THE CONDUCTANCES OF ZINC PERCHLORATE AND POTASSIUM OCTACYANOMOLYBDATE (IV) AND THE TRANSFERENCE NUMBER OF ZINC SULFATE IN AQUEOUS SOLUTION AT 25° C.

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY

Mary Patricia Faber

1961

This is to certify that the

thesis entitled

The Conductances of Zinc Perchlorate and Potassium Octacyanomolybdate (V) and the Transference Number of Zinc Sulfate in Aqueous Solution at 25°C.

presented by

Mary Patricia Faber

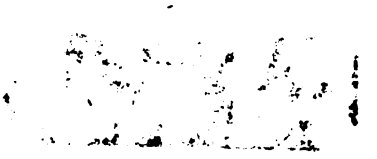
has been accepted towards fulfillment of the requirements for

Ph. D. degree in Chemistry

James L. Dye
Major professor

Date Aug 16, 1961

O-169



ABSTRACT

THE CONDUCTANCES OF ZINC PERCHLORATE AND POTASSIUM OCTACYANOMOLYBDATE (IV) AND THE TRANSFERENCE NUMBER OF ZINC SULFATE IN AQUEOUS SOLUTION AT 25°C.

by Mary Patricia Faber

An outline of the history of the method of conductance and transference number measurements, as well as a history of the interionic attraction theory of electrolytic solutions is presented.

As a test of the theoretical expressions which have been developed for the description of the conductance phenomenon, an attempt was made to fit the conductance data of zinc sulfate. Three parameters are involved, one of which is the equivalent conductance of zinc sulfate. To reduce the number of arbitrary parameters, the equivalent ionic conductance of zinc ion was sought by an independent measurement of the equivalent conductance of aqueous zinc perchlorate. The conductance of this salt was found to deviate markedly from the Onsager equation even in dilute solution. Attempts made to explain this behavior on the basis of ion-pairing, hydrolysis and purely electrostatic interactions were entirely unsatisfactory.

As a further test of the theory the transference number of zinc sulfate in water as a function of concentration was measured by the moving boundary method at 25° C.

The conductance data for zinc sulfate can be adequately fit by either the Fuoss-Onsager theory including ion association or by including terms of the electrophoretic equation which are usually neglected. The former treatment also gives a fairly suitable limiting form for transference numbers. However, when the limiting ionic conductance for zinc ion from measurements on zinc perchlorate is used, it is much too high for either theory to describe the behavior adequately.

We conclude that zinc salts do not form typical dilute solutions but that, perhaps due to the covalent bonding tendencies of the zinc ion, there are deviations from any theory which is based on the assumption of hard, non-polarizable ions.

While the primary objective of determining λ_0 for zinc ion thus could not be achieved, the new phenomenon observed will require a new approach to this conductance problem. It also indicates that not all electrolytes can be treated in the conventional fashion.

In addition to these considerations, the equivalent conductance of potassium octacyanomolybdate (IV) was determined. Large deviations from the limiting equation of Onsager occur, so that the limiting ionic conductance could not be accurately determined by the methods now available. We attempted to obtain the transference number of this salt from the moving boundary method. No reproducible transference number could be determined. It was concluded from examination of much self-consistent data that perhaps some immediate decomposition was occurring even in freshly prepared solutions.

THE CONDUCTANCES OF ZINC PERCHLORATE AND POTASSIUM OCTACYANOMOLYBDATE (IV) AND THE TRANSFERENCE NUMBER OF ZINC SULFATE IN AQUEOUS SOLUTION AT 25°C.

By

Mary Patricia Faber

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

ACKNOWLEDGMENTS

The author wishes to express her sincere appreciation to Professor J. L. Dye for his guidance and assistance throughout the course of this work, and to the National Science Foundation for grants subsidizing this research.

****

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

The modern theory of the nature of solutions of strong electrolytes is based on the following model which was developed into a practical formulation by Debye and Hückel (1). The electrolyte in solution consists of individual ions which are free to move about independently. In the neighborhood of each ion of a given charge is a local excess concentration of ions of opposite charge. These ions exert a net force on the central ion whenever the spherical symmetry of this 'ionic atmosphere' is destroyed by motion of the central ion. Onsager and Fuoss (2, 3) have used this model to construct a general theory of irreversible processes in electrolytic solutions, which allows the prediction of the conductance of these solutions at low concentrations. Bjerrum (4) had shown that the existence of tightly bound pairs of ions of opposite charge in equilibrium with free ions may noticeably reduce the conductance, especially in solvents of low dielectric constant. Onsager and Fuoss (8, 9, 10, 11) made additional extensions to the theory especially dealing with the "time of relaxation" effect in conductance. The idea of "ion pairs" was later incorporated into the treatment by Fuoss (5, 6, 7).. The resulting theory now is applicable to symmetrical electrolytes in solvents of dielectric constant higher than about twenty.

Onsager and Fuoss have neglected powers of concentration higher than the first for both practical and theoretical reasons. However, Dye and Spedding (12) have shown the importance of these terms for unsymmetrical electrolytes in water. Also Karl and Dye (13) have considered the contribution of these terms to the conductance of symmetrical electrolytes in water and dioxane mixtures.

The Fuoss-Onsager theory for symmetrical electrolytes has been tested with favorable results, on the conductance of 1-1 electrolytes in water. It seemed desirable, then, to further test the accuracy of the theory in predicting the conductance of 2-2 electrolytes. Zinc sulfate was chosen since accurate conductance data already were available (14).

An attempt to fit the conductance data alone by the Fuoss-Onsager method would require three parameters: (1) the limiting equivalent conductance of zinc sulfate, (2) the ion size parameter $\underline{\mathring{a}}$, and (3) the ion-association constant $\underline{K}$. In order to reduce the arbitrariness of fit, it was decided to determine the limiting equivalent conductance of zinc ion by measuring the equivalent conductance of zinc perchlorate as a function of concentration. The limiting ionic conductance of sulfate ion is already known accurately (15). The perchlorate salt was chosen since the limiting ionic conductance of perchlorate ion is also known (16) and the ion itself is stable and unhydrolyzed.

To further test the theoretical expressions, the transference number of zinc sulfate was determined as a function of concentration. The only data available for transference numbers are those of Purser and Stokes (17) based on the E.M.F. method, and of Gold (18) based on the Hittorf method. These methods are subject to rather large errors and we employed the more accurate moving boundary method.

The success of Dye and Spedding (12) using the extended electrophoretic correction to conductance of unsymmetrical electrolytes, led to interest in the investigation in this laboratory of other higher charge electrolytes. Potassium octacyanomolybdate (IV), a 1-4 electrolyte was chosen as an example of this charge type. For successful application of theory it was necessary that the salt exhibit a minimum tendency to form ion-pairs, undergo no hydrolysis and be sufficiently soluble so that measurements could be made over a range of concentration.

II. HISTORY

A. Method of Conductance Measurements

The transfer of electrons involved in the passage of electricity is accomplished by mechanisms which may be distinguished in two limiting cases: (1) metallic or electronic conduction and (2) electrolytic or ionic conduction. In electronic conductors, conduction takes place by direct migration of electrons through the conductor under the influence of applied voltage. Electrolytic conduction involves the migration of both positive and negative ions which results in the transfer of matter, as well as electricity, from one part of the conducting solution to another.

The earliest measurements employed the same d.c. methods as were used for determinations of resistance in metallic solid conductors (19, 20, 21). Since the passage of current causes changes in the electrolytic solution such as concentration gradients and the setting up of back e.m.f. due to polarization at the electrodes, it appeared to early investigators that Ohm's law, valid for metallic conductors, was not obeyed by electrolytic solutions.

The resistance (or its reciprocal, the conductance) should depend only on the temperature and on the area and distance between the electrodes of the measuring cell.

$$\text{Conductance} = \frac{1}{R} = \frac{A}{\rho\, l_s} = L_s \frac{A}{l_s} \quad \text{ohm}^{-1} \qquad (1)$$

where R is the resistance of the solution, A is the area of the electrodes, l_s is the distance between electrodes, ρ is the specific resistance, which is equal to the inverse of L_s, the specific conductance.

Kohlrausch (22), believing that polarization was due to adsorption of gas on the electrode, began using alternating current sources and an a.c. Wheatstone bridge for measuring resistances. To further reduce the effect of polarization, he plated the platinum electrodes with finely divided platinum black. The dimensions of the cell were measured to determine the cell constant $l_s/A = k$. It was soon apparent that it is more convenient to employ a secondary standard of known specific conductance in the cell and calculate k, the cell constant. The specific conductance of potassium chloride was measured by Kohlrausch (22) to be used as a standard. Between 1868 and 1880, Kohlrausch made a long series of carefully controlled conductivity measurements over a wide range of concentrations, temperatures and pressures. His data, especially on potassium chloride, are still accepted today.

Kohlrausch defined the quantity called the equivalent conductance Λ. Λ is defined as the conductance of a volume of solution containing one equivalent weight of dissolved substance between parallel electrodes one centimeter apart, large enough to contain all of the solution between them. The quantity, Λ, is never measured directly but is calculated from the specific conductance

$$\Lambda = \frac{1000\ L_S}{c^*} \qquad (2)$$

where c^* is the normality of the solution. Another quantity, Λ_0, was defined as the equivalent conductance at infinite dilution. The value of Λ_0 cannot be obtained directly from experiment, but is obtained by extrapolation of a suitable function of equivalent conductances and concentrations. Kohlrausch (23, 24) also determined that Λ_0 was the sum of the equivalent ionic conductances, λ_j^0, of the cation and anion such that

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \qquad (3)$$

The work of Kohlrausch disclosed the many sources of error in prior work and hence the accuracy of any earlier results is very questionable. Improvements in conductance measurements since the work of Kohlrausch have been limited to better design of equipment rather than method change.

The most important and extensive work in this line was carried out by Jones (25, 26, 27, 28) and co-workers who published a series of papers concerned with the problem of eliminating errors from conductance measurements. Jones made an experimental and theoretical study of the design of the conductance bridge. Resulting from this analysis were recommendations on the design of resistance boxes, shielding of bridge components, sources of alternating current, detector circuits, oscillator circuits and bridge grounding. This latter was a modification of a method developed by Wagner (29).

The use of oil rather than water as a thermostat liquid was recommended following the discovery of the sensitivity of the resistance measurements to the presence of water, a conductor, near the cell. The use of oil gave results independent of the resistance being measured, of the specific conductivity of the bath liquid and of the frequency.

Experimental work by Wien (30), Taylor and Acree (31), and Kraus and Parker (32, 33) indicated that an increase in conductance with moderate increase in field strength can occur. Jones and Bollinger (27) investigated these phenomena to determine whether variation was due to experimental error or failure of Ohm's law. The results of this investigation indicated that there was no measurable variation of the resistance with change in applied voltage if proper experimental precautions eliminated (1) heating, (2) polarization, and (3) secondary effects of conductance and capacitance.

In 1923 Parker (33) observed that in many cases cell constants varied with the resistance and frequency being measured. In 1930 Shedlovsky (34) investigated the design of conductance cells as an approach to the problem of the 'Parker effect.' He designed a four electrode cell to determine whether cell constant variation would be eliminated if similar electrodes were included in two arms of the bridge during measurements. The following year Jones and Bollinger (35) continued this study of cell design. Analysis of the cell reactance as a function of frequency, resistance, amount of platinization, and size of electrodes led to the proof that the Parker effect was due, for the most part, to faulty design of conductance cells. The error was due to a series capacitance and resistance shunt built into the cell by constructing the filling tubes and mercury contact tubes parallel and too close together. Shedlovsky, (36) following the recommendations of Jones, constructed a cell for the high dilution range which was independent of frequency.

Some of the Parker effect was deduced to be due to polarization. The platinization of electrodes to minimize polarization was studied by Jones and co-workers who published papers in 1935 on this subject (37, 38). Summarized, the results of this investigation were:

(1) Polarization resistance is inversely proportional to the square root of the frequency.

(2) Polarization may be treated as a capacitance which decreases with increasing frequency, in series with the cell resistance.

(3) Both polarization capacitance and resistance are dependent upon the metal used for electrodes, the electrolyte and the temperature, but independent of the current density and degree of electrode separation.

(4) Platinization from a solution of chloroplatinic acid with a small amount of lead acetate can reduce polarization to a

negligible amount. However, in very dilute solutions platinization must be reduced greatly or eliminated altogether.

(5) Sufficiency of platinization may be ascertained by plotting resistance versus the square root of the frequency, the intercept on the resistance axis giving the true resistance. The difference between the apparent resistance and the true resistance gives the error due to polarization. If the error thus determined is negligible for the purpose of the measurement, then platinization is adequate.

Kohlrausch had used standard potassium chloride solution to determine cell constants. Later workers continued to use this as a reference salt since it was easily purified, non hygroscopic, soluble and stable. However, several definitions of the standard reference were accepted at the time when Jones, Bradshaw and Prendergast (39, 40) began investigation of this problem. This study resulted in a definition of a standard reference solution of potassium chloride in terms of weight in grams per kilogram of solution corrected to vacuum. They then determined the specific conductance of standard potassium chloride reference solutions at $0^{\circ}C$, $18^{\circ}C$, and $25^{\circ}C$. The cells were first calibrated with mercury, a primary standard of resistance. Nearly all subsequent work in this field is now based upon these standards.

In 1959 Fuoss and co-workers (135) published a recommendation for calibration of the cell over a range of cell resistances rather than the previous method of calibrating at one resistance only with a solution prepared precisely to a predetermined value. The now rather well-developed theory for 1-1 electrolytes furnishes a method of extroplating linearly from the Jones and Bradshaw 0.01 demal solution to lower concentrations. Fuoss has presented an equation which permits the calculation of the conductance of potassium chloride in water at any

concentration up to about 0.012 N. They recommend the use of this equation for cells with constants of the order of unity, for calibration at several high resistances of the magnitude encountered in actual experimental work.

B. Method of Transference

When an electric field is applied to an electrolytic solution the ions experience a force and are initially accelerated toward the anode or cathode according to the sign of their charge. Their final velocity is a result of this acceleration and the counter force of friction with the surrounding solvent molecules. This directed motion is superimposed on their random Brownian movement and therefore the net transfer of ions is due only to the applied field. The ionic mobility of an ion is a quantity characteristic of the given ionic species and is dependent upon temperature, pressure, type of solvent and concentration.

Experiments by Daniell (41, 42) using a three compartment cell, showed the concentration changes that would be expected with a migration of ions. He also found the first indication that positive and negative ions in a solution do not carry equal amounts of the total current. The fraction that each ion carries of the total is defined as the transference number of the cation or anion. Since the ions in a solution must carry all of the current, the sum of the transference numbers of the ions in solution must always be unity.

Conductivity measurements yield the sum of the ionic mobilities of an electrolyte, but individual values cannot be obtained from these measurements alone. They can be evaluated from a knowledge of the concentration changes which take place around the anode and cathode during electrolysis. Hittorf (43, 44, 45) first utilized this fact and began an extensive study of transference numbers which continued from 1853 to 1903. It is particularly interesting that many of these measurements were made before the ionic theory of Arrhenius was formulated in 1884.

The experimental methods available for measuring transference numbers are divided into three types: (1) the Hittorf method, (2) the electromotive force method (E.M.F.) which depends on the measurement of the potentials of cells with and without transference, and (3) the moving boundary method.

The Hittorf apparatus consists essentially of an electrolysis cell divided into an anode and a cathode compartment which are separated by a third compartment. Initially, the concentration of electrolyte is the same in each compartment. Electricity, measured by a coulometer in series with the cell, is passed and the change in composition of the anode and cathode compartment is determined. Assuming that conditions are met so that the central compartment concentration does not change, the change of equivalents in the anode or cathode compartments after electrolysis will give the transference number calculated from the expression (45)

$$T_j = \frac{N_0 + N - N_f}{N} \qquad (4)$$

where N_0 is the initial number of equivalents of the jth ion per gram of solvent, N_f is the final number of equivalents of that ion and N the number of equivalents of ion that are introduced into the solution (or correspondingly deposited) by electrode reaction. Early measurements contained several sources of error making uncertain the validity of the results. This early work has been summarized by McBain (46) and Noyes and Falk (47).

The application of the Hittorf method is limited principally by three factors; (1) at least one, and preferably both electrodes must be reversible, (2) mixing of the electrode and middle compartment solutions during electrolysis must be prevented, and (3) the analytical procedure must be highly accurate. More recent work by Jones and Dole (48) MacInnes and Dole (49) Jones and Bradshaw (50) and Steel and

Stokes (51) gave quite good results. More accurate data obtained more speedily have been obtained by the moving boundary method.

A potentiometric method for the determination of transference numbers was first proposed by Helmholtz (52). A concentration cell with transference of the form:

$$M\text{-}MX \mid A^{2+}_{\nu+}\ X^{2-}_{\nu-}\ (c_1) \mid A^{2+}_{\nu+}\ X^{2-}_{\nu-}\ (c_2) \mid MX - M \qquad (5)$$

where M-MX represent electrodes reversible to X^- ions and concentration c_1 is greater than concentration c_2. When one faraday of current is passed through the cell, E_t will be the electromotive force, accompanied by the transfer of T_+ equivalents of salt from c_1 to c_2. A concentration cell without transference of the type

$$M\text{-}MX \mid A^{2+}_{\nu+}\ X^{2-}_{\nu-} \mid A(Hg)_x - A(Hg)_x \mid A^{2+}_{\nu+}\ X^{2-}_{\nu-} \mid MX\text{-}M \qquad (6)$$

involves the reversible transport of one equivalent of salt from concentration c_1 to c_2 per faraday of current passed, with an electromotive force of E. Combination yields the result that

$$T_+ = \frac{E_t}{E} \qquad (7)$$

which gives a method of direct calculation of the transference number. The transference number thus obtained is a mean value and can therefore only be valid if the number is constant in the concentration range c_1 to c_2. When the transference number varies rapidly with concentration, graphical methods or empirical fitting of the data have been used. The E.M.F. method has been studied with some success by Pearce and Mortimer (53) and MacInnes and Beattie (54) investigating lithium ion; MacInnes and Parker (55) and Jones and Dole (48) studying potassium ion. In most cases the method does not yield as accurate data as obtained by either the Hittorf or moving boundary method.

The moving boundary method depends on the phenomenon described as follows. Two solutions can be placed in an electrolytic cell so that a boundary is observed between them, due to differences in color or refractive indices. The solutions may or may not have a common ion, but for the purposes of this work it is sufficient to consider the case of two electrolytes M^+A^- and N^+A^- with the common anion A^-, forming a boundary at a-a in Figure I. As Q coulombs of electricity are passed through the cell the boundary between the solution will move to a position represented by b-b. The effect of the passage of current is to replace the solution of M^+A^-, of volume V milliliters, in the region between the two positions of the boundary, by a solution of N^+A^-. M^+A^- is designated as the "leading" solution and N^+A^- as the "indicator" or "following" solution. For a solution containing c equivalents per liter, then cV/1000 equivalents of M^+ pass through a given cross section of the tube and carry cVF/1000 elementary charges. This is also $T_+ Q$ = (T_+ it) coulombs of electricity passed. Therefore

$$T_+ i\, t = \frac{c\, V\, F}{1000} \quad \text{and} \qquad (8)$$

$$T_+ = \frac{c\, V\, F}{1000\, i\, t}$$

This is the fundamental equation for the moving boundary method.

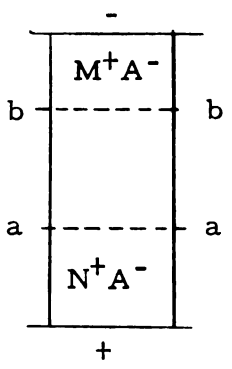


Figure 1. Schematic representation of transference cell.

Lodge (57) in 1886 made the first studies of the motion of individual ions. A gelatin gel held both the ion being studied and an indicator ion with which it formed a precipitate or colored complex. Assuming that the potential gradient was constant throughout the gel, he measured the velocity of the boundary formed. In 1893 an error was pointed out by Whetham (58, 59) who showed that the gradient was dependent upon the conductivity of the ionic species and was not the same on both sides of the boundary. Both Whetham and Nernst (60) began observations on boundaries between colored and uncolored ions in solutions without gelatin. Masson (61) in 1899 delineated the conditions necessary for quantitative work with moving boundaries.

Kohlrausch (62) in 1897 published the first theoretical treatment of moving boundaries. He deduced that in order to obtain a stable boundary it is necessary that

$$\frac{T_+}{c} = \frac{(T_+)_f}{c_f} \tag{9}$$

where T_+ and c refer to the transference number and concentration, respectively, of the leading solution and $(T_+)_f$ and c_f to the same quantities of the following solution. This relationship is known as the Kohlrausch ratio.

Diffusion and mixing of the two solutions in contact must tend to occur, but in actual practice there is a self-sharpening mechanism operating so that it appears that no diffusion occurs. The leading and following solutions are chosen such that the mobility of M^+, the leading cation, is greater than that of N^+. The following solution is in a region of higher potential than the leading solution because of its higher specific resistance. If any M^+ ions lag behind, the higher potential gradient will increase their velocity until they again enter the leading solution. The converse process will take place if the following ions

N^+ diffuse ahead of the boundary. Extensive investigations by MacInnes (63, 64) and co-workers have experimentally proven the existence of such a mechanism.

According to the Kohlrausch treatment the concentration of following solution immediately behind the boundary will adjust to the concentration given by the Kohlrausch ratio under the influence of an electric field. There is no such effect on the leading solution. This permits the transference number to be ascertained accurately even if conditions set by the Kohlrausch ratio are not fulfilled. However, studies by MacInnes and Smith (65, 66) showed that, while theory sets no limits on the concentration of the following solution, the concentration adjustment can take place properly only if the following solution is within three to eight percent of the Kohlrausch ratio. The properties necessary for an indicator solution have been summarized by Dye (67) as follows:

(1) The solution must not react with the ion under investigation.

(2) The transference number of the following ion must be less than that of the leading ion.

(3) The following solution must be less dense than the leading solution for falling boundaries and of greater density for rising boundaries.

(4) There must be a sufficient difference in properties of the solutions, such as color or refractive index, to permit the boundary to be observed and its movement followed.

In order to observe boundary motion it is, of course, necessary to form a sharp stable boundary between two species. The first very successful boundaries not in a gel were observed by Steele (68, 69) in 1901. Steele formed the boundaries by using a gelatin gel plug. The boundaries were allowed to move into a gelatin-free tube where they were observed.

The formation of a boundary by the "autogenic" method was first used in 1904 by Franklin and Cady (70). This method consisted of placing the solution to be observed in the cell over a metal plug or disk serving as the anode. The metal must form a soluble salt in combination with the anion of the solution. When current is passed the boundary between these ions will move up the tube. The concentration was automatically adjusted to the Kohlrausch ratio by the electric field.

In 1906 Denison and Steele (71, 72) made significant advances in measuring the boundaries between two uncolored solutions. The boundary was illuminated with a light from behind and viewed with a telescope as in the method used today. They replaced the gelatin plugs used by Steele (68) to form the boundary by a cone covered by a membrane of parchment. This method was later simplified by MacInnes and Smith in 1923 (65) who replaced the cone and parchment paper with a flattened glass rod and soft rubber disk. A sharper initial boundary was obtained two years later by MacInnes and Brighton (73) who used a "shearing disk" apparatus. The technique was further simplified by Spedding, Porter and Wright (74) using a hollow-bore stopcock to form the boundary. These methods may be used with either a rising or falling boundary.

Early workers in the field considered the possibility that electrode reactions which occur with the passage of current, might be accompanied by significant changes in volume. These would affect the observed movement of the boundary. Denison and Steele considered the effect negligible, which conclusion was proved to be in error by the calculations first made by Lewis (75). Unlike the Hittorf method which measures the transference number of an ion with reference to the solvent, the moving boundary method measures the motion relative to a fixed mark on the tube. The computation of the volume change, ΔV, is simplified if one side of the cell is left open to the atmosphere and the other side closed. Then only the changes which occur between the boundary and

the closed side need to be considered. An example of this computation is to be found under the experimental section of this work. The volume change ΔV means that the boundary has swept out a volume $V' + \Delta V$ such that

$$V_{observed} = V' + \Delta V \tag{10}$$

where V' is the volume swept out by the boundary corrected for any change due to electrode reaction. The expression for the transference number then becomes

$$(T_+)_{corr.} = T_+ - \frac{c^*\Delta V}{1000} \tag{11}$$

The validity of the correction has been experimentally demonstrated by two independent methods (64, 76) which are briefly described by MacInnes (77).

In 1932 Longsworth (78) proposed an additional correction to correct for the experimental fact that the sum of the cation and anion transference number was not exactly unity. He deduced that this was due to the small fraction of the total current which was carried by solvent impurities, and derived the following expression to correct for these impurities:

$$\Delta T_+ = \frac{T_+ (L_{solvent})}{(L_{solution})} \tag{12}$$

where $\underline{\Delta T_+}$ is the correction to the transference number $\underline{T_+}$ and $\underline{L_{solvent}}$ and $\underline{L_{solution}}$ are the specific conductances of the solvent and of the solution respectively. The final expression for the transference number is then given by:

$$T_+ = \frac{F\ c\ V}{1000\ i\ t} - \frac{c\ \Delta\ V}{1000} + T_+ \frac{L_{solvent}}{L_{solution}} \tag{13}$$

The transference numbers thus determined agree with those obtained by the Hittorf method within the limit of the experimental error.

III. THEORY

The foundation of the theories and investigations which ultimately led to the present concepts of interionic theory, were laid by Arrhenius (79). The then current theory, based upon the earlier work of Faraday and Hittorf, viewed the applied E.M.F. as the cause of the splitting up of the molecules of the solution into ions which could carry current. Since Ohm's law was found to be obeyed by electrolytic solutions, it had to follow that some small fraction of the solute existed in an ionized state. This fraction of "active" molecules were assumed to be short-lived basic and acid radicals of the solvent, free to move in an electric field.

Arhennius' own work on mineral acids and van't Hoff's study of the colligative properties of solutions supported the ideas Arhennius advanced in his theory of ionic dissociation which is summarized as follows:

(1) An electrolyte upon dissolving, dissociates into ions.

(2) The degree of dissociation, α, depends on the concentration and in infinitely dilute solutions the dissociation is complete. The extent of dissociation is indicated by the deviation from van't Hoff's laws.

