed, indicating a rearrangement of the ion structure. It is possible that the NH_3OH^+ ion formed a complex ion with the platinum electrode.

It is recommended that future investigations be made to verify the ionic structure of aqueous solutions of $NH_2OH \cdot HCl$. One method of doing this would be to measure the freezing point depression of various dilute

solutions of $NH_2OH \cdot HCl$. This would indicate the number of ions in the solution and would possibly substantiate the presence of a cyclic trimer ion as shown in Fig. 5.

A method to determine if there is complex ionization is to place a d-c potential on the conductance cell in addition to the already present a-c potential. The wave on the oscilloscope should be an undistorted sine wave, and the resistance should decrease with time. A reversal of the d-c leads should not change the shape of the wave. If a distorted wave appears this would indicate that the NH_3OH^+ ion is complexing with the platinum electrode and in effect causing the conductance cell to act as a rectifier.

Density

Values obtained in the density measurements varied approximately linearly with changes in concentration. No unusual deviations were observed or difficulties encountered that would give cause to question the validity of results obtained.

Viscosity

The method of measuring viscosity was very precise. The temperature was accurately controlled ($\pm 0.02^\circ C$), the viscometers were precision instruments calibrated and certified by the manufacturer, and the efflux times of at least three runs agreed to within a few tenths of a second. In view of the above the only possible difference in viscosity would be due to the difference in the conductance water used and the water used by the U. S. Bureau of Standards. A correction factor was used to adjust the experimental

data to a more correct value which would be obtained if U. S. Bureau of Standards water was used. The experimental value obtained for the conductance water was within 2.4 percent of the value given by U. S. Bureau of Standards for pure water.

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Appendix A

Conductance Measuring Method

General

Conductance was determined by taking resistance measurements of a solution contained in a Jones Conductance Cell (see Fig. 8). The cell was immersed in an aquarium-type thermostat bath with a controlled temperature of 25.00° ± .015°C (see Fig. 9). Resistance readings were made by balancing a Leeds and Northrup Jones Conductance Bridge (see Fig. 11). One leg of the bridge contained the Jones Conductance Cell. A Hewlett-Packard Oscillator (Model 201-C) was used to provide a 2000 cps frequency at a voltage of approximately 3 volts. Bridge balancing was done by using a General Radio Corporation Type 1231-B Amplifier and Null Detector. In conjunction with the amplifier, a General Radio Corporation Type 1231-P5M Adjustable Filter was used to reduce harmonics and background noise. A Dumont Type 304-H Oscilloscope was used for a quick visual indication of the null point when balancing the bridge. A schematic diagram of the conductance measuring apparatus is shown in Fig. 10.

The bridge has a capability of measuring resistance with an accuracy of ± 0.02 percent. For all readings of resistance, five or six significant figures were recorded. The amplifier sensitivity is less than 8 microvolt input at 1 kc for 1 percent indication on meter, which made possible the

