

UNIVERSITY OF CINCINNATI

June 2 1930

I hereby recommend that the thesis prepared under my supervision by Alfred J. Berger entitled The Electrical Conductance of Aqueous Solutions of Cobalt Sulfate

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

Approved by:

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- 1 -

THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS
OF
COBALT SULFATE

A THESIS

Presented to the Faculty
of the
Graduate School
of the
University of Cincinnati

in partial fulfillment of the requirements for the
degree of
Doctor of Philosophy

by

Alfred J. Berger.

"

A. B. St. Xavier College 1927

M. A. University of Cincinnati 1928

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INTRODUCTION AND THEORY

The conductance of a body is by definition the reciprocal of its resistance, or expressed in absolute units, conductance is the number of coulombs that pass thru a conductor per second when the potential difference is one volt. Provided that a certain minimum voltage is exceeded the familiar law of Ohm, $E = IR$ holds equally as well for solutions that conduct a current as for metallic conductors. Hence if L represents the conductance of the solution, it follows that $I = EL$.

The conductance of a homogeneous body of uniform cross-section varies directly with the area of the cross-section and inversely with the length of the conductor. Specific conductance is defined as the conductance of a one centimeter cube between electrodes one centimeter apart, hence the relation between L the conductivity of any body and $\bar{L}$ its specific conductance is $L = \bar{L} \frac{a}{l} (1)$.

As resistance is measured in ohms, conductance is measured in reciprocal ohms called mhos. An ohm is the resistance of a column of mercury at 0°C , one square millimeter in cross-section and 106.3 centimeters long, the mho, is its conductance.

In comparing the conductances of electrolytes it is more convenient to use the equivalent conductivity which is the conductivity of the amount of solution which contains one chemical equivalent, when placed between parallel

electrodes one centimeter apart. Thus for a 1 N solution the equivalent conductivity Λ would be 1000 times the specific conductivity $\bar{L}$. To generalize $\Lambda = \frac{1000\bar{L}}{N}$ (2), where N = the normality of the solution, or $\Lambda = \frac{\bar{L}}{C}$ where C = the number of equivalents per cubic centimeter of the solution.

The equivalent conductivity (Λ) increases with the dilution of the electrolyte and with strong electrolytes approaches a maximum. This maximum value Λ_0 is called the equivalent conductivity at infinite dilution or what is equivalent at zero concentration. As measurements cannot be made with accuracy beyond a certain concentration, the value for Λ_0 is of necessity an extrapolated value. Various methods of lessening the error of extrapolation will be discussed later.

The equivalent conductance Λ of a salt at any concentration may be considered to be due to two factors.

- (a) the conductance Λ_c of the cation constituent,
- (b) the conductance Λ_A of the anion constituent.

By ion constituent is meant the electrolyte present both as ions and as undissociated molecules. Therefore $\Lambda = \Lambda_c + \Lambda_A$ (3) at any concentration and $\Lambda_0 = \Lambda_{0c} + \Lambda_{0A}$, (4) at infinite dilution or zero concentration. According to Arrhenius' theory, the ion constituents are present wholly in the form of ions at zero concentration, therefore using this hypothesis $\Lambda_0 = \Lambda_{0c^+} + \Lambda_{0A^-}$ (5).

The conductance of a solution depends upon, (1) the

charge $\underline{F}$ carried by each ion, (2) the concentration $\underline{C}$ of the ions in the solution, and (3) the mobilities $\underline{U}$ of the ions, if the concentrations of the ion constituents are expressed in electro-chemical equivalents, then by Faraday's Law, $\underline{F}$ the current carried, is the same for one equivalent of ions of any electrolyte. This value $\underline{F}$ is called the Faraday and has been determined to be 96,500 coulombs of electricity. Hence $\underline{L} = F (C_A U_A + C_B U_B + \dots)$, (6). The mobility U_A of the ions depends upon the fraction of the electrolyte ionized γ_A , and upon the individual speed of the ions $U_A \pm$, therefore $U_A = \gamma_A U_{A\pm}$ (7)

When there is only one salt present in the solution, $C_C = C_A = C$ and $\gamma_c = \gamma_A = \gamma$, therefore combining equation (6) and (7) we may write, $\underline{L} = C F \gamma (U_{c+} + U_{A-})$, (8), or $\underline{\Lambda} = \frac{\underline{L}}{C} = F \gamma (U_{c+} + U_{A-})$ (9). As $C \rightarrow 0$; $\gamma \rightarrow 1$, therefore $\underline{\Lambda}_0 = F (U_{c+})_0 + F (U_{A-})_0$ (10), where the electrolyte is assumed to exist only in the form of ions and the mobilities of the ions are their mobilities in pure water.

Any change in $\underline{\Lambda}$ with increasing concentration must be due to a change either in γ (that is, a change in the concentration of the ions,) or in the mobilities of the ions, as the concentration term C does not appear in the equation.

The ratio of the conductance at any concentration to the conductance at zero concentration, from equations (9) and (10)

$$\text{is } \frac{\underline{\Lambda}}{\underline{\Lambda}_0} = \gamma \frac{U_{c+} + U_{A-}}{(U_{c+})_0 + (U_{A-})_0} \quad (11).$$

Arrhenius (1) assumed that the mobilities were constant hence $\frac{\Lambda}{\Lambda_0} = f$ and thus the conductance ratio was used as a measure of the degree of ionization. This value obtained for f was found to hold very well giving a constant in the mass action equation when applied to weak electrolytes at low concentrations. However the mass action equation did not hold for concentrated solutions of weak electrolytes above 0.1 N hence there must have been some change in the mobilities of the ions, as was pointed out by Jahn (2) and later by Lewis (3).

The resistance to motion of the ions is different in more concentrated solutions from that in pure water. Viscosity is a measure of the resistance offered by the molecules of a liquid to the motion of similar molecules past one another. Hence it might be assumed that the resistance offered to the motion of ions through the solution is roughly proportional to the viscosity of the solution. Thus the change in mobility of the ions at a definite concentration from their mobility at zero concentration may be assumed to be inversely proportional to the viscosity of that solution relative to the viscosity of pure water.

$$\frac{U_{C^+} + U_{A^-}}{(U_{C^+})_0 + (U_{A^-})_0} = \frac{\eta_0}{\eta} \quad , \quad \text{or} \quad \frac{\Lambda}{\Lambda_0} = f \frac{\eta_0}{\eta} \quad , \quad \text{whence}$$

$$f = \frac{\Lambda}{\Lambda_0} \cdot \frac{\eta}{\eta_0} \quad , \quad (12).$$

This conductivity-viscosity ratio was found to give a constant in the mass action equation when applied to concentrations as high as 1 N.

For strong electrolytes, even in dilute solution, the transference numbers change with the concentration. This change of transference number is evident even in the range where the viscosity change is too slight to be significant. The change of transference number of cobalt sulfate with concentration is under investigation at this institution by E. C. Payne. (4)

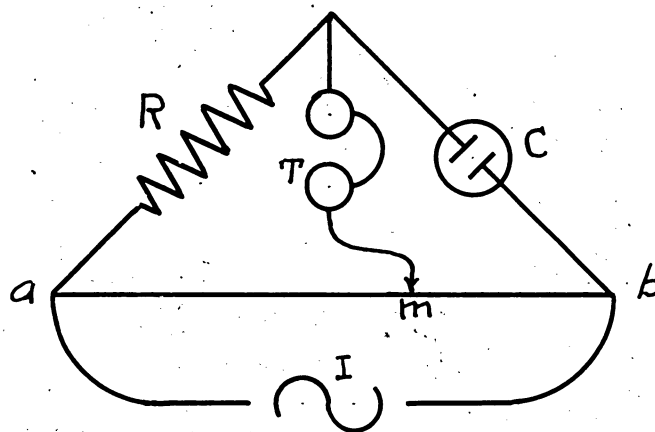
If the transference numbers of strong electrolytes change with the concentration it follows that the mobilities must also change with the concentration (although the converse does not follow of necessity, as the mobilities could vary without changing the proportion between them). Hence the conductance-viscosity ratio cannot be used as an accurate measure of the degree of ionization of strong electrolytes. Noyes and Falk (5) however point out that even if the ratio $\frac{\Lambda}{\Lambda_0}$ does not have the significance of a degree of ionization, it is a convenient empirical expression of the change of conductance with concentration, without reference to ionization.

Another objection to Arrhenius' theory of constant ion mobility is the fact that it leads to a uniformity of ionization values for substances of the same valence type. That is, if $\gamma = \frac{\Lambda}{\Lambda_0}$, the values of γ so obtained at equal concentrations indicate that the extent to which ions combine in solution to form unionized molecules is determined not by the chemical nature of the ions, but by the

charge carried by the ion. However all chemical reactions depend in a highly specific manner upon the nature of the atoms or groups reacting. For reasons such as these, the theory of complete ionization has been brought forth and has been developed by Sutherland (6) and Noyes (7) and more recently by Bjerrum, (8) Debye and Huckel (9), Bronsted and LaMer (10) and others. (11)

The chief difficulty in measuring the conductivity of electrolytes, met by early investigators was that, due to polarization a cell with a back electromotive force is set up in opposition to the current as soon as a finite amount of ions have been deposited on the electrodes. Direct current measurements were tried by Horsford (12) who used metal plates as electrodes in a trough of the electrolyte. By altering the distance between the plates, he calculated the resistance of the solution, assuming polarization to be equal in the various positions. Many improvements were made on the method by his followers. Beetz (13) eliminated electrodes entirely by using currents induced by a moving magnet. Newbery (14) devised a direct current measurement of conductivity by potentiometric methods which was later used and improved by Eastman (15) who showed that the values obtained by use of 1000 cycle alternating current do not differ more than 0.02-0.03% from those obtained by the direct current method, in the cases investigated. However the direct current method is much more complicated and hence not as readily applicable as the alternating current method.

Kohlrausch (16) developed the most satisfactory method of eliminating polarization. His method of using high frequency alternating current is with many refinements the one in use at present. His method was an arrangement of the Wheatstone Bridge whereby the resistance of the electrolyte in a conductivity cell was balanced against a known resistance by means of a slide-wire. A diagrammatic representation of his apparatus is shown in Fig. I.



C = conductivity cell

R = known resistance

ab = slide-wire

m = sliding contact

T = telephone

I = source of alternating current

From the principle of the Wheatstone Bridge it follows that,

$$\frac{\text{resistance of } R}{\text{resistance of } C} = \frac{am}{mb}$$

or if the slide-wire reading be x and the total divisions

be 100,

$$\frac{\text{resistance of R}}{\text{resistance of C}} = \frac{X}{100 - X}$$

$$\text{or } \frac{1}{C} = \frac{X}{(100 - X) R}$$

but the reciprocal of the resistance of the solution equals its conductance, therefore $L = \frac{X}{(100 - X) R}$

As stated previously, Kohlrausch was the first to substitute high frequency alternating current for direct current in conductivity measurement. His source of current was a small induction coil. This necessitated replacing the galvanometer formerly used by a telephone. This step in itself greatly increased the accuracy of the measurements as the sensitivity of the telephone is far greater than that of the galvanometer.