(3) The degree of dissociation can be calculated from conductivity measurements by means of the relationship:

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (14)$$

where Λ is the equivalent conductance of the solution and Λ_0 is the equivalent conductance at infinite dilution.

There was some agreement between values of α calculated from equation (14) and from methods depending upon colligative properties,

gaining much support for the theory. The relationship expressed by equation (14) involves the assumption that ion mobilities do not vary with concentration. Rarely can this be true, as accurate data obtained on transference numbers could later show. In addition it was found that the law of mass action apparently obtained for electrolytes that are only slightly dissociated. If one considers the partial dissociation of $M^+A^- \rightleftharpoons M^+ + A^-$, the law of mass action implies that

$$K = \frac{[M^+][A^-]}{[M^+A^-]} \tag{15}$$

If M^+A^-, whose concentration is c, is dissociated to a degree α then upon substitution in equation 15 and also combination with equation 14,

$$K = \frac{\Lambda^2 c}{\Lambda_0 (\Lambda_0 - \Lambda)} \tag{16}$$

which is a form of Ostwald's dilution law. This relationship involves the assumption, not then considered, that concentration and "active mass" are equivalent. Equation 16 was tested for constancy of $\underline{K}$ by a number of workers. In strongly associated solution (weak electrolytes) early work appeared to be in close accordance with the equation. However, the later, very accurate work of MacInnes and Shedlovsky (80) showed a small change of $\underline{K}$ with concentration. For intermediate and strongly dissociated electrolytes, $\underline{K}$ was shown to be less constant (36, 81). It was concluded that the Ostwald dilution law was true only in the limiting case, an infinitely weak electrolyte. The failure of the highly conducting solutions to follow the dilution law was for some time known as the "anomaly of the strong electrolyte."

There were two explanations advanced for the anomaly; (1) all electrolytes obey the dilution law but this is obscured by disturbing factors such as complex ion and unstable ion-hydrate formation, and (2) equation (14) is not valid and a fundamental change was needed in

the ionization theory for strong electrolytes. Fruitful pursuit of the latter led to modern theory. J. J. van Laar (82) first recognized that coulombic forces between ions must affect such properties of a solution as conductance, freezing point depression and osmotic pressure. Noyes (83) and Jahn (84) attacked the assumption that the mobilities of the ions are independent of concentration, proposing that the electrostatic charges on the ions must alter the properties of the solvent and affect ionic speeds. That strong electrolytes should be considered as totally dissociated was suggested first by Sutherland (84) and Lewis (85). The latter felt that "additive" properties of salts, which show no physical properties for the undissociated portion, should lead us to a theory of complete dissociation. The evidence that concentration was not equivalent to "active mass" led to the conception of "activity" and "activity coefficients" of Lewis (87). Only in an ideal solution would the activities of the ions be equal to their concentrations. Sutherland (88) made calculations which were only approximate, on the magnitude of the coulombic force between ions assuming complete dissociation, and showed that these forces could produce the observed decrease in conductance with concentration. In an attempt to account for the variation of activity coefficients from unity on the basis of interionic attraction and repulsion, Milner (89) developed a mathematical theory based on statistical methods. This theory was essentially correct in the light of present day ideas, but the difficult mathematical analysis prevented its wide use. He did show that at low concentrations the deviations from ideal behavior should be proportional to the square root of the concentration.

The first considerations of ionic interaction assumed that the ions formed a lattice not unlike a crystal lattice. The lattice energy would simply be reduced by the effect of the dielectric constant of the solvent. However, the theory neglects the effect of thermal motion

which would break down any structural configuration the ions might tend to assume. They do, however, tend to have a limited structural arrangement brought about by the interionic attraction which causes the mean distance between ions of like charge to be greater than that of oppositely charged ions. In a time average there would be more negative ions in the region of a positive ion and more positive ions in the region of a negative ion. This "ionic atmosphere" can be regarded as a spherical region around a given ion having a charge of sign opposite to that of the central ion. The attraction between the ion and its atmosphere gives rise to the deviation from ideal behavior because it imposes a slight degree of order on an otherwise random system. Debye and Hückel in 1923 (1), following Milner's formulation, developed their theory of interionic attraction upon this model. The assumptions concerning the solution involved in the development of the theory may be summarized as follows:

(1) Strong electrolytes in solution exist as ions with no undissociated salt present at any concentration.

(2) The solutions would show ideal behavior if there were no interionic attraction.

(3) The ions can be regarded as point charges, unpolarizable and possessing a symmetrical coulombic field.

(4) Only coulombic forces are important in interionic attraction; any other intermolecular forces are negligible.

(5) The dielectric constant of the solution is the same as that of the solvent.

(6) The interionic attractive coulombic energy is small compared with the energy of thermal motion.

In the theoretical consideration of the interionic attraction the fundamental statistical property is the distribution function (corresponding to the equations of motion in a simple mechanical system). The distribution

function defines the distribution of ions in the ionic atmosphere. The desired distribution function for this system may be defined by

$$f_{ji} = n_j n_{ji} = f_{ij} = n_i n_{ij} \qquad (17)$$

where f_{ji} is the time average distribution of i - ions in the vicinity of n_j central j-ions. The quantity n_{ji} gives the number of i-ions in the vicinity of a central j-ion. Since material must be conserved in the system as a whole, the converse expression for f_{ij} may also be written. f_{ji} and n_{ji} depend, in general, upon the location in solution of the central j-ion as well as the position relative to the central ion at which the concentration of i-ions is specified.

In the special case where there are no impressed forces on the system, this distribution will be spherically symmetrical and independent of location in solution. It can, therefore, be written as a function only of distance r from the central ion. Knowledge of this fundamental property would provide the basic equation for computing the limiting laws of equilibrium properties such as activity and osmotic coefficients and, subsequently, partial molar heats of dilution and heat capacities.

In the more general case when there is present a perturbing force such as an impressed E.M.F. causing conductance, the distribution will not be spherically symmetrical. Then, it is necessary to consider position in solution and position relative to the central ion.

The early Debye-Hückel theory presented below, considers only the former case of the unperturbed ionic atmosphere and is therefore applicable only for the calculation of those properties dealing with equilibrium processes.

In order to calculate an equilibrium value of the function n_{ji} one may set up a differential equation. The forces between the ions are coulombic in nature and it may be reasonable, for the distances we are considering, and taking a time average, to treat the distribution of ions

as a smooth charge density function. The appropriate equation would then be the Poisson equation of electrostatics:

$$\nabla^2 \psi = \frac{-4\pi}{D} \rho \tag{18}$$

For our system we can identify ψ with $\psi_j^0(r)$, the spherically symmetrical equilibrium value of electrostatic potential in the neighborhood of a central j-ion. $\underline{D}$ is the dielectric constant of the solution. $\underline{\rho}$ is defined, then, as $\underline{\rho_j}$, the charge density function in the neighborhood of the central j-ion which can be written in terms of $\underline{n^0_{ji}}$ and summed over all the kinds of ions in the solution as

$$\rho_j = \sum_{i=1}^{s} n^0_{ji} e_i = \sum_{i=1}^{s} n^0_{ji} z_i \epsilon \tag{19}$$

where $\underline{e_i}$ is the charge on the ion of type i, $\underline{\epsilon}$ is the magnitude of the charge on the electron and $\underline{z_i}$ is the valence of the i-ion. It can be seen that upon substitution of ρ_j of equation (19) into equation (18) both ψ_j^0 and ρ_j are unknown functions of position and charge and therefore equation (18) is not completely defined.

There are two independent lines of reasoning which allow us to write ρ_j as a function of ψ_j^0 which would result in a differential equation with ψ_j^0 as the only unknown function.

(1) Considering the fact that the ionic atmosphere is the result of electrostatic attraction opposed by random thermal agitation, one might assume that the distribution is governed by the Maxwell-Boltzmann law. This would depend on the energy $\underline{U^0_{ji}}$ of the "atmosphere" ions as a function of their separation from the central j-ion as

$$n^0_{ji} = n_i \exp\left(-U^0_{ji}/kT\right) \tag{20}$$

where $\underline{n_i}$ is the average concentration of i-ions computed assuming uniform distribution. $\underline{U^0_{ji}}$, moreover, can be approximated by $e_i \psi_j^0$, which is the energy the i-ions would have, subject to the equilibrium potential function ψ_j^0.

$\underline{n}_{ji}^{0}$ reduces to $\underline{n}_i$ when separation between i and j-ions goes to infinity (i.e. when ψ_j^0 goes to zero). Finally, then

$$\rho_j = \sum_{i=1}^{s} e_i n_i \exp(-e_i \psi_j^0 / kT) \tag{21}$$

(2) The second alternative proceeds from the nature of the Poisson equation itself. If ρ_1, ρ_2 and ρ_3 are three charge density functions and ψ_1, ψ_2 and ψ_3 the corresponding potential functions obtained by solution of the Poisson equation, and if $\rho_3 = \rho_1 + \rho_2$, then ψ_3 turns out to be equal to $\psi_1 + \psi_2$. Hence, since ρ is actually a function of ψ then

$$\rho_1(\psi_1) + \rho_2(\psi_2) = \rho_3(\psi_3) = \rho_3(\psi_1 + \psi_2) \tag{22}$$

This is the defining relation for a linear function; hence $\rho \propto \psi$.

Since the first alternative leads to an exponential relationship between ρ and ψ, and the second alternative to a linear relationship, the two methods are obviously not compatible. Since both contain approximations, (1) that $U_{ji}^0 = e_j \psi_j^0$ and (2) that a smooth charge density function is valid for the times and very small distances involved, neither solution gives unequivocal results. These difficulties can be circumvented by expanding the exponential function in equation (21) as a power series in the exponent $e_i \psi_j^0 / kT$ and retaining only the first two terms, i.e. the constant plus the first linear term. Because of charge neutrality, $\sum_{i=1}^{s} n_i e_i = 0$ and substitution into equation (21) results in

$$\rho_j = \frac{1}{kT} \sum_{i=1}^{s} n_i e_i^2 \psi_j^0 = \left(\frac{\epsilon^2}{kT} \sum_{i=1}^{s} n_i z_i^2 \right) \psi_j^0 \tag{23}$$

Substitution of this equation into equation (18) gives the result

$$\nabla^2 \psi_j^0 = \varkappa^2 \psi_j^0 \tag{24}$$

where

$$\chi^2 = \frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \qquad (25)$$

The term χ has the dimensions of cm^{-1}. The length $1/\chi$ is called the radius of the ionic atmosphere.

The solution of the differential equation (24) is shown in detail by Harned and Owen (90). The final result is given by

$$\psi_j^0(r) = \frac{e_j e^{\chi a}}{D(1 + \chi a)} - \frac{e^{-\chi r}}{r} \qquad (26)$$

which for point charges reduces to

$$\psi_j^0 = e_j \, e^{-\chi r}/Dr \qquad (26a)$$

From equation (20) and the discussion following it,

$$n_{ji}^0 = n_i \exp\left(-e_i \psi_j^0/kT\right) \qquad (27)$$

This exponential function may also be expanded in a power series and retention of only the first two terms yields,

$$n_{ji} = n_i \left(1 - e_i \psi_j^0/kT\right) \qquad (28)$$

Substitution in equation (17) for the values of n_{ji}^0 and ψ_j^0 given by equations (28) and (26) respectively, yields the final expression for the distribution function characteristic of the equilibrium case considered,

$$f_{ji}^0 = n_j n_i \left(\frac{1 - e_i e_j e^{\chi a}}{D\,k\,T(1 + \chi a)} \cdot \frac{e^{-\chi r}}{r}\right) \qquad (29)$$

On the basis of equation (29) Debye and Hückel computed successfully the limiting law for the activity coefficient. The Debye-Hückel theory gave a theoretical basis for the concept of ionic strength which had been derived empirically by Lewis (87). The interionic attractions postulated would be expected to be even more effective in determining the properties of

solutions at high concentrations but, as the theory has been developed, its validity is limited to dilute solutions. The ratio of the coulombic to the thermal energy of the ions must be small i.e. $e_i \psi_j^0 << kT$. This will not be true if the ions are very small or highly charged or if the dielectric constant is very low. In such cases higher terms in the expansion of equation (21) should not be neglected. The first modification to the evaluation of the potential was made by Müller (91) and by Gronwall, LaMer and Sandved (92). Müller obtained the solutions of the integrals by a graphical method rather than by means of a series expansion. Gronwall et al. expanded the series and kept higher terms. They were able to account for some experimental results on solutions of highly charged electrolytes with relatively small ions. The mathematical difficulties associated with this method led Bjerrum (4) to suggest a much simpler improvement. In part the concept may be considered to represent a real phenomenon and in part to circumvent inherent mathematical inadequacies.

Bjerrum suggested that all oppositely charged ions within a certain distance of one another, possessing sufficient energy to be a stable physical entity, are associated into ion-pairs which act as a single unit in solution. Two ions which are closer than a critical distance apart are considered to form an ion-pair. Bjerrum chose this distance, q, to be

$$q = \frac{|z_1 z_2| \epsilon^2}{2\,DkT} \qquad (30)$$

At this distance the electrostatic potential energy of the oppositely charged ions is 2kT. Bjerrum arrived at this value for q by computing the time average probability of finding an oppositely charged ion in any point within an infinitestimal spherical shell of thickness dr and radius r as a function of r, the distance from the reference ion. He noted that the function has a minimum at r = q. This involved the assumption that the number of oppositely charged ions per unit volume would follow the Boltzmann

distribution function

$$n_{ji} = n_i \exp(- e_i \psi_j/kT) \qquad (31)$$

where ψ_j was taken to be the simple coulombic potential of the central ion

$$\psi_j = z_j \epsilon/Dr$$

On the basis of this he calculated (1 - α) the degree of association, and K, the association constant, as a function of a, the distance of closest approach and D, the dielectric constant of the solvent. Calculations showed that ion pairing makes a significant contribution to the behavior of an electrolyte when the ion size is small (including the solvation sheath) and/or the dielectric constant is low. This has been experimentally substantiated by the study of lanthanum ferricyanide in various solvents (93, 94, 95) and the investigation of tetraisoamylammonium nitrate in water-dioxane mixtures by Kraus and Fuoss (96).

Fuoss (97) has suggested a modification of the approach by redefining the criterion for an ion-pair. Two ions are to be considered as an ion-pair only if they are in contact without intervening solvent molecules. While Bjerrum's treatment gives good results in solutions of low dielectric constant, in general, the theoretical expressions for K have proven unreliable. As a result, the constant is now treated as an adjustable parameter chosen to give the best fit.

Debye and Hückel were also able to make an important contribution to the theory of electrolytic conductance (98). This problem becomes more difficult since the equilibrium condition will be destroyed and the ions will move under an applied E.M.F.

The equivalent conductance of a solution has earlier been defined by

$$\Lambda = 1000\ L/c \qquad (32)$$

Λ is also obtained by summing the ionic conductances over all types of

ions in a given solution. The equivalent conductance $\underline{\lambda_j}$ of a given ion may be defined as the current produced by one gram equivalent of the ion under a potential gradient of one volt per centimeter. $\underline{\lambda_j}$ is related to the ionic mobility $\underline{u_j}$

$$\lambda_j = 96,500\ u_j \tag{33}$$

The mobility $\underline{u_j}$, of an ion is its velocity under a potential gradient of one volt per centimeter whereby

$$u_j = v_j/300\underline{X} \tag{34}$$

where $\underline{X}$ is the electric potential gradient expressed in the appropriate cgs units. It then follows that

$$\Lambda = \sum_j \lambda_j = \frac{96,500}{300\ \underline{X}} \sum_j v_j \tag{35}$$

To obtain a value for the mobility experimentally, the limiting equivalent ionic conductance at infinite dilution is obtained from measurements of the conductance at a number of concentrations. A suitable extrapolation function will give the conductance at infinite dilution. The problem in the conductance theory which is evident from equation (35) is to determine a value for the average ionic velocities. The knowledge of the distribution of the ions relative to each other, the electric potential at any point in the solution and the hydrodynamic equation of continuity are used to derive a theoretical expression for the conductance of a solution.

Debye and Hückel, using their distribution and electrical potential function as a basis for this new theory, found average ionic velocities by considering the perturbation caused by an applied E.M.F.

Onsager and Fuoss in a number of papers from 1927 to 1958 have developed a conductance theory along the same lines as the original Debye-Hückel theory. In presenting this theory here, we will follow the development as it is now known and used, indicating the points of deviation from the historical presentation.

Two underlying physical concepts concerning a central ion and its surrounding atmosphere were first considered by Debye and Hückel. As ions move in the field of a perturbing electric force those of opposite sign will be moving in opposite directions. Since each tends to drag some solvent molecules with it, the overall effect will be a local solvent flow in the direction opposite to that of any particular ion. The average speed of all ion types will then be lowered. This is called the electrophoretic effect.

A second effect may be considered when there is an applied E.M.F. As the ion travels through the solution, its ionic atmosphere of opposite sign must be tending to move away from it, and will therefore no longer possess a spherically symmetrical structure. A finite time is required for the atmosphere to build up and then decay about the moving central ion. This is known as the time of relaxation. The net effect will be an excess of oppositely charged ions behind a given central ion and can be considered an opposing force to the applied force. The applied force is the product of the ion charge and the potential gradient X. The small restoring force is described in terms of a correction to the field, ΔX, called the relaxation field. The result is a lowering of the ion's mobility. Both of these effects depend upon the density of the ionic atmosphere.

In addition to these two effects, Onsager and Fuoss (11) recently modified the concept to include consideration of a kinetic effect. Due to the time of relaxation a larger number of ions are behind the central ion than are in front of it. Thermal motion will cause the central ion to be struck more often from behind than from in front, resulting in an increased velocity of the central ion. This effect then acts as a force, ΔP, in the direction of the field, and is considered as an osmotic pressure on the reference ion which moves it with the field.

The original model used considered the solvent as a structureless continuum. However, at finite concentrations there will be ions of solute

which will act as obstacles to the moving ion. This effect was treated by Fuoss (5) as an additional correction to the physical concepts conceived by Debye and Hückel. It can be treated as a correction to the viscosity, which is inversely proportional to the conductance itself.

Following the method of Fuoss (7) we would like to write in symbolic form the conductance equation derived from considerations of the four effects described above. An isolated j-ion in a solution to which an E.M.F. is applied will move with a velocity $\underline{v_j}$ proportional to the applied force field $\underline{e_j X}$, where the proportionality constant is the reciprocal of the coefficient of friction of the ion.

$$v_j = \omega_j \mid e_j \mid X \tag{36}$$

Due to the relaxation and electrophoretic effects, the average velocity of the j-ion will be reduced. If $\underline{v_{js}}$ is the retarding velocity of the solvent in the neighborhood of the j-ion resulting from the electrophoretic solvent drag by j-ions, and the actual force felt by the ions is $\underline{e_j}$ $\underline{(X + \Delta X)}$ then

$$v_j = \omega_j \mid e_j \mid (X + \Delta X) - \mid v_{js} \mid \tag{37}$$

Combination of equations (35) and (37), considering only one ion, gives

$$\lambda_j = \frac{96,500}{300} \omega_j \mid e_j \mid (1 + \Delta X/X) - \frac{96,500}{300X} \mid v_{js} \mid \tag{38}$$

At infinite dilution where there would be no interacting ions present, $\Delta X/X$ and $\underline{v_{js}}$ are both zero and therefore

$$\lambda_j = \frac{96,500}{300} \omega_j \mid e_j \mid \equiv \lambda_j^0 \tag{39}$$

where $\underline{\lambda_j^0}$ if the limiting equivalent conductance at infinite dilution. Since $\underline{v_{js}}$, the solvent velocity, is dependent upon the velocity of the i-ions and therefore is proportional to the applied field $(X + \Delta X)$, the last term on the right-hand side of equation (38) may be written as

$$\frac{96,500}{300\,X} |v_{js}| = (\Delta\lambda_e)_j (1 + \Delta X/X) \tag{40}$$

where $(\Delta\lambda_e)_j$ is the electrophoretic contribution to the conductance. Summing equation (38) over all kinds of ions in the solution one obtains the total equivalent conductance as

$$\Lambda = (\Lambda_0 - \Delta\Lambda_e) \left(1 + \frac{\Delta X}{X}\right) \tag{41}$$

where $\Delta\Lambda_e$ is the term due to the electrophoretic effect and $\Delta X/X$ the term due to the time of relaxation effect. The contribution of the kinetic effect, a force in the direction of the field, and the viscosity correction which is inversely proportional to the conductance, results in the final form of the conductance equation,

$$\Lambda = \frac{(\Lambda_0 - \Delta\Lambda_e) \left(1 + \frac{\Delta X}{X} + \frac{\Delta P}{X}\right)}{1 + Fc} \tag{42}$$

An outline of the considerations involved in the derivation for each of the expressions which appear in equation (42), following the procedure used by Fuoss and Onsager, will be presented here.

I. The Electrophoretic Effect

The electrophoretic correction has been calculated in two ways. One method is based on the use of Stoke's law for the moving ions and is described fully by Harned and Owen (90). The second method is that of Onsager and Fuoss (19) which was later slightly modified by Fuoss and Accascina (99). This method proceeds by way of a calculation of the solvent velocity as a function of position about the central ion. The basic hydrodynamic equation for the flow of solvent is

$$\eta \nabla^2 \vec{v}_{js} = \nabla p - \vec{F} \tag{43}$$

where $\underline{\eta}$ is the viscosity of the solvent, $\underline{v}_{js}$ is the solvent velocity at a

distance r from a particular ion and p is the pressure. $\vec{F}$ is the force per unit volume of the solution due to the electrostatic force on the ions contained in it. Its magnitude may be written in terms of the field strength and the charge density $F = X\rho$, in the direction of the impressed E.M.F.

The solution of this differential equation is found in the original paper (10) and has been discussed in some detail by Karl (13). We are interested only in the radial component of $\vec{v}_{js}$ which will be needed in the calculation of the time of relaxation effect, and in the component of $\vec{v}_{js}$ along the direction of the applied E.M.F. The latter is of interest because its value at a distance a, represents the velocity of solvent in contact with the ion in question and therefore the velocity of the ion itself.

The radial component is given by

$$v_r = \frac{Xe\cos\theta}{4\pi\eta}\left\{2\left[1 + \varkappa a + \frac{\varkappa^2 a^2}{2} + \frac{\varkappa^3 a^3}{6}\right] - \frac{2e^{\varkappa(a-r)}(1-\varkappa r)}{\varkappa^3 r^3 (1+\varkappa a)} - \frac{R^2}{3r^3}\right\} \quad (44)$$

R is the hydrodynamic radius of the ion and is set by Fuoss and Accascina (99) equal to a.

The velocity v in the direction of the applied field, evaluated at r equal to a, is given by

$$v_x(a) = \frac{Xe_j}{6\pi\eta a} - \frac{Xe_j\varkappa}{6\pi\eta(1+\varkappa a)} \quad (45)$$

The first term on the right-hand side of equation (45) represents the Stoke's law limiting velocity of an ion subject to an impressed force e_jX and moving in a medium of viscosity η. The second term, a retarding velocity, must represent the correction to the velocity due to the electrophoretic effect. It has been shown that

$$\lambda_j = \frac{96,500}{300\,X} v_j \quad (35)$$

and therefore

$$\lambda_j = \frac{96,500}{300} \left(\frac{e_j}{6 \pi \eta a} \right) - \frac{96,500}{300} \left(\frac{e_j \varkappa}{6 \pi \eta (1 + \varkappa a)} \right) \tag{46}$$

which may be written as

$$\lambda_j = \lambda_j^0 - (\Delta \lambda_e)_j \tag{47}$$

where

$$(\Delta \lambda_e)_j = - \frac{96,500}{1800 \pi \eta} | e_j | \frac{\varkappa}{1 + \varkappa a} \tag{48}$$

For point charges where a = 0 the correction may be written

$$(\Delta \lambda_e)_j = - \frac{96,500}{1800 \pi \eta} | e_j | \varkappa \equiv - \beta_j \sqrt{c^*} \tag{49}$$

The total correction to the conductance $\Delta \Lambda_e$ can be obtained by summing over all kinds of ions.

II. The Time of Relaxation Effect

The relaxation effect is mathematically more difficult to evaluate. It will be recalled that the electric field due to the ionic atmosphere may be expressed as $X = -\nabla \psi_j$. The quantity ψ_j is equal to $\psi_j^0 + \psi_j'$, where ψ_j^0 is the spherically symmetrical equilibrium potential function, and ψ_j' is the asymmetric contribution to this function. Hence, the relaxation field ΔX, evaluated at the central j-ion and due entirely to this asymmetric portion, is given by

$$\Delta X = - \nabla \psi_j' \tag{50}$$

ψ_j' must be obtained by solution of a differential equation formed by the following series of steps.

(1) Since we can write the distribution function $f_{ji} = f_{ji}^0 + f_{ji}'$, Poisson's equation can be applied simply to the asymmetric quantities as

$$\nabla^2 \psi_j' = - \frac{4 \pi}{D} \sum_{i=1}^{s} f'_{ji} \; e_i / n_j \tag{51}$$

(2) To find f_{ji}' we need the hydrodynamic equation of continuity for stationary states (100) namely,

$$\nabla^2 = (f_{ji}\ \vec{v}_{ji}) + \nabla_1 - (f_{ij}\ \vec{v}_{ij}) = 0 \tag{52}$$

(The total distribution functions are used in this equation.)

(3) We now need the quantities $\vec{v}_{ji}$ and $\vec{v}_{ij}$ and they can be obtained from the general expression for the relative velocity,

$$\vec{v}_{ji} = \vec{v}_{js} + \omega_i (\vec{K}_{ji} - kT \nabla_2 \ln f_{ji}) \tag{53}$$

where $\vec{v}_{js}$ is the solvent velocity in the neighborhood of a j-ion

$\vec{K}_{ji}$ is the force on an i-ion in the neighborhood of a j-ion.

$kT\nabla_2 \ln f_{ji}$ is a term that was not considered by Debye and Hückel, which arises from the Brownian motion of the ions. Onsager considered this a restoring force to the symmetry of the ionic distribution.

The remaining terms have previously been defined. A completely analogous expression may be written for $\vec{v}_{ij}$. The force $\vec{K}_{ji}$ may be further defined as a sum of three forces

$$\vec{K}_{ji} = e_i X \vec{i} - e_i \nabla_2 \psi_i'(a) - e_i \nabla_2 \psi_j \tag{54}$$

The first term is the x-component of the applied external force. The second is the force of its own atmosphere on the central i-ion. The third is the force on this i-ion due to the neighboring j-ion and the atmosphere of this j-ion.