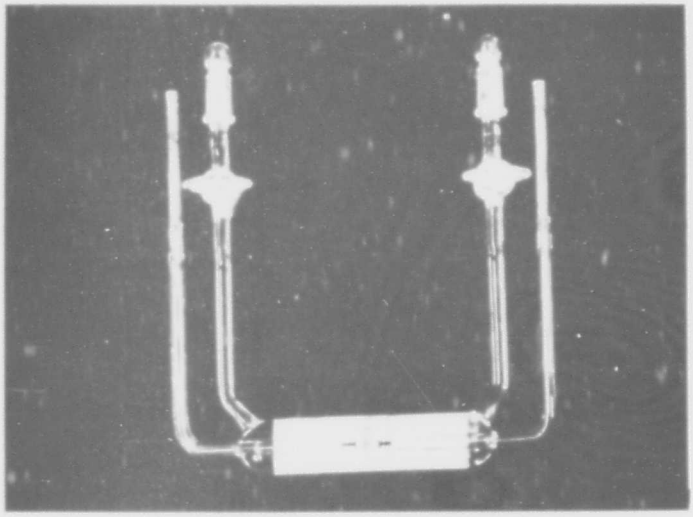

Fig. 8 Jones Conductance Cell

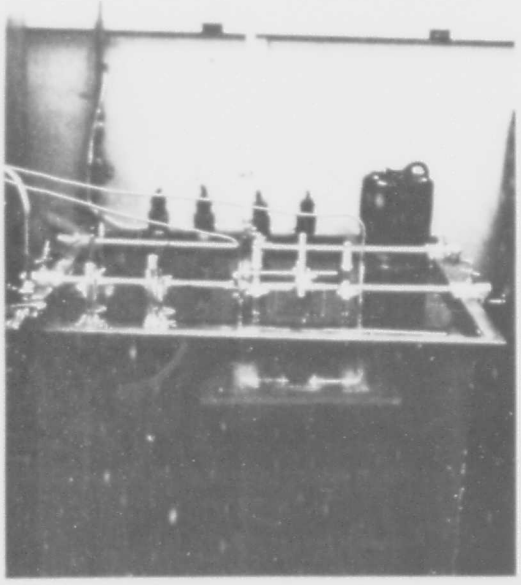

Fig. 9 Aquarium-Type Constant-Temperature Bath

Fig. 10 Schematic Diagram of Conductance Measuring Equipment

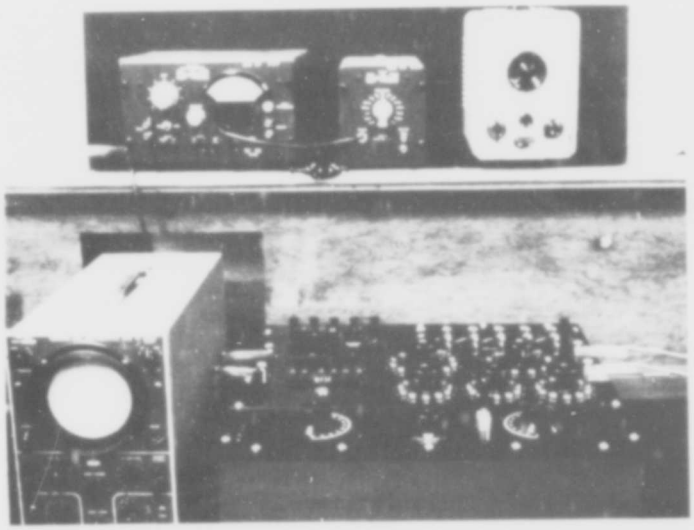

Fig. 11 Conductance Measuring Equipment

large number of significant figures. Since concentration could not be measured with a high degree of accuracy or significance, it was the controlling parameter in determining the number of significant figures for equivalent conductance.

Procedure

To determine a value of resistance a known solution was put in a Jones Conductance Cell and immersed for 20 minutes in a controlled-temperature bath to insure an equilibrium temperature of 25°C. At the end of this time interval the electrodes were connected to the electrical circuit of the bridge, and bridge balancing was started immediately. Due to an irreversible reaction which caused resistance to decrease with time, readings were taken at 30 seconds, 1 minute, and 2 minutes. These readings were then extrapolated back to zero time to obtain resistance at the start of the reaction. Several determinations at various frequencies were made and indicated no differences in resistance due to polarization.

After a determination, the cell was emptied, rinsed and refilled with the same solution and the above procedure repeated. An average value of resistance (R) was then obtained for several determinations. Specific conductance (L_s) was calculated by use of the equation

$$L_s = \frac{K_c}{R} \tag{5}$$

where K_c is a cell constant. Equivalent conductance (Λ) was obtained by use of the equation

$$\Lambda = \frac{1000\ L_s}{C} \tag{6}$$

where C is the concentration in equivalents/liter.

Appendix B

Density and Viscosity Measurement Methods

Density

The density of each solution was determined at 25°C with a glass pycnometer of the "specific gravity bottle" type shown in Fig. 12. The pycnometer was dried carefully, weighed, and then filled with conductance water. It was suspended in the thermostat bath for 15 minutes, and as the water expanded with rise in temperature the excess was wiped off with a piece of filter paper. When the water was at the temperature of the bath, the pycnometer was removed, wiped with a lintless paper napkin, and allowed to stand for five minutes inside a desiccator filled with dry silica gel. The pycnometer was then placed in the balance case and weighed. A little more water was added, and the determination repeated. At least three determinations were made to obtain the weight of the water in the pycnometer. This established the volume of the pycnometer.

The calibrated pycnometer was rinsed thoroughly with one of the solutions and the weight of the solution required to fill the pycnometer was determined in the manner described above.

The volume of the pycnometer at 25°C was calculated from the weight of water that it contained. The density of water at 25°C is 0.99707 gm/ml (Ref. 9). The density of the solution was calculated by dividing the weight of the solution by the volume of the pycnometer.

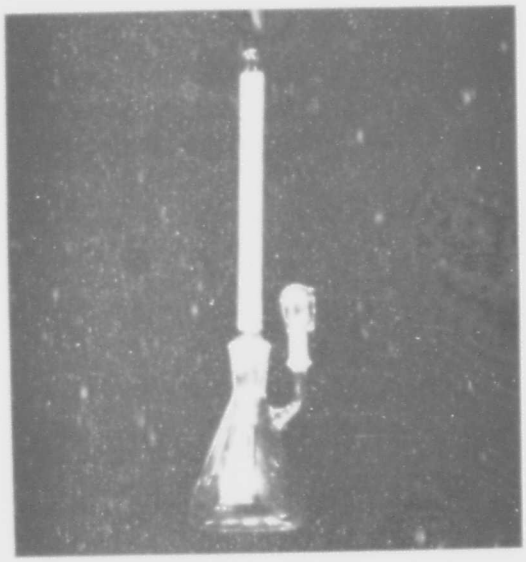

Fig. 12 Pycnometer (approx. 25 ml)