The sources of error in Kohlrausch's work have been studied by many investigators among the first of whom was Washburn (17) who described notable advances in technique by use of tuned telephones, pure resistances, specially designed cells, 1000 cycle alternating current of pure sine wave form, better capacities and methods of grounding.

A slide-wire constructed of a manganin wire mounted on a meter stick was used in Kohlrausch's measurements. Evidently the accuracy of the readings would increase in proportion to the length of the wire, but a very long wire would be inconvenient. In order to combine length with ease of manipulation, slide-wires have been wound on marble drums and a sliding contact made by rotating the drum. In addition, two coils of

equal resistance may be connected at the ends of the slide-wire thus making the effective length many times its actual length and increasing the accuracy of the readings proportionally.

Taylor and Acree (18) eliminated the helically wound slide-wire by a method in which the resistance of the cell is obtained by substitution as suggested by Dr. Curtis (19) of the U. S. Bureau of Standards. They recommend this method because of self induction which is a source of error in the helically wound slide-wire. This fact was also noted by Morgan and Lammert (20). This source of error has recently been attacked again, this time by Jones and Joseph (21) who have made a very careful study of the imperfections in the design of conductivity apparatus in an attempt to reduce such errors to 0.001%. They maintain that owing to self induction a helically wound slide-wire may introduce considerable error when used with high frequency alternating current. When the circuit is brought to balance at the mid-point of the bridge, the induction will be equally divided in the two halves of the bridge. However, in any other position the induction will be unequal. These authors give graphs showing the variation in error with the bridge reading. If the balance point is within the middle tenth of the bridge the error is less than 0.02%. They have designed a special resistance bridge to replace the slide-wire. However, a slide-wire bridge was used by Parker and Parker (22) in their very careful redetermination of the specific conductance of several standard solutions.

For a source of high frequency alternating current Kohlrausch used an induction coil. The circuit breaker was adjusted to give a high mosquito-like note. There are certain disadvantages in using an induction coil. There is a mechanical disadvantage in that the note emitted, therefore also the frequency, does not remain constant and often changes erratically. As will be shown later, the conductivity varies with the frequency of the current, especially if the electrodes are not properly platinized. In addition, an intrinsic disadvantage of the induction coil is that the current is slightly unidirectional as Washburn and Bell (17) proved by inserting a silver coulometer in the circuit. This of course would produce polarization just as a direct current. The current should be small in quantity and exactly equal in both directions or in other words a pure sine wave of high frequency. An article by Taylor and Acree (23) discusses critically the various sources of current in detail. Many devices for generating current have been recommended. High frequency generators especially designed for conductivity measurement provide a suitable current but must be far removed from the apparatus due to the unavoidable noise of the motor; another objection is that the speed of the motor and consequently the frequency may vary with the motor current.

The Vreeland Oscillator has been highly recommended as a source of current, but it is very expensive. It supplies a pure sine wave of any desired frequency and is unaffected by the load. Morgan and Lammert (20) however have shown that the

frequency is not very constant over long period of time and varies considerably the first few hours. Jones and Joseph (21) have further investigated this source of current and find several disadvantages in it. Owing to electromagnetic induction it must be removed as far as possible from the conductivity apparatus. These authors explain in detail the construction of an audion tube oscillator first suggested by Hall and Adams. (24) Oscillators of this type are not yet manufactured commercially but would be much cheaper than the Vreeland Oscillator over which this type has several distinct advantages.

Leeds and Northrup manufacture a Microphone Hummer which emits a sufficiently pure sine wave for ordinary purposes at 1000 cycles. It operates on four dry cells and the alternating current may be taken from any one of three taps of varying intensity. The frequency is kept constant by a tuning fork arrangement. This piece of apparatus proved entirely satisfactory in the present investigation.

For very accurate work special resistances with very low inductance and capacity have been designed. Washburn (25) made resistances of colloidal platinum deposited in glass tubes, but unfortunately their temperature coefficient was quite large. Curtis (19) designed specially wound coils to be used for very accurate work. He found that the errors from induction and capacity may amount to 0.05% with 1000 ohm coils of various makes. A more recent investigation of the errors in using different types of resistances in conductivity

work was undertaken by Jones and Josephs (21) who show that the apparent resistance of 5000 ohm coils of the plug type may be in error by as much as 0.012% at 1100 cycles and that in every case the error increases rapidly with the frequency. None of the commercial resistances investigated were found free from alternating current error. These authors give specifications for new coils with very low percentages of error.

The conductivity cell acts both as a resistance and as a capacity due to the infinitesimal amount of polarization and depolarization of the electrodes on each reversal of the current, hence this capacity must be balanced by a variable condenser shunted across the terminals of the resistance box, as suggested by Kohlrausch.

The sensitivity of the telephones is increased by tuning to the frequency of the current as discussed by Washburn and Parker (25). Special telephones are made for this purpose. However, if the phones are tuned, the frequency must remain very constant or the intensity will vary with the frequency. To increase the sensitivity of the phones and to simplify the location of the minimum, Hall and Adams (24) recommend the use of an amplifier in the phone circuit. This, according to Jones and Joseph (21), is much preferable to tuning the phones.

There have been many articles published concerning the importance of shielding the various parts of the apparatus from one another and from stray electrical currents.

However, Jones and Joseph discuss the various views and conclude that electromagnetic and electrostatic shielding of the bridge is not to be recommended, but that shielding of any source of outside disturbance, such as the Oscillator, motors, etc. is preferable.

These authors claim that all previous methods of grounding are erroneous and advise a somewhat complicated method in which the bridge is shunted by a resistance with a variable connection to the ground. By a switch a variable condenser, also grounded, may be connected to either one of the leads from the source of current. They found that the position of the balance point varied on reversing the current leads and hence came to the conclusion that ground should be connected to one or the other of the leads by a variable condenser. The condensers and the resistance in the ground connections must be adjusted at each bridge setting as explained by the authors. This need of balancing the capacity to the ground is due to the fact that when the leads from the oscillator are enclosed in a grounded metal sheath, the condenser action between each of the leads and the sheath is not equal due to their different positions.

Notwithstanding the fact that most conductivity measurements have been made in water baths, Jones and Joseph advise the use of oil baths for very accurate work and give experimental data to show that with high frequency current and a grounded water bath the errors may be very appreciable. If a water bath be used it should not be grounded as the error due

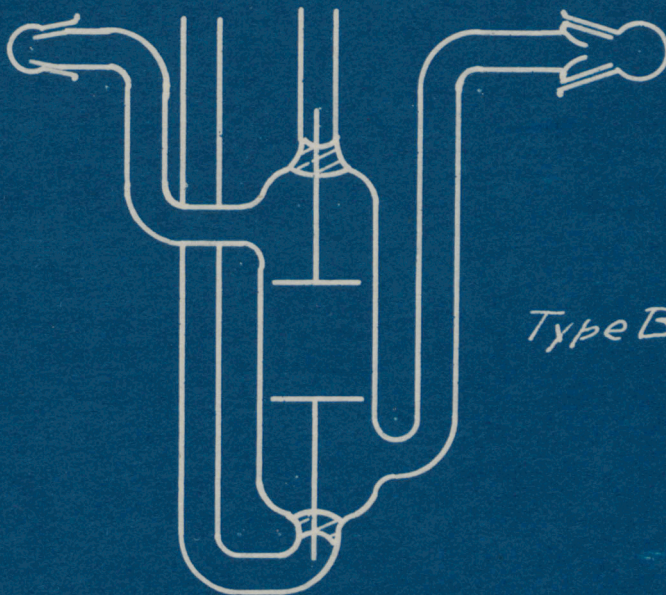
to grounding the thermostat was found to be the most important and was increased by moving the cell near the walls of the bath. These authors state, "The grounding of the bath also had a marked influence upon the necessary adjustment in the grounding of the bridge and upon the reactance balance in the bridge proper." Thus it is seen that an oil bath is preferable, though it is more inconvenient, and if water be used the bath should not be grounded.

In a comprehensive treatise by Washburn (26) the theory of the design of conductivity cells is undertaken in detail, and the dimensions of four cells of the pipette form, to cover the range from conductivity water up to concentrated solutions, are given. For the range between 1.6×10^{-7} to 1×10^{-5} reciprocal ohms the electrodes consist of two platinum discs 4 cm. in diameter and 2 mm. apart. The electrodes are not platinized but are roughened by the sand blast. The cell covering the range 10^{-6} to 10^{-4} reciprocal ohms should have slightly platinized electrodes of the same dimensions but 3 mm. apart. A cell of this type was used in the present investigation, and also one for the range 10^{-4} - 10^{-2} mho.⁻¹ which was provided with well platinized electrodes 1.5 cm. in diameter and 1.8 cm. apart. The electrodes must not change their relative positions and hence must be made of heavy platinum. Jena glass is sufficiently resistant and insoluble for all ordinary purposes. All apparatus must be thoroughly cleaned with warm chromic acid solution, steamed and washed repeatedly with conductivity water.

Fig. 2.

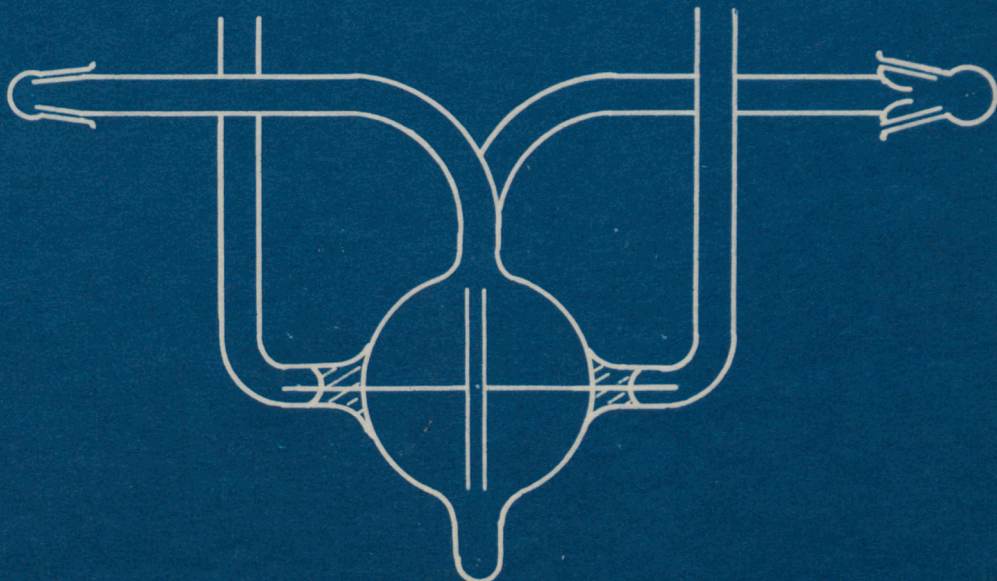


Type of Cell used by
Jones and Jacobson⁽²¹⁾



Washburn Cells

Type B



Type A

To prevent polarization and the consequent poor determination of the point of minimum sound in the phones, the electrodes must be coated with platinum black. The effect of platinizing the electrodes is discussed by Taylor and Acree (18), who show that the measured conductivity changes with the frequency if the electrodes are not platinized. Too thick a layer of platinum black might possibly promote catalytic action in some cases or selective adsorption and is only washed free of the electrolyte with great difficulty, hence the proper thickness must be determined by trial. The effect of platinization is partly due to accelerating the reversibility of the cell set up by the infinitesimal polarization and partly due to the increased effective area of the electrodes. The cell constant does not change on platinizing the electrodes.