Combination of the equations discussed above results in a very complicated differential equation, the method of whose solution we will briefly indicate. This equation is solved subject to the following four boundary conditions:

(1) The gradient of the potential function of the central ion must become zero at an infinite distance from this ion.

(2) and (3) Both the potential and its gradient, the field strength, must be continuous at the surface of the central ion where r = a.

(4) At the moment when two ions strike each other the radial component of their relative velocity must be zero because they are considered to be rigid spheres. This latter condition was introduced by Falkenhagen (101).

The terms of this differential equation were then classified by Fuoss according to the power to which $\varkappa$ will appear in the unknown solution. For the first order solution he retained terms of order $\varkappa^4$ and for a second order solution terms giving $\varkappa^5$, neglecting any higher order terms. The problem was then further limited to a single electrolyte with only two kinds of ions.

A first approximation to the solution for the asymmetric distribution function is then found ignoring the higher order terms, as follows: We set

$$\psi_j' = \Psi_j + p_j \tag{55}$$

and

$$f_{ji}' = F_{ji} + g_{ji} \tag{56}$$

where Ψ and F_{ji} are the first order approximate asymmetric potential and distribution functions. The contributions of higher order terms are denoted by p_j and g_{ji}. The functions ψ_j' and f_{ji}' are related by Poisson's equation. The solutions for Ψ_j and Ψ_i are identical and are denoted by Ψ. The exact expression for Ψ is shown in the original paper (102). The relaxation field is found from

$$-\nabla_x \Psi = \Delta X \tag{57}$$

For the first approximation we consider only the case of point charges

and thus obtain ΔX_0, which was the result first obtained by Onsager in 1927. Since i = 1 and j = 2 then

$$\frac{\Delta X_0}{X} = \frac{e_1 e_2 q^2 \varkappa}{3DkT(1+q)} = -a\sqrt{c^*} \tag{58}$$

The next approximation, which gives ΔX_1, is made when the ions are considered as hard spheres of radius a, instead of point charges. This approximation is expressed as a correction, $-\Delta X_0 \Delta_1$, to the previous solution. This results in the expression

$$\Delta X_1 = \Delta X_0 (1 - \Delta_1) \tag{59}$$

where

$$\Delta_1 = \frac{\varkappa a(1+q)}{p_3(1+\varkappa a)} + \frac{\varkappa a(1+q)}{2bp_3} + \frac{\varkappa^2 a^2}{p_3(1+\varkappa a)} \quad (q + q^2/3) \tag{60}$$

where

$$b = \frac{|e_1 e_2|}{a\,DkT}$$

$$p_3 = 1 + q\,\varkappa a + q^2 \varkappa^2 a^2/3$$

Now

$$\frac{\Delta X_1}{X} = -a\sqrt{c^*}\ (1 - \Delta_1) \tag{61}$$

A second order approximation could now be made by substitution of the known value of ψ and F_{ji} into the original differential equation to obtain p_j and g_{ji} and so obtain the exact correction to ΔX. The mathematical complications involved thereby led Fuoss (10) to approach a solution in another way. He divided the contribution g_{ji} into a sum of four terms and devised a method for deriving the second order approximation for ΔX directly, without computing ψ_j' as an intermediate step. Of the four terms thus obtained, one, ΔX_v, requires knowledge of the radial component of the solvent velocity which has been previously given by equation (45). The contributions from the other three terms are all proportional to ΔX_0 and are combined as

$$\Delta X_B \; \alpha \; \Delta X_a + \Delta X_{2,3} = \Delta X_0 \Delta_2 \qquad (62)$$

where, for symmetrical electrolytes

$$\Delta_2 = \left[\frac{b(1+q)\chi a}{(1+\chi a)^2}\right]\left[\frac{11\sqrt{2}-3}{24\, p_2\, p_3} + \frac{1}{4\, p_2} + F(\chi a)\right] - \frac{(1+q)\chi a}{2p_2(1+\chi a)} \qquad (63)$$

A complete description of the rather complicated terms involved in this expression and for the three terms on the left-hand side of equation (62) are given by Fuoss and Accascina (103). The part of the relaxation term due to the velocity field is given by

$$\frac{\Delta X_V}{X} = \frac{\beta\sqrt{c^*}}{\Lambda_0}\,\Delta_3' \qquad (64)$$

where Δ_3' is included in the description by Fuoss and Accascina (103). The complete relaxation term can now be expressed as,

$$-\frac{\Delta X}{X} = \alpha\sqrt{c^*}\left(1 - \Delta_1 + \Delta_2 + \frac{\beta\Delta_3'}{a\Lambda_0}\right) \qquad (65)$$

III. The Viscosity Correction.

The viscosity correction is only applied when large ions are involved. "Bulky" ions interfere with motion of a particular ion through the solvent which, in effect, increases the viscosity of the solvent. The mobility of the ion is inversely proportional to the viscosity of the solvent medium. Since the equivalent conductance is proportional to the mobility we conclude that it is also inversely proportional to the viscosity. In order to estimate the correction, Fuoss (5) used the Einstein viscosity expression

$$\eta = \eta_0 (1 + 5\phi/2) \qquad (66)$$

where ϕ is the ion volume fraction, η_0 the solvent viscosity and η the viscosity experienced by the ion. If we assume the ion to have a radius R, then

$$\phi = \frac{4}{3}\pi R^3 \,(N\,c/1000) \equiv \mathcal{S}\,c \qquad (66)$$

Let $5\delta/2$ be equal to **F**. Then the conductance equation becomes

$$\Lambda = \frac{(\Lambda_0 - \Delta\Lambda_e)\left(1 + \frac{\Delta X}{X}\right)}{1 + Fc} \tag{67}$$

IV. The Kinetic Correction.

The kinetic term of Fuoss and Onsager (11) has already been described as an increase in probability of collision from behind due to the asymmetry of the atmosphere of the reference ion. Alternatively, it can be considered a local osmotic pressure at the reference ion. If the distribution function is given by the approximation

$$f_{ji} = F_{ji} + f^0_{ji} \tag{68}$$

then the osmotic pressure π, due to the field is given by

$$\pi = F_{ji}\, kT/n_i \tag{69}$$

The force ΔP is given by the directed component of the osmotic pressure π integrated over the surface of the sphere of radius a. The resulting ΔP for a symmetrical 1-1 electrolyte is

$$\Delta P = X\left(\frac{\chi^2 a^2 (b-1)}{12b}\right) \tag{70}$$

The ionic velocity then becomes

$$v_j = (X + \Delta X + \Delta P)(e_j \omega_j) - v_{js} \tag{71}$$

The conductance equation (67) with this additional term then becomes the complete conductance equation,

$$\Lambda = \frac{(\Lambda_0 - \Delta\Lambda_e)\left(1 + \frac{\Delta X}{X} + \frac{\Delta P}{X}\right)}{1 + Fc} \tag{72}$$

This conductance equation is limited in application to symmetrical electrolytes and to concentrations of less than 0.1 normal. No less than

two adjustable parameters, the limiting equivalent conductance Λ_0 and the distance of closest approach a, are contained in the equation. The ion-pairing constant K may also appear as an adjustable parameter.

Fuoss and Accascina (104) have shown that equation (72) may be expanded with the use of several approximations, to a convenient form of

$$\Lambda = \Lambda_0 - S\sqrt{c^*} + Ec^*\log c^* + Jc^* - F\Lambda_0 c^* \qquad (73)$$

where expressions for the constant S, E, J and F are summarized by the same authors and are also discussed later in this thesis. Equation (73) has two familiar limiting forms. At low concentrations in solvents of high dielectric constant it reduces to the Onsager limiting law

$$\Lambda = \Lambda_0 - S\sqrt{c^*} \qquad (74)$$

Onsager derived this in 1927 from a general treatment of the motion of ions. In solvents of low dielectric constant where considerable ion pairing might be expected, it reduces to Ostwald's dilution law. Fuoss feels that this equation (73) "bridges the gap between systems with negligible association and those with marked association and provides a mathematical description of the transition."

Empirical Extensions of the Onsager Limiting Law.

While Onsager's limiting law adequately described the behavior of many dilute 1-1 electrolytes up to 0.001 normal, several attempts were made in the succeeding years to modify the equation to represent data at higher concentrations and for higher charge-type ions. Shedlovsky (105) proposed an equation to be used for extrapolation by simple rearrangement of Onsager's limiting equation. The latter may be written in the form

$$\Lambda = \Lambda_0 - (a\Lambda_0 + \beta)\sqrt{c} \qquad (75)$$

which Shedlovsky rearranged to

$$\Lambda_0 = \frac{(\Lambda + \beta\sqrt{c})}{(1 - \alpha\sqrt{c})} \equiv \Lambda_0' \tag{76}$$

Since the fraction above varies almost linearly with concentration he defined an extrapolation function Λ_0'. Then Λ_0' is plotted versus concentration and extrapolated to zero concentration. The values of Λ_0' should become constant through the concentration range in which Onsager's equation is valid and should therefore have zero slope near zero concentration. Its intercept with the Λ_0' axis should be the true value of Λ_0.

Onsager (2) and Onsager and Fuoss (3) in 1932 proposed an empirical extension by adding two terms to the limiting law such that

$$\Lambda = \Lambda_0 - S_{(\lambda)}\sqrt{c} + A\,c\log c + B\,c \tag{77}$$

The constants are evaluated by rearrangement to

$$\frac{\Lambda_0' - \Lambda_0}{c} = A\log c + B \tag{78}$$

followed by plotting the left-hand side of equation (78) against log c. The value of Λ_0 must be adjusted and Λ_0' recalculated, until a straight line is finally obtained giving the slope A and intercept B. Owen (56) used this method extensively and with marked success for such salts as potassium, barium, and lanthanum chlorides. The method has subsequently often been referred to by other authors as the Owen method or Owen plot.

It is noteworthy that equation (73) now gives some theoretical justification for use of the additional terms of the form used in equation (77).

Dye and Spedding (12) found that much better agreement with theory was obtained for certain higher charge-type electrolytes if higher terms

in the distribution function were retained in considering the complete electrophoretic effect. It will be recalled that the potential function obtained by consideration of equilibrium systems was

$$\psi_j^0 = \frac{e_j e^{\varkappa a}}{D(1 + \varkappa a)} \cdot \frac{e^{-\varkappa r}}{r} \tag{26}$$

and that

$$n_{ji}^0 = n_i \exp(- e_i \psi_j^0 / kT) \tag{27}$$

The exponential was then expanded in a power series to be substituted into the final expression for the distribution function. Dye and Spedding alternatively suggest using the complete exponential so that the expression for the distribution function becomes

$$f_{ji}^0 = n_i n_j \exp \left(\frac{-e_i e_j e^{\varkappa a}}{DkT(1 + \varkappa a)} \right) \frac{e^{-\varkappa r}}{r} \tag{79}$$

It is this distribution function which is then used in the treatment of the electrophoretic effect. From the Stoke's law development of this effect the ionic velocity correction due to electrophoresis is known

$$\Delta v_j = \frac{2X}{3\eta} \int_a^\infty r \left[\sum_i (n_{ji} - n_i) e_i \right] dr \tag{80}$$

Since $n_{ji} = f_{ji}^0 / n_j$, the new distribution function is substituted into this expression. The correction $\Delta \lambda_j$ to the conductance is

$$\Delta \lambda_j = \frac{96,500}{300 X} \Delta v_j \tag{81}$$

Considering an electrolyte which dissociates into only two kinds of ions and defining

$$\rho = \varkappa r$$

$$X = \varkappa a$$

$$P = \varkappa e^x / DkT (1 + x)$$

$$M = \frac{96,500 \, D \, k \, T}{1800 \, \pi \, \eta \, \epsilon (|z_+| + |z_-|)}$$

and using the relationships that

$$n_+ e_+ = \frac{\nu_+ z_+ cN\epsilon}{1000} \quad \text{and} \quad n_- e_- = \frac{\nu_- z_- c\, N\epsilon}{1000}$$

$$| \nu_+ z_+ | = | \nu_- z_- | ,$$

Dye and Spedding obtained

$$\Delta\lambda_+ = M \int_x^\infty \rho \left[\exp\left[-Z_+^2 P \frac{e^{-\rho}}{\rho} \right] - \exp\left[| Z_1 Z_2 | P \frac{e^{-\rho}}{\rho} \right] \right] d\rho \quad (82)$$

and an analogous expression for $\Delta\lambda_-$ where Z_- is used instead of Z_+. Experimental conductances of unsymmetrical rare earth electrolytes were found to have much better agreement with theory using this extension. Karl (13) has also evaluated this effect for univalent electrolytes in water-dioxane mixtures.

A test of any interionic attraction theory may be made through experimental measurements of the transference numbers. Transference numbers are simply related to the individual ionic conductances so that a correct conductance theory should yield correct transference numbers. The transference number of the j-ion is defined as

$$T_j = \frac{i_j}{\sum_{i=1}^{s} i_i} \quad (83)$$

where i_j is the current carried by the j-ions and $\sum_i i_i$ is the total current carried by all ions in the solution. The transference number may also be expressed as

$$T_j = \frac{\mu_j}{\sum_i \mu_i} = \frac{\lambda_j}{\sum_i \lambda_i} = \frac{\lambda_j}{\Lambda} \quad (84)$$

We can write therefore, using equation 40,

$$T_j = \frac{(\lambda_j^0 - (\Delta\lambda e)_j)(1 + \Delta X/X)}{\Lambda_0 - \Delta\Lambda e)\ (1 + \Delta X/X)} = \frac{\lambda_j^0 - (\Delta\lambda e)_j}{\Lambda_0 - \Delta\Lambda e} \quad (85)$$

Simultaneous with the development of the conductance theory described, two other effects were theoretically investigated, based upon the interionic attraction theory. The limiting law for the viscosity of an electrolytic solution was deduced by Falkenhagen (106, 107). This verified the conclusions reached experimentally that the viscosity of the solution was proportional to the square root of concentration. It was also shown by Onsager and Fuoss (3) that, to a first approximation, the relative increase in the viscosity is proportional to the ratio of the radius of the ion to that of its atmosphere. The viscosity increase due to large solute particles was explained by Einstein (108) as due to the interference of particles to the flow of an ion. This has been dealt with earlier in this paper.

The second effect was the influence of high intensity fields upon the properties of solutions. This is known as the Wien effect. Under very high potentials, ions move so quickly that the ionic atmosphere does not have time to form completely or, in fact, may not form at all. Wilson (109) has obtained a complete solution for this problem in the case of electrolytes which dissociate into two kinds of ions. Onsager (110) has shown that at high field strength the ionization constant will increase and has obtained an equation relating this constant to the field strength.

As this brief survey has indicated, the interionic attraction theory has been applied with some success to equilibrium and irreversible processes in solution.

IV. EXPERIMENTAL

A. Materials

Zinc sulfate: Mallinckrodt analytical grade reagent was recrystallized twice from boiling conductivity water and once from cold conductivity water. From this, stock solution was prepared. The stock solution was filtered and the pH determined as 5.8. The pH of the unrecrystallized salt solution was 5.1. Concentration of the stock was determined by ignition to the anhydrous sulfate at 400°C as recommended by Cowperthwaite (111). The samples were also ignited to the oxide at 860°C. for twenty-four hours in a furnace which had previously been calibrated. A somewhat higher temperature can give a yellow modification of the oxide. Molality of the stock solution was found to be 0.2297 ± .03%.

Lithium chloride stock solution was prepared according to the method of Scatchard and Prentiss (112). A solution of lithium carbonate c.p. in conductance water was treated with hydrochloric acid and flushed with nitrogen until the pH was 6.5. The solution was then filtered and aliquots were taken to be analyzed by the silver chloride gravimetric method. Normality was found to be 1.747 ±0.5%. Subsequent solutions were prepared from this stock solution by weight dilution.

Potassium chloride was prepared from Baker c.p. reagent by recrystallizing twice from conductivity water followed by fusion in platinum ware under a stream of nitrogen, following the recommendation of Pinching and Bates (113). The resulting salt was dissolved in carbon dioxide free conductivity water. Subsequent solutions were made by weight dilution of the stock solution.

Tetra-n-butylammonium sulfate was prepared by the conversion to the sulfate of the iodide salt. The iodide salt was recrystallized once from conductivity water. It is only moderately soluble in water. Silver oxide was prepared from seven grams of sodium hydroxide and twenty-three grams of silver nitrate. The oxide was washed about thirty times with hot water and was then added to the tetra-n-butylammonium iodide solution. This was mixed under a nitrogen atmosphere for 15 hours to give the tetra-n-butyl ammonium hydroxide. The solution was then filtered through sintered glass and titrated with standard sulfuric acid to a pH of 7.0 as recommended by Fowler et al. (114) to convert to the tetra-n-butylammonium sulfate. The most concentrated solution we were able to prepare was 0.04867 N. Volume dilutions were made as necessary.

Zinc perchlorate stock solution was prepared from G. F. Smith Chemical Co. salt, recrystallized three times from conductivity water. The stock solution was analyzed by adding sulfuric acid to weighed aliquots, and evaporating to fumes of SO_3. The residues were dried to both zinc sulfate at 400°C. and zinc oxide at 860°C. Molality of the stock solution was determined as 0.4450 ± 0.09%.

Conductivity water was prepared by the distillation of demineralized water from alkaline permanganate solution. This distillate was subsequently redistilled under nitrogen. The water was transferred under nitrogen pressure directly to the conductance cells or solution flasks. The exit from the distilling receiver was fitted with a stopcock followed by a piece of tygon tubing which could be connected directly to a conductance cell. The specific conductance never exceeded 7.3×10^{-7} ohm^{-1} cm^{-1}.

Potassium octacyanomolybdate prepared according to the method given in "Inorganic Synthesis," was obtained from Dr. F. B. Dutton (115).

The salt was then recrystallized from conductivity water by the addition of ethanol. Stock solutions were made up by weight dilution. The concentration was checked by titration with standard ceric sulfate solution. This was standardized by the method of Willard and Furman (116). The concentration was in agreement to within $\pm$ 0.06%.

B. Apparatus

1. Transference. The transference number of zinc sulfate was obtained using the sheared boundary technique (64). A modification of the equipment used by Spedding, Porter and Wright (74) was employed. The transference cell consists of an anode compartment fitted to the end of a Pyrex hollow-bore stopcock at which the boundary was formed. The stopcock was connected through a middle opening to a two millimeter Corning measuring pipette. The pipette was connected to the cathode compartment through another hollow-bore stopcock, which permits use of the same cell with a rising boundary. The anode and cathode compartments were provided with female ground glass joints to accommodate the male joints into which the electrodes were sealed. Side arms with stopcocks were attached to the electrode compartments. Removable glass cups were used to prevent the products of the electrode reactions from contaminating the measuring tube. The measuring pipette was marked by a diamond stylus with fine semi-circular cuts, with a gap left both front and back to facilitate accurate and reproducible timing. The tube was calibrated three times with mercury as recommended by Longsworth (78). The measuring pipette was filled with clean mercury and mounted vertically with a stopcock at the bottom to allow mercury to be withdrawn into a weighing flask. A cathetometer was used to measure vertical distance in the pipette and was fitted with a micrometer microscope with 90° crosshairs. The vertical position on the graduated scale was measured by means of a vernier which was in no particular

units and henceforth will be referred to as 'turns.' The temperature variation with time (in the constant temperature room) was plotted along with the variation in meniscus reading with this temperature fluctuation. Since maximum and minimum of temperature and meniscus height occur together, we recorded the temperature simultaneously with each reading made on the pipette. Later a temperature correction was made and will be described. Calibration was done from top to bottom of the pipette starting with the first split mark. The mercury was run out to just slightly above the first mark and the weighing bottle weight recorded. The microscope crosshairs were then set on the split mark with the vernier on the zero position. The turns necessary to bring the crosshairs to the level of the mercury mensicus were determined. These were recorded as positive turns. The temperature was recorded.

The mercury was then allowed to run into the weighing bottle until the meniscus was just below the split mark and the new weight of weighing bottle recorded. The vernier was then returned through zero and the crosshairs again aligned with the meniscus. This reading was recorded as negative turns. The temperature was recorded at the same time. The mercury was then run out to just above the second mark and the procedure repeated. Typical data are shown in Table 1.

Since it was necessary to make a temperature correction, a relationship between the number of turns and the temperature was derived as follows:

The coefficient of thermal expansion for mercury is

$$\alpha = \frac{1}{V} \cdot \frac{\Delta V}{\Delta T} \tag{86}$$

where ΔT is $25^{\circ}C$ minus the temperature at the time of reading, and $\underline{V}$ is the volume of the mercury. The total volume $\underline{V}$ is 2.90 milliliters at the zero mark. The volume may then be expressed as

$$V = 2.90 - (0.10)\,(\text{number of the mark}) \tag{87}$$

The quantity ΔV is then expressed as

$$\Delta V = \alpha V \Delta T = \Delta h A \tag{88}$$

where h is the height of the mercury and A is the cross sectional area of the tube. If r is the number of turns and k is equal to the turns/inch, then

$$\Delta r = \Delta h\, k = \frac{k}{A} \Delta V = \frac{k \alpha}{A} \cdot V \Delta T \tag{90}$$

but ΔV is also equal to $\Delta m/\rho$, where m is the mass of the mercury and ρ is the density. Following from this we can write therefore

$$\Delta r = \frac{k}{A} \cdot \frac{\Delta m}{\rho} \tag{91}$$

and

$$k/A = \rho \Delta r/\Delta m \tag{92}$$

The number of turns (uncorrected for temperature) and the weight, enables one to calculate an average value for $\Delta m/\Delta r$, grams per turn. This value was used to give a first approximation to k/A. Then, by successive approximations, an expression for Δr was determined where $\Delta m/\Delta r = 0.0156$ grams per turn. From equation (90)

$$\Delta r = \frac{\rho \Delta r}{\Delta m} \alpha V \Delta T \tag{93}$$

where ρ is 13.53 grams per cubic centimeter and α is 0.1817×10^{-3} deg^{-1}. The final expression then for Δr is

$$\Delta r = 0.157\, V \Delta T \tag{94}$$

This correction on the number of turns, r, was made for each reading and tabulated in Table 1. The number of grams per turn was calculated and averaged for all three of the calibrations.

It is now possible to calculate what the weight of mercury would have been had the meniscus been exactly at the zero mark for each reading, as follows.

Table 1. Data Used in Calibration of Transference Tube.

Mark	Turns	Weight	Temp.	Corrected Turns	gm/Turn
0	+7.922	20.6413	23.35	+8.67	0.0153
0	-5.100	20.8491	24.65	-4.94	
1	+3.798	22.1364	22.50	+4.89	0.0165
1	-3.077	22.2625	24.50	-2.66	
2	+8.155	23.5113	23.00	+9.00	0.0157
2	-3.843	23.6928	22.00	-2.58	

	Average Wt at Zero	Interval Wt.	Interval Vol.
0	20.7743	1.4426	.1066
1	22.2169	1.4353	.1061
2	23.6522	1.4338	.1059
3	25.0860		

Weight of mercury with meniscus +8.67 turns above zero - 20.6413 gm.

+ 8.67 turns x 0.0156 gm/turn .1353 gm.

Weight of mercury with meniscus at zero 20.7766 gm.

The same procedure was followed, by subtracting the amount of mercury from the amount that was actually weighed:

Weight of mercury with meniscus - 4.94 turns below zero - 20.8491 gm.

-4.94 turns x 0.0156 gm/turn .0771 gm.

Weight of mercury with mensicus at zero 20.7720 gm

These two values were averaged. In the same way, average values were obtained for each mark. The difference between two successive marks are listed in Table 1 as the interval weight. Since the density of mercury is known at 25°C, the corresponding interval volume was calculated and tabulated in Table 1.

The boundary between two solutions of different refractive indices can be detected by placing a light source behind and slightly below this boundary and viewing the tube from the front. The light source used was a vertically mounted fluorescent light covered by a cloth shield with a one quarter inch horizontal slit. This shield was lowered or raised to position the slit as the boundary movement was followed, by attachment to the drive shaft of a 110 volt reversible d.c. motor. The boundary was viewed through a thirty power telescope placed about 10 feet from the cell. Constant temperature was maintained in the cell by placing it in an aquarium-type water bath where the temperature was maintained at 25.00°C $\pm$ 0.05°C as determined by a platinum resistance thermometer calibrated by the National Bureau of Standards. The calibration was rechecked by determining its resistance at 0°C. This was done by immersing the thermometer in a Dewar flask containing conductivity water in equilibrium with ice made from the same water. The constant temperature bath was stirred by a Gorman-Rupp pump fitted with glass tubing intake and exhaust. A 150 watt infra-red bulb was used as a heat

source. A constant head of water fed to copper coils was used for cooling. A precision Micro-set Differential Range thermoregulator was used to control the temperature.

The boundary movement was timed by two stopwatches mounted in a stand with an adjustable hinged top so that one watch could be simultaneously started while the other was stopped. The watches were checked with the standard WWV time signal and were accurate to three seconds over a twenty-four hour period.

Constant current was obtained with an electronic controller and balancing motor. A complete description and a diagram of the current controller is given by Karl (13).

The entire apparatus was checked at intervals by measuring the transference number of potassium chloride followed by lithium chloride. These results agreed with published values to within 0.05%.

2. Conductance. Conductivity measurements were made using a bridge designed by Thompson and Rogers (117) modified by the addition of a Wagner ground circuit. The source of the alternating current to the bridge was supplied by the oscillator shown in Figures 2A and 2B, designed to produce essentially sinusoidal wave forms from 400 to 4000 cps. The unbalance signal from the bridge was amplified by the narrow band amplifier shown in Figure 3. The output of this amplifier was applied to the vertical input terminals of a cathode ray oscilloscope. The horizontal input of the oscilloscope was driven by a signal of adjustable phase taken directly from the oscillator. The power supplies for these circuits are shown in Figure 4.

Because the two fixed resistors R_1 and R_2, in the bridge circuit shown in Figure 5 are equal, the bridge is balanced when the impedance of the cell is equal to the impedance of the parallel R-C arm consisting of R_3 and C_1. Thus, at balance, the resistance of the cell is equal to R_3, which is read directly on the decade dials on the face of the instrument.