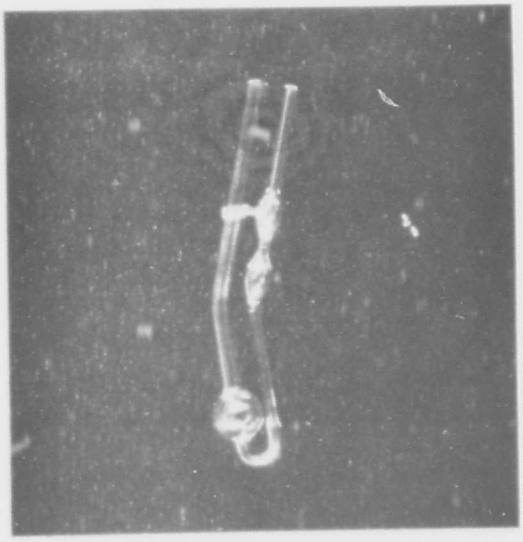

Fig. 13 Cannon-Fenske-Oswald Viscometer

Viscosity

The viscosity of each solution was determined at 25°C with a viscometer of the Cannon-Fenske-Oswald type shown in Fig. 13. The viscometer was cleaned with hot sulfuric acid and potassium dichromate and then rinsed and dried by aspirating through clean air. The viscometer was then clamped vertically in the thermostat bath in such a position that it could be viewed easily, and 5.0 ml of conductance water was added from a pipette. A dust-free rubber hose was attached to the smaller tube of the viscometer, and the liquid was drawn up into the enlarged bulb and above the upper mark. The quantity of liquid was sufficient to fill the lower bend and extended up slightly into the larger tube.

The liquid was then allowed to flow down through the capillary, and a stop watch was started when the meniscus passed the upper mark and stopped when it passed the lower mark. Three or four determinations of the time of efflux were made. When they agreed closely it was assumed that the viscometer was clean.

The above measurements were repeated with the solutions of the experiment. To obtain the viscosity of a solution in centistokes the efflux time in seconds was multiplied by the viscometer constant. The viscometer constant was calibrated by the manufacturer according to standards established by the U. S. Bureau of Standards. The standards specify that viscosities will be based on the new value for water adopted by the U. S. Bureau of Standards and The American Society for Testing Materials, July 1, 1953. The new viscosity basis is 1.0038 centistokes for water at 68°F.

Appendix C

Preparation and Standardization of Hydroxylamine Hydrochloride Solutions

General

The $NH_2OH \cdot HCl$ solutions were prepared by dilution from a master solution. This master solution was prepared by weighing a sample of the salt and dissolving it in conductance water that had a measured specific conductance of less than 7×10^{-7} mho/cm. This water was obtained by use of Bantam Demineralizer (see Fig. 1) with distilled water as starting material. All solutions were stored in polyethylene bottles which were tightly capped and placed in a dark cabinet when not in use. Solutions were standardized and used as soon as possible after preparation to prevent their possible deterioration. The $NH_2OH \cdot HCl$ solutions were standardized by reducing a $Fe_2(SO_4)_3$ solution and titrating the Fe^{+2} with standard 0.1 N $KMnO_4$.

Preparation of Standard 0.1 N $KMnO_4$ Solutions

A method as outlined by Willard (Ref. 26:222) was followed in the preparation of a standard potassium permanganate solution. A sample of approximately 3.3 g. of $KMnO_4$ was dissolved in 200 ml of warm distilled water. When all of the crystals had dissolved the solution was poured into a Kimax 1000 ml volumetric flask and distilled water added up to the mark. The solution was thoroughly mixed and allowed to stand for 24 hours

or more to allow all organic matter in the water to be oxidized and manganese dioxide (MnO_2) to precipitate out of solution. The clear portion of solution was siphoned off thru a glass siphon and poured into a stoppered clean glass bottle. The solution was stored in a dark cabinet to prevent deterioration.

The $KMnO_4$ solution was standardized by the sodium oxalate method. A special grade of sodium oxalate of known purity factor (1.0012) was used. The sodium oxalate was dried for a minimum of two hours in a drying oven at 105° - 110°C. Three samples of the material weighing about 0.3g each were placed in 400 ml erlenmeyer flasks. Each sample was labeled and the exact weight of the sample recorded. A dilute solution of 5 percent sulfuric acid had previously been prepared by boiling for 10-15 minutes and cooling to room temperature (27° to 30°C). To each sample 250 ml of the acid solution was added and stirred until all of the sodium oxalate dissolved. The $KMnO_4$ solution to be standardized was placed in an automatic Machlett burette (see Fig. 14) and 39-40 ml of the $KMnO_4$ was titrated into the sodium oxalate solution. The solution was allowed to stand until all pink color disappeared. If this color did not disappear in approximately 45 seconds the sample was discarded and another begun adding a few ml less of permanganate solution. The solution was then heated to 55°-60°C and the titration performed at these temperatures until a faint pink color persisted for 30 seconds. Particular care was taken to allow each drop of $KMnO_4$ to decolorize before the next drop was added. When the end-point was reached the amount of $KMnO_4$ used was recorded. The normality of the

Fig. 14 Automatic Machlett Burette

$KMnO_4$ solution was calculated by the following equation

$$\text{Normality of } KMnO_4 = \frac{(\text{Wt. of Sodium Oxalate})(\text{Purity Factor})}{(\text{ml of } KMnO_4)\ (\text{Milliequivalent Wt. of Sodium Oxalate})} \qquad (7)$$

The standardization reaction is

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 10CO_2 + 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Standardization of Hydroxylamine Hydrochloride Solutions

A method as outlined by Bray (Ref. 2:1363) was followed in the standardization of $NH_2OH \cdot HCl$ solutions. A Kimax pipette was used to measure 3 samples of $NH_2OH \cdot HCl$ solution into three 400 ml Erlenmeyer flasks (different sized samples were used to keep the volume of the titration products from becoming too large, and to prevent a side reaction caused by concentrated $NH_2OH \cdot HCl$ reacting with the acid solution of $Fe_2(SO_4)_3$ forming NO). The sample was diluted with approximately 50 ml of conductance water, then 15 ml of 12N H_2SO_4 and 50 ml of $Fe_2(SO_4)_3 \cdot 9H_2O$ solution (40 g/liter) were added.