HISTORICAL

"The Conductivity and Ionization of Electrolytes in Aqueous Solutions as Conditioned by Temperature, Dilution and Hydrolysis", an investigation by H. C. Jones and C. A. Jacobson (27) contains data on the conductivity of Cobalt Sulfate solutions at 25°C. The purpose of their research was to study the influence of temperature upon the dissociation of electrolytes. The conductivity of thirty-four substances was investigated by the authors at the four temperatures, 0°; 10°; 25°; and 35°C., and at various concentrations from 1 N to N/1024. The value for N/1024 was assumed to be Λ_0 and the degree of dissociation calculated for each concentration by dividing Λ of that concentration by the assumed Λ_0 value. Their apparatus included:

- (a) a manganin wire on a meter stick
- (b) an induction coil as the source of alternating current
- (c) plug resistances
- (d) cells of a type in which condensation of solvent on the walls might change the concentration of the solution appreciably. The electrodes were not sealed into the walls of the cell, hence might have suffered during manipulation. The authors mention that the cell constants checked to within 0.2-0.3%.

Their solutions were made by successive dilution in the conductivity cell, a method which is not capable of high accuracy.

A table of Jones and Jacobson's (27) data for CoSO_4 at 25°C is given below. Their results have been recalculated from molecular concentrations to normalities and from molecular conductance to equivalent conductance.

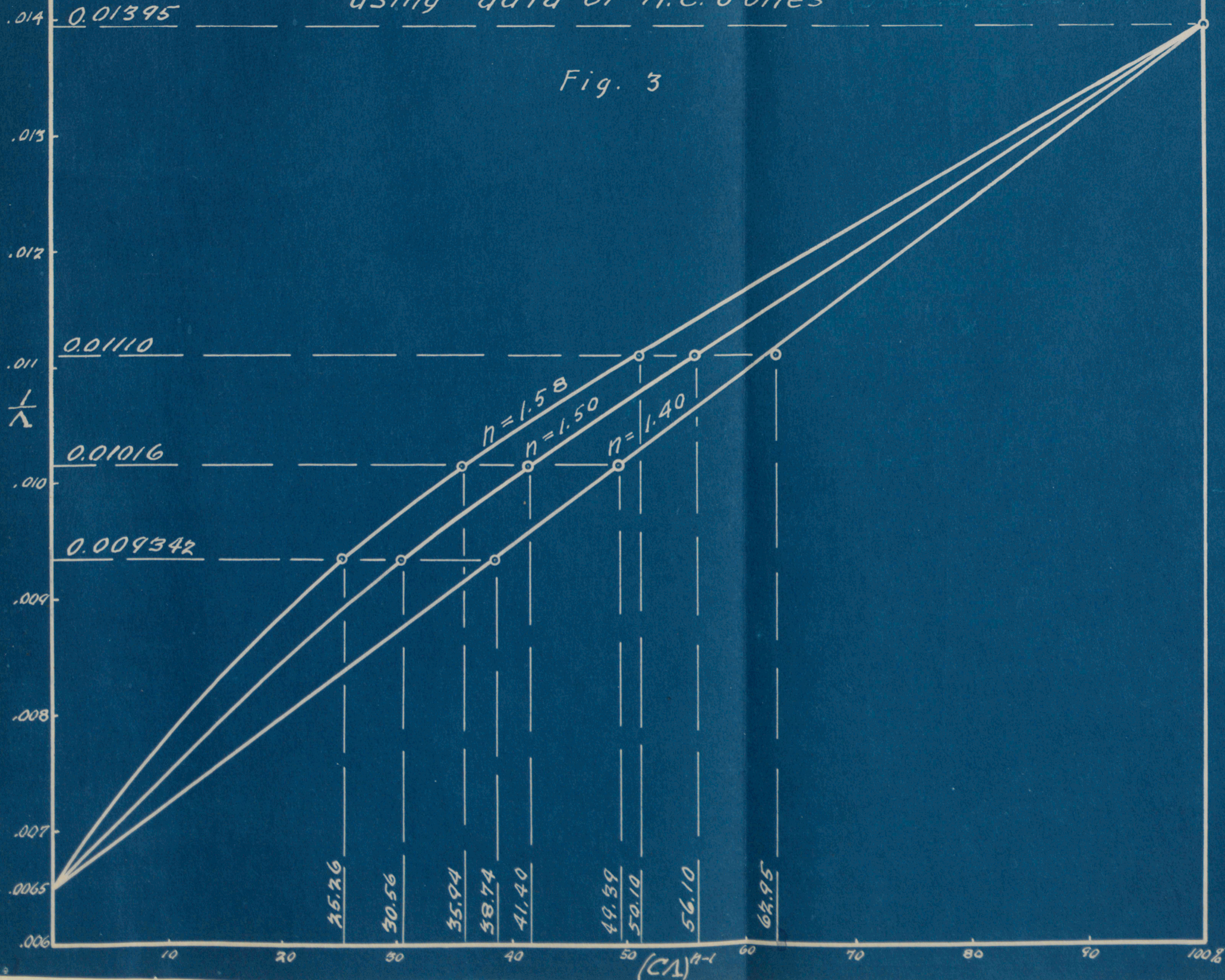
Table I
 CoSO_4 ; 25°C Jones and Jacobson (27)

N	Λ	% Dissociation
1 N	27.55	25.7
1/4 N	39.18	36.6
1/8 N	45.98	43.0
1/16 N	52.70	49.2
1/64 N	71.70	67.0
1/256 N	90.10	84.2
1/512 N	98.45	92.0
1/1024 N	107.05	100

An attempt was made to apply the graphic method of extrapolating conductivity data for low concentrations to obtain Λ_0 , according to A. A. Noyes (28). The values of $(C\Lambda)^{n-1}$ in the range $C=0.0001$ to 0.02 N are plotted against the corresponding values of $1/\Lambda$ and that value of $n-1$ taken which makes the plot as linear as possible. The value for Λ_0 is obtained graphically by extrapolating the plotted line to zero concentration. This method will be discussed in detail in a later paragraph. In Fig. 3, page 22, in order to make the three curves comparable the value of $(C\Lambda)^{n-1}$ for $C=1/64$ N, the highest normality used in the plot, was made 100 for each

Plot of $\frac{1}{\Lambda}$ against $(c\Lambda)^{n-1}$
for Cobalt Sulfate
using data of H.C. Jones⁽²¹⁾

Fig. 3



value of n and the other values each multiplied by the necessary factor to reduce to per cent of this value. Curves for $n = 1.58$, $n = 1.50$ and $n = 1.40$ are shown, and it may be seen that the plot for $n = 1.40$ most nearly approximates a straight line as alternate points lie on opposite sides of a straight line. By extrapolating this curve for $n = 1.40$ to $C = 0$ the corresponding value for is 0.0065, hence Λ at $C = 0$ or Λ_0 is the reciprocal of 0.0065 or 154. However the value of N in the equation has been found to be very near 1.60 for most bi-bivalent salts. In addition the extrapolation from the last point on the curve, $\Lambda = 107.05$ to $\Lambda_0 = 154$ is of such a magnitude as scarcely to admit of accuracy. From these and other reasons concerned with the apparatus used, it was thought necessary to repeat the former research with modern apparatus.

OBJECT

The object of this research was to determine the equivalent conductivity of cobalt sulfate solutions of various concentrations, thence by extrapolation of the conductivity data to arrive at a value for the equivalent conductance at zero concentration or infinite dilution; and also to obtain the value of N in the equation

$$\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - (C \Lambda)^{n-1} \quad \text{for cobalt solution.}$$

EXPERIMENTAL

Preparation of Cobalt Sulfate and Standard Solutions.

Chloro-purpureo-cobalti-chloride $\text{Co}(\text{NH}_3)_5\text{ClCl}_2$ was prepared by the method of Sorensen (29) from cobalt chloride. This was washed several times with half diluted hydrochloric acid and then washed free of acid with alcohol. The salt was then redissolved in 2% ammonia, filtered, precipitated with hydrochloric acid and washed exactly as previously. The chloro purpureo cobalti chloride was calcined to the chloride and then precipitated with ammonium oxalate according to Chaudron (30), filtered and dried. The oxalate crystallizes with two molecules of crystallization. Apparently this salt is stable in air at ordinary temperatures as the yield of cobalt on analysis by the electrolytic method described by Treadwell and Hall (31) was as follows:

<u>Cobalt oxalate taken</u>	<u>Cobalt found</u>	<u>Cobalt found</u>	<u>Cobalt theory</u>
0.6757 gm.	0.2177 gm.	32.22%	32.23%
0.7081 gm.	0.2263 gm.	31.95%	32.23%

Difficulties encountered in the electrolytic method will be discussed later.

The oxalate was dissolved in hydrochloric acid as it is only slightly soluble in sulfuric acid, and converted to the carbonate with sodium carbonate. This after filtering and thorough washing was treated with slightly less than the theoretical amount of sulfuric acid, filtered and concentrated by evaporation. The cobalt sulfate was crystallized by ethyl

alcohol and finally twice recrystallized from conductivity water. Since cobalt sulfate may exist in various stages of hydration, it is not possible to make up a standard solution by weighing. Instead a solution, known to be more than 0.5 N, was made and the amount of cobalt per c.c. determined by electro-analysis of 10 c.c. of the solution. Much trouble was experienced with this method as the last traces of cobalt ion are extremely hard to remove and the anode loses weight on electrolysis in the strongly ammoniacal solution. As long as the analyses are run strictly in duplicate as to time and current density, the results will check very closely. This ease of obtaining checks in duplicate runs undoubtedly accounts for the fact that it has been recommended as being highly accurate in the literature. However, the cathode continually gains weight so that the end point when all the cobalt has been plated out is always uncertain. Treadwell and Hall (31) state that the analysis should not be run too long as the cathode continually gains weight, but no mention of weighing the anode was found in the literature. This seemed advisable as a check on the error due to deposition of platinum on the cathode. When the loss of platinum was excessive at the anode it was usually found that the analysis was in poor agreement with the other values. Treadwell and Hall advise determining the end point by testing a small amount of the solution with ammonium sulfide. However the excess ammonia must first be boiled off or cobalt sulfide will not precipitate. In order to determine the best conditions a series of duplicates were

run. The results of a few of the determinations are given in order to show that checks could very easily be obtained under like conditions. Ten cubic centimeters of the same solution was taken in each analysis.