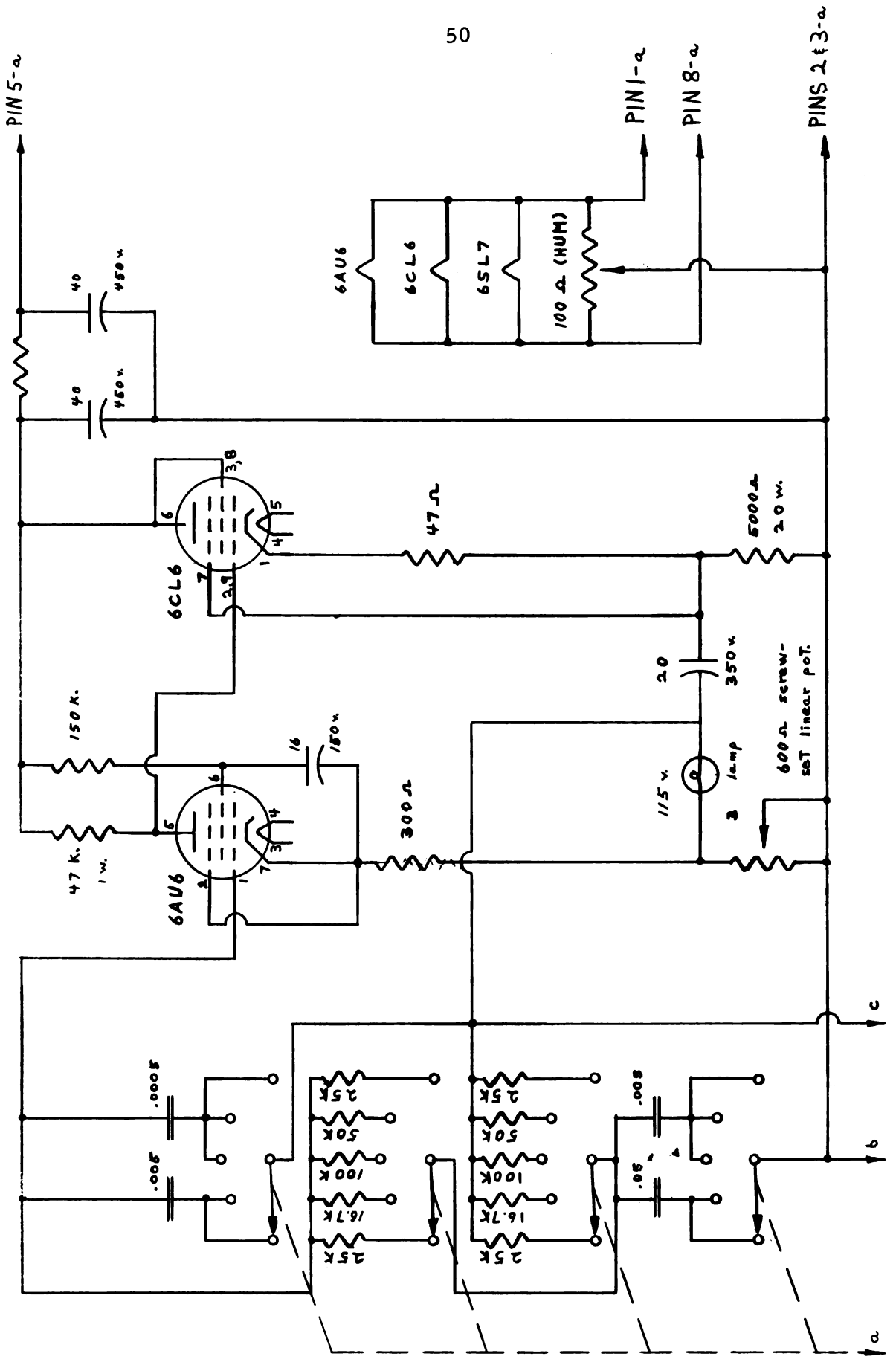


Figure 2a. Conductance Bridge Oscillator.

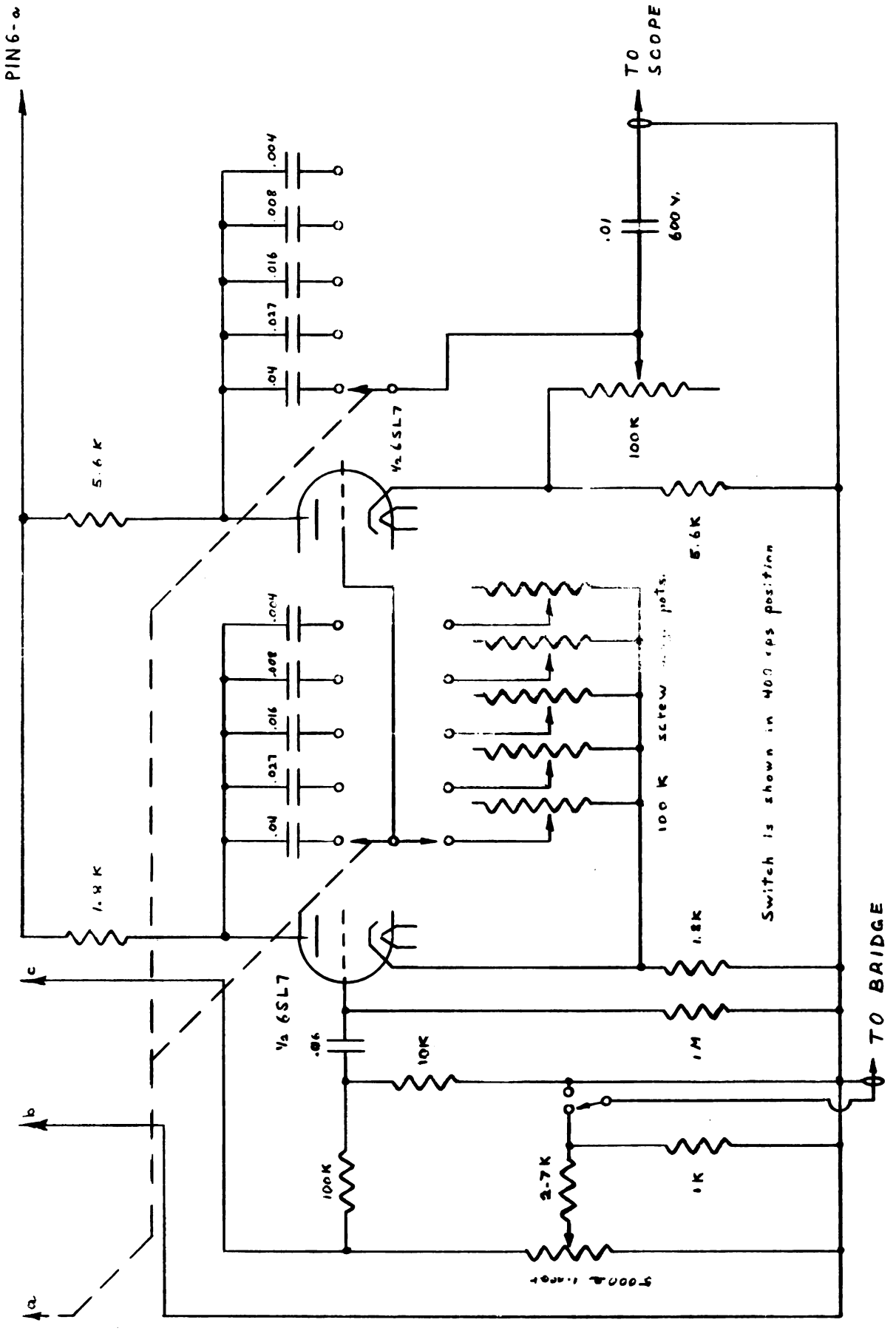


Figure 2b. Conductance Bridge Oscillator.

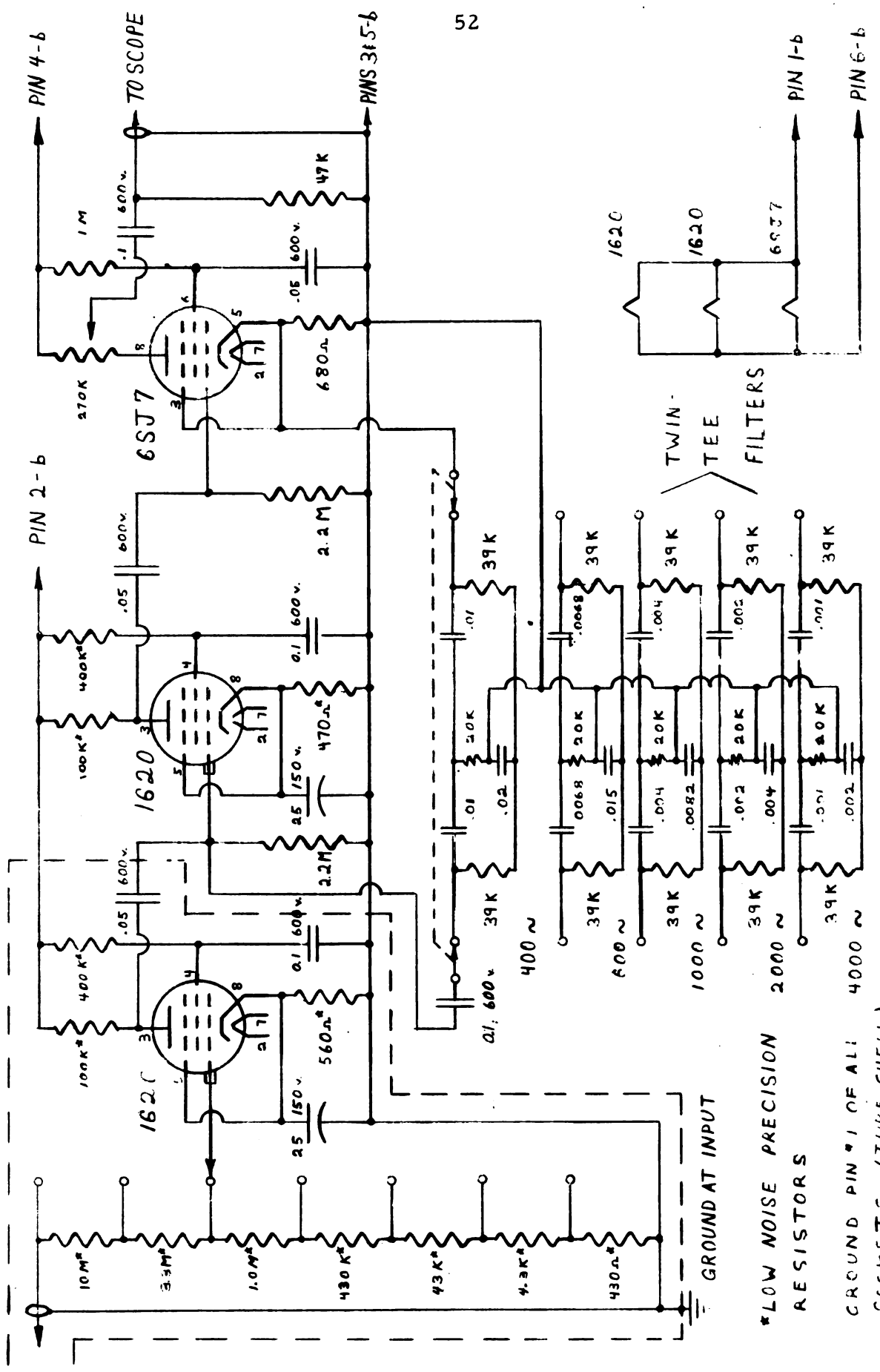


Figure 3. Conductance Bridge Detector Circuit.

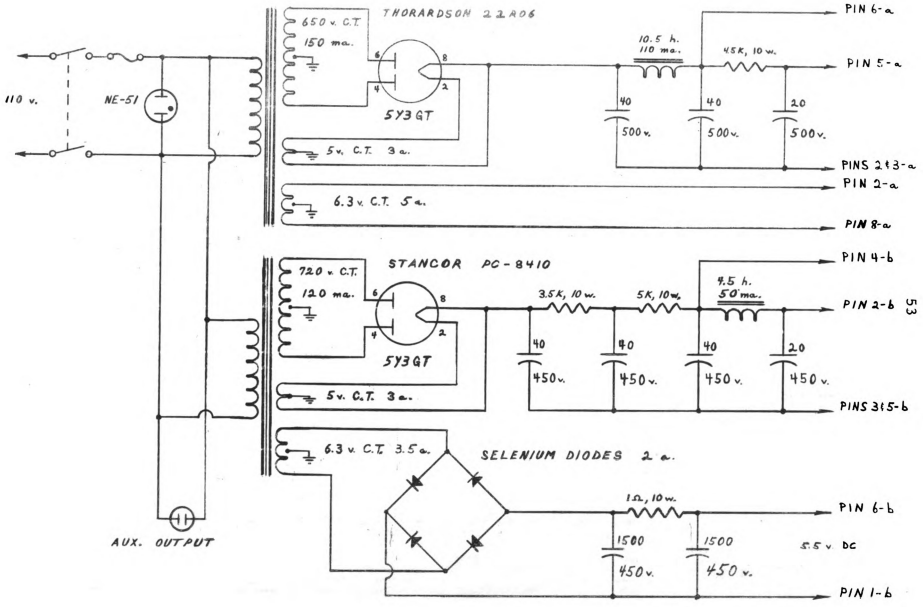


Figure 4. Conductance Bridge Power Supply.

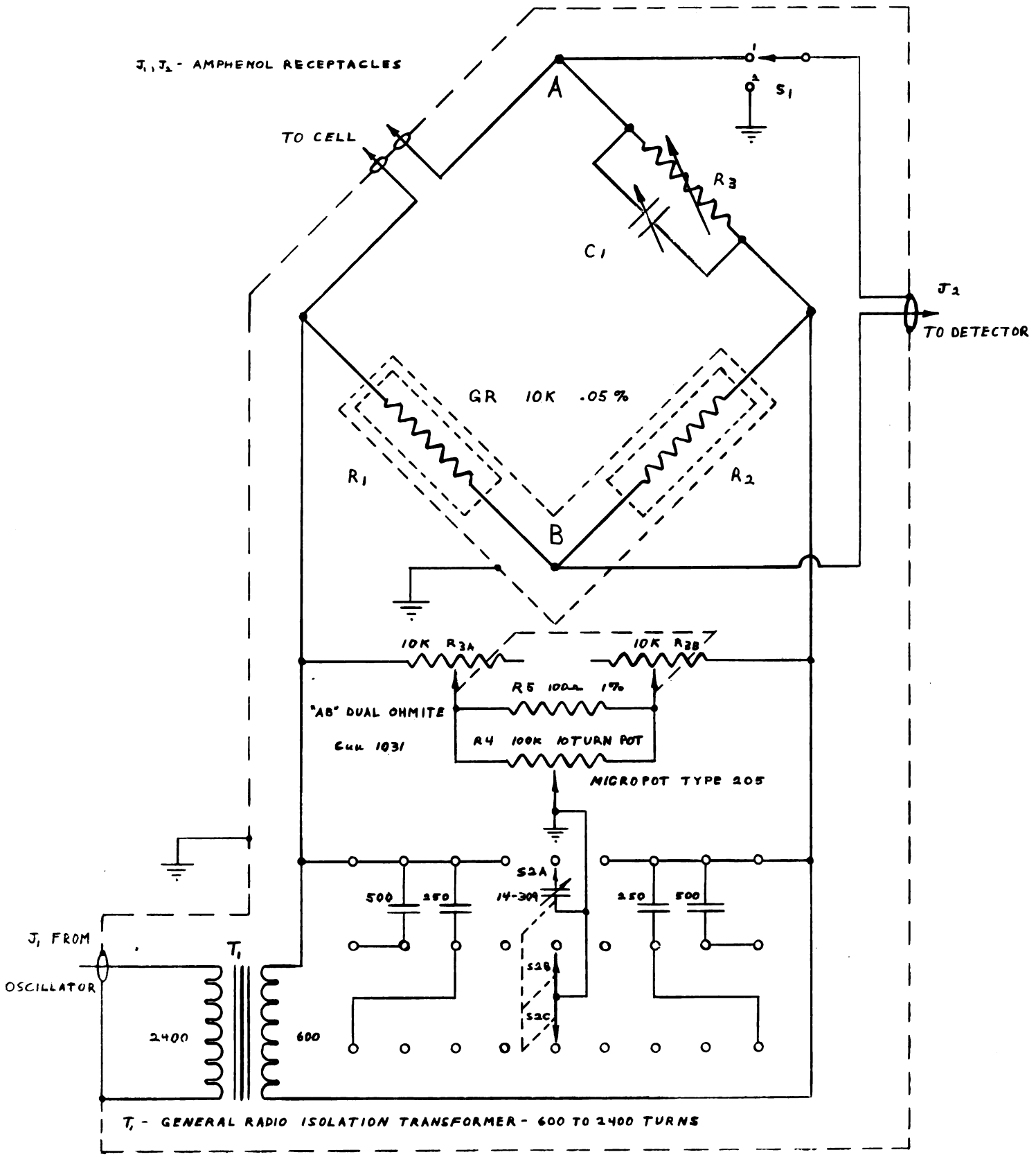


Figure 5. Conductance Bridge Bridge Circuit.

The noise level in the unbalance signal is minimized by the Wagner ground circuit which allows the point B to be set at ground potential without being connected to ground. By successive balancing of the Wagner ground circuit with switch S_1 in position 2, and of the bridge circuit with S_1 in position 1, a balance point is achieved where $R_{cell} = R_3$, $C_{cell} = C_1$, and points A and B are both at ground potential.

The set of decade resistors, R_3, was calibrated internally by the method prescribed for internal calibration of Mueller Bridges. It was not necessary to perform an absolute calibration of the bridge against external resistors, for the conductance cells were always calibrated with standard potassium chloride solutions.

The constant temperature bath was filled with transformer oil to minimize capacitive effects. The temperature was maintained at $25.000^{\circ}C \pm 0.015^{\circ}C$ as determined by a platinum resistance thermometer. The bath was shielded by copper screen encircling it, the screen being at ground potential. A metal baffle covered with black baked-on enamel was placed towards the edge of the circular bath to facilitate stirring, which was done with a Gorman-Rupp liquid pump. For work at low concentrations, conductivity cells were constructed from Leeds and Northrup type "A" cells, by sealing the cell into a 500 milliliter Erlenmeyer flask as shown in Figure 6. Modifications from similar cells used by Kraus et al. (118) included a side arm with a stopcock as well as a stopcock exit in the cap. This arrangement allowed conductivity water to be pumped directly into the cell from the receiving vessel of the still. It also provided a means of insuring an atmosphere of nitrogen over the solution in the cell during the further addition of solute. To reduce polarization effects caused by the alternating current, the electrodes were very lightly platinized according to the recommendations of Jones and Bollinger (28). The electrolytic platinizing solution was about three percent chloroplatinic acid and 0.02 percent lead acetate. About twenty

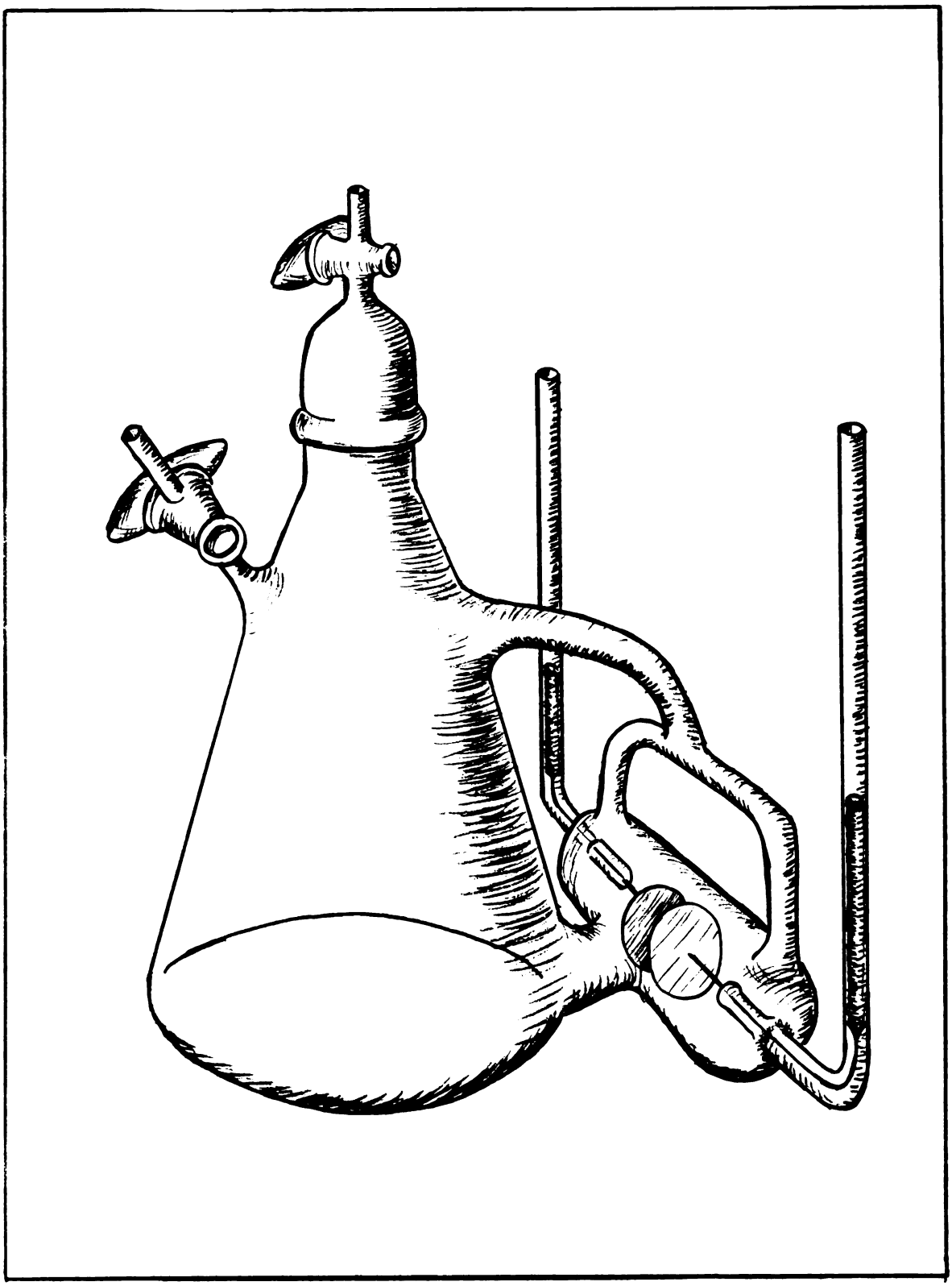


Figure 6. Conductance Cell.

milliamperes of current were used, with the polarity reversed every ten seconds for a total period of forty seconds. The cell showed very little Parker effect upon calibration over the same range of resistances as were used with the samples.

C. Procedure

1. Transference. The transference tube was cleaned with alcoholic KOH and acid cleaning solution after every four or five determinations. After thorough rinsing with distilled water it was allowed to stand with water for twelve hours to insure removal of the acid from the glass. Between other determinations it was thoroughly rinsed and allowed to stand with distilled water in it. Silicone grease was used on the stopcocks. The cell was rinsed several times with zinc sulfate and then filled, the electrode cup and the silver-silver chloride electrode inserted and the side-arm stopcock closed. The anode compartment was then shut off by the upper hollow-bore stopcock, rinsed with water, followed by tetra-n-butyl ammonium sulfate solution made up to the concentration given by the Kohlrausch ratio with an estimated value of the transference number of the zinc ion. When the cadmium electrode was in place, the cell was completely rinsed on the outside with distilled water. The side-arm stopcocks were then opened until temperature equilibrium could be reached.

The cell was checked for electrical leaks to the bath by a vacuum tube ohmmeter and aligned vertically with the light and telescope. The Leeds and Northrup potentiometer was balanced against the standard cell, the leads connected, the hollow-bore stopcock opened and the current turned on. The current was adjusted to allow about 170 to 250 seconds for the traversal of the volume between approximately .1 ml. markings. Temperature equilibrium was reached by the time the boundary reached the first mark since this always took more than one-half

hour. The side-arm stopcock in the cathode compartment was left open during the run, the anode closed. Only the volume changes which occur between the boundary and the closed side then need to be considered. Stopwatches were used to determine the time for the boundary to pass each mark.

The zinc sulfate solutions were made up by weight dilution of a .2298 molal stock solution. Densities of three solutions were measured in a 50 ml pycnometer. The equation of the line giving density as a function of molality, m, was found to be:

$$\rho = .9970 + .1607\ m \qquad (96)$$

This equation allowed calculation of the normalities of the solutions from the known molalities, as well as evaluation of the partial molar volume of zinc sulfate.

2. Conductance. A standard resistor, about 24K ohms, enclosed in glass and immersed in the oil bath, was permanently mounted so that it might be connected in parallel with conductivity cells when their resistances were very high. The resistance of this standard was recorded with each run, through a range of 400 to 4000 cycles per second. The conductance cells were cleaned with detergent and water, followed by rinsing with distilled water, conductivity water and oven drying. When it became necessary to replatinize the cell, it was cleaned with fuming nitric acid followed by rinsing with water before platinizing. The cell afterwards was then rinsed about thirty times before proceeding as before.

The cells were calibrated with potassium chloride solution using a technique described below which was later used with both zinc perchlorate and potassium octacyanomolybdate (IV).

The stopcocks of the dried cool flask were coated lightly with Dow Corning High vacuum grease. The cell was then weighed and conductivity water was forced into it under nitrogen pressure. The total weight was

then determined and, from this, the weight of water, which was then corrected to weight in vacuum according to the equation

$$\text{Weight}_{(\text{vacuum})} = \text{Weight}_{(\text{air})} + k\ \text{Weight}_{(\text{air})}/1000 \quad (97)$$

where k for brass weight and solution density of approximately one, is 1.06 (119).

The cell was then placed in the oil bath in parallel with the standard resistor. Occasional gentle mixing was found desirable to shorten the time required to attain temperature equilibrium. Care was taken that no water or solution was ever allowed as high as the side arm outlet since additional mixing would then be difficult and solution strength inaccurate. The equilibrium point was determined by the constancy of the resistance measurement. When a constant value was obtained, the resistance of the standard resistor was then recorded for frequencies of 400, 600, 1000, 2000 and 4000 cycles per second. There was always a small amount of frequency dependence of the resistance so that resistance versus the reciprocal of the square root of the frequency was plotted and extrapolated to infinite frequency following the method of Jones and Christian (37). Reasonably straight lines were thus obtained as shown in Figure 7. The uncertainty of the extrapolation is estimated as less than $\pm$ 0.02%. Whenever the value of resistance at infinity differed from that at 400 cps by more than 0.3% the cells were cleaned and replatinized and the cell constant redetermined.