The solution was then boiled vigorously for at least 10 minutes (high values of concentration were obtained if boiling time was shorter). The boiling destroys the NH_2OH by converting the $Fe_2(SO_4)_3$ to $FeSO_4$ by the following reaction

$$2NH_2OH \cdot HCl + 2Fe_2(SO_4)_3 \rightarrow N_2O + 4FeSO_4 + 2H_2SO_4 + H_2O + 2HCl$$

The solution was diluted to approximately 250 ml with distilled water and cooled to room temperature (27° to 30°C). The sample was titrated with

the approximately 0.1N standard $KMnO_4$ solution. The amount of $KMnO_4$ used for each sample was recorded. The molarity of $NH_2OH \cdot HCl$ was calculated by the following equation

$$\text{Molar Conc. of } NH_2OH \cdot HCl = \frac{(\text{ml of } KMnO_4)(\text{Normality of } KMnO_4)}{(\text{ml of } NH_2OH \cdot HCl)\ (2)} \qquad (8)$$

Appendix D

Calibration of Jones Conductance Cells and Beckman Thermometer

Jones Conductance Cells

The electrodes were platinized by filling the cells with a solution containing 3g of platinic chloride and 0.02g of lead acetate in 100 ml of water, and connecting them to two dry cells connected in series. Valves on the conductance cells were left open to permit evolved gases to escape. After the electrodes were coated with platinum black, the solution was removed and the cells were washed thoroughly with distilled water. Traces of chlorine adsorbed from the plating solution were removed by continuing the electrolysis, with the same connections, in a dilute solution of sulfuric acid.

The cells were rinsed thoroughly and filled with conductance water and the resistance was determined. The cells were removed, rerinsed, and refilled until the measured resistance was constant, showing that any contaminating electrolytes had been rinsed out.

When a cell was clean as determined by a constant resistance with conductance water, it was rinsed three times with a 0.01N potassium chloride solution, and then the resistance was determined with this solution filling the cell. Additional readings were taken, using fresh samples of the solution until successive determinations agreed closely.

The specific conductance (L_s) for 0.01N potassium chloride is 0.001413 reciprocal ohms (mho) at 25°C. (Ref. 3). The observed resistance (R) for

the 0.01N potassium chloride solution was multiplied by its specific conductance to obtain the cell constant. Mathematically,

$$K_c = L_s R \tag{9}$$

The specific conductance of other solutions was calculated by using the above relation and substituting the value of the cell constant and the observed resistance.

Beckman Thermometer

An aquarium-type thermostat bath was used to maintain an exact temperature of 25.00° ± .015°C. The bath is provided with a Beckman Thermometer which is used to determine temperatures to one-hundredth of a degree centigrade. This thermometer can be made to read at high or low temperatures by simply removing or adding mercury to the column as the case may be. The thermometer must be calibrated after any change in the mercury column.

An initial calibration was performed by use of a Leeds and Northrup Precision Potentiometer No. 8662 and a copper vs. constantan thermocouple. A bath of crushed ice made from distilled water was used as a zero temperature reference junction. In calibration, the potentiometer was set to the predetermined emf for 25.00°C and the bath temperature was changed to correspond to this emf. This temperature was maintained for a period of time sufficient to insure equilibrium, at which time the reading on the Beckman was noted. This procedure was repeated twice as a check with identical readings obtained each time. This reading was the calibrated value for 25.00°C. Temperatures accurate to four significant figures were easily maintained.

Appendix E

Tabulated Data

Table I

Conductance Data of Aqueous Solutions of Hydroxylamine Hydrochloride at 25°C

$NH_2OH \cdot HCl$ Concentration C (moles/liter)	Conductance Cell Constant K_c (cm^{-1})	Resistance R (ohm)	Specific Conductance L_s ($mho\text{-}cm^{-1}$)	Equivalent Conductance (mho/cm-equiv)
0.000535	1.0753	13,928	0.0000772	144.3
		13,948*	0.0000777	145.2
0.00102	1.0753	7,373	0.000146	143.0
		7,365	0.000146	143.0
0.00475	1.0753	1,665.0	0.0006459	135.8
		1,665.9	0.0006455	135.9
		1,666.6	0.0006452	135.9
0.0100	1.0753	835.99	0.001286	128.6
		836.00	0.001286	128.6
0.0152	169.63	90,838	0.001860	122.7
		91,212	0.001868	123.2
0.02067	1.0753	449.00	0.002395	115.85
		448.86	0.002396	115.90
0.03032	1.0753	307.55	0.003496	115.3
		307.56	0.003496	115.3
0.03046	1.0753	307.75	0.003494	114.7
0.04023	1.0753	233.67	0.004602	114.4
		233.58	0.004603	114.4
0.05050	1.0753	190.30	0.005650	111.9
		190.63	0.005640	111.7