<u>Analysis</u>	<u>A</u>	<u>B</u>
1	0.01509 gm. per c.c.	0.01509 gm. per c.c.
2	0.01535 " " "	0.01536 " " "
3	0.01534 " " "	0.01539 " " "
4	0.01547 " " "	0.01562 " " "

It will be noted that the longer the electrolysis the greater the deviation between the duplicates.

Next, blank runs were made with the usual amounts of ammonium sulfate and ammonia and the loss and gain in weight of the electrodes noted.

<u>Time</u>	<u>Anode</u>	<u>Cathode</u>
1 hour	-0.0027 gm.	+0.0005 gm.
3 hours	-0.0067 gm.	+0.0019 gm.

Then a chemically pure platinum wire was made into a spiral electrode and a blank run made with it.

<u>Time</u>	<u>Current</u>	<u>Anode</u>	<u>Cathode</u>
1 hour	3.2 v. - 2.8 amp.	-0.0039 gm.	+0.0001 gm.
2 hours	" "	-0.0057 gm.	+0.0020 gm.

This seemed a definite improvement as a stronger current was used and the pure platinum anode was used thereafter. It is to be noted that there can be no mathematical correction for the amount of platinum deposited on the cathode because even if there were a definite ratio discovered between the weight

of platinum dissolved and the amount plated out when no cobalt were present, it would in all probability not hold in the presence of the easily reduced cobalt ion because no weighable quantity of platinum would be deposited before the cobalt ion concentration became very low.

The electrolytic apparatus used was made by the Fischer Scientific Co. of Pittsburgh, and operated on 110 volt alternating current. The direct current was supplied by a Tungar rectifier and could be regulated by variable resistances. An ammeter and a voltmeter were provided in the circuit. The platinum wire anode which was in the form of a spiral was revolved by an electric motor operating on the 110 volt circuit. The cathode was a cylinder of platinum gauze which surrounded the rotating anode.

The method finally adopted for the analyses was as follows: To 10 c.c. of the solution, (an amount which would give less than 0.2 gm. of cobalt) were added 10 c.c. concentrated sulfuric acid and 50 c.c. of concentrated ammonia. The excess of ammonia is necessary as the cobalt must be present in the form of the complex cobalt-ammonia ion or cobalt oxide will be deposited on the anode. The solution was diluted to a volume of 150 c.c. and electrolyzed while warm at 2 amperes and 2-3 volts. A better deposit is obtained if a much weaker current is used at the beginning of the electrolysis. The cathode was weighed after 1-3/4 - 2 hours and then once or twice at 20 minute intervals until the gain in weight was only about 0.0005 gm. When removing the

electrodes for weighing, the direct current must not be turned off until they have been washed free of the electrolyte.

An average of the values obtained in this way 0.01558 gm. per c.c. was taken in calculating the standard. A half normal solution of cobalt sulfate should contain 14.735 gm. of cobalt per liter, hence $14.735 \div 0.01558$ or 946.37 c.c. of a solution containing 0.01558 gm. cobalt per cubic centimeter will contain one half of a gram-equivalent (or 14.735 gms.) of cobalt and to this may be added 53.63 c.c. of conductivity water to make one liter of 0.5 N solution. This amount of water was run into a liter flask from a calibrated burette and then a sufficient amount of the original solution added to bring the volume to one liter. All volumetric apparatus, including the pipette used to deliver the 10 c.c. of solution in the electroanalysis was calibrated for 20°C. The temperature of the room, which was always near 25°C owing to the care necessary in regulating the water bath, would therefore require the same correction to each piece of apparatus. But since the same correction would be applied to every volume, and all quantities including the amount of cobalt taken for analysis are measured by volumes, the normality of the resulting liquid would be unchanged; the final volume only, would be less than a liter at 25°C if no correction for the difference in temperature were made. The normality would be the normality at 25°C and not at 20°C, this is of course as desired.

Conductivity Water

Ordinary distilled water cannot be used in making up solutions for conductivity measurements as it has a very appreciable conductivity due to dissolved electrolytes, especially ammonia and carbon dioxide. Another disadvantage is that it contains small amounts of organic materials which would gradually be adsorbed on the electrodes.

Kohlrausch and Heydweiller (32) prepared the purest water known, with a conductivity of only 0.043×10^{-6} mhos. at 18°C , by redistilling water 42 times in vacuo into a conductivity cell that had been left standing for ten years in conductivity water. Water of such purity has never been duplicated. In air, even the best conductivity water rises to a value around 0.7×10^{-6} mhos. due to carbon dioxide dissolved from the air. That this rise in conductivity is due almost entirely to carbon dioxide is proved by the fact that the conductivity can be very considerably lowered by passing purified (CO_2 free) air thru it. Water with a conductivity near 1×10^{-6} mhos is sufficiently pure for all but the most exact measurements which are to be carried out in air. Ordinary distilled water, redistilled from potassium permanganate solution and condensed in a block-tin condenser was used in this investigation. The distillation was regulated so that some liquid was continually condensing in the long neck of the flask and the upper part of the block-tin condenser. This condenser was made from a three foot length of half inch block-tin pipe, that is made of

solid tin and seamless. It was bent in such a way as to allow six inches to project vertically from the four-liter distilling flask allowing partial condensation of the vapors. Part of the inclined portion of the condenser was equipped with a water jacket, and the flow of water so regulated that a continual flow of steam passed thru the two-liter volumetric flask which was used as a receiver. In this way any vapors from the room were unlikely to find their way into the conductivity water. The water was collected at a rate of about one liter per hour, after the whole apparatus had been thoroughly steamed. The conductivity water was kept in a six liter pyrex flask fitted with a siphon and soda lime tube. A summary of the various methods of preparation of conductivity water is given by Kendall (33). He concluded that if the water were perfectly pure there would be no need of correction due to the conductivity of the water, but Washburn (34) maintained that even with water having a conductivity of 0.04×10^{-6} the correction might be as high as 0.3% at 0.0001 N. Since very pure water is difficult to keep, if working in the presence of air, the best procedure would be to use a water of constant conductance in equilibrium with the carbon dioxide always present in the air, but even this may vary greatly.

The conductivity of the solvent is usually subtracted from the measured conductivity of the solution assuming the value for the solvent to remain unchanged in the solution. Laue (35) suggested a very complicated equation for computing

the water correction which includes the effect of the electrolyte under investigation. Since the conductivity of the water is small in comparison with that of the solutions, its value need only be known to two or three significant figures. Thus for this measurement, dipping electrodes may be used. In this research, since the value of the correction becomes very appreciable at the very low concentrations, the cell B was used both for the dilute solutions and to obtain the conductivity of the water used. It was quite difficult to obtain a constant value for the conductivity of the water as adsorption on the electrodes of cobalt sulfate from the solutions was very hard to eliminate. For this reason and due to the uncertainty of the water correction due to handling the solutions in air, only two figures were thought significant and applied in the water correction. The water used in this investigation had a conductivity of between 1.2×10^{-6} and 2.0×10^{-6} mhos. The conductivity of the water in the six liter flask was taken at frequent intervals and the proper corrections recorded for the solutions as made up.

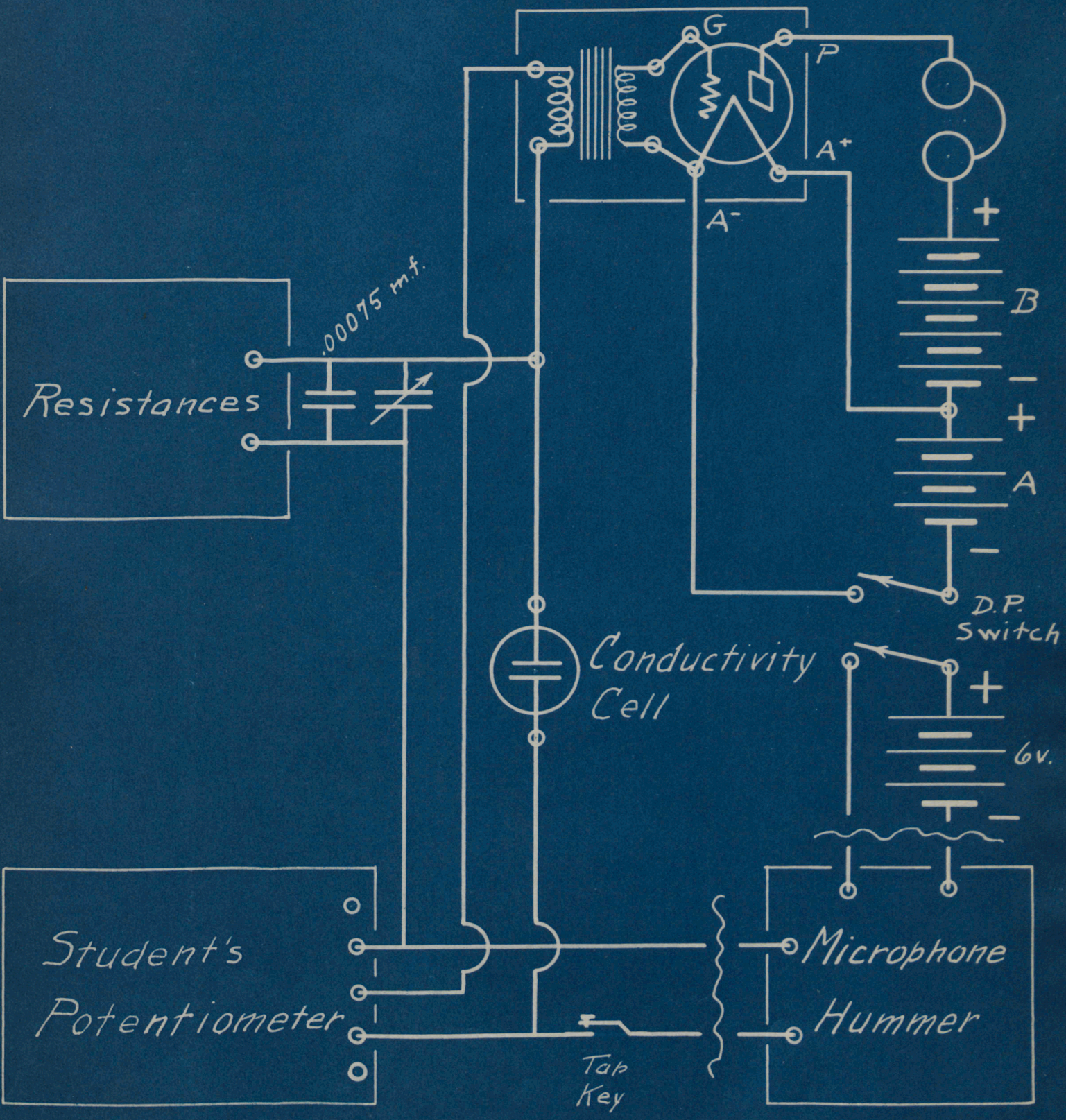
Arrangement of Apparatus

The apparatus was connected as shown in Fig. 3. The technique used in this research was one which could be used in any well equipped laboratory, and was based on that of Randall and Scallione ⁽³⁶⁾ with the following differences.