The resistance of the water was then measured and calculated from the relationship

$$1/R_{\text{total}} = 1/R_{\text{water}} + 1/R_{\text{standard}} \quad (98)$$

The cell was then removed from the bath and connected to the nitrogen line, with the cap off. Stock solution was added from a weight burette while nitrogen was flowing through the cell. The cell was then closed

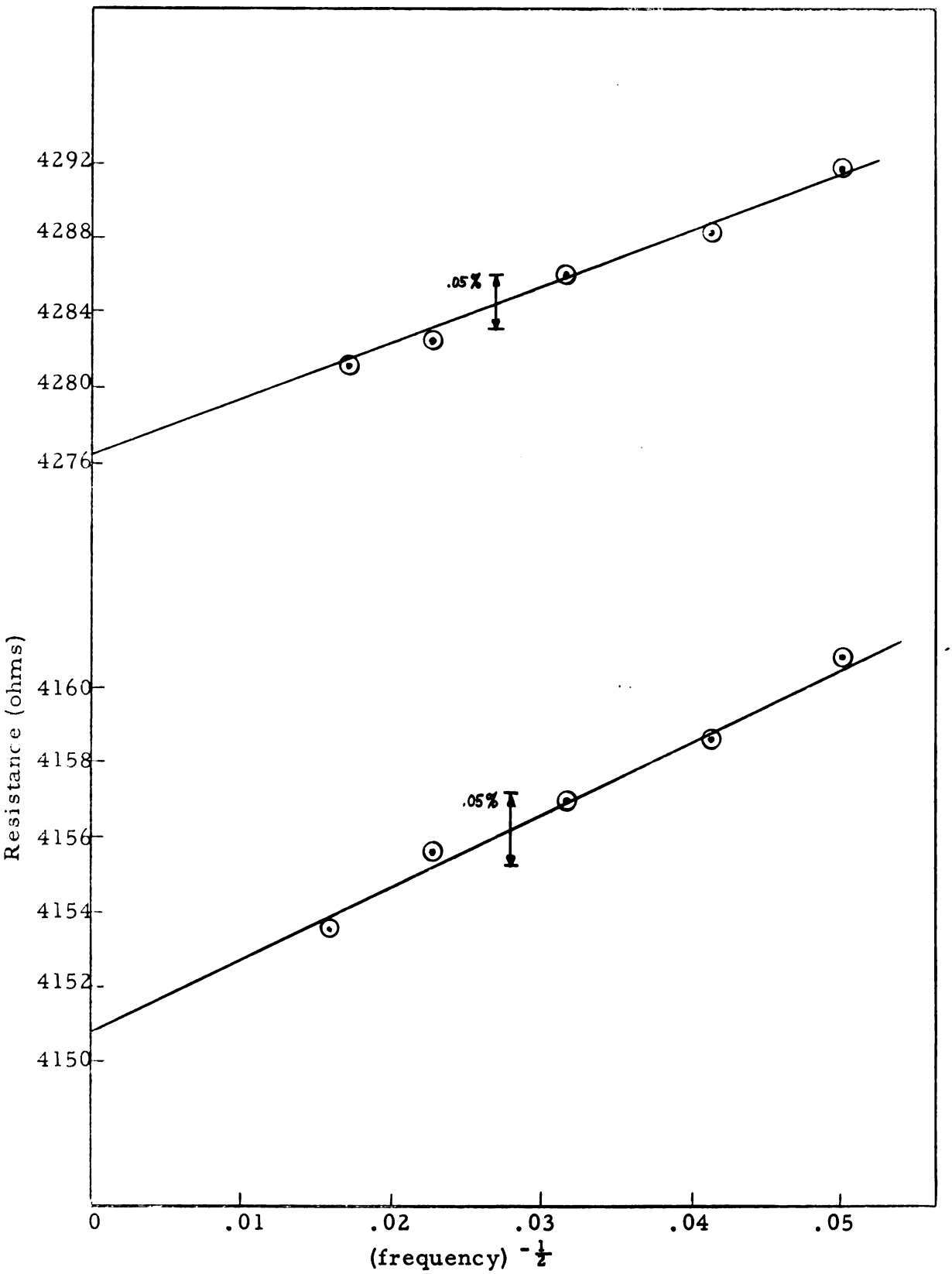


Figure 7. Cell resistance as a function of frequency extrapolated to infinite frequency.

off and the solution thoroughly mixed before returning it to the bath. Repeating this procedure gave resistance readings over a range of increasing concentrations.

All weights used were previously calibrated against a ten gram National Bureau of Standards calibrated weight.

The potassium chloride solutions which were used for weight dilution were prepared according to the method of Jones and Bradshaw (39). They contained 0.74526 grams of potassium chloride per kilogram of solution in vacuum.

D. Results

1. Sample Calculation to determine a cell constant.

Weight of water in vac.	341.72 g.
Weight of solution in first addition	9.12 g.
Total solution weight	350.84 g.

$$\text{Weight of solute added} = \frac{0.74526}{1000} \times 9.1237 = 6.7995 \times 10^{-3} \text{ g.}$$

Total solution weight	350.84 g.
Solute weight	0.01 g.
Solvent weight	350.83 g.

$$\text{Molality of new solution} = \frac{\text{gm. of solution}}{\text{molecular wt. of solute}} \cdot \frac{1000}{\text{weight of solvent}}$$

$$m = 2.5995 \times 10^{-4} \text{ moles/1000 gm of solvent}$$

The molarity, c, of the solution is related to the molality m by the relationship

$$c = m(d_0 - Am + Bm^2) \cdot \qquad (99)$$

where the constants are given by Harned and Owen (120) as

$$d_0 = 0.99707, \quad A = 0.0284 \text{ and } B = 0.0003 \text{ for KCl at } 25^\circ\text{C.}$$

It then follows that

$$c = 2.5914 \times 10^{-4} \text{ equivalents/liter}$$

The value of Λ was then evaluated from an empirical expression of Onsager (3)

$$\Lambda = \Lambda_0 - S_{(\lambda)} \sqrt{c} + Ac \log c + Bc \qquad (77)$$

where

Λ is the equivalent conductance of KCl

$\Lambda_0 = 149.87$, the limiting equivalent conductance

c = molarity of the solution

A = 31.8 (reference 121)

B = 144 (reference 121)

$S_{(\lambda)} = \alpha^* \Lambda_0 + \beta^*$ where $\alpha^* = .2289$ (reference 122)

$\beta^* = 60.19$ (reference 122)

From this $\Lambda = 148.35$ ohm^{-1} cm^2 equivalent^{-1}

The specific conductance of potassium chloride is

$$L_{KCl} = c \Lambda / 1000$$
$$= 2.5914 \times 10^{-4} \times 148.35/1000 \qquad (2)$$
$$= 3.8448 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$$

We know that

$$(L_{solution})\,(R_{solution}) = k = (L_{H_2O})\,(R_{H_2O}) \qquad (100)$$

where L_{sol} and L_{H_2O} are the specific resistances of the solution and of the water respectively, and R_{sol} and R_{H_2O} are the resistances of the solution and the water respectively, and k is the cell constant.

Then

$$L_{H_2O} = (L_{sol})\,(R_{sol}) / R_{H_2O} \qquad (101)$$

But $L_{sol} = L_{KCl} + L_{H_2O}$ (102)

It then follows that

$$L_{sol} = \frac{L_{KCl}}{1 - \frac{R_{sol}}{R_{H_2O}}} \qquad (103)$$

$$= \frac{3.8448 \times 10^{-5}}{1 - \frac{2.6483 \times 10^4}{2.0400 \times 10^6}} = 3.8919 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$$

From equation (100) it then follows that

$$k = (3.8919 \times 10^{-5}) \ (2.6483 \times 10^{4}) = 1.0307$$

The water which was added in the stock solution from the weight burette was at equilibrium with the carbon dioxide of the air and its conductance was found to be about 1×10^{-6} ohm^{-1} cm^{-1}. To correct for the added conductivity due to this impure water, the specific conductance of the pure water was calculated, using the approximate $\underline{k}$ obtained above.

$$L_{H_2O} = 1.0307 \ / \ 2.04 \times 10^{6} = 0.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$

The correction Δk on the cell constant was then

$$\Delta k = [(L_{\text{impure water}}) - (L_{\text{pure water}})] \left(\frac{\text{wt of solution added}}{\text{total wt. of solution}} \right) \tag{104}$$

$$(R_{sol}) = (1 - .5) \ 10^{-6} \ \left(\frac{9.124}{341.7}\right) \ (2.6483 \times 10^{4}) = 3.5 \times 10^{-4}$$

Therefore the correct cell constant becomes $k + \Delta k$

$$k_{corr.} = 1.0307 + 0.0004 = 1.0311$$

The results of the cell constant determination are shown in Table 2. Figure 8 shows graphically the scatter in determining the constant of cell 2. A check on the cell constant determination was made with one of the cells using standard barium chloride solution. The equivalent conductance was determined for five different concentrations. These agree well with the results of Shedlovsky and Brown (123) on the same salt. The equivalent conductances they obtained at the same concentrations are shown with those determined in this laboratory in Table 3.

Table 2. Conductance Cell Calibration with KCl.

Run No.	N x 10^4	k
I - cell 2	3.0325	0.25028
	5.2551	0.25028
	7.6917	0.25013
	9.8326	0.24998
II	2.4124	0.25031
	3.9681	0.25017
	5.7619	0.25026
	7.8759	0.25023
	10.0597	0.25007
III	1.8854	0.25009
	3.9054	0.24995
	6.4277	0.24995
I - cell 3	4.1094	1.0339
	6.8161	1.0365
	10.216	1.0357
	12.409	1.0356
	15.841	1.0341
II	5.8979	1.0336
	10.652	1.0347
	17.393	1.0362

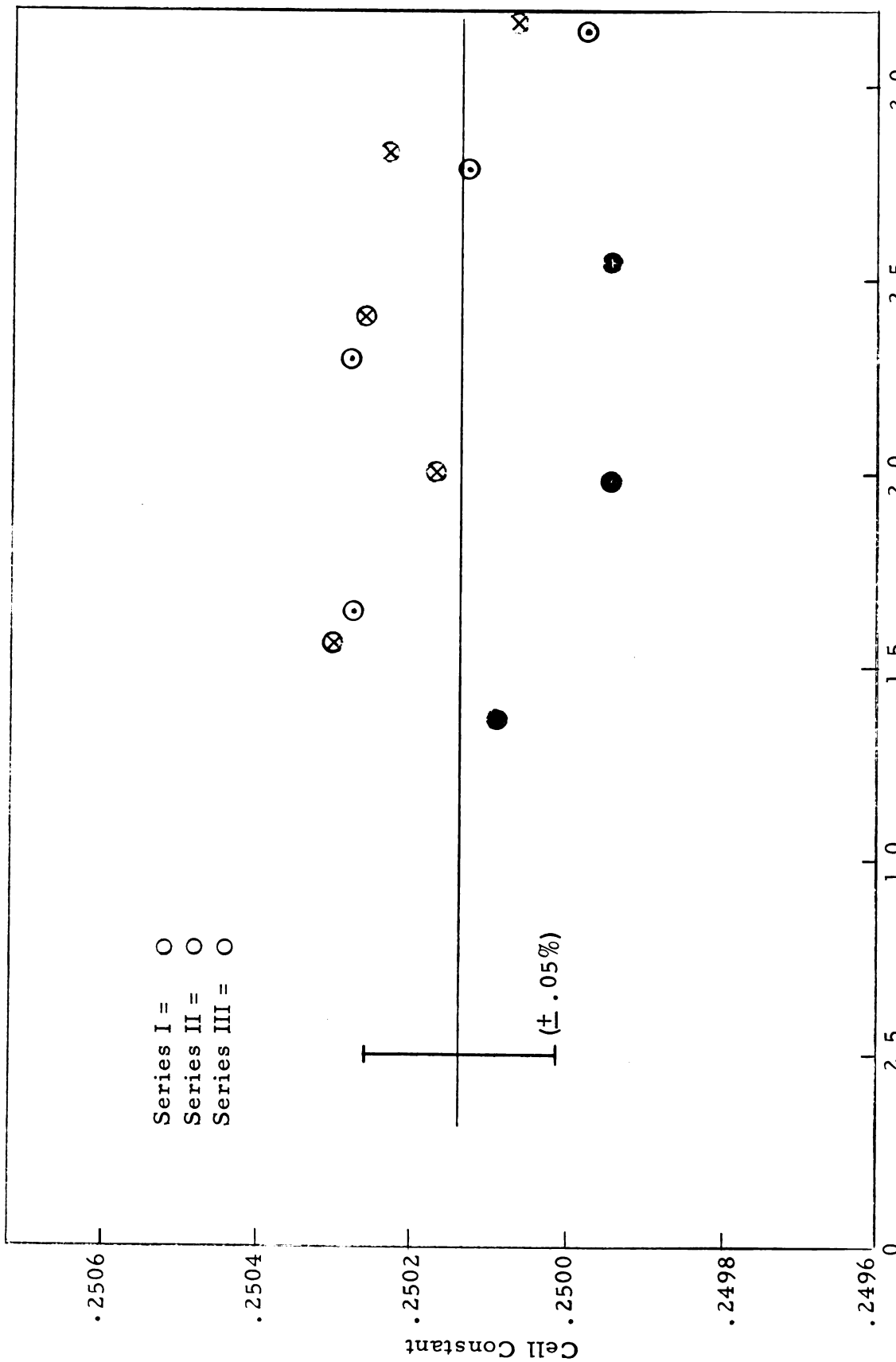


Figure 8. Cell constant determination at varying concentrations of potassium chloride.

Table 3. The Equivalent Conductance of $BaCl_2$.

$\sqrt{c^*}$ x 10^2	Λ Shedlovsky	Λ This Lab.
1.83	136.76	136.44
2.196	136.06	136.06
2.49	135.55	135.57
2.95	134.72	134.63
3.30	134.10	134.06

2. The Equivalent Conductance of Zinc Perchlorate.

The equivalent conductance of zinc perchlorate was determined using the same experimental procedure used to determine the cell constant. Since the cell constant k was known, the specific conductance of water and of each solution could be calculated from the relationship $L = k/R$, where R is the resistance in ohms of the solution. The density of zinc perchlorate was determined using a fifty milliliter pycnometer. This enabled the conversion from molality to normality to be made. The density change with molality can be represented by the equation

$$\rho = 0.99707 + 0.1985\ m \tag{105}$$

Sample calculations

Weight of flask + water	612.92 g.
Weight of flask	291.90 g.
Weight of water	321.02 g. = 321.36 in vacuum

Weight of first addition of stock solution = 0.3818 in vacuum

The molality of the resulting solution can be found from the relationship

$$m = \frac{m_s\ g}{g + w\ \left(\frac{1 + m_s M}{1000}\right)} \tag{106}$$

where m is the molality of the new solution, m_s is the molality of the stock solution, g is the weight of stock solution added, w is the weight of pure water in vacuum and M is the formula weight of zinc perchlorate.

$$m = \frac{0.03798\ (0.3818)}{.3818 + 321.36\ \left(1 + \frac{.03798(264.29)}{1000}\right)} = 4.3575 \times 10^{-5} \text{ moles/1000 grams solvent.}$$

The normality of this solution can then be calculated from the relationship

$$\text{normality} = c^* = \frac{2\rho\ m}{1 + \frac{mM}{1000}} \tag{107}$$

where ρ is the density of the solution

$$c^* = 8.6896 \times 10^{-5} \text{ equivalent/liter.}$$

Now $L_{H_2O} = k/R = \frac{1.0350}{1.420 \times 10^6 \text{ ohm}} = 0.729 \times 10^{-6} \text{ ohm}^{-1}$

and $L_{sol} = k/R_{sol} = \frac{1.0350}{9.234 \times 10^4 \text{ ohm}} = 1.1209 \times 10^{-5} \text{ ohm}^{-1}$

Then $L_{Zn(ClO_4)_2} = (L_{sol}) - (L_{H_2O}) = 1.0480 \times 10^{-5} \text{ ohm}^{-1}$

The specific conductance of the bulk of the water was much lower than that of the water in the stock solution which was in equilibrium with carbon dioxide in the air, and had a specific resistance of 1×10^{-6} ohm^{-1}. For this reason a correction, ΔL, was made on the L of $Zn(ClO_4)_2$ as follows:

$$L_{corrected} = L_{measured} - \Delta L \tag{108}$$

where

$$\Delta L = (L \text{ of water in stock}) - (L \text{ of solution water}) \frac{(\text{weight of stock solution water})}{(\text{total weight of water})} \tag{109}$$

$$\Delta L = (1 - .7)\ 10^{-6}\ \frac{(.38)}{(321)} = .00008 \times 10^{-5}$$

$$L_{corrected} = (1.0480 - 0.000004) \times 10^{-5} \text{ ohm}^{-1}$$

$$= 1.0480 \times 10^{-5} \text{ ohm}^{-1}$$

This correction is negligible here and only becomes significant at higher concentrations.

$$Zn(ClO_4)_2 = \frac{L_{corrected}\ 1000}{c} = \frac{1.0480 \times 10^{-5} \times 10^3}{8.6896 \times 10^{-5}} =$$

$$120.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalents}^{-1}$$

The extent of hydrolysis of zinc perchlorate was checked in two ways. (1) The pH of the stock solution and several dilutions were determined using a Beckman Model B pH meter. (2) These solutions were acidified to pH of 3 with perchloric acid and were titrated with standard sodium hydroxide. The equivalence pH was determined graphically by plotting Δ pH/Δ ml versus $\overline{\text{pH}}$. The maximum in the curve, where the slope

is equal to zero, is the equivalence pH. This method was used because there was no sharp break apparent in the titration curve of milliliters versus pH. The two methods agreed to within 0.05 pH units, indicating little or no free acid in the zinc perchlorate samples. The average value of the hydrolysis constant corrected for activity coefficients, for the equation, $Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+$, was found to be $0.94 \pm .03 \times 10^{-9}$. This is only approximate because of the irreversibility of the glass electrode and the uncertainty arising because of the chloride-perchlorate junction potential. Kolthoff and Kameda (124) using a hydrogen electrode obtained a value of 2.65×10^{-10} from measurements on zinc sulfate. A hydrolysis correction, $\Delta\Lambda$, was then made on the basis of their hydrolysis constant. The method of this correction is developed below.

Correction of Λ of $Zn(ClO_4)_2$ for Hydrolysis

$$\Lambda_{\text{corrected}} = \Lambda - \Delta\Lambda \tag{110}$$

To derive expression for $\Delta\Lambda$:

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+ \tag{111}$$

$$K = K_c K_\gamma = \frac{[ZnOH^+][H^+]}{[Zn^{++}]} = K_\gamma \tag{112}$$

using $K = 2.65 \times 10^{-10}$ from Kolthoff and Kameda (124)

$$K_\gamma = \frac{\gamma_{H^+} \gamma_{ZnOH^+}}{\gamma_{Zn^{++}}} \tag{113}$$

then $\log K_\gamma = \log \gamma_{H^+} + \log \gamma_{ZnOH^+} - \log \gamma_{Zn^{++}}$

but for dilute solutions

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{\Gamma}}{1 + B a_i \sqrt{\Gamma}} \simeq - A z_i^2 \sqrt{\Gamma} \tag{114}$$

therefore we may now express

$$\log K_\gamma = 2 A \sqrt{\Gamma}$$

and

Now $L_{H_2O} = k/R = \frac{1.0350}{1.420 \times 10^6 \text{ ohm}} = 0.729 \times 10^{-6} \text{ ohm}^{-1}$

and $L_{sol} = k/R_{sol} = \frac{1.0350}{9.234 \times 10^4 \text{ ohm}} = 1.1209 \times 10^{-5} \text{ ohm}^{-1}$

Then $L_{Zn(ClO_4)_2} = (L_{sol}) - (L_{H_2O}) = 1.0480 \times 10^{-5} \text{ ohm}^{-1}$

The specific conductance of the bulk of the water was much lower than that of the water in the stock solution which was in equilibrium with carbon dioxide in the air, and had a specific resistance of 1×10^{-6} ohm^{-1}. For this reason a correction, ΔL, was made on the L of $Zn(ClO_4)_2$ as follows:

$$L_{corrected} = L_{measured} - \Delta L \tag{108}$$

where

$$\Delta L = (\text{L of water in stock}) - (\text{L of solution water}) \frac{(\text{weight of stock solution water})}{(\text{total weight of water})} \tag{109}$$

$$\Delta L = (1 - .7)\, 10^{-6} \frac{(.38)}{(321)} = .00008 \times 10^{-5}$$

$$L_{corrected} = (1.0480 - 0.000004) \times 10^{-5} \text{ ohm}^{-1}$$

$$= 1.0480 \times 10^{-5} \text{ ohm}^{-1}$$

This correction is negligible here and only becomes significant at higher concentrations.

$$Zn(ClO_4)_2 = \frac{L_{corrected}\ 1000}{c} = \frac{1.0480 \times 10^{-5} \times 10^3}{8.6896 \times 10^{-5}} =$$

$$120.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalents}^{-1}$$

The extent of hydrolysis of zinc perchlorate was checked in two ways. (1) The pH of the stock solution and several dilutions were determined using a Beckman Model B pH meter. (2) These solutions were acidified to pH of 3 with perchloric acid and were titrated with standard sodium hydroxide. The equivalence pH was determined graphically by plotting Δ pH/Δ ml versus $\overline{\text{pH}}$. The maximum in the curve, where the slope

is equal to zero, is the equivalence pH. This method was used because there was no sharp break apparent in the titration curve of milliliters versus pH. The two methods agreed to within 0.05 pH units, indicating little or no free acid in the zinc perchlorate samples. The average value of the hydrolysis constant corrected for activity coefficients, for the equation, $Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+$, was found to be $0.94 \pm .03 \times 10^{-9}$. This is only approximate because of the irreversibility of the glass electrode and the uncertainty arising because of the chloride-perchlorate junction potential. Kolthoff and Kameda (124) using a hydrogen electrode obtained a value of 2.65×10^{-10} from measurements on zinc sulfate. A hydrolysis correction, $\Delta\Lambda$, was then made on the basis of their hydrolysis constant. The method of this correction is developed below.

Correction of Λ of $Zn(ClO_4)_2$ for Hydrolysis

$$\Lambda_{\text{corrected}} = \Lambda - \Delta\Lambda \tag{110}$$

To derive expression for $\Delta\Lambda$:

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+ \tag{111}$$

$$K = K_c K_\gamma = \frac{[ZnOH^+][H^+]}{[Zn^{++}]} = K_\gamma \tag{112}$$

using $K = 2.65 \times 10^{-10}$ from Kolthoff and Kameda (124)

$$K_\gamma = \frac{\gamma_{H^+} \gamma_{ZnOH^+}}{\gamma_{Zn^{++}}} \tag{113}$$

then $\log K_\gamma = \log \gamma_{H^+} + \log \gamma_{ZnOH^+} - \log \gamma_{Zn^{++}}$

but for dilute solutions

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{\Gamma}}{1 + B a_i \sqrt{\Gamma}} \simeq - A z_i^2 \sqrt{\Gamma} \tag{114}$$

therefore we may now express

$$\log K_\gamma = 2 A \sqrt{\Gamma}$$

and

$$\Gamma = \sum_{i=1}^{2} c_i z_i^2$$

$A = 0.509/\sqrt{2}$ (reference 125)

and $C_{Zn^{++}} = C_{salt} = C^*/2$

and $C_{ClO_4^-} = 2C_{salt} = C^*$

Then $\mu = 3/2\ C^*$

and $\log K\gamma = 1.247\sqrt{c^*}$ (115)

For charge balance the total charge before hydrolysis must equal the total charge after hydrolysis.

(1) Before hydrolysis

Species	(conc)(charge)
Zn^{++}	$2C_s$
H^+	$Kw/2$
OH^-	$-Kw/2$

(2) After Hydrolysis

Zn^{++}	$2(C_s - [ZnOH^+])$
$ZnOH^+$	$[ZnOH^+]$
H^+	$[H^+]$
OH^-	$-[OH^-]$

Then

$$2C_s = 2C_s - 2[ZnOH^+] + [ZnOH^+] + [H^+] - [OH^-]$$

$$\therefore [ZnOH^+] = [H^+] - \frac{K_w}{[H^+]} \quad (116)$$

$$[ZnOH^+][H^+] = [H^+] - K_w$$

But from equation (112)

$$[ZnOH^+][H^+] = \frac{K[Zn^{++}]}{K\gamma} \simeq \frac{K C_s}{K\gamma} \quad (117)$$

and therefore

$$[H^+] = \sqrt{\frac{K C_s}{K_\gamma} + K_w} \qquad (118)$$

Now $\Lambda_0 = \lambda^0_{H^+} + \lambda^0_{OH^-} + \lambda^0_{ZnOH^+} + \lambda^0_{Zn^{++}}$

The total conductance per liter is

$$\sum_i \lambda^0_i c_i^* = 1000\ L = c_s^* \Lambda$$

then $c^* \Delta\Lambda = \sum_i \lambda^0_i (c_i^*)_{hydrolyzed} - \sum_i \lambda^0_i (c_i^*)_{unhydrolyzed}$

$$= 2\lambda^0_{Zn^{++}} [Zn^{++}]_{hyd.} + \lambda^0_{H^+} [H^+]_{hyd.} + \lambda^0_{OH^-} [OH^-]_{hyd.}$$

$$+ \lambda^0_{ZnOH^+} [ZnOH^+]_{hyd.} - \lambda^0_{H^+} [H^+]_{unhyd.} - \lambda^0_{OH^-} [OH^-]_{unhyd.}$$

$$- 2\lambda^0_{Zn^{++}} [Zn^{++}]_{unhyd.}$$

However,

$$[Zn^{++}]_{hyd.} - [Zn^{++}]_{unhyd.} = - [ZnOH^+]_{hyd.}$$

$$[H^+]_{unhyd.} = [OH^-]_{unhyd.} = 10^{-7} \text{ at } 25^\circ C.$$

Then

$$c^* \Delta\Lambda = \lambda^0_{H^+} [H^+]_{hyd.} + \lambda^0_{OH} [OH^-]_{hyd.} + (\lambda^0_{ZnOH^+} - 2\lambda^0_{Zn^{++}})$$

$$[ZnOH^+] - (\lambda^0_{H^+} + \lambda^0_{OH^-})\ 10^{-7} \qquad (119)$$

We know that

$\lambda^0_{H^+} = 350$ (reference 23)

$\lambda^0_{OH^-} = 200$ (reference 24)

$\lambda^0_{Zn^{++}} = 53$ (reference 14)

$\lambda^0_{ZnOH^+} = 32$ (reference 14)

Therefore

From equation (100) it then follows that

$$k = (3.8919 \times 10^{-5}) \ (2.6483 \times 10^{4}) = 1.0307$$

The water which was added in the stock solution from the weight burette was at equilibrium with the carbon dioxide of the air and its conductance was found to be about 1×10^{-6} ohm^{-1} cm^{-1}. To correct for the added conductivity due to this impure water, the specific conductance of the pure water was calculated, using the approximate $\underline{k}$ obtained above.

$$L_{H_2O} = 1.0307 \ / \ 2.04 \times 10^{6} \ = \ 0.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$

The correction Δk on the cell constant was then

$$\Delta k = [(L_{\text{impure water}}) - (L_{\text{pure water}})] \left(\frac{\text{wt of solution added}}{\text{total wt. of solution}} \right) \qquad (104)$$

$$(R_{sol}) = (1 - .5) \ 10^{-6} \ \left(\frac{9.124}{341.7}\right) \ (2.6483 \times 10^{4}) = 3.5 \times 10^{-4}$$

Therefore the correct cell constant becomes $k + \Delta k$

$$k_{corr.} = 1.0307 + 0.0004 = 1.0311$$

The results of the cell constant determination are shown in Table 2. Figure 8 shows graphically the scatter in determining the constant of cell 2. A check on the cell constant determination was made with one of the cells using standard barium chloride solution. The equivalent conductance was determined for five different concentrations. These agree well with the results of Shedlovsky and Brown (123) on the same salt. The equivalent conductances they obtained at the same concentrations are shown with those determined in this laboratory in Table 3.