$NH_2OH \cdot HCl$ Concentration C (moles/liter)	Conductance Cell Constant K_c (cm^{-1})	Resistance R (ohm)	Specific Conductance L_s ($mho\text{-}cm^{-1}$)	Equivalent Conductance (mho/cm-equiv)
0.05955	1.0753	161.21	0.006670	112.0
		161.09	0.006675	112.1
0.07071	1.0753	139.51	0.007708	109.0
		139.64	0.007701	108.9
0.07937	1.0753	123.33	0.008719	109.9
		123.23	0.008726	110.1
0.09190	1.0753	110.73	0.009711	105.7
		110.85	0.009705	105.6
		110.85	0.009705	105.6
0.1051	1.0753	99.84	0.01077	106.1
		99.67	0.01079	106.3
		99.77	0.01078	106.2
0.5280	169.63	3353.1	0.05058	95.8
		3352.0	0.05061	95.9
1.078	169.63	1879.7	0.09026	83.7
		1878.9	0.09028	83.8
1.445	169.63	1465.8	0.1157	80.1
		1465.8	0.1157	80.1
1.872	169.63	1223.3	0.1387	74.1
		1223.2	0.1387	74.1
3.507	169.63	791.8	0.2142	61.1
		792.3	0.2141	61.1
		792.2	0.2141	61.1

*The second and third values are for different samples of the same concentration.

Table II

Viscosity Data of Aqueous Solutions of Hydroxylamine Hydrochloride at 25°C

$NH_2OH \cdot HCl$ Concentration C (moles/liter)	Viscometer Constant K_v (Centistokes/sec)	Efflux Time T (sec)	Viscosity Uncorrected η_u (Centistokes)	Viscosity Corrected* η_c (Centistokes)
0.0505	0.001767	520.0	0.9188	0.8977
		519.7	0.9183	0.8972
		519.7	0.9183	0.8972
0.0707	0.001641	561.5	0.9214	0.9003
		561.7	0.9217	0.9006
		561.1	0.9208	0.8997
0.1015	0.001641	562.6	0.9232	0.9021
		562.4	0.9229	0.9018
		562.3	0.9227	0.9016
0.5280	0.001641	572.8	0.9400	0.9189
		572.8	0.9400	0.9189
		572.8	0.9400	0.9189
1.078	0.001767	541.7	0.9572	0.9361
		541.5	0.9569	0.9358
		541.7	0.9572	0.9361
1.445	0.001767	550.2	0.9722	0.9511
		549.8	0.9715	0.9504
		549.7	0.9713	0.9502
1.872	0.001641	603.3	0.9900	0.9689
		603.5	0.9903	0.9692
		603.1	0.9897	0.9686
3.507	0.001767	606.3	1.071	1.050
		606.3	1.071	1.050
		606.0	1.071	1.050

*The United States Bureau of Standards lists the viscosity of pure water at 25°C as 0.8963 centistokes. The viscosity of conductance water used in this study was measured as 0.9174 centistokes, a difference of 0.0211 from that of pure water. The corrected value was obtained by subtracting 0.0211 from the measured uncorrected value.

Table III

Density Data of Aqueous Solutions of Hydroxylamine Hydrochloride at 25°C

$NH_2OH \cdot HCl$ Concentration C (moles/liter)	Volume Pycnometer V (cm^3)	Weight of Solution W (g)	Density D (g/cm^3)
0.00102	25.961	25.8861	0.99711
	25.961	25.8862	0.99712
0.00475	25.961	25.8918	0.99733
	25.961	25.8909	0.99728
0.0100	25.961	25.8938	0.99741
	25.961	25.8948	0.99745
	25.961	25.8946	0.99744
0.02067	25.961	25.9017	0.99772
	25.961	25.9017	0.99772
0.03032	26.263	26.2162	0.99818
	26.264	26.2163	0.99818
0.04023	26.264	26.2221	0.99840
	26.264	26.2221	0.99840
0.0505	26.264	26.2319	0.99877
	26.264	26.2328	0.99881
	26.264	26.2320	0.99878
0.05955	25.961	25.9368	0.99906
	25.961	25.9364	0.99905
0.07071	26.264	26.2527	0.99957
	26.264	26.2510	0.99950
0.07937	25.961	25.9550	0.99976
	25.961	25.9550	0.99976
0.09190	26.264	26.2627	0.99995
	26.264	26.2617	0.99991

$NH_2OH \cdot HCl$ Concentration C (moles/liter)	Volume Pycnometer V (cm^3)	Weight of Solution W (g)	Density D (g/cm^3)
0.1015	25.961	25.9649	1.0002
	25.961	25.9684	1.0003
	25.961	25.9699	1.0003
0.5280	26.264	26.4205	1.0176
	26.264	26.4203	1.0177
1.078	25.961	26.7172	1.0291
	25.961	26.7175	1.0291
1.872	25.961	27.2633	1.0502
	25.961	27.2633	1.0502
3.507	25.961	28.3530	1.0921
	25.961	28.3530	1.0921