(1) Two Leeds and Northrup dial resistances, Catalogue No. 4723 were used in place of the expensive Curtis

Fig. 4

Arrangement of Apparatus for Conductivity Measurement



compensated resistance coils. The Curtis coils are specially designed and are preferable for very accurate work but the dial type resistances have been recommended as suitable for most purposes. As mentioned previously, Jones and Joseph (21) found none of the commercial resistances free from error but from his data it may be assumed that the maximum error from this source in the present investigation was -0.012% for a plug resistance of 5000 ohms, which was used in but three of the measurements, namely 0.002 N, 0.001 N and in determining the cell constant of cell A.

(2) Standard radio telephones with a one step audio frequency amplifier in place of a set of telephones tuned to 1000 cycles. The former is preferable according to Jones and Joseph (21). In the present research an amplifier of conventional radio design was assembled using one 201A radio tube and a 3-1 audio transformer. The current for the tube was supplied by a storage battery and a 45 volt B battery was used for the plate circuit. The leads usually connected to the phones were connected to the primary of the transformer and the phones inserted in the plate circuit as shown in the diagram, Fig. 2. The amplifier alleviates the strain on the nerves and makes tuning of the phones undesirable. The point of minimum sound is much more easily determined with its help.

(3) A Leeds and Northrup Microphone Hummer instead of the Siemens-Schuchart high frequency generator. The microphone hummer is not as expensive as more elaborate apparatus, is very efficient and does not easily get out of adjustment.

(See Experimental Physical Chemistry, Daniels et al., McGraw-Hill Book Co., 1929, p. 387). The hummer was packed in a sound proof box so that no sound was heard except thru the phones.

(4) The instruments were not shielded but were well separated from one another as recommended by Jones and Joseph (21).

(5) The leads were heavy stranded lamp cord. However, the leads from the microphone hummer were not shielded.

There is no mention in the paper by Randall (36) of grounding the bridge, the water bath, or the phones, yet very satisfactory minima were obtained at all times. The reason for grounding different parts of the apparatus is to equalize capacity effects and thus make the point of silence sharper. Partington (56) states that as long as a sharp minimum is obtained in the phones, it may be assumed that inductance, capacity and polarization are negligible, unless the resistances to be measured are very large or very small. While grounding the apparatus according to the method of Jones and Joseph (21) is undoubtedly preferable, owing to its complication it was not followed in this investigation. Very satisfactory minima were observed in this investigation as reported also by Randall, probably due to the fact that in both cases the water bath was not grounded. It will be recalled that Jones and Joseph found that the error introduced by imperfect grounding was greatly increased when the water bath was grounded. Unless a very carefully designed system of grounding,

such as that proposed by Jones and Joseph, is followed, the authors are of the opinion that no ground at all is preferable to obsolete forms of grounding.

The capacity necessary to balance that of the cell A was determined by a large calibrated radio condenser and this capacity was obtained by means of a 0.00075 m.f. fixed condenser shunted by a conventional 11 plate variable condenser. This assured a good minimum in the phones at all times. The capacity necessary to balance that of cell B was of such a low value that hardly any appreciable difference in sharpness of the bridge setting was noticed whether or not a capacity was used. The variable condenser alone without the fixed condenser was sufficient to supply this low capacity.

As a slide-wire bridge, a new Leeds and Northrup Students Potentiometer (No. 164593) was used. The slide-wire has a resistance of 10 ohms and the extension coils on either side have a resistance of 45 ohms so that when the extension coils are used the total resistance of the slide-wire is only one tenth that of the entire bridge. The slide-wire has 100 uniform divisions with a guaranteed accuracy of .5 division, therefore when the end coils are in the circuit the accuracy in reading the bridge is 0.05% or less. Actually the point of minimum sound could be read to tenths of a division, as the bridge balance was very sharp. The end coils may be cut out for approximate adjustment of the resistances necessary to make the bridge balance near the mid-point of the bridge.

The usual intercomparisons of slide wire and resistance coils were made before the measurements. Strouhal and Barus (37) give an exact method of calibration.

The conductivity cells were hung in the middle of the bath as suggested by Jones and Joseph (21) and connections were made by means of heavy insulated stranded wires which dipped into small test tubes of mercury which also were submerged in the bath. This was to prevent the leads from conducting heat to or from the cell. The ends of the leads dipping into the mercury were amalgamated. This method of connecting the cell is recommended by Washburn (26).

The constant temperature bath was a large galvanized iron container 18" by 14" and 13" in depth, filled with water. The circulation of the water was provided for by an electric stirrer which was fitted with a large baffle so that efficient stirring was obtained with the motor running at a slow speed without noise or sparks. The temperature was maintained at $25^{\circ}\text{C} \pm .01^{\circ}$ with a toluene-bulb gas regulator, illustrated in Fig. 5, page 51, which proved very satisfactory. On warm days a cooling coil was used allowing tap water to run slowly thru the coil. The temperature was determined with a thermometer graduated in 20ths of a degree and which could be easily read to 0.01° with an attached telescope. Variations in temperature could be more easily read by a neighboring Beckman thermometer. As stated previously, the bath was not grounded.

Determination of Cell Constant

Since the electrodes are not exactly one square centimeter in area and exactly one centimeter apart, the resistance measured is not the specific resistance of the solution. However, as the resistance varies in proportion to the distance between the electrodes and inversely as the square of the area, the resistance is some constant times the specific resistance. This constant is called the cell constant. As it is impossible to accurately measure the area of the electrodes and the distance between them, the universal method of determining the cell constant is to measure the conductivity of a standard solution, the specific conductivity of which has been measured accurately in special cells of known dimensions. From the value (k) of the standard solution measured in the cell to be calibrated and the previously determined specific conductance (L) of the standard, the cell constant (C) is determined as follows:

$$k = CL \quad \therefore \quad C = \frac{k}{L}$$

Kohlrausch (16) (32) (38) and his co-workers give data for calibrating conductivity cells with solutions of potassium chloride as standards. Recent investigators have found an error in the directions given by Kohlrausch and Holborn (16), for making up some of the more dilute solutions by the weight method. Thus Kraus and Parker (39) found a difference in cell constant of 0.48% determined with a 0.1 N and 0.01 N HCl solutions made according to the directions

(by weight) of Kohlrausch and Holborn, which was much too large to blame upon experimental error. They maintain that standard solutions are made most conveniently by the weight method, thus avoiding the necessity of calibrating volumetric apparatus. Kohlrausch and Maltby (38) give the most complete data for KCl solutions, but give no directions for making up the solutions. Kohlrausch and Holborn (16) give directions by the weight method which for 1 N are correct, but for 0.1 N (as also for 0.02 N and 0.01 N which are made from the first by dilution) the directions, namely 7.430 gms. KCl to 1000 gms. solution, Kraus and Parker calculate to be 0.10% in error owing to neglecting the density of the solution. These authors corrected this error in the preparation by the weight method and then the cell constants using 0.01 N and 0.1 N KCl solutions checked to within 0.016%. They give the following directions for the preparation of the KCl solutions. "The salt after two recrystallizations from conductivity water is placed in a porcelain crucible and heated over a Meeker burner, and cooled over phosphorous pentoxide; half the KCl melts and the rest forms a crust. The KCl is weighed quickly on a watch glass to the exact quantity calculated and added to the water and the solution kept in stoppered bottles. Approximately 1000 gms. of conductivity water are weighed and this weight multiplied by 0.007494 will give the weight of KCl required to make a 0.1 N solution.

A 0.1N KCl solution was made in this manner but the resistance necessary to keep the bridge balance near the mid-

point was so low that a good minimum in the phones could not be obtained owing to polarization. Therefore the solutions made in this manner were diluted with nine volumes of conductivity water, thus making a 0.01 N solution and a satisfactory minimum was obtained. However, as Kohlrausch and Maltby do not give a value for 0.01 N KCl at 25°C, two alternatives remained. One, to use their data for 18°C and calibrate the cells at this temperature and assume that the cell constant is independent of temperature between 18°C and 25°C (Kraus and Parker loc. cit. page 2428); or to accept other data, e.g. the value for 0.01 N KCl at 25°C as calculated by Bray and Hunt (40) from Kohlrausch and Maltby's value for 0.01 N KCl at 18°C. Following the method of Randall (36) the later method was used. In addition to the solutions made up by the corrected weight method a 0.01 N KCl solution was made according to Randall (36) by a volumetric method as follows: "—cell constant — 1.4912 g (weighed in air) of Kahlbaum's potassium chloride recrystallized to a constant conductance and powdered and dried to a constant weight, was dissolved to make two liters of solution at 25°C. This solution according to Kohlrausch, with temperature coefficients of Dequene, and as used by Bray and Hunt (40) has a specific conductance of 0.0014142 mho. From the work of Parker and Parker (22) we calculate the standard of Bray and Hunt to be 0.152% too high. The original results have been corrected by this amount. Atomic weights of 1926 and vacuum corrections have been used."

Since the value given by Bray and Hunt is actually 0.0014142 mho, it is evident that Randall corrected his results obtained by using this value by the 0.152% which he mentions; or what is equivalent Bray and Hunt's value should be 0.0014120 mho. which value was used as the conductance of 0.01 N KCl in this investigation.

As stated previously, 0.01 N KCl solutions were made up both by the corrected weight method of Kraus and Parker and by a volumetric method suggested by Randall. If both methods are correct they should result in identical solutions and the cell constants calculated from each should prove identical. The values obtained using the two methods of preparation agreed to within 0.05% and the average 0.80373 was taken as the cell constant of cell B. As explained previously, Bray and Hunt's corrected value for the conductivity of 0.01 N potassium chloride, namely 0.0014120 mho, was used in the calculations.