Table 2. Conductance Cell Calibration with KCl.

Run No.	N x 10^4	k
I - cell 2	3.0325	0.25028
	5.2551	0.25028
	7.6917	0.25013
	9.8326	0.24998
II	2.4124	0.25031
	3.9681	0.25017
	5.7619	0.25026
	7.8759	0.25023
	10.0597	0.25007
III	1.8854	0.25009
	3.9054	0.24995
	6.4277	0.24995
I - cell 3	4.1094	1.0339
	6.8161	1.0365
	10.216	1.0357
	12.409	1.0356
	15.841	1.0341
II	5.8979	1.0336
	10.652	1.0347
	17.393	1.0362

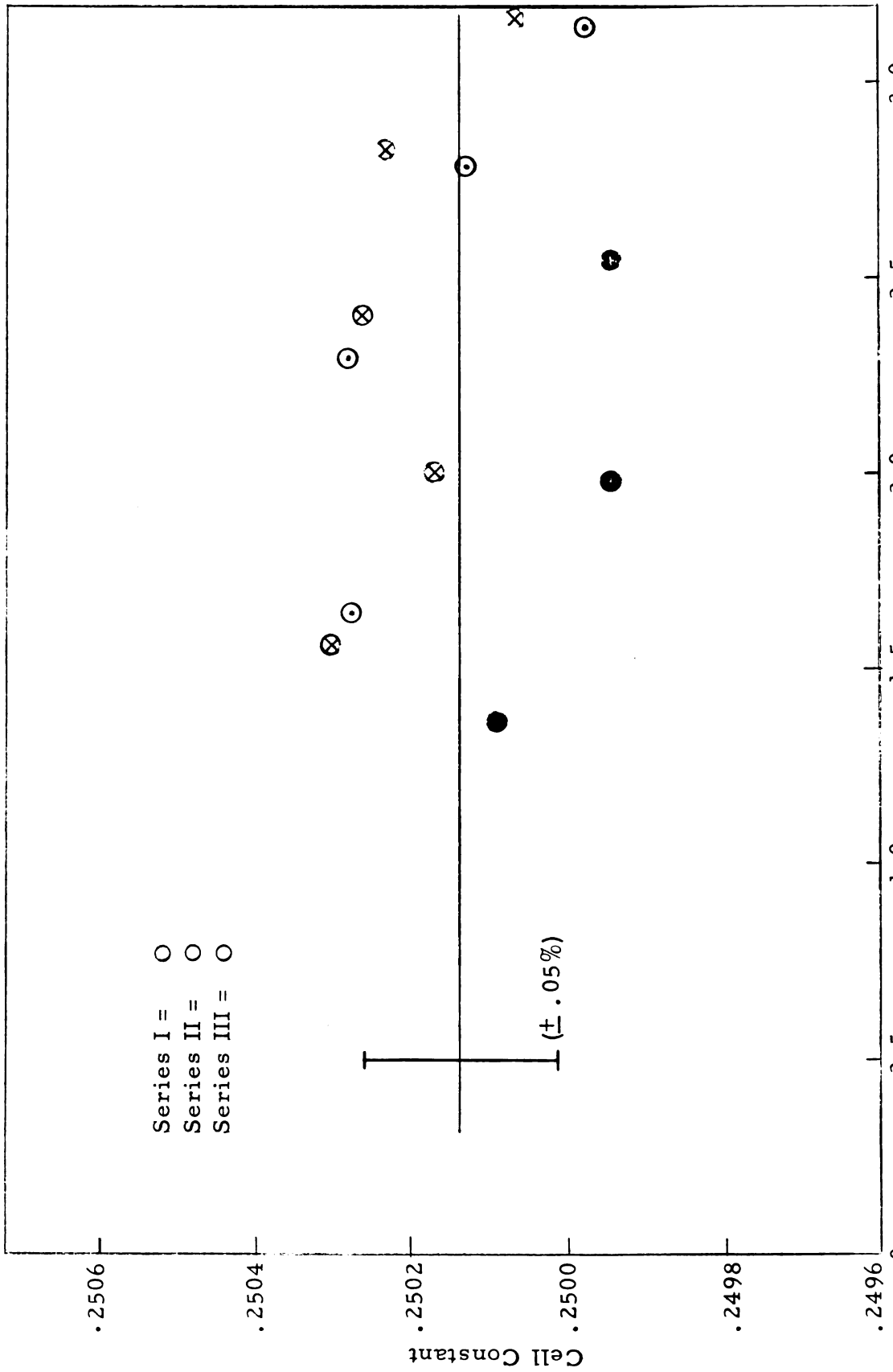


Figure 8. Cell constant determination at varying concentrations of potassium chloride.

Table 3. The Equivalent Conductance of $BaCl_2$.

$\sqrt{c^*}$ x 10^2	Λ Shedlovsky	Λ This Lab.
1.83	136.76	136.44
2.196	136.06	136.06
2.49	135.55	135.57
2.95	134.72	134.63
3.30	134.10	134.06

2. The Equivalent Conductance of Zinc Perchlorate.

The equivalent conductance of zinc perchlorate was determined using the same experimental procedure used to determine the cell constant. Since the cell constant k was known, the specific conductance of water and of each solution could be calculated from the relationship $L = k/R$, where R is the resistance in ohms of the solution. The density of zinc perchlorate was determined using a fifty milliliter pycnometer. This enabled the conversion from molality to normality to be made. The density change with molality can be represented by the equation

$$\rho = 0.99707 + 0.1985\ m \tag{105}$$

Sample calculations

Weight of flask + water	612.92 g.
Weight of flask	291.90 g.
Weight of water	321.02 g. = 321.36 in vacuum

Weight of first addition of stock solution = 0.3818 in vacuum

The molality of the resulting solution can be found from the relationship

$$m = \frac{m_s\ g}{g + w\ \left(\frac{1 + m_s M}{1000}\right)} \tag{106}$$

where m is the molality of the new solution, m_s is the molality of the stock solution, g is the weight of stock solution added, w is the weight of pure water in vacuum and M is the formula weight of zinc perchlorate.

$$m = \frac{0.03798\ (0.3818)}{.3818 + 321.36\ \left(1 + \frac{.03798(264.29)}{1000}\right)} = 4.3575 \times 10^{-5} \text{ moles/1000 grams solvent.}$$

The normality of this solution can then be calculated from the relationship

$$\text{normality} = c^* = \frac{2\rho\ m}{1 + \frac{mM}{1000}} \tag{107}$$

where ρ is the density of the solution

$$c^* = 8.6896 \times 10^{-5} \text{ equivalent/liter.}$$

Now $L_{H_2O} = k/R = \frac{1.0350}{1.420 \times 10^6 \text{ ohm}} = 0.729 \times 10^{-6} \text{ ohm}^{-1}$

and $L_{sol} = k/R_{sol} = \frac{1.0350}{9.234 \times 10^4 \text{ ohm}} = 1.1209 \times 10^{-5} \text{ ohm}^{-1}$

Then $L_{Zn(ClO_4)_2} = (L_{sol}) - (L_{H_2O}) = 1.0480 \times 10^{-5} \text{ ohm}^{-1}$

The specific conductance of the bulk of the water was much lower than that of the water in the stock solution which was in equilibrium with carbon dioxide in the air, and had a specific resistance of 1×10^{-6} ohm^{-1}. For this reason a correction, ΔL, was made on the L of $Zn(ClO_4)_2$ as follows:

$$L_{corrected} = L_{measured} - \Delta L \tag{108}$$

where

$$\Delta L = (L \text{ of water in stock}) - (L \text{ of solution water}) \frac{(\text{weight of stock solution water})}{(\text{total weight of water})} \tag{109}$$

$$\Delta L = (1 - .7)\, 10^{-6} \frac{(.38)}{(321)} = .00008 \times 10^{-5}$$

$$L_{corrected} = (1.0480 - 0.000004) \times 10^{-5} \text{ ohm}^{-1}$$

$$= 1.0480 \times 10^{-5} \text{ ohm}^{-1}$$

This correction is negligible here and only becomes significant at higher concentrations.

$$Zn(ClO_4)_2 = \frac{L_{corrected}\ 1000}{c} = \frac{1.0480 \times 10^{-5} \times 10^3}{8.6896 \times 10^{-5}} =$$

$$120.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalents}^{-1}$$

The extent of hydrolysis of zinc perchlorate was checked in two ways. (1) The pH of the stock solution and several dilutions were determined using a Beckman Model B pH meter. (2) These solutions were acidified to pH of 3 with perchloric acid and were titrated with standard sodium hydroxide. The equivalence pH was determined graphically by plotting Δ pH/Δ ml versus $\overline{\text{pH}}$. The maximum in the curve, where the slope

is equal to zero, is the equivalence pH. This method was used because there was no sharp break apparent in the titration curve of milliliters versus pH. The two methods agreed to within 0.05 pH units, indicating little or no free acid in the zinc perchlorate samples. The average value of the hydrolysis constant corrected for activity coefficients, for the equation, $Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+$, was found to be $0.94 \pm .03 \times 10^{-9}$. This is only approximate because of the irreversibility of the glass electrode and the uncertainty arising because of the chloride-perchlorate junction potential. Kolthoff and Kameda (124) using a hydrogen electrode obtained a value of 2.65×10^{-10} from measurements on zinc sulfate. A hydrolysis correction, $\Delta\Lambda$, was then made on the basis of their hydrolysis constant. The method of this correction is developed below.

Correction of Λ of $Zn(ClO_4)_2$ for Hydrolysis

$$\Lambda_{corrected} = \Lambda - \Delta\Lambda \tag{110}$$

To derive expression for $\Delta\Lambda$:

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+ \tag{111}$$

$$K = K_c K_\gamma = \frac{[ZnOH^+][H^+]}{[Zn^{++}]} = K_\gamma \tag{112}$$

using $K = 2.65 \times 10^{-10}$ from Kolthoff and Kameda (124)

$$K_\gamma = \frac{\gamma_{H^+} \gamma_{ZnOH^+}}{\gamma_{Zn^{++}}} \tag{113}$$

then $\log K_\gamma = \log \gamma_{H^+} + \log \gamma_{ZnOH^+} - \log \gamma_{Zn^{++}}$

but for dilute solutions

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{\Gamma}}{1 + B a_i \sqrt{\Gamma}} \simeq - A z_i^2 \sqrt{\Gamma} \tag{114}$$

therefore we may now express

$$\log K_\gamma = 2 A \sqrt{\Gamma}$$

and

$$\Gamma = \sum_{i=1}^{2} c_i z_i^2$$

$A = 0.509/\sqrt{2}$ (reference 125)

and $C_{Zn^{++}} = C_{salt} = C^*/2$

and $C_{ClO_4^-} = 2C_{salt} = C^*$

Then $\mu = 3/2\ C^*$

and $\log K\gamma = 1.247\sqrt{c^*}$ (115)

For charge balance the total charge before hydrolysis must equal the total charge after hydrolysis.

(1) Before hydrolysis

Species	(conc)(charge)
Zn^{++}	$2C_s$
H^+	$Kw/2$
OH^-	$-Kw/2$

(2) After Hydrolysis

Zn^{++}	$2(C_s - [ZnOH^+])$
$ZnOH^+$	$[ZnOH^+]$
H^+	$[H^+]$
OH^-	$-[OH^-]$

Then

$$2C_s = 2C_s - 2[ZnOH^+] + [ZnOH^+] + [H^+] - [OH^-]$$

$$\therefore [ZnOH^+] = [H^+] - \frac{K_w}{[H^+]} \quad (116)$$

$$[ZnOH^+][H^+] = [H^+] - K_w$$

But from equation (112)

$$[ZnOH^+][H^+] = \frac{K[Zn^{++}]}{K\gamma} \simeq \frac{K C_s}{K\gamma} \quad (117)$$

and therefore

$$[H^+] = \sqrt{\frac{K C_s}{K_\gamma} + K_w} \qquad (118)$$

Now $\Lambda_0 = \lambda^0_{H^+} + \lambda^0_{OH^-} + \lambda^0_{ZnOH^+} + \lambda^0_{Zn^{++}}$

The total conductance per liter is

$$\sum_i \lambda^0_i c_i^* = 1000\, L = c_s^* \Lambda$$

then $c^* \Delta\Lambda = \sum_i \lambda^0_i (c_i^*)_{hydrolyzed} - \sum_i \lambda^0_i (c_i^*)_{unhydrolyzed}$

$$= 2\lambda^0_{Zn^{++}} [Zn^{++}]_{hyd.} + \lambda^0_{H^+} [H^+]_{hyd.} + \lambda^0_{OH^-} [OH^-]_{hyd.}$$

$$+ \lambda^0_{ZnOH^+} [ZnOH^+]_{hyd.} - \lambda^0_{H^+} [H^+]_{unhyd.} - \lambda^0_{OH^-} [OH^-]_{unhyd.}$$

$$- 2\lambda^0_{Zn^{++}} [Zn^{++}]_{unhyd.}$$

However,

$$[Zn^{++}]_{hyd.} - [Zn^{++}]_{unhyd.} = - [ZnOH^+]_{hyd.}$$

$$[H^+]_{unhyd.} = [OH^-]_{unhyd.} = 10^{-7} \text{ at } 25^\circ C.$$

Then

$$C^* \Delta\Lambda = \lambda^0_{H^+} [H^+]_{hyd.} + \lambda^0_{OH} [OH^-]_{hyd.} + (\lambda^0_{ZnOH^+} - 2\lambda^0_{Zn^{++}})$$

$$[ZnOH^+] - (\lambda^0_{H^+} + \lambda^0_{OH^-})\, 10^{-7} \qquad (119)$$

We know that

$\lambda^0_{H^+} = 350$ (reference 23)

$\lambda^0_{OH^-} = 200$ (reference 24)

$\lambda^0_{Zn^{++}} = 53$ (reference 14)

$\lambda^0_{ZnOH^+} = 32$ (reference 14)

Therefore

$$c^{*}\,\Delta\Lambda = 350\,[H^{+}] + 200\,[OH^{-}] - 74\,[ZnOH^{+}] - 550 \times 10^{-7} \quad (120)$$

and

$$\Delta\Lambda = \frac{10^{2}}{c^{*}}\,[3.50\,[H^{+}] + 2.0\,[OH^{-}] - 0.74\,[ZnOH^{+}] - 5.50 \times 10^{-7}] \quad (121)$$

Since $[OH^{-}] = K_{w}/[H^{+}]$ and using equation (116)

$$\Delta\Lambda = \frac{10^{2}}{c^{*}}\,[2.76\,[H^{+}] + 2.74\,\frac{K}{[H^{+}]} - 5.50 \times 10^{-7}]$$

Now defining $\overline{[H^{+}]} = \dfrac{[H^{+}]}{\sqrt{K_{w}}}$ (122)

$$K' = \frac{K}{K_{w}} = K \times 10^{14} \quad (123)$$

Combining these expressions and equation (118) we have

$$\overline{[H^{+}]} = \sqrt{\frac{C_{s}K'}{K\gamma} + 1} \quad (124)$$

and finally

$$\Delta\Lambda = \frac{10^{-5}}{c^{*}}\,[2.76\,\overline{[H^{+}]} + \frac{2.74}{\overline{[H^{+}]}} - 5.50] \quad (125)$$

The values of Λ for zinc perchlorate were corrected for hydrolysis using equation (125) above. The equivalent conductance, Λ, the hydrolysis correction, $\Delta\Lambda$, and $\Lambda_{(\text{corrected})}$ as a function of concentration are given in Table 4. The equivalent conductance Λ_{corr}, as a function of concentration, is shown graphically in Figure 9.

Since the conductance measurements were undertaken to determine λ_{0}^{++} for zinc ion, the limiting equivalent conductance Λ_{0}', was calculated from the Onsager equation

$$\Lambda = \Lambda_{0}' - S_{(\lambda)}\sqrt{c} \quad (74)$$

where the calculated Λ_{0}' is distinguished from the usual Λ_{0} obtained by extrapolation to infinite dilution.

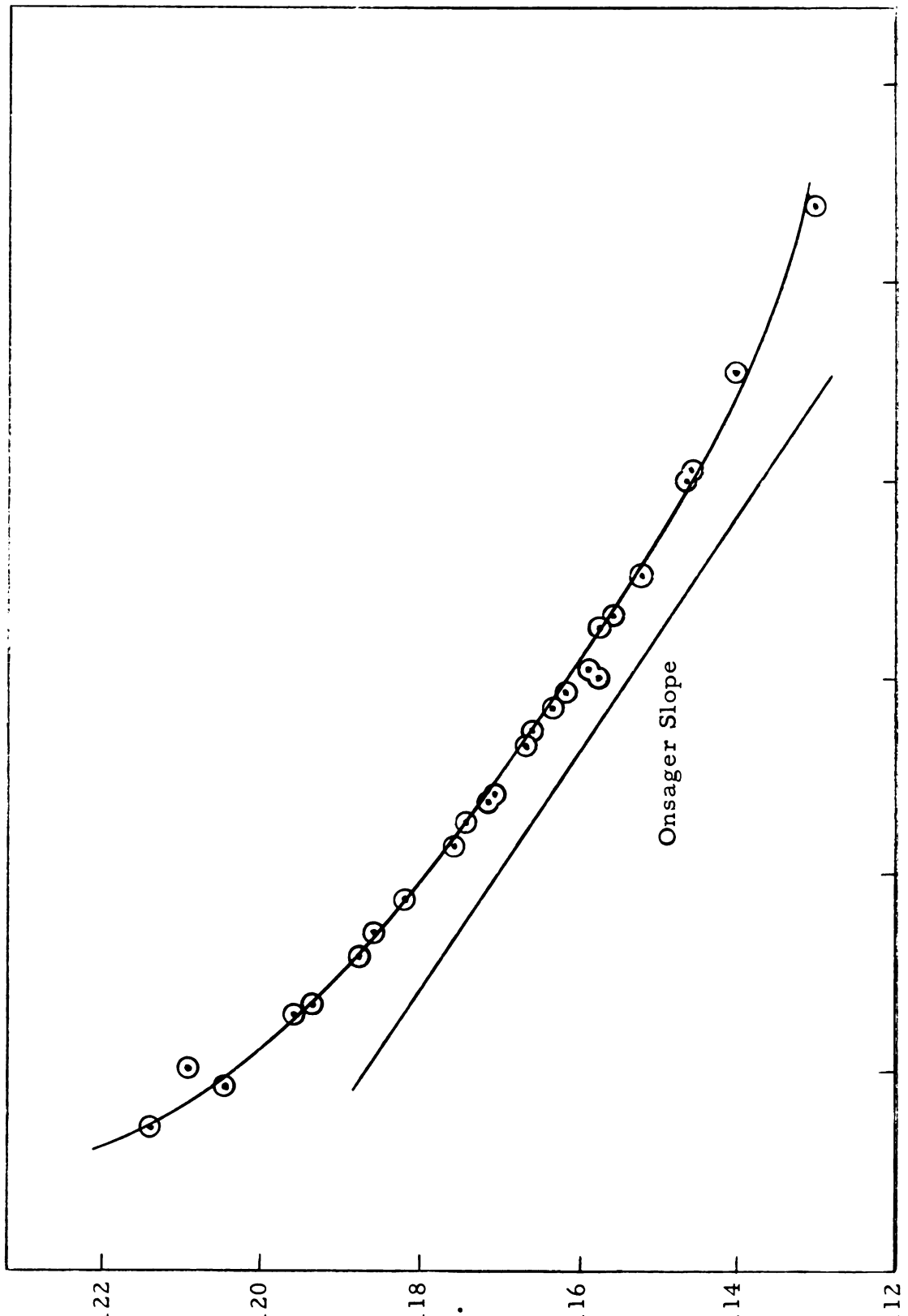


Figure 9. Phoreogram for $Zn(ClO_4)_2$ at 25°C.

$$S_{(\lambda)} = a^* \Lambda_0' + \beta^*$$

where $a^* = 0.2289\ \omega' Q$

$\beta^* = 60.19\ \omega^*$

and $\omega' = z_1 z_2 \left(|z_1 z_2|\ \nu/2 \right)^{\frac{1}{2}} = 3.464$

$$Q = \frac{q^*}{.2929\ (\ 1 + \sqrt{q^*}\ )}$$

and $q^* = \dfrac{|z_1 z_2| \Lambda_0}{(|z_1| + |z_2|)\ (|z_1|\ \lambda_2^0 + |z_2|\ \lambda_1^0)}$

$= 0.42776$ where $\lambda_1^0 = 67.3$

$\lambda_2^0 = 53.2$

$\Lambda_0 = 120.5$

then $Q = 0.8829$ and $a^* = 0.70005$

and $\omega^* = \dfrac{(|z_1| + |z_2|)}{2} \left(\dfrac{\nu (|z_1 z_2|)}{2} \right)^{\frac{1}{2}} = 2.598$

hence $\beta^* = 156.37$

$$\Lambda_0' = \Lambda_{\text{corrected}} + 170.22\ \sqrt{c^*} \qquad (126)$$

Λ_0' as a function of concentration is given in Table 4 and shown graphically in Figure 10.

An estimate of the precision of the experimental data in dilute solution was obtained from examination of the experimental points below 9×10^{-4} normal. The standard deviation of these points from the Onsager equation (77), repeated here for clarity, was determined.

$$\Lambda = \Lambda_0 - S_{(\lambda)} \sqrt{c^*} + A\ c^* \log c^* + B c^* \qquad (77)$$

By rearrangement and substitution this may be expressed as

$$\frac{\Lambda_0' - \Lambda_0}{c^*} = A \log c^* + B \qquad (78)$$

Table 4. Conductance Data for $Zn(ClO_4)_2$.