Table IV

Resistance Change with Time at Constant Potential* of 0.1M Hydroxylamine Hydrochloride at 25°C

Time (hr)	Resistance (ohm)
0.0	98.91
2.0	96.22
3.0	95.29
3.5	94.88
4.0	94.53
4.5	94.18
5.0	93.83
5.5	93.57
6.0	93.33
6.5	93.05
7.0	92.81
22.5	88.03
23.5	87.91
25.0	87.54

*5 volt potential on a Jones Conductance Cell (K_c = 1.0753 cm^{-1})

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Table V

Calibrated Constants for Measuring Equipment

Jones Conductance Cells

Cell No.	Constant K_c (cm^{-1})	Accuracy (cm^{-1})*
1	1.0486	±0.0002
2	0.24827	±0.00007
3	1.0753	±0.0001
4	0.26717	±0.00005
5	169.630	±0.001

Specific Gravity Bottles

Bottle No.	Volume (ml)	Accuracy (ml)*
16	25.961	±0.002
45	26.264	±0.001

Viscometers Cannon-Fenske-Oswald Type

Cell No.	Constant K_v (Centistokes/sec)
25-J-288	0.001641**
25-J-328	0.001767

*Maximum deviation of constant for all samples measured.

**As specified by calibration certificate of manufacturer.

Jones Conductance Bridge

Range	1 to 60,000 ohms.
Ratio Arms	Two 1000 ohm resistors adjusted to equality of d-c resistance within ±0.01 percent.
Adjustable Capacitors	50 to 1000 micro-micro farad and 10 to 120 micro-micro farad connected across rheostat and "X" arm of bridge respectively.
Limits of Error	±0.02 percent.

Beckman Thermometer Constant Temperature Bath

Accuracy	±0.015°C
Reading for 25.00°C	0.18

Burette-Automatic Machlett

Capacity	50 ml
Reservoir	2000 ml
Accuracy	±0.05 ml

Transfer Pipettes-Kimax

Each pipette has been retested by the manufacturer and its error found to be less than half the tolerance required by U. S. National Bureau of Standards Circular #602.

Balance - Type S "Right-A-Weigh"

Accuracy	±0.0001 g

Volumetric Flasks - Kimax

Size (ml)	Tolerance (ml)
500	±0.30
1000	±0.60
2000	±1.00

Appendix F

Sample Calculations

Standardization of $KMnO_4$

The $KMnO_4$ solution was standardized by titration against a known amount of $Na_2C_2O_4$ with a purity factor of 1.0012.

$$\text{Normality } (KMnO_4) = \frac{(\text{wt. of } Na_2C_2O_4 \text{ sample})\ (\text{Purity Factor})}{(\text{ml of } KMnO_4 \text{ titrated})\ (\text{Milliequivalent wt. of } Na_2C_2O_4)} \qquad (7)$$

where: (a) Wt. of $Na_2C_2O_4$ = 0.3013 gm

(b) ml of $KMnO_4$ titrated = 42.75 ml

(c) Purity Factor $Na_2C_2O_4$ = 1.0012

(d) Milliequivalent wt. of $Na_2C_2O_4$ = 0.0670 gm/ml

$$\text{Normality } (KMnO_4) = \frac{(0.3013)(1.0012)}{(42.75)(0.0670)} = 0.1058 \text{ N}$$

Standardization of $NH_2OH \cdot HCl$

The molar concentration of the $NH_2OH \cdot HCl$ solution was calculated by titration of a prepared solution against a standard solution of $KMnO_4$.

$$\text{Molar Concentration } (NH_2OH \cdot HCl) = \frac{(\text{ml of } KMnO_4 \text{ titrated})(\text{Normality of } KMnO_4)}{(\text{ml of } NH_2OH \cdot HCl \text{ Sample})\ (2)} \qquad (8)$$

where: (a) Amount $KMnO_4$ titrated = 19.15 ml

(b) Normality $KMnO_4$ = 0.1056 N (average value)

(c) $NH_2OH \cdot HCl$ Sample Size = 20 ml

$$\text{Molar Concentration } (NH_2OH \cdot HCl) = \frac{(19.15)(0.1056)}{(20)\ (2)} = 0.0505 \text{ molar}$$

Calculation of Viscosity

A Cannon-Fenske-Oswald type viscometer was used to measure the kinemetic viscosity of $NH_2OH \cdot HCl$ solutions. A calibrated viscometer was used.

$$\text{Viscosity (Centistokes)} = (\text{Viscometer Constant } K_v)(\text{Efflux Time}) \qquad (10)$$

where: (a) Viscometer Constant K_v = 0.001767 Centistokes/sec

(b) Efflux Time = 550.2 sec

$$\text{Viscosity} = (0.001767)(550.2) = 0.9722 \text{ centistokes}$$

Calculation of Volume of Pycnometer

The bottle was weighed empty and then filled with pure conductance water and allowed to reach an equilibrium temperature of 25°C in the constant-temperature bath. The full bottle was weighed and the net weight of water was obtained by subtracting empty weight from full weight.