The cell constant of cell A could not be determined with 0.01 N KCl solution as the resistance was far too low. Therefore the method of intercomparison as explained by Weiland (41) was used. In brief, the method is to measure the conductance of a solution somewhere near the lower limit of concentration allowable, in a cell whose cell constant has already been determined by a standard KCl solution, then the same solution is measured in the cell of lower concentration range, and from the measured conductivity of the solution as determined in the already calibrated cell, the cell constant

of the second cell may be calculated just as though the solution were a standard. The concentration ranges of the cells designed by Washburn overlap sufficiently so that this method is readily applicable. In the present research, the solutions used for intercomparison of Cell A and cell B were cobalt sulfate solutions 0.001-0.0005 N which resulted in good minima in the phones with both cells. The average value for the cell constant of cell A as determined in this manner using five different solutions was 0.023206.

Measurement of Conductivity. After the water bath had become constant at $25^{\circ}\text{C} \pm 0.01^{\circ}$ for several hours the cell was rinsed with the solution under investigation and then filled and allowed to attain the temperature of the bath for from 15 - 30 minutes. The conductivity measurements were then made and repeated at 15 minute intervals until a constant value was obtained. Then the cell was refilled two or three times and the same procedure of measurement repeated until a further filling did not change the value of the conductance. The number of such fillings and the constancy of the value obtained depended upon the concentration as the absorption on the platinum black became more or less important. Between measurements the cells were kept filled with conductivity water.

The 0.5 N. cobalt sulfate solution was made as described previously under the standardization of the solutions. From this were made all the less concentrated solutions by dilution.

The Ostwald (42) Method of dilution in which the solution is progressively diluted in the conductivity cell itself by withdrawal of solution and addition of conductivity water by means of calibrated pipettes was much used by the early workers on conductivity. But for many reasons the accuracy of this method is very limited. Since 10 c.c. pipettes are used and the total volume of solution in the cell is only 20 c.c., the chance in error upon each successive dilution is very great. This combined with the possibility of contamination, displacing the electrodes and insufficient mixing make this

method applicable only as a laboratory experimental or technical method at the present time. However, the speed with which measurements could be obtained by this simple method of dilution enabled early workers in this field to investigate a very great number of solutions and to report voluminous quantities of data. As mentioned previously, this method was used by Jones and Jacobson (27) in their investigation of the conductivity of many salts including cobalt sulfate.

The method of dilution used in the present investigation was as follows: from the standard 0.5 N CoSO_4 solution prepared as explained previously, the 0.2 N solution was prepared by diluting 100 c.c. of the 0.5 N solution to a volume of 250 c.c. In a similar manner the 0.1 N solution was made by diluting 100 c.c. of the 0.5 N solution to a volume of 500 c.c. The 0.05 N solution was made by dilution of 100 c.c. of 0.5 N solution to 1000 c.c.; and in a like manner all the more dilute solutions. In each case two or more solutions were made up and concordant results were obtained. Whenever possible these duplicate solutions were made by dilution in a different ratio, e.g. the 0.1 N from the 0.2 N, the 0.05 N from the 0.1 N etc., in which case duplicate values would prove that both the solution used and the solution prepared were concordant with the other solutions. In this manner a constant check on the method of dilution was obtained and any error immediately detected. Thus one dilution was found to be at fault owing to the fact that the solution used and the

conductivity water added were not at the same temperature. This was immediately corrected by keeping the solutions and the conductivity water next to one another and far from the window. The faulty solution was rejected and after due precautions concordant results were obtained with new solutions. Since the dilution is by volume ratios, the variation in room temperature has no effect on the liquids provided that they be at equal temperatures.

When the cell and its contents had attained the temperature of the bath the double throw switch (as shown in Fig. 4, page 33) was closed and the microphone hummer and the amplifier started. A tap key T prevented the alternating current from passing thru the cell except for short intervals while the bridge was being set, in order to avoid appreciable heating of the solution by the current. Since an amplifier was used it was possible to use the lowest output current of the microphone hummer so that the heating of the cell would be at the lowest possible value. Five different resistances were used with each filling of the cell and the values chosen so that the bridge reading would lie well within the middle tenth of the bridge. At first much trouble was experienced in trying to reproduce closely the values for the conductivity of concentrations 0.01 N and below. It was noticed that the conductivities of these solutions gradually rose. At first the effect was thought to be due to solution of the salt adsorbed on the platinum black of the electrodes from the more concentrated solutions but even after allowing the cell to

remain standing for several days in conductivity water, the conductance value steadily rose. Hence it was concluded that the solution in the volumetric flask had itself increased in conductivity due to solution of some of the free alkali in the glass. This effect was almost entirely eliminated by allowing conductivity water to remain in the vessels for several days prior to their use.

Whenever the conductivity of a new concentration was to be measured, the cell had to be rinsed very carefully with conductivity water and then filled several times with the solution to be observed as the platinum black on the electrodes tends to retain the salt adsorbed from the more concentrated solution. On the contrary, in the case of the extremely dilute solutions, if the cell has been allowed to remain filled with conductivity water for many hours, the first few fillings with the dilute solution show too low a value due to adsorption of the salt and consequent lowering of the concentration of the already extremely dilute solution. Thus it is seen that at low concentrations it is extremely difficult to obtain concordant results. If more than a few days elapsed between the measurement of the conductivity of a solution and its use to prepare a solution of lower concentration, the conductivity was re-determined and should any change be noted the solution was discarded and a solution used which checked with previous measurements. This was only necessary in the more dilute regions 0.01 N and below, owing to the slight solubility of the glass as explained above. Another effect noticed in the

dilute solutions on standing for several weeks was the formation of a crystalline flaky precipitate in those bottles which had large amounts of air above the liquid. As this was noted only in the cobalt sulfate solutions and not in pure water or potassium chloride solutions and only in those flasks containing much air, it was assumed that the crystals were the very slightly soluble cobalt carbonate formed from carbon dioxide present in the air. The appearance of such crystals was noted only some weeks after all the conductivity measurements had been completed but they may have constituted a source of error in the very dilute solutions. One entire set of measurements on solutions of concentrations below 0.2 N was made a month after the first values had been obtained.

Viscosity Measurements

As explained previously, an approximate correction for the term $\frac{(U_{C+})_{\infty} + (U_{A-})_{\infty}}{U_{C+} + U_{A-}}$ in the equation, $\gamma = \frac{\Delta}{\Delta_{\infty}} \frac{(U_{C+})_{\infty} + (U_{A-})_{\infty}}{U_{C+} + U_{A-}}$ is the viscosity ratio $\frac{\eta}{\eta_0}$, where η = the viscosity of the solution and η_0 is the viscosity of pure water. The viscosity correction is discussed at length by Washburn (43). Although this correction is only a rough approximation, it amounts to a considerable value at moderate concentrations. Accordingly, it was thought of sufficient interest to apply the correction to the values of the equivalent conductance.

The only data available for the viscosity of cobalt sulfate solutions at 25°C was that of Wagner (44) whose measurements were upon a very limited number of concentrations, namely 1 N, N/2, N/4 and N/8. Accordingly, a check on the viscosity of the 0.5 N solution was attempted along with the value for the other concentrations used in the conductance measurements. Table II records Wagner's data for cobalt sulfate at 25°C.

Table II

<u>Normality</u>	<u>Specific Gravity</u>	<u>Relative viscosity</u>
1.0	1.0750	1.3543
0.5	1.0383	1.1598
0.25	1.0193	1.0766
0.125	1.0110	1.0402

For the flow of a homogeneous liquid through a capillary tube, the following expression may be deduced, $\eta = \frac{\pi p r^4 t}{8 V l}$

where p = driving force,

r = radius of tube,

t = time required for a given volume,

V = volume of the liquid,

l = length of tube

It is evident that if only the relative viscosity of the solution is desired, that is the ratio of its viscosity to that of pure water, the characteristics of the instrument used, namely the radius and length of the capillary, being constant, will cancel out, in the resulting value for the relative viscosity $\frac{\eta}{\eta_0}$. Now if the volume of the liquid is kept the same in all cases, the ratio of the driving forces may be shown to depend only on the ratio of the two densities, so that the relative viscosity of a solution to that of pure water may be measured by the relative times of flow multiplied by the relative densities, or, $\frac{\eta}{\eta_0} = \frac{S_1}{S_0} \frac{t_1}{t_0}$, provided only that the temperatures, characteristics of the viscosimeter, and the volumes are constant.

The type of viscosimeter used in these measurements was the Ostwald modification of Poiseuille's apparatus, illustrated in Fig. 5, page 51, an instrument quite generally used in laboratory determinations. The instrument was carefully cleaned with chromic acid solution and dried before introduction of the liquid to be investigated. The constant temperature bath was the same one as used for the conductivity measurement. A stop watch graduated in tenths of a second was

used to determine the times of flow.

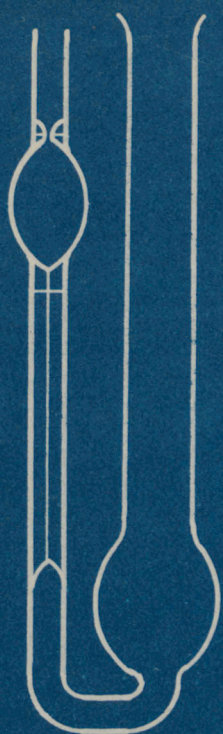
The time of flow for pure water was checked after every few determinations and at one time a distinct change in the value was observed. This was no doubt due to the enlarging of the capillary by drawing cleaning solution through it with suction, as the time of flow was definitely shortened by 0.65 seconds after this treatment. After this displacement of the water constant measurement on a previously determined solution were repeated and checked very closely the values determined with the old constant. The densities were obtained by a pycnometer of 60 c.c. capacity (also illustrated in Fig. 5, page 51). The same water bath was used.

In order to test the values of the viscosity, the Jones and Dale (45) function has been plotted in Fig. 6, page 53. These authors found that the graph of $\phi - 1/\sqrt{C}$ plotted against $\sqrt{C}$, (where ϕ = the reciprocal of the relative viscosity or the fluidity) closely approximated a straight line for many salts. In table III the values for the densities referred to water at 25°C, and the viscosity ratios of the solutions are recorded and the calculated percentage deviation from the straight line function.