Run Number	10^4 N	$10^2\sqrt{N}$	Λ	Hydrolysis $\Delta\Lambda$	$\Lambda_{corr.}$	$\Lambda'_{0_{corr}}$
1	20.566	4.535	114.02	0.04	113.98	121.75
L_{H_2O}= 0.530 x 10^{-6}	29.123	5.397	112.97	0.04	112.93	122.18
2	1.0190	1.009	120.97	0.05	120.92	122.65
L_{H_2O}= 0.641 x 10^{-6}	2.5296	1.590	118.88	0.05	118.83	121.56
	5.6920	2.386	117.23	0.06	117.17	121.23
	7.4784	2.735	116.66	0.05	116.60	121.30
	8.9795	2.997	115.82	0.05	115.77	120.91
	15.9383	3.992	114.65	0.05	114.60	121.44
3	0.5556	0.7454	121.44	0.04	121.40	122.68
L_{H_2O} = 0.349 x 10^{-6}	1.6844	1.298	119.65	0.05	119.60	121.82
	3.5303	1.879	118.28	0.06	118.22	121.44
	5.0971	2.258	117.51	0.06	117.45	121.32
	6.9506	2.636	116.75	0.06	116.69	121.21
	8.6128	2.935	116.26	0.05	116.21	121.24
	10.505	3.241	115.83	0.05	115.78	121.34
	12.582	3.547	115.21	0.05	115.16	121.24
	16.309	4.038	114.64	0.05	114.59	121.51
4	.86897	0.9322	120.60	0.05	120.55	122.15
L_{H_2O} = 0.729 x 10^{-6}	1.8144	1.347	119.44	0.06	119.38	121.69
	2.9193	1.709	118.68	0.06	118.62	121.55
	4.6545	2.157	117.67	0.06	117.61	121.31
	5.8167	2.412	117.17	0.06	117.11	121.24
	8.0631	2.840	116.37	0.05	116.32	121.19
	9.3703	3.061	115.97	0.05	115.92	121.17
	10.9866	3.315	115.64	0.05	115.59	121.27

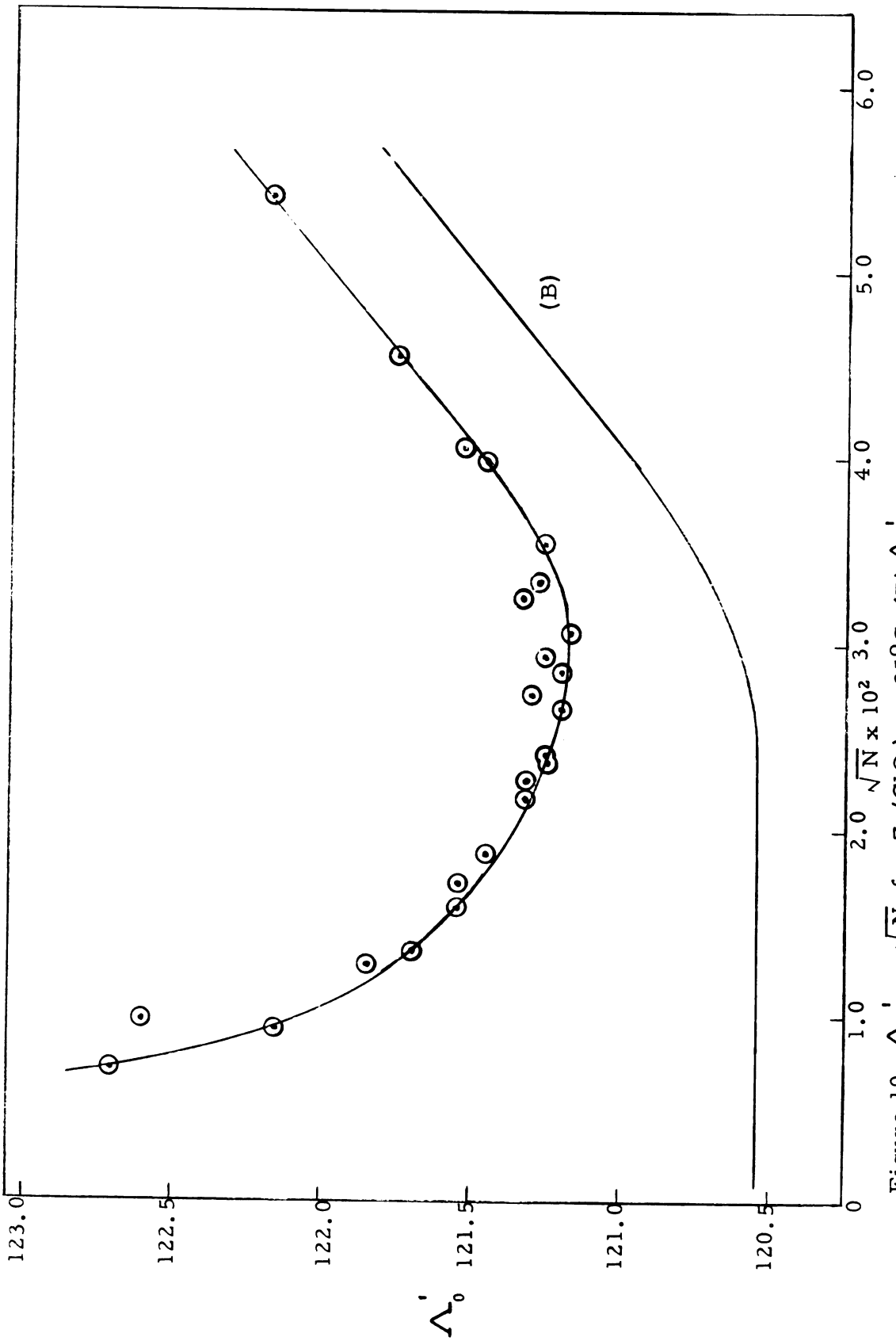


Figure 10. Λ_0' vs $\sqrt{N}$ for $Zn(ClO_4)_2$ at 25°C (B) Λ_0' corrected using a hypothetical hydrolysis constant.

The constants A and B were evaluated from the plot of $\frac{\Lambda_0' - \Lambda_0}{c^*}$ versus $\log c^*$, the slope and intercept of the best line drawn through the experimental points yielding A and B respectively. A preliminary value of Λ_0 and therefore also of α^*, is obtained from the simple extrapolation of Λ versus c^*. This value was used to calculate the first approximation of Λ_0'. The value of Λ_0 was then altered until the resulting computations yielded a straight line. A was thus determined to be 5,130 and B 14,120 for a corresponding $\Lambda_0 = 122.70$ cm^2 ohm^{-1} equiv^{-1}. The standard deviation of fourteen experimental points involving three runs and two different cells is 0.06Λ units. The accuracy is limited by the analysis of the stock solution, four determinations giving a standard deviation from the mean of 0.10%.

3. Transference number of zinc sulfate.

The transference number of zinc ion was measured using tetra-n-butyl ammonium sulfate following solution (abbreviated $[(Bu)_4N]_2SO_4$). In order to obtain a stable boundary Kohlrausch (62) deduced that the condition expressed by the relationship $c^*/c^*_f = T_+/T_{+_f}$ must be met. c^* and c^*_f are the concentrations of the zinc sulfate and $[(Bu)_4N]_2SO_4$ solutions respectively, and T_+ and T_{+_f} are the transference numbers of the zinc and tetra-n-butylammonium ion respectively. In order to determine the desirable concentration, the cation transference numbers of both leading and following ion were estimated from the limiting ionic conductances where

$\frac{1}{2}\lambda_+$ of $Zn^{++} \simeq 53$ (reference 14)

$\frac{1}{2}\lambda_-$ of $SO_4^{=} \simeq 80$ (reference 126)

λ_+ of $(Bu)_4N^+ \simeq 19.5$ (reference 13)

then T_+ for $Zn^{++} \simeq 53/133 \simeq 0.397$

T_+ for $(Bu)_4N^+ \simeq 19.5/99.5 \simeq .197$

This enables one to calculate the ratio of various concentrations of leading to following solution.

The moving boundary method, which measures the motion of the solution relative to a fixed mark on a tube, must have a correction made for any change in volume caused by electrode reaction since the bulk of the solution would move to accommodate any volume change. The computation in this case was simplified since one side of the cell was left open to the atmosphere and the other side closed. Only the volume changes which occur between the closed side and the boundary need then to be considered.

We employed a falling boundary between zinc sulfate and $[(Bu)_4N]_2SO_4$. The cathode, with the silver-silver chloride electrode, was open to the atmosphere. The volume changes which take place between the boundary and the closed anode with the cadmium electrode during the passage of one faraday of electricity are:

(1) $\frac{1}{2}$ mole of Cd^o is lost $\quad \Delta V_1 = - V_{Cd}/2$

(2) $\frac{1}{2}$ mole of $CdSO_4$ is formed $\quad \Delta V_2 = \frac{1}{2} \bar{V}_{CdSO_4}$

(3) $\frac{1}{2} T_+$ moles of $ZnSO_4$ are lost $\quad \Delta V_3 = - \frac{1}{2} T_+ \bar{V}_{ZnSO_4}$

$\bar{V}_{CdSO_4}$ and $\bar{V}_{ZnSO_4}$ are the partial molar volumes of cadmium and zinc sulfate respectively. This thermodynamic property may be defined in general by the expression

$$\bar{V}_j - \left(\frac{\partial V}{\partial n_j}\right)_{P, T, n_1, n_2, \ldots,}$$

Summing the volume changes (1) through (3) above, the total volume change between the closed side and the boundary is

$$\Delta V = \frac{1}{2} [\bar{V}_{CdSO_4} - T_+ \bar{V}_{ZnSO_4} - V_{Cd}] \qquad (127)$$

The volume change ΔV means that the boundary has swept out a volume $V' + \Delta V$, such that

$$V_{obs} = V' + \Delta V \tag{128}$$

where V_{obs} is the measured volume in milliliters, and V' the volume swept out by the boundary, corrected for any change due to the electrode reaction. To compute ΔV we used the value $V_{Cd} = 13.0$ ml. (reference 78). The partial molar volumes of $CdSO_4$ and $ZnSO_4$ were calculated from the equation derived below. The density, ρ, of the solution is given by

$$\rho = \frac{n_1 M_1 + n_2 M_2}{1000\ V} \tag{129}$$

where n_1 is the number of grams of solvent, n_2 the grams of solute, M_1 and M_2 are the molecular weights of solvent and solute respectively and V is the volume in liters. Rearranging and then differentiating at constant temperature and pressure

$$\frac{dV}{dn_2} = \frac{M_2/1000 - V\, d\rho / dn_2}{\rho} \tag{130}$$

Since n_1 is equal to 1000 grams than n_2 is equal to the molality m. The volume V may be expressed in cubic centimeters v, where $v = \frac{1000 + m_2 M_2}{\rho}$. The partial molar volume in cubic centimeters per mole is then

$$\bar{V} = \frac{M_2\, \rho - (1000 + m_2 M_2)\, d\rho / dm}{\rho^2} \tag{131}$$

The partial molar volume $\bar{V}$, of zinc sulfate was then determined using equation (131) and equation (96) for the relationship between density and molality.

$$\bar{V}_{ZnSO_4} = \frac{(161.39)(1.0057) - (1000 + 161.39\ (0.05015)\ (0.1607))}{(1.0057)^2}$$

$$= 0.3\ cm^3 mole^{-1}$$

The density of cadmium sulfate as a function of concentration was taken from the International Critical Tables (127). The concentrations were

converted from percentage to molality and can be expressed by the equation

$$\rho = .99862 + 0.2037\ m \qquad (132)$$

Then $\bar{V}_{CdSO_4} = \dfrac{(208.48)\,(1.00454) - (1000 + 0.02895\,(208.48)\,(.2037))}{(1.00454)^2}$

$= 4.5\ cm^3 mole^{-1}$

From equation (127) then,

$$\Delta V = \tfrac{1}{2}\ [4.5 - 13.0 - 0.4(0.3)] = -4.6\ cm^3 mole^{-1}$$

In addition to the volume correction it is necessary to make the solvent correction proposed by Longsworth (78). It may be recalled that, since impurities in the solvent carry some small fraction of the total current,

$$\Delta T_+ = T_+ (L_{solvent}/L_{solution}) \qquad (12)$$

The average value of the specific conductance of the solvent was 2×10^{-6} ohm^{-1}. The specific conductance of zinc sulfate was obtained from the work of Owen and Gurry (14).

Sample calculation for the transference number of zinc sulfate.

For each experimental determination of the transference number, the time that the boundary took to pass each volume mark was recorded. The entire run was done at constant current, the value recorded in milliamperes. The volume between each mark had previously been determined. These were grouped together in larger volume increments of 0-8, 1-9 ... 9-17. For each of these sub totals the corresponding total time was determined. A $\underline{T}_+$ value was then calculated from

$$T_+ = \frac{F\ c^*\ V}{1000\ it} = \frac{96,500\ (.009692)\ (0.8552)}{1000\ (1.10)\ (1899.8)} = 0.3827$$

This calculation was repeated for each volume increment. The value of T_+ for the run was taken as the average value from the results thus

obtained, which, for this example, was equal to 0.3825.

The volume correction was then made to this average transference number from the evaluation

$\frac{c^*\Delta V}{1000} = \frac{0.009692\ (-\ 4.6)}{1000} = 0.000044$, which is negligible at this particular concentration, and, therefore, for this example no correction was necessary. The value of the solvent correction at the same concentration is found from

$$T_+\ (L_{solvent}) / (L_{solution}) = 0.38\ \frac{(2 \times 10^{-6})}{(0.78 \times 10^{-3})}$$

$$= 0.97 \times 10^{-3} \simeq 0.0010$$

Therefore the corrected transference number is

$$T_+ = 0.3825 + 0.0010 = 0.3835$$

The transference number of zinc sulfate as a function of concentration, with the solvent and volume corrections, is given in Table 5. The transference number versus concentration is shown graphically in Figure 11. It proved to be a linear function of the square root of the normality. The least squares equation was determined to be,

$$T_+ = 0.3900 - 0.0628\ (N)^{\frac{1}{2}} \qquad (133)$$

with a standard deviation of 0.07% for ten determinations. For those concentrations in Table 5 involving duplicate runs, the current and/or indicator concentration differ by 10 to 20 percent. The results of Purser and Stokes (17) based upon the E.M.F. method are also given in Figure 11 for comparison.

Table 5. Transference Number of $ZnSO_4$ as a Function of Concentration.

Norm.	$(N)^{\frac{1}{2}}$	$T_{+(obs)}$	Vol. Correction	Solvent Correction	T_+ Corrected	T_+ Calculated	ΔT_+
0.009692	0.09845	0.3825	+.0000	+.0010	0.3835	0.3838	+3
0.009692	0.09845	0.3829	+.0000	+.0010	0.3839	0.3838	-1
0.02270	0.1507	0.3800	+.0001	+.0005	0.3806	0.3805	-1
0.03549	0.1884	0.3774	+.0002	+.0003	0.3779	0.3782	+3
0.03549	0.1884	0.3781	+.0002	+.0003	0.3786	0.3782	-4
0.05095	0.2257	0.3750	+.0002	+.0002	0.3754	0.3758	+4
0.07510	0.2740	0.3723	+.0003	+.0002	0.3728	0.3728	0
0.07510	0.2740	0.3724	+.0003	+.0002	0.3729	0.3728	-1
0.09027	0.3004	0.3703	+.0004	+.0002	0.3709	0.3711	+2
0.07510	0.2740	0.3725	+.0003	+.0002	0.3730	0.3728	-2

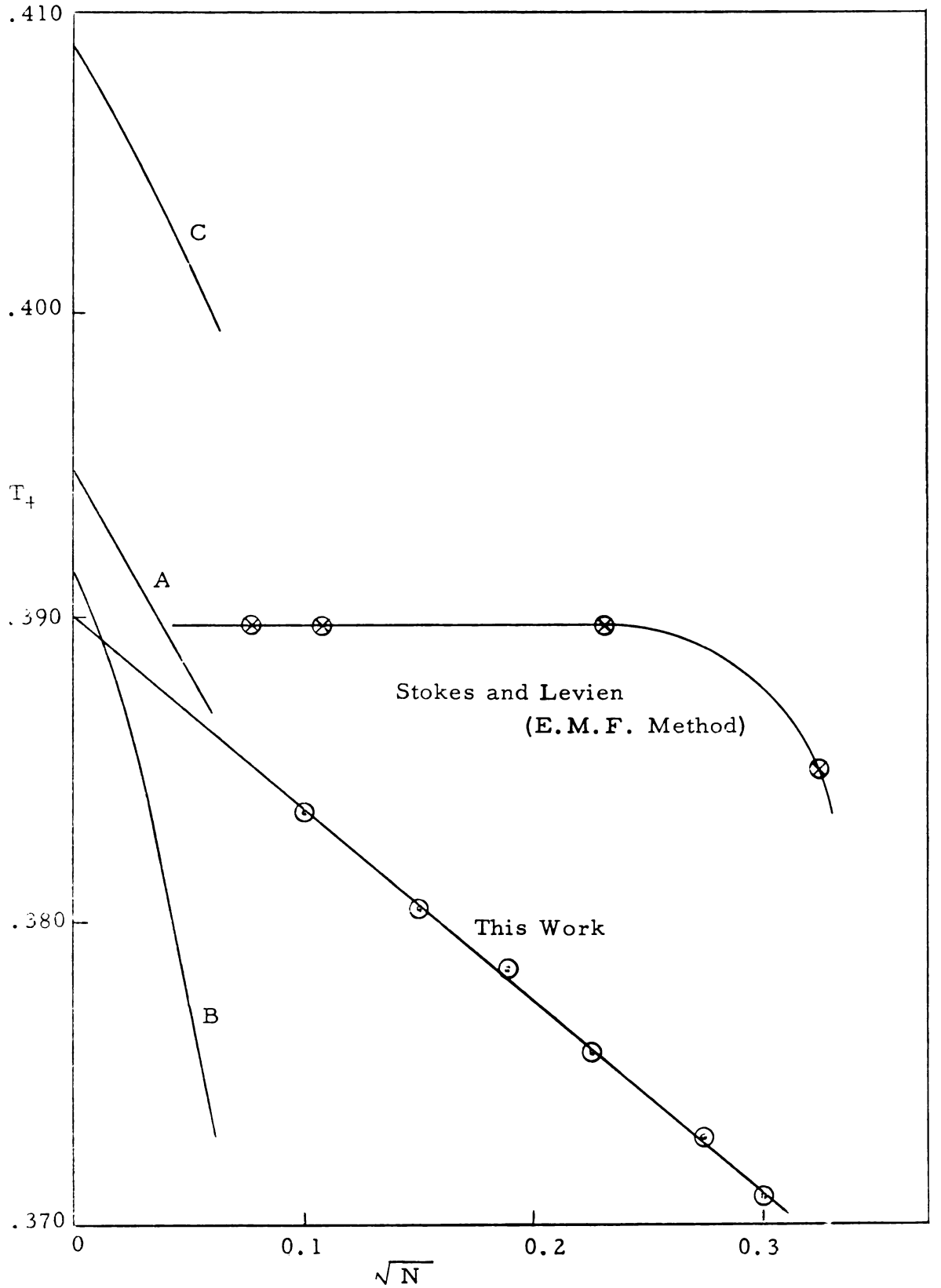


Figure 11. Transference Number of Zinc Sulfate versus $\sqrt{N}$ compared with Various Theoretical Curves.

4. Equivalent Conductance of Potassium Octacyanomolybdate (IV).

The conductance of $K_4Mo(CN)_8$ was determined using the same experimental procedure as that described for zinc perchlorate.

The densities of the $K_4Mo(CN)_8$ solutions were determined using a fifty milliliter pycnometer. The relationship between density and concentration at 25°C may be expressed by the linear equation,

$$\rho = 0.99707 + 0.2505 \ m \qquad (134)$$

Using this equation, the normalities of the solutions were calculated. The specific conductance of water was determined with each run and used to correct for the specific conductance of the salt. A correction was also made for the added contribution to the conductance by the water which was added with solute. This water was at equilibrium with the carbon dioxide of the air and the correction is analogous to that made for zinc perchlorate.

The equivalent conductance, Λ, as a function of concentration is given for three separate runs in Table 6 and shown graphically in Figure 12. Extrapolation to infinite dilution gives a value of 188.5 cm^2 ohm^{-1} $equivalent^{-1}$ for Λ_0. If the Onsager equation is obeyed, it is possible to express the equivalent conductance by the equation

$$\Lambda = \Lambda_0 - \tfrac{1}{2} (\alpha^* \Lambda_0 + \beta^*) \sqrt{c^*} \qquad (75)$$

Rearranging this equation, following the method of Shedlovsky (105) and using experimental values of Λ from equation (75), it is possible to calculate values of Λ_0 which we designate Λ_0' to distinguish them from the limiting conductances obtained by extrapolation to infinite dilution. Equation (75) then becomes,

$$\Lambda_0' = \Lambda + \tfrac{1}{2} (\alpha^* \Lambda_0 + \beta^*) \sqrt{c^*} \qquad (135)$$

Table 6. Equivalent Conductance and Λ_0' for $K_4Mo(CN)_8$ as a Function of Concentration.

$N \times 10^4$	$\sqrt{N} \times 10^2$	$\times 10^4$ $L_{corrected}$	Λ	Λ_0'
0.45219	0.67245	0.083467	184.58	187.62
1.7798	1.3341	0.32189	180.86	186.89
4.0222	2.0055	0.71090	176.74	185.80
5.3133	2.3051	0.92967	174.97	185.38
6.7887	2.6055	1.1754	173.14	184.91
8.0381	2.8352	1.3811	171.82	184.63
10.020	3.1654	1.7018	169.84	184.14
8.8095	2.9681	1.5081	171.19	184.60
13.195	3.6325	2.2087	167.39	183.80
17.293	4.1585	2.8446	164.49	183.27
20.982	4.5806	3.4041	162.24	182.93
23.967	4.8956	3.8526	160.75	182.86
27.035	5.1995	4.3035	159.18	182.67
32.422	5.6940	5.0822	156.75	182.47
39.239	6.2641	6.0451	154.06	182.35
50.972	7.1395	7.6574	150.23	182.48
7.5185	2.7420	1.2964	172.43	184.82
10.3603	3.2187	1.7567	169.56	184.10
16.5437	4.0674	2.7251	164.72	183.09
22.2890	4.7211	3.5915	161.13	182.45

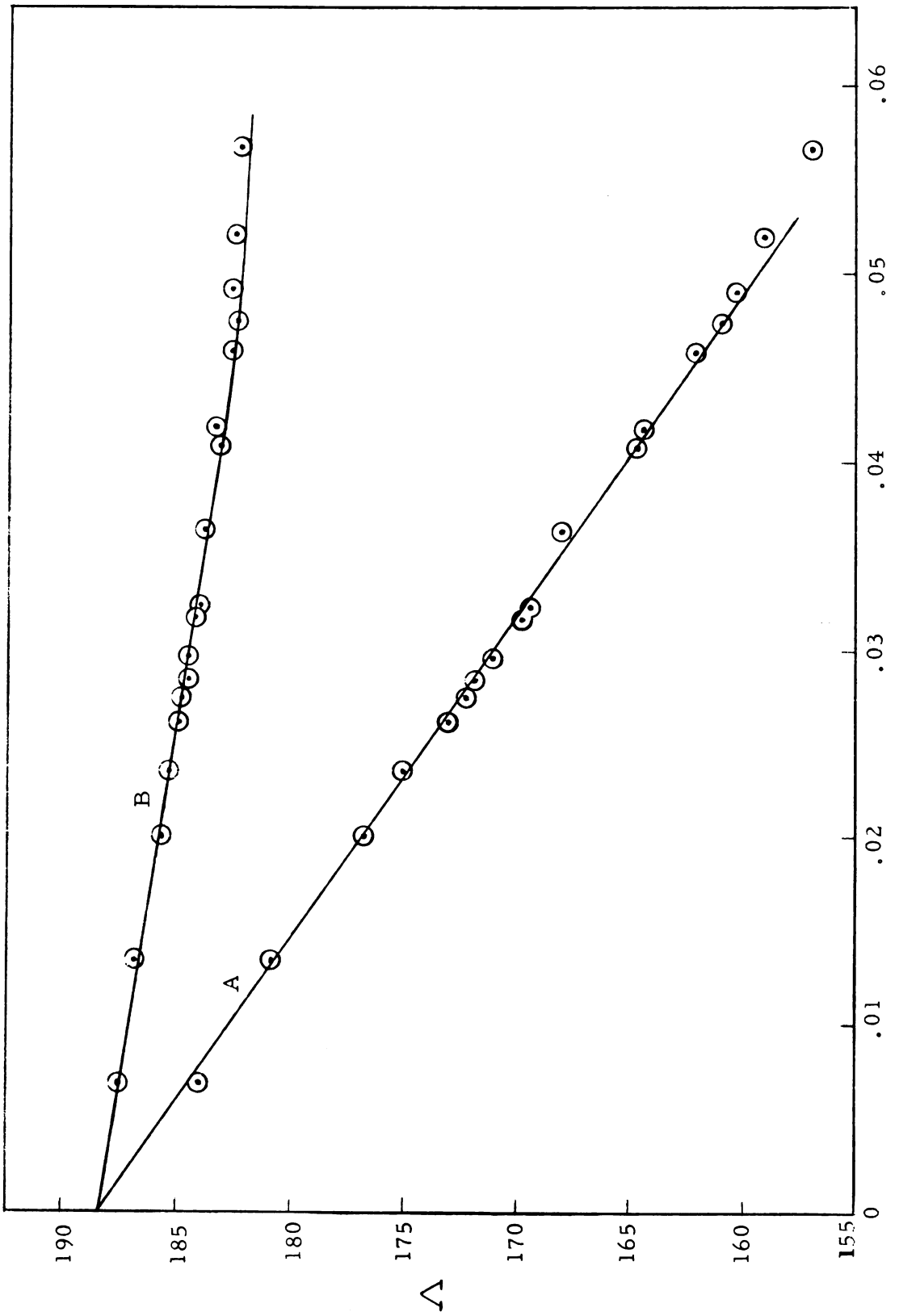


Figure 12. (A) Phoreogram for $K_4Mo(CN)_8$ at 25°C. (B) Λ_0' vs. $\sqrt{N}$ for $K_4Mo(CN)_8$ at 25°C.

where Λ_0 = 188.5 which was the value obtained from the simple extrapolation of Λ versus c^*

λ_0^+ = 73.4 (reference 128)

λ_0^- = 115

α^* = .2289 w'Q and β^* = 60.19 w^* (reference 122)

where w', Q and w^* have previously been defined.

For potassium octacyanomolybdate (IV), the value of α^* is 2.2680 and β^* is 475.86. The resulting equation then becomes,

$$\Lambda_0' = \Lambda + 451.69 \sqrt{c^*} \qquad (136)$$

The values of Λ_0' thus obtained from equation (136) as a function of concentration are given in Table 6 for three different runs. These extrapolate at infinite dilution to the same value of Λ_0 (188.5 cm^2 ohm^{-1} $equivalent^{-1}$) with a somewhat less steep curve, as shown in Figure 11.

It is also possible to try the Onsager function (3) to determine the limiting value of the equivalent conductance of $K_4Mo(CN)_8$. This equation has the form as shown before

$$\Lambda = \Lambda^0 - \tfrac{1}{2} S \sqrt{c^*} + A\, c^* \log c^* + Bc^* \qquad (77)$$

which can be rearranged as shown previously in equation (78) to permit evaluation of the constants A and B. These are obtained by plotting $\Lambda_0' - \Lambda_0/c^*$ versus $\sqrt{c^*}$, finally yielding a straight line whose slope is A and intercept B. The value of Λ_0 first tried was 188.5. A preliminary value of α^* was then calculated. The value of Λ_0 was then altered until a straight line was obtained. The best line was for Λ_0 equal to 188.0 cm^2 ohm^{-1} $equivalent^{-1}$. This results in a value of A equal to 4217 and B equal to 8811. This is shown in Figure 13.