where: (a)

Full Weight	57.2049 gm
Empty Weight	31.0175 gm
Net Weight =	26.1874 gm

The density of pure water at 25.0°C is listed as 0.99707 in Handbook of Physics and Chemistry.

$$\text{Volume (ml)} = \frac{\text{Net Weight of Water, gm}}{\text{Density of Water 25°C, gm/ml}} \qquad (11)$$

$$\text{Volume} = \frac{26.1874 \text{ gm}}{0.99707 \text{ gm/ml}} = 26.264 \text{ ml}$$

Calculation of Density of $NH_2OH \cdot HCl$ Solution

Calibrated specific gravity bottles were weighed empty, then filled with $NH_2OH \cdot HCl$ solution to be measured, allowed to come to equilibrium in the constant-temperature bath, weighed full and the net weight was obtained by subtracting empty weight from full weight. As an example,

where: Full weight $NH_2OH \cdot HCl$ solution and bottle = 58.4730 gm

Empty weight of bottle = 32.5046 gm

Net weight of $NH_2OH \cdot HCl$ solution = 25.9684 gm

$$\text{Density (gm/ml)} = \frac{\text{Weight of Solution, gm}}{\text{Volume of Solution, ml}} \qquad (12)$$

$$\text{Density (gm/ml)} = \frac{25.9684 \text{ gm}}{25.961 \text{ ml}} = 1.0003 \text{ gm/ml}$$

Calculation of Conductance Cell Constant

The Leeds-Northrup Jones Conductance Cells constants were calculated by using 0.01 molar KCl in aqueous solution. The solution of KCl was poured into the cell and the cell immersed in the constant temperature bath. When equilibrium temperature of 25.0°C was assured the resistance

of the solution was measured.

$$K_c,\ cm^{-1} = (\text{Specific Conductance KCl, mho-cm}^{-1})(\text{Resistance, ohm}) \quad (9)$$

where: Specific conductance 0.01 molar KCl at 25°C = 0.001413 mho-cm^{-1}

Resistance of Solution = 761.06 ohm

$$K_c,\ cm^{-1} = (0.001413,\ \text{mho-cm}^{-1})(761.06\ \text{ohm}) = 1.0754\ cm^{-1}$$

Calculation of Specific Conductance of $NH_2OH \cdot HCl$ Solution

The solution to be measured was poured into a calibrated conductance cell and allowed to reach an equilibrium temperature of 25.0°C. The resistance was recorded at 30 seconds, 1 minute, and 2 minutes from the time the electrodes were connected. The resistance was plotted vs. time and a value of resistance at zero time was obtained by extrapolation. This was the resistance that was used for calculation.

$$L_s,\ \text{mho-cm}^{-1} = \frac{(\text{Conductance Cell Constant } K_c,\ cm^{-1})}{(\text{Resistance of Solution, ohm})} \quad (5)$$

where: Conductance Cell Constant, K_c = 1.0753 cm^{-1}

Resistance of Solution (0.1051 molar) = 99.772 ohms

$$L_s,\ \text{mho-cm}^{-1} = \frac{1.0753\ cm^{-1}}{99.772\ \text{ohm}} = 0.01078\ \text{mho-cm}^{-1}$$

Calculation of Equivalent Conductance of $NH_2OH \cdot HCl$ Solution

$$\Lambda,\ \text{mho-cm}^{-1}\text{-equiv}^{-1} = \frac{1000\ (L_s,\ \text{mho-cm}^{-1})}{(C,\ \text{equiv/liter})} \quad (6)$$

where: $L_s = 0.01078$ mho-cm^{-1}

$C = 0.10511$ equiv/liter

$$\Lambda, \text{ mho-cm}^{-1}\text{ equiv}^{-1} = \frac{(1000)(0.01078 \text{ mho-cm}^{-1})}{0.10511 \text{ equiv/liter}} = 106.2 \text{ mho-cm}^{-1}\text{-equiv}^{-1}$$

Least Squares Method of Calculating Slope and Intercept from Experimental Data

Experimental Data

Λ	$(C)^{\frac{1}{2}}$
135.89	0.0689
128.62	0.1000
115.87	0.1435
122.95	0.1231
144.76	0.0232
143.02	0.0319

b = intercept

a = slope (13)

Assume: $Y = ax + b$ where $Y = \Lambda$ and $x = (C)^{\frac{1}{2}}$

$b + 0.0689\ a = 135.89$	
$b + 0.1000\ a = 128.62$	
$b + 0.1435\ a = 115.87$	
$b + 0.1231\ a = 122.95$	
$b + 0.0232\ a = 144.76$	
$b + 0.319\ a = 143.02$	
Sum $6b + 0.4906\ a = 791.11$	(14)