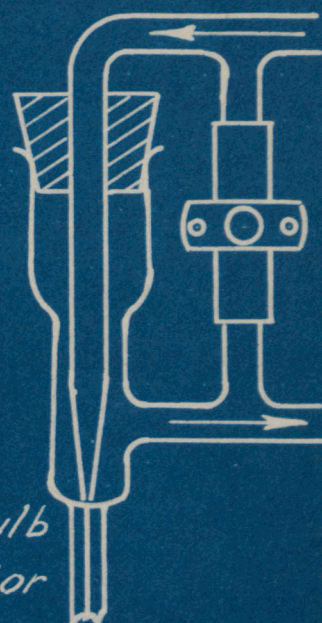
Table III

<u>Normality</u>	<u>d 25°</u>	<u>η/η_0</u>	<u>Deviation</u>
0.5	1.0380	1.1613	+0.38%
0.2	1.0158	1.0579	-0.56%
0.1	1.0079	1.0337	+0.09%

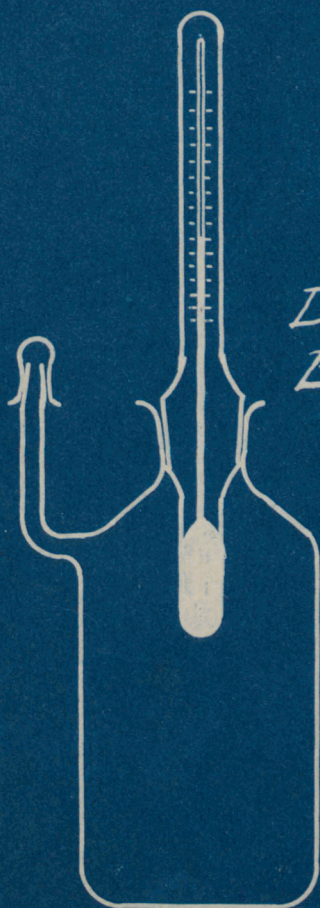
Fig 5.



*Ostwald
Viscosimeter*



*Toluene Bulb
Gas Regulator*



*Density
Bottle*



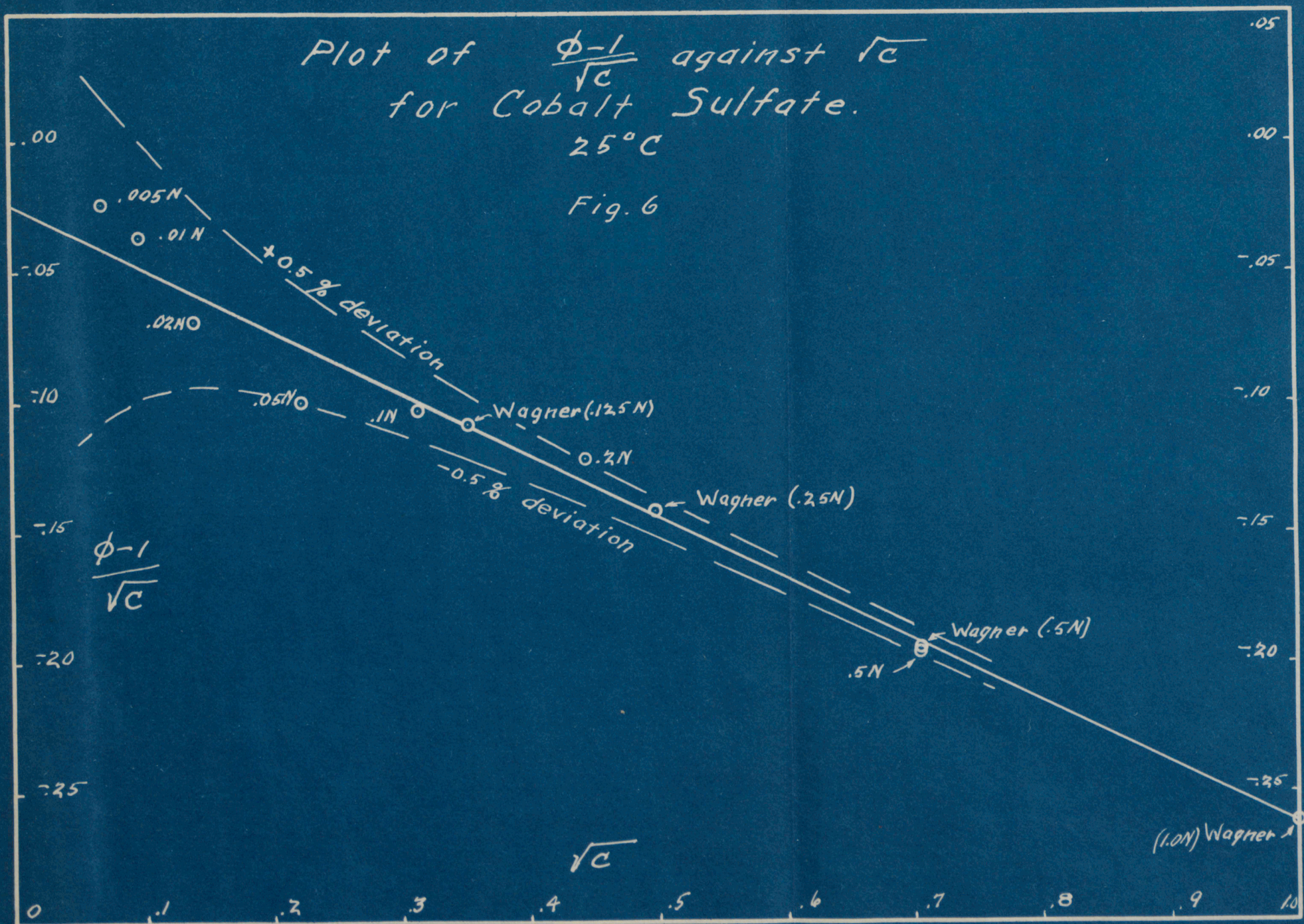
Table III (cont)

<u>Normality</u>	<u>d_{25}^{25}</u>	<u>η/η_0</u>	<u>Deviation</u>
0.05	1.0040	1.0230	+0.50%
0.02	1.0020	1.0099	+0.16%
0.01	1.0009	1.0035	-0.13%
0.005	1.0004	1.0017	-0.13%
0.002	1.0000	1.0000	
0.001	1.	1.0000	

In the plot of Jones and Dale's function the four determinations by Wagner ⁽⁴⁴⁾ are included. His value for 0.5 N (the only one directly comparable to a concentration investigated in this research) is 1:1598 or 0.13% lower than the value obtained by the authors. Assuming the data of Wagner to be the most nearly correct, as his purpose was to test the viscosity function of Arrhenius ⁽⁴⁶⁾, a straight line has been drawn as nearly as possible to his points. The maximum deviation of the data obtained in the present investigation from that required by the straight line relation - for 0.2 N - is 0.56% while the greatest deviation in Wagner's data - for 0.5 N - is 0.23%. The nature of the plot is such as to magnify the apparent percentage of deviation at the low concentrations. The percentage deviations as well as the values for plotting the 0.5% curve were obtained by using a value for $\phi - 1/\sqrt{C}$ read from the straight line and solving for ϕ . As suggested by Jones and Doyle ⁽⁴⁵⁾ the value for $\phi - 1/\sqrt{C}$ was found to be negative at the intersection of the $c = 0$ axis.

Plot of $\frac{\phi-1}{\sqrt{c}}$ against $\sqrt{c}$
for Cobalt Sulfate.
25°C

Fig. 6



Results and Calculations

Table IV contains the averages of the specific conductances obtained and the equivalent conductances calculated from them. The values have been corrected for the conductance of the solvent, as explained previously. For purposes of comparison the corresponding values for nickel sulfate solutions, as determined by Murata (47) are also included.

Table IV

Conductance of Cobalt Sulfate Solutions at 25°C

Concentration	Specific Conductance	Equivalent Conductance	NiSO ₄ (Murata)
1.0 N			29.091
0.5	17718 X 10 ⁻⁶	35.436	35.222
0.2	8778 "	43.890	43.585
0.1	5111.8 "	51.118	50.755
0.05	2978.8 "	59.576	59.160
0.02	1448.2 "	72.410	72.254
0.01	827.76 "	82.778	82.69
0.005	466.2 "	93.24	93.16
0.002	210.0 "	105.0	105.49
0.001	112.7 "	112.7	113.05
0.0005	59.35 "	118.7	118.66
0.0002	24.74 "	123.7	124.14
0.0001	12.39 "	123.9	126.90

In Table V are given the densities, relative viscosities and the calculated conductance viscosity ratios.

Table V

Normality	$d_{25}^{25^\circ}$	η/η_0	$\frac{\Lambda}{\Lambda_0}$	$\frac{\Lambda}{\Lambda_0} \cdot \frac{n}{N_0}$
0.5	1.0380	1.1613	0.26327	0.30574
0.2	1.0158	1.0579	.32608	.34496
0.1	1.0079	1.0337	.37978	.39258
0.05	1.0040	1.0230	.44262	.45280
0.02	1.0020	1.0099	.53797	.54330
0.01	1.0009	1.0035	.61499	.61714
0.005	1.0004	1.0017	.69272	.69390
0.002	1.0000	1.0000	.78009	.78009
0.001	1.	1.0000	.83730	.83730
0.0005	1.	1.	.88187	.88187
0.0002	1.	1.	.91902	.91902
0.0001	1.	1.	.92051	.92051

As explained previously, the value of the equivalent conductance at infinite dilution (Λ_0) is of necessity an extrapolated value. Even salts which are highly ionized do not approach this value at low concentrations with sufficient speed that the value may be read from a smooth curve of the equivalent conductance values with much accuracy. Many empirical functions have been proposed by which the inaccuracy of this extrapolation to zero concentration may be diminished. In general, with several assumptions, these equations may be derived from the law of mass action. Thus, for a binary salt, $MX \rightarrow M^+ + X^-$ the mass action equation, assuming the ions as well as undissociated molecules behave as perfect solutes, becomes

$$\frac{C_{M+} \times C_{X-}}{C_{MX}} = K \quad (13)$$

If γ equals the degree of dissociation then the mass action expression becomes

$$\frac{C\gamma \times C\gamma}{C(1-\gamma)} = K \quad (14) \quad \text{or} \quad (C\gamma)^2 = KC(1-\gamma)$$

Ostwald (48) assumed that $\gamma = \frac{\Lambda}{\Lambda_0}$, where Λ is the equivalent of a given concentration and Λ_0 is the equivalent conductance of the solution at zero concentration. Then the

above equation may be simplified as follows:

$$C(\gamma)^2 = K - K\gamma$$

$$C \left(\frac{\Lambda}{\Lambda_0} \right)^2 = K - K \frac{\Lambda}{\Lambda_0}$$

multiplying by $\frac{\Lambda_0}{K}$ the equation becomes,

$$\frac{C}{K} \frac{\Lambda_0}{\Lambda_0} \left(\frac{\Lambda}{\Lambda_0} \right)^2 = \Lambda_0 - \Lambda$$

$$\text{or} \quad \Lambda = \Lambda_0 - \frac{C\Lambda^2}{K\Lambda_0} \quad (15)$$