Now if each above equation is multiplied by xi then:

$$
\begin{aligned}
0.0689\ b + 0.00475\ a &= (0.0689)(135.89) = 9.362 \\
0.1000\ b + 0.01000\ a &= (0.1000)(128.62) = 12.862 \\
0.1435\ b + 0.02067\ a &= (0.1435)(115.87) = 16.273 \\
0.1231\ b + 0.01516\ a &= (0.1231)(122.95) = 15.135 \\
0.0232\ b + 0.00054\ a &= (0.0232)(144.76) = 3.351 \\
0.0319\ b + 0.00102\ a &= (0.0319)(143.02) = 4.562
\end{aligned}
$$

$$
\text{Sum} \quad 0.4906\ b + 0.05214\ a = 61.545 \tag{15}
$$

$$
b = \frac{791.11}{6} - \frac{0.4906}{6}\ a = 131.85 - 0.08176\ a
$$

Then substitute for b in Equation (15)

$$
(0.4906)(131.85 - 0.08176\ a) + 0.05214\ a = 61.545
$$

$$
\begin{aligned}
64.680 - 0.04011a + 0.05214\ a &= 61.545 \\
0.01203\ a &= 3.135 \\
a &= -260.5 \quad \text{Slope}
\end{aligned} \tag{16}
$$

$$
b = 131.85 - (0.08176)(-260.5) = 131.85 + 2130 \tag{17}
$$

$$
b = 153.15, \text{ Y-axis intercept } (\Lambda_o) \tag{18}
$$

Onsager Equation Calculation

Maron (Ref. 18:457) gives the Onsager Equation:

$$
\Lambda = \Lambda_o - \left[\frac{(0.9834 \times 10^6)}{(DT)^{3/2}}\ w\ \Lambda_o + \frac{28.94\ (z_+ + z_-)}{\eta (DT)^{\frac{1}{2}}}\right]\left[(z_+ + z_-)\ C\right]^{\frac{1}{2}} \tag{2}
$$

where: Λ_o = equivalent conductance at infinite dilution, mho-cm^{-1}-$equiv^{-1}$

D = dielectric constant of solvent (no units)

T = absolute temperature, °K

η = viscosity of solvent, poise

z_+ = charge of positive ion (no units)

z_- = charge of negative ion (no units)

C = concentration of solution, equiv/liter

$$w = \frac{(z_+)(z_-)\ (2q)}{(1 + (q)^{\frac{1}{2}})} \qquad (3)$$

$$q = \frac{(z_+)(z_-)\ (1^o_- + 1^o_-)}{(z_+ + z_-)\ (z_+\ 1^o_- + z_-\ 1^o_+)} \qquad (4)$$

$\Lambda_o = (1^o_- + 1^o_+)$

1^o_- = equivalent negative ionic conductance at infinite dilution

1^o_+ = equivalent positive ionic conductances at infinite dilution

Now assume the aqueous solution of $NH_2OH \cdot HCl$ is a 3-1 electrolyte and Cl^- is the negative ion.

Then: Λ_o = 153.15 (see Equation 18)

D = 78.55 (no units)

T = 298.°K

η = 0.008949 poise

z_+ = 3 (no units)

z_- = 1 (no units)

1^o_- = 76.34 (Cl^-) mho-cm^{-1}-$equiv^{-1}$

$1^o_+ = \Lambda_o - 1^o_- = 153.15 - 76.34 = 76.81$

$$q = \frac{(3)(1)\ 153.15}{(3 + 1)\ (3 \times 76.34 + 1 \times 76.81)} = \frac{(3)(153.15)}{(4)(305.33)} = 0.372$$

$$\alpha^{\frac{1}{2}} = 0.609$$

$$w = \frac{(3)(1)(2)(0.374)}{1 + .609} = 1.386$$

So the theoretical slope of the curve of Λ vs $(C)^{\frac{1}{2}}$ of a 3-1 electrolyte would be

$$-\text{Slope} = \left[\frac{(0.9834 \times 10^6)(1.386)(153.15)}{(78.55 \times 298)^{3/2}} + \frac{(28.94)(3+1)}{(0.008949)\ (78.55 \times 298)^{\frac{1}{2}}}\right](4)^{\frac{1}{2}}$$

$-\text{Slope} = (58.2 + 84.2)(2) = \underline{284.8}$ (theoretical)

$-\text{Slope (Experimental)} = \underline{260.5}$ (from least squares method)

Difference = 24.3

$$\text{Percent Difference} = \frac{284.8 - 260.5}{284.8}(100) = \frac{24.3}{284.8}(100) = \underline{\underline{8.17}} \text{ percent} \quad (18)$$

GAW/Mech 62-15

Vita

Jimmie J. Nelson was born on 1 February 1928 in McLoud, Oklahoma. He attended grade school in Oklahoma City, Oklahoma and graduated from Northeast High School, Oklahoma City, Oklahoma, 25 May 1945. In September 1945 he enrolled in the School of Chemical Engineering at the University of Oklahoma. On 6 June 1949 he received a Bachelor of Science Degree in Chemical Engineering from that institution. He entered the United States Air Force 1 March 1950. His military education includes, pilot training and the undergraduate Aeronautical Engineering Program (1EP-57) at the Institute of Technology. His military assignments include, duties as an aircraft maintenance officer and a multi-engine pilot. The three years prior to his return to the Institute of Technology were spent in Tokyo, Japan, where he was a Weapon Systems Planning Officer for Headquarters Fifth Air Force. He is married to the former Beth C. Carlsson of Karlsborg, Sweden, and they have one son, Paul Carl-Gustaf.

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This thesis was typed by Helen E. Creek.

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