For salts dissociating into N ions, the equation $(C\gamma)^N = KC(1-\gamma)$ in a similar manner becomes

$$C^N \gamma^N = KC - \gamma KC$$

$$C^{N-1} \gamma^N = K - \gamma K$$

Again assuming $\frac{\Lambda}{\Lambda_0} = \gamma$

$$C^{N-1} \left(\frac{\Lambda}{\Lambda_0} \right)^N = K - \frac{\Lambda}{\Lambda_0} K$$

multiplying by $\frac{\Lambda_0}{K}$

$$\frac{C^{N-1}}{K} \frac{\Lambda_0}{\Lambda_0} \left(\frac{\Lambda}{\Lambda_0} \right)^N = \Lambda_0 - \Lambda$$

Thus equation (15) in the more general form becomes

$$\Lambda = \Lambda_0 - \frac{C^{N-1} \Lambda^N}{K \Lambda_0^{N-1}} \quad (16)$$

corresponding to Storch's Equation (48)

But if $\Lambda \rightarrow \Lambda_0$ and N is large, then $\frac{\Lambda^N}{\Lambda_0^{N-1}} \simeq \Lambda_0$

so that with this assumption equation (16) may be written

$$\Lambda \simeq \Lambda_0 - \frac{\Lambda_0 C^{N-1}}{K} \quad (17) \text{ or letting } \frac{\Lambda_0}{K} = B$$

$$\Lambda \simeq \Lambda_0 - BC^{N-1} \quad (18)$$

Several equations have been proposed of this form. Kohlrausch⁽⁵⁰⁾ gives $\Lambda = \Lambda_0 - BC^M$ where $M = 1/3$ or $M = 1/2$ Lorenz⁽⁵¹⁾ and Walden⁽⁵²⁾ suggest that $M = 0.45$. Debye and Huckel⁽⁹⁾ deduce an equation of this form and show that M should have the value $1/2$, this value being independent of the nature of the electrolyte. A. A. Noyes and his associates⁽²⁸⁾ employ a graphical method to evaluate N in the equation (18), which will be referred to later.

One objection to Kohlrausch's equation and all those based upon it, is that it involves the assumption that strong electrolytes do not obey the Mass Action law even at high dilutions. In fact Bates⁽⁵³⁾ has pointed out that in this method the value of K is implicitly assumed to decrease without limit and to approach zero when the concentration becomes zero.

For this reason Kraus⁽⁵⁴⁾ suggests a four-parameter empirical equation

$$\frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda_c)} = K = K_0 + k \left(C \frac{\Lambda_c}{\Lambda_0} \right)^h \quad (19)$$

where Λ_c is the equivalent conductance corrected for viscosity. They have applied this equation to all the conductivity data available at that time and have found it applicable with but few exceptions, one of these however being in the case of

strong electrolytes, e.g. potassium chloride as determined by Kraus and Bray. Washburn (55) discusses this equation critically and concludes that the only advantage over the Kohlrausch equation is that at high dilutions it approaches the mass action equation.

A more complicated three-parameter equation, due to Bates (52) expresses the change of conductivity with concentration with great exactness for Kohlrausch and Maltby's potassium chloride solutions between 1.0 N and 0.0001 N. This function, namely

$$\log \frac{\Lambda_c^2 C}{\Lambda_o(\Lambda_o - \Lambda_c)} = \log K = \log K_o + K'(C \frac{\Lambda_c}{\Lambda_o})^{h'} \quad (20)$$

as well as the Kohlrausch, and the Kraus equations are compared graphically by Washburn (55), using the above mentioned data.

Washburn proposes a graphical method whereby the values of the equilibrium constant are plotted against the concentration, employing different assumed values of Λ_o and rejecting those values which cause the curve to exhibit radical changes in direction at low concentrations. That is, curves are plotted with assumed values of Λ_o until one which approaches $K = \text{a constant at infinite dilution}$. Using Kohlrausch and Maltby's data (38) which extend to 0.0001 N he maintains the accuracy of this method to be 0.2%, and if sufficiently accurate data extends to 0.00002 N the extrapolation would be only $\pm 0.01\%$ in error.

The method used in this investigation was that due to A. A. Noyes (28) (5). This is a graphical method of evaluating N in equation (18).

Equation (16) $\Lambda = \Lambda_0 - \frac{C^{N-1} \Lambda^N}{K \Lambda_0^{N-1}}$, multiplying thru by $\frac{1}{\Lambda \Lambda_0}$

is evidently equal to $\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - \frac{C^{N-1} \Lambda^{N-1}}{K \Lambda_0^N}$

or $\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - K' (C \Lambda)^{N-1}$ (21)

Accordingly, in Figure 7, page 60, the values of $(C \Lambda)^{N-1}$ in the range from 0.0001 to 0.2 normal have been plotted as abscissae against the values of $\frac{1}{\Lambda}$ as ordinates, by varying the values of N-1 until a plot as linear as possible was obtained. In this plot it was found necessary to omit the values for 0.0002 and 0.0001 normal, as these are evidently in much greater error than are the other determinations. The value of Λ_0 was obtained graphically by extrapolation of the curves to zero concentration, where $C \Lambda = 0$. In Figure 7, in order to make the various curves comparable, the value of $(C \Lambda)^{N-1}$ for the highest concentration (0.02 normal) was made 100 for each value of N, and the other values proportionally varied, that is, changed to the per cent of the value for 0.02 N corresponding to that value of N taken.

As may be seen from the graphs, the value of the exponent for cobalt sulfate at 25°C was found to be 1.58 as with this value the curve very closely approximates a straight line. The value of $\frac{1}{\Lambda}$ at zero concentration was found, by extrapolation of the N = 1.58 curve, to be 0.00743 hence Λ at zero concentration or $\Lambda_0 = 134.6$ at this temperature.

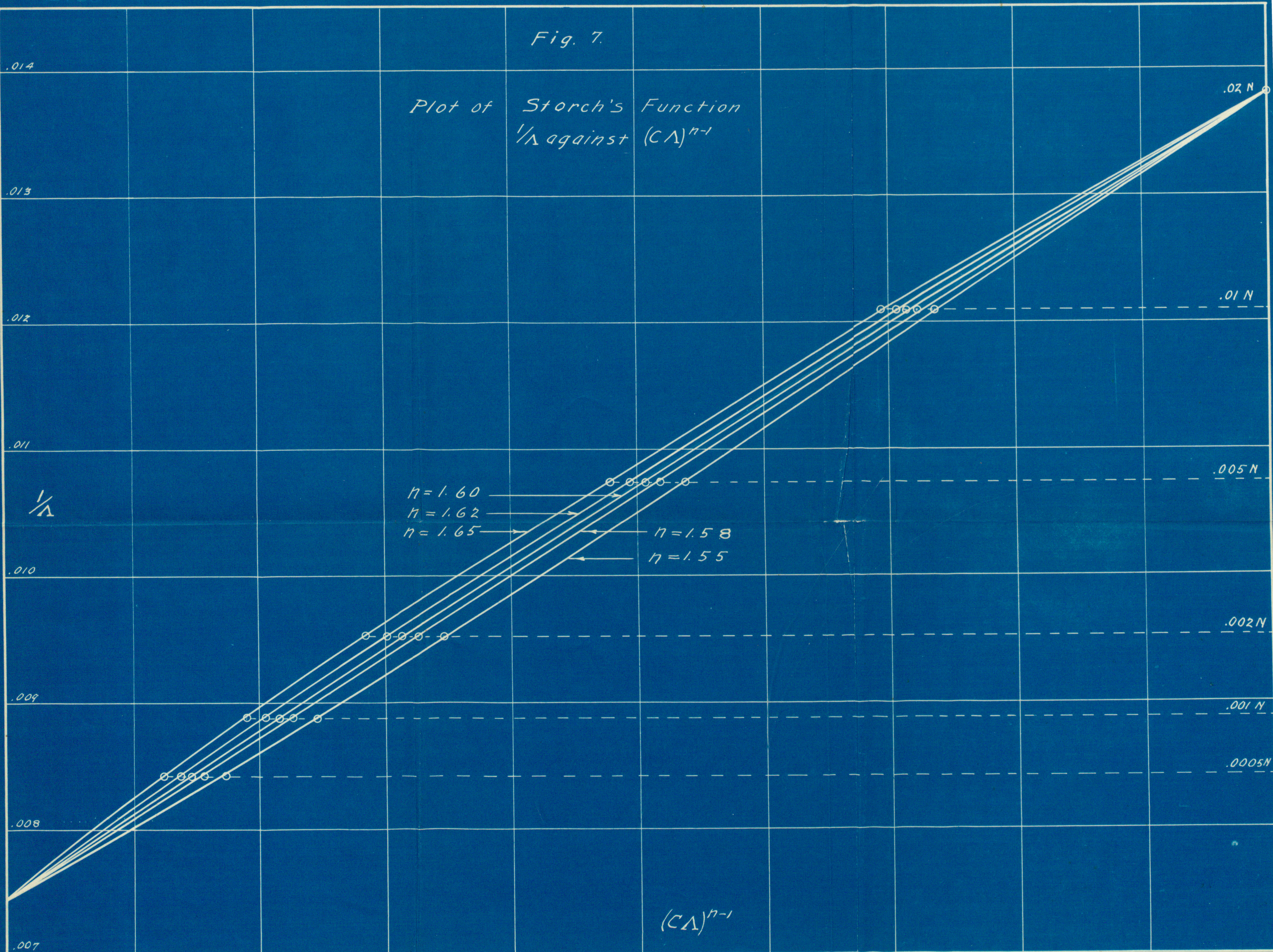
It is interesting to note that Murata (47) found the exponent N = 1.60, for nickel sulfate at 18°C and at 25°C.

Plot of Storch's Function

Electrical Conductance of Cobalt Sulphate Solutions by R.C. Cantelo and A.J. Berger

Fig. 7.

Plot of Storch's Function
 $1/\Lambda$ against $(C\Lambda)^{n-1}$



According to Noyes and Falk (5), for all bi-bivalent sulfates N takes a value not far from 1.6 for the concentration interval from 0.001 to 0.02 normal. Noyes also points out that the variation of N with the temperature is negligible.

Summary And Conclusions

The conductances of aqueous cobalt sulfate solutions at concentrations 0.0001 to 0.5 normal have been measured at 25°C; and the equivalent conductance at zero concentration has been determined by extrapolation of the data.

The value of the exponent M in the equation $\Lambda = \Lambda_0 - BC^M$ (18) has been found to equal 0.58 for cobalt sulfate.

The densities and the relative viscosities have been determined for the solutions, and the conductance-viscosity ratios have been calculated.

Acknowledgement

The author wishes to express his sincere gratitude for the assistance and encouragement of Dr. R. C. Cantelo, who suggested this research and who by his careful supervision and constructive criticism guided and directed the course of this investigation.

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