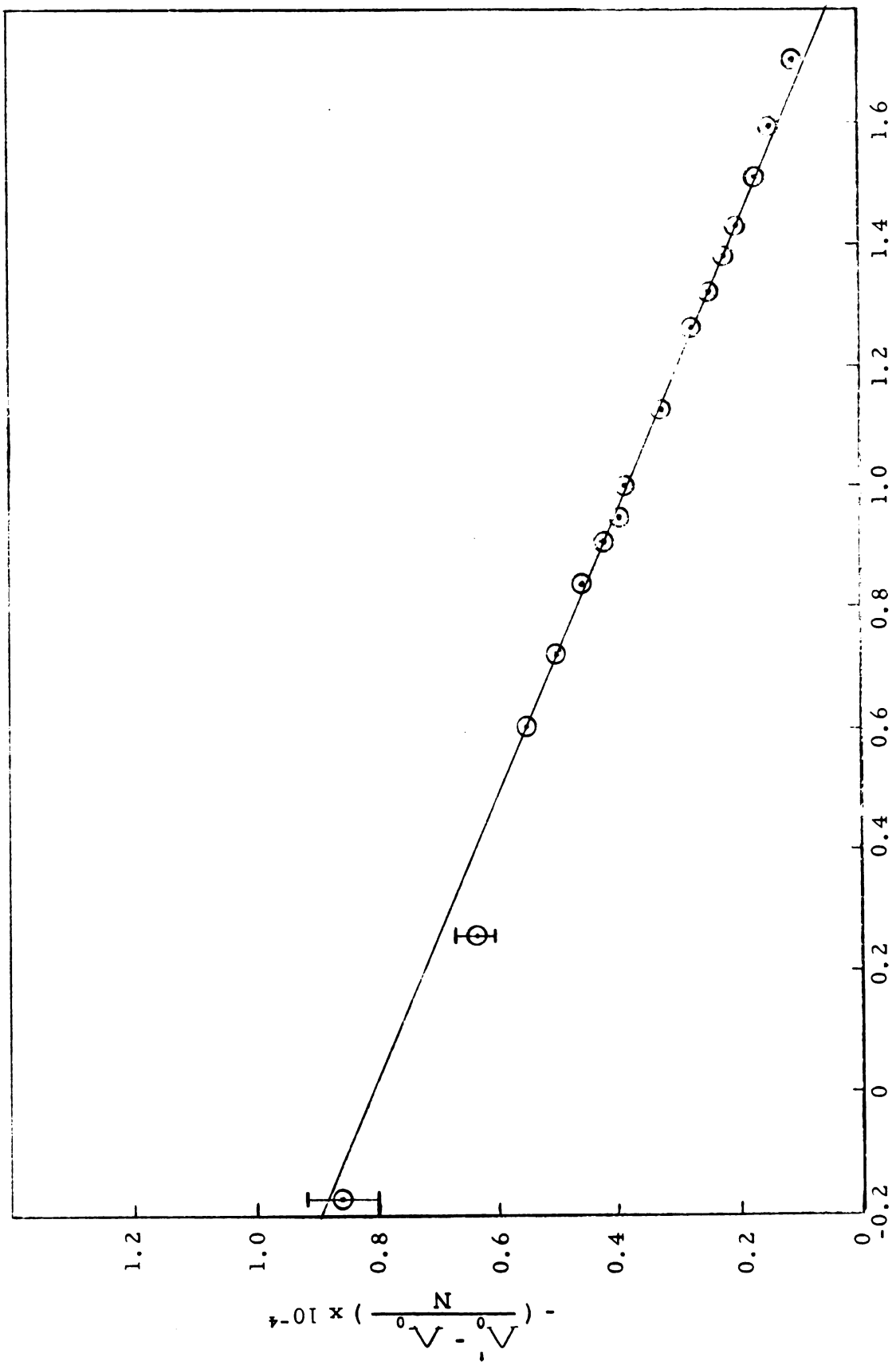


Figure 13. Determination of the Constants A and B in the Owen Function for $K_4Mo(CN)_8$ at 25°C.

DISCUSSION OF RESULTS

A. Zinc perchlorate.

It may be recalled that the conductance measurements on the zinc perchlorate system were undertaken to determine the limiting ionic conductance, λ_0^{++}, for zinc ion, so that this parameter could be used to calculate the theoretical conductance curve for zinc sulfate.

As shown in Figure 10, the minimum in the curve shows the very marked deviation from the Onsager equation. If the system obeyed the Onsager limiting law Λ_0' would be constant. While such deviations occur for many higher charge type electrolytes such as $K_4Fe(CN)_6$ and $Co(en)_3Cl_3$ (129) they had not been found previously for 2-1 electrolytes. A slight effect of this type was observed by Jenkins and Monk (15) with sodium and potassium sulfate. They attributed this behavior to ion-pair formation. A pronounced deviation of this type has been found for $K_2Pt(CN)_4$ (130). It appears then, that this effect is not unique to the zinc perchlorate system.

The most obvious choice of explanation for this behavior involves the assumption of ion-pair formation of the type $ZnClO_4^+$. There are, however, several difficulties involved in making this calculation for this salt which are not present in calculations for simple symmetrical electrolytes. The first of these is the lack of knowledge of the behavior to be expected of a completely dissociated 2-1 electrolyte. One method is to arbitrarily select some conductance curve to represent the completely dissociated electrolyte. All deviations of the electrolyte from the hypothetical salt are then considered as resulting from incomplete dissociation. Some knowledge of the activity coefficient of the electrolyte as a function of concentration is also required. While $\gamma_\pm$ would

be known for the salt under investigation the value for the ion-pair would have to be estimated. The other difficulty is that the ion-pair carries a charge and therefore contributes to the total conductance of the solution. The selection of a mobility for the ion-pair involves assumptions of uncertain validity as to size and shape of the ion and the amount of solvation. In spite of these difficulties, by following the method of Davies (131), it should be possible to obtain a reasonable value for K, the association constant.

Inspection of the Λ_0' curve of Figure 10 shows that a value of no less than 123 conductance units is required for $Zn(ClO_4)_2$, which gives a value of 56 or greater for λ_0^{++} of zinc ion. Using three points from the conductance curve at concentrations lower than that giving a minimum in the Λ_0' curve, trial values of 56 and 59 conductance units for λ_0^{++} of zinc ion, with λ_0^{+} for $Zn(ClO_4)^+$ arbitrarily set at 30 conductance units, values of K were determined as described below.

Consider the equilibrium

$$Zn^{++} + ClO_4^- \rightleftharpoons ZnClO_4^+ \qquad (139)$$

The association constant K for this system is

$$K = \frac{a_{+_1}}{a_{+_2}\ a_{-_1}} = \frac{c_{+_1}}{c_{+_2}\ c_{-_1}} \cdot K\gamma \qquad (140)$$

where the subscrips denote the species of corresponding charge, a their activities and c their molar concentrations. $K\gamma$ denotes the activity coefficient ratio

$$K\gamma = \frac{\gamma_{+_1}}{\gamma_{+_2}\ \gamma_{-_1}} = \frac{(\gamma_\pm)_{1-1}^2}{(\gamma_\pm)_{2-1}^3} \qquad (141)$$

where $(\gamma_\pm)_{ij}$ is the mean ionic activity coefficient of a salt of charge-type i-j calculated by the Debye-Hückel theory. The Debye-Hückel limiting law for activity coefficients in its most general form is

$$\log \gamma_\pm = - \frac{S_{(\gamma)}\sqrt{\Gamma}}{1 + aA\sqrt{\Gamma}} \qquad (142)$$

where $S_{(\gamma)}$ has been shown to be (132)

$$S_{(\gamma)} = \frac{1}{\nu} \sum_{j=i}^{\rho} \nu_j Z_j^2 \quad \frac{1.283 \times 10^6}{(DT)^{\frac{3}{2}}} \qquad (143)$$

This reduces to 0.3582 for a 1-1 electrolyte and is equal to 2(0.3582) for a 2-1 electrolyte at 25°C. The quantity $\underline{A}$ is expressed as

$$A = \frac{35.57}{(DT)^{\frac{1}{2}}} = 0.2325 \text{ at } 25^\circ C \qquad \text{(reference 132)}$$

The ional strength, Γ, of the solution is defined by

$$\Gamma = \sum_i c_i Z_i^2 \qquad (144)$$

The distance of closest approach $\underline{a}$ for the salt and the ion-pair were considered to be equal, and a value of 4.5 Angstrom units was chosen. The quantity $\underline{K}_{(\gamma)}$ may then be obtained from

$$\log K_\gamma = \frac{4(0.3582)\sqrt{\Gamma}}{1 + 4.5(.2325)\sqrt{\Gamma}} \qquad (145)$$

The values of $\underline{K}_\gamma$ are given in Table 7 with the values of $\Gamma^{\frac{1}{2}}$ and the three corresponding concentration points which had been chosen.
If $\underline{c}$ is the stoichiometric molarity, then the concentrations of the various species may be expressed as

$$\begin{aligned} [ZnClO_4^+] &= c_2 \\ [Zn^{++}] &= c - c_2 \\ [ClO_4^-] &= 2c - c_2 \end{aligned} \qquad (146)$$

and then the association constant $\underline{K}$ is given by

$$K = \frac{c_2}{(c - c_2)(2c - c_2)} \cdot K_\gamma \qquad (147)$$

The concentration $\underline{c_2}$ may be found from a consideration of the conductance data. The total specific conductance may be expressed as

$$L_T = l_{Zn^{++}} + l_{ClO_4^-} + l_{ZnClO_4^+} \qquad (148)$$

Table 7. Data Used in the Calculation of the Association Constant for Zinc Perchlorate,

$N^{\frac{1}{2}} \times 10^2$	$\Gamma^{\frac{1}{2}} \times 10^2$	$K\gamma$	Λ_{corr}	Λ_0'	Species	λ_0	λ_j
2.840	4.9183	1.1660	116.32	121.19	Zn^{++}	56	53.13
					Zn^{++}	59	56.09
					ClO_4^-	67.36	65.79
					$ZnClO_4^+$	30	28.77
1.590	2.7548	1.0724	118.83	121.56	Zn^{++}	56	54.39
					Zn^{++}	59	57.37
					ClO_4^-	67.36	66.48
					$ZnClO_4^+$	30	29.31
0.7454	1.2910	1.0429	121.40	122.68	Zn^{++}	56	55.25
					Zn^{++}	59	58.24
					ClO_4^-	67.36	66.95
					$ZnClO_4^+$	30	29.68

since $\Lambda = 1000\ L_T/c^*$ it follows that

$$L_T = \frac{2(c - c_2)\,\lambda_{++}}{1000} + \frac{(2c - c_2)\,\lambda_-}{1000} + \frac{c_2\lambda_+}{1000}$$

$$L_T = \frac{c_2(\lambda_+ - \lambda_- - 2\lambda_{++}) + 2c(\lambda_{++} + \lambda_-)}{1000} \qquad (149)$$

The ionic conductances at various concentrations can be calculated with a knowledge of the limiting ionic conductances from the equation

$$\lambda_j = \lambda^0 - S_{(\lambda)} \Gamma^{\frac{1}{2}} \qquad \text{(reference 133)} \qquad (150)$$

where

$$S_{(\lambda)} = \frac{1.970 \times 10^6}{(DT)^{\frac{3}{2}}} \left(\frac{q^*}{1 + \sqrt{q^*}} \right) |Z_1 Z_2|\, \lambda_j^0 + \frac{28.98\,|Z_j|}{\eta\,(DT)^{\frac{1}{2}}}$$

where $T = 298.16^oC$

$D = 78.54$

$\eta = .008949$ poises

$$q^* = \frac{|Z_1 Z_2|}{(|Z_1| + |Z_2|)} \cdot \frac{(\lambda_1^0 + \lambda_2^0)}{(|Z_2|\lambda_1^0 + |Z_1|\lambda_2^0)}$$

A value of 30 was assumed for λ^0 of $ZnClO_4^+$ and both 56 and 59 for Zn^{++}. The value 67.36 was used for λ^0 of ClO_4^- (16)

For ClO_4^- and $ZnClO_4^+$ ions then

$$S_{(\lambda)} = 0.16102\,\lambda_j^0 + 21.161$$

and for Zn^{++} where $\lambda^0 = 56$ then $S_{(\lambda)} = 58.348$

where $\lambda^0 = 59$ then $S_{(\lambda)} = 59.207$

The value for λ_j for each of the ionic species was then calculated at each concentration from equation (150) and the resulting values are shown in Table 7. Also shown in the same table for convenience are the values of Λ_{corr} and Λ'_0 from Table 4 for the same concentration points.

Solving equation (149) for c_2 and making the substitution $2c\Lambda = 1000\ L_T$ we obtain the expression

$$c_2 = \frac{2c\Lambda - 2c\ (\lambda_{++} + \lambda_-)}{\lambda_+ - \lambda_- - 2\lambda_{++}} \qquad (151)$$

Calculated values of c_2 at the three concentrations are tabulated in Table 8.

Table 8. Concentration of $ZnClO_4^+$ With Varying Concentrations of Zinc Perchlorate.

$c \times 10^4$	c_2	
	$\lambda_{Zn} = 56$	$\lambda_{Zn} = 59$
4.0316	1.4608×10^{-5}	3.0055×10^{-5}
1.2648	3.5357×10^{-6}	8.3595×10^{-6}
0.2778	3.0079×10^{-7}	1.3700×10^{-6}

Subsequent substitution into equation (147) for the values of $\underline{c}$, $\underline{c}_2$ and $\underline{K}\gamma$ yield the values of $\underline{K}$ tabulated in Table 9.

Table 9. Association Constants for Zinc Perchlorate as a Function of Concentration.

$c^* \times 10^4$	$\underline{K}$	
	$\lambda_{Zn} = 56$	$\lambda_{Zn} = 59$
8.0631	55.4	121
2.5296	120	300
0.5556	206	998

This four-fold variation of $\underline{K}$ over a narrow range of concentration shows that simple ion-pair formation is not entirely responsible for the deviation observed. Although $\underline{K}$ is rather large for ion association it must be borne in mind that a value of $\underline{K}$ of about 100 corresponds to having 3% of the ions associated when the concentration is about 1.2×10^{-4} molar.

The type of behavior observed here could be expected of system undergoing extensive hydrolysis according to

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^{+} + H^{+} \qquad (152)$$

However, all data already had been corrected for hydrolysis (see experimental section). It is possible to calculate an "hydrolysis constant" which would bring the conductance data in accord with the Onsager equation at low concentrations. Using trial values of $\underline{K}$ in equation (125) a value of $\Delta\Lambda$ is obtained for various concentrations. Λ_0 minus this new $\Delta\Lambda$ is shown in Figure 9 as the lower curve. This is unsatisfactory since the hydrolysis constant required to give this curve has a value of $1.1 \pm .1 \times 10^{-8}$ while that obtained by pH measurements averaged 0.094×10^{-8} and the value obtained by Kolthoff and Kameda was 0.0265×10^{-8}. This discrepancy in $\underline{K}$ values is very large and essentially eliminates hydrolysis as a cause of the deviations from the Onsager equation. Only if some mechanism were operating which greatly suppressed hydrolysis at higher concentrations could these results be compatible. The value of Λ_0 given by this "hydrolysis constant" is 120.55 which gives a value of 53.19 for λ^0_{++} for zinc ion.

Another possible explanation for these deviations from the theory is the inadequacy of this theory to deal with unsymmetrical electrolytes. The neglect of pair-wise interaction implied by the linear distribution function is partially compensated for by the introduction of Bjerrum's ion-pair concept. Karl (13) has shown that deviations from the Fuoss-Onsager conductance equations which previously had been attributed to ion-pair formation, may possibly depend upon higher order terms of the concentration. The significance of higher order terms of the electrophoretic correction to the conductance has been pointed out by Dye and Spedding (12). As was indicated earlier, it is possible to make use of the Owen function (56) to fit the data below the minimum. This gave a

value of 122.70 cm^2 ohm^{-1} $equivalent^{-1}$ for Λ_0 and 55.34 for λ_0^{++} of zinc ion (see experimental). Owen and Gurry (14) obtained the much lower value of 52.8 for λ_0^{++} of zinc ion using the assumption of ion-pair formation. Alternatively, the assumption of hydrolysis gave us a value of 53.19. It is obvious we do not obtain the unequivocal value of limiting conductance of zinc ion which was sought.

The Fuoss-Onsager extended equation is not applicable to an unsymmetrical electrolyte so that it can not properly be used for an extrapolation function. Direct use of equation (73) as if it were valid for unsymmetrical electrolytes does not eliminate the upswing. Since the correction given by electrostatic theory is very small in dilute solutions, it is doubtful whether this approach would be helpful even if the correct equation were known. The result is that we have no theoretical extrapolation function to use to evaluate Λ_0.

B. Zinc sulfate.

It is possible in several ways to treat theoretically the zinc sulfate transference data using an adjustable Λ_0 and the conductance data of Owen and Gurry (14). The standard Fuoss-Onsager calculation (5, 6, 8, 9, 10) was first made using the conductance equation as given earlier in this paper by

$$\Lambda = (\Lambda_0 - \Delta\Lambda_e)\left(1 + \frac{\Delta X}{X}\right) \qquad (41)$$

This was combined with an ion-pair constant. The idea of ion association, first suggested by Bjerrum (4), involves the postulation of an equilibrium caused solely by electrostatic interactions between "free" ions and neutral ion-pairs according to the equation

$$C^+ + A^- \underset{}{\overset{K}{\rightleftharpoons}} (C^+A^-)^0 \qquad (155)$$

This leads to an expression for the association constant K,

$$K = \frac{(1 - \gamma)}{c\,\gamma^2 f^2} \qquad (156)$$

where γ is the fraction of ions which are free and f is the ionic activity coefficient given by the Debye-Hückel expression. The activity coefficient of the neutral species is assumed to be unity. The concentration terms in the Onsager expression refer to ion concentrations. The presence of pairing equilibrium means that the average concentration of ions is less than the stoichiometric amount, and that c^* everywhere in the conductance equation should be replaced by the ion concentration c_i where

$$c_i = \gamma\, c^* \qquad (157)$$

The ion-pairing constant K is treated as a parameter chosen to give the best fit to the data. The ionic conductance is then given by

$$\Lambda_i = \frac{\Lambda}{\gamma} \qquad (158)$$

where Λ is the experimental equivalent conductance for the solution. From equation (156)

$$\frac{1}{\gamma} = \frac{1 + \sqrt{1 + 4Kcf^2}}{2} \qquad (159)$$

where $\log f_{\pm}^2 = \dfrac{-\sqrt{2}\, S_{(f)} \sqrt{c_i}}{(1 + \varkappa a)}$

and $S_{(f)} = 0.5091$ at $25^{\circ}C$

a is the distance of closest approach

$c_i = \gamma\, c^*$ where c^* is the normality of the salt

$\varkappa$ is defined earlier in this paper. In this case it reduces to the expression, $\varkappa = 0.46466 \sqrt{c_i}$

Equation (41) may be rewritten

$$\Lambda_i = (\Lambda_o - \Delta\Lambda_e)\left(1 + \frac{\Delta X}{X}\right) \qquad (160)$$

where Λ_i is defined by equation (158), $\Delta\Lambda_e$ is the electrophoretic correction given by equation (48) which is repeated here for clarity

$$\Delta\Lambda_e = \frac{-96,500\,(|e_i| + |e_j|)\chi}{1800\,\pi\,\eta\,(1 + \chi a)} \qquad (48)$$

which for this case reduces to

$$\Delta\Lambda_e = \frac{-170.44\,\sqrt{c_i}}{1 + \chi a} \qquad (161)$$

The term $\Delta X/X$ has previously been defined by equation (65) as

$$\frac{\Delta X}{X} = -\left[\alpha\sqrt{c_i}\,(1 - \Delta_1 + \Delta_2) + \frac{\Delta_3'\,\beta\sqrt{c_i}}{\Lambda_0}\right] \qquad (65)$$

The values of Δ_1, Δ_2 and Δ_3' were calculated by IBM 704 computer for varying concentrations and distances of closest approach, a. These values and the resulting $\Delta X/X$ values were calculated and tabulated for use in these calculations. Equation (160) then contains three adjustable parameters, a, K and γ. To find suitable values of these parameters we first assumed trial values of each and then computed a new $\gamma = \gamma'$, according to equation (159) for a particular value of c. Then, γ' will give a new value for $c_i = c_i'$, from equation (159). Using this c_i' we again computed a new $\gamma = \gamma''$. This procedure was repeated until successive calculations yielded constant values for γ.

To choose the best value for K, we first assumed a value for a. Then various values were assumed for K, and for each value a Λ_0' was computed from equation (160) rearranged to

$$\Lambda_0' = \frac{\Lambda_i}{1 + \frac{\Delta X}{X}} + \Delta\Lambda_e \qquad (162)$$

where Λ_i is obtained from the Owen and Gurry (14) data for Λ using equation (158). Three different concentrations were used for each value of K that was tried. K versus Λ_0' was then plotted and lines were drawn through points (K, Λ_0') for the same value of concentration. The three

lines nearly cross (minimizing variation in Λ_0' with concentration) at a K value of 51.

Then, with K equal to 51 we assumed various values of a. For each value of a we calculated and plotted Λ_0' for three concentrations. Again lines were drawn through points (a, Λ_0') for the same concentration to determine where the spread was a minimum. The value of a equal to 3.6 was chosen for the best fit. Using a K of 51 and a of 3.6, the average value of Λ_0' was calculated to be 132.24. This was taken as the value for Λ_0 in equation (158) from which Λ_i was then calculated. A value of $\Lambda_{calculated}$ was then determined using equation (158). The values of $\Lambda_{calc.}$ for various concentrations are given in Table 10 column II. The values of Λ from the data of Owen and Gurry (14) are also shown in Table 10 for comparison. The fit of the conductance data is too close to be shown graphically. It is now possible to calculate a transference number for zinc ion. From equation (85) we know that

$$T_+ = \frac{\lambda_0^+ - \frac{1}{2}\Delta\Lambda e}{\Lambda_0 - \Delta\Lambda e} \qquad (163)$$

where $\Delta\Lambda e$ is defined by equation (49), $\Lambda_0 = 132.24$ and $\lambda_0^+ = \Lambda_0 - \lambda_0^-$. The value of λ_0^- for sulfate ion is 80.02 (reference 126). The calculated transference number is given in Table 10 Column III, and is shown graphically in Figure 11 (A).

The Fuoss-Onsager treatment does not take into account the possible dependence of conductance upon higher powers of concentration than the first. Dye and Spedding (12) pointed out the significance of the higher terms of the electrophoretic correction to the conductance. Accordingly, the Fuoss-Onsager calculation of the time of relaxation effect was combined with the calculation of the higher electrophoretic terms. This calculation involved two adjustable parameters a and Λ_0.

The final expression for $\Delta\Lambda_e$ as developed by Dye and Spedding (12) are integrals which are functions of the charge type, dielectric

Table 10. Conductance and Transference Data for Varying Concentrations of Zinc Sulfate from Several Theoretical Determinations.

$\sqrt{N}$	I Owen and Gurry	II Fuoss-Onsager + Ion-Pairing	III T_+	IV Fuoss-Onsager + Extended $\Delta\Lambda_e$	V T_+	VI Combined	VII T_+
0			.3949		.3915		.4088
.03	116.55	116.52	.3909	116.37	.3843	116.51	.4047
.04	110.65	110.66	.3897	110.70	.3810	109.69	.4033
.05	105.15	105.14	.3884	105.26	.3776	103.04	.4016
.06	100.20	100.37	.3872	100.06	.3740	97.53	.4005

constant, viscosity, temperature, concentration and distance of closest approach. Their derivation has been discussed earlier in this thesis. The evaluation of the electrophoretic integral was done by IBM 704 computer and tabulated tables prepared of the resulting $\Delta\Lambda_e$ with varying concentrations and a values. The Fuoss-Onsager functions were calculated for 2-2 electrolytes in water at 25°C for varying ion size also using the IBM 704 computer. These results were combined with the electrophoretic correction. Using equation (41), with $\Delta\Lambda_e$ redefined according to Dye and Spedding (12), various combinations of Λ_0 and a values were tried. The best fit for the data was obtained for a of 4.3 and Λ_0 of 131.5. The results are shown in Table 10 column IV. The transference number of the zinc ion was again calculated from equation (163) using the redefined $\Delta\Lambda_e$. The results are given in Table 10 column V and are shown graphically in Figure 11 (B).

It is seen that both treatments satisfactorily can reproduce the conductance behavior of zinc sulfate and that the theory using the extended electrophoretic terms gives a fairly suitable limiting form for the transference number. However, as soon as the zinc perchlorate data are examined one can see that the λ_0^{++} for zinc ion is much too high for either method alone to fit conductance or transference data for zinc sulfate. The transference data yields a value of 51.16 for λ_0^{++} of zinc ion. Using the value of 55.34 as the limiting equivalent conductance for zinc ion as demanded by the perchlorate data, it is possible to fit the conductance data only at the lowest concentration by a combination of the two treatments just described. The procedure to find K is not as complex, however, since the limiting ionic conductance was fixed and therefore also Λ_0. The best fit was obtained for an a of 6.0 and a K of 95. The results are shown in Table 10 column VI and the fit is not good. The transference number is also given in Table 10 column VII and shown graphically in Figure 11 (C).

One should not overlook the possibility of inadequacies in the theory. It might be interesting in this connection to briefly review the fundamental assumptions and approximations inherent in the "Poisson-Boltzmann" equation, which is the basis of the ionic atmosphere treatment. The Boltzmann distribution function is based on a statistical model in which the number of particles able to be accommodated in a given energy state is unlimited. This assumption is not in accord with the physical system, however, for an "exclusion principle" exists - not a quantum mechanical one, but a volume exclusion. Consider, for example, the energy level corresponding to the distance $\underline{r} = \underline{a}$ between the central ion and an atmosphere ion. In this energy state, the number of particles is limited to the number of ions that can be accommodated on a sphere of radius $\underline{a}$, about six. Further, the Boltzmann function is here used in its simplest form, without a weighting function. This implies that all energy levels are equally likely to be occupied, which is not necessarily the case.

Also implied by the Boltzmann distribution function is a fixed, continuous set of energy levels which exists independently of the distribution of particles (ions) among them. This energy level continuum is, in the equilibrium case, related by a smooth function to the distance from the central ion. Hence, the equation does not take into account the fact that U_{ji} depends not only on $\underline{r}$ but also on the presence of other atmosphere ions in the vicinity; i.e. the energy level system is altered according to its state of occupancy. This approximation is stated more specifically when U_{ji} is related to the potential function by $U_{ji} = e_i \psi_j$. Here, ψ_j is defined as the average potential due to the central ion and the other atmosphere ions. The assumption is made that the presence of a given atmosphere ion does not alter the distribution of the other atmosphere ions. This is commonly called the "linear superposition of fields approximation."

The Poisson equation, which is used to relate the potential function to the charge distribution, involves the idea of a continuous distribution which, in view of the discrete charges carried by the ions, must be meaningful on the time average only. The time of averaging, then, must be short compared with the time spent by a given ion in the atmosphere of a chosen central ion. For example, if at some concentration, a given atmosphere ion is the only ion in the vicinity of the central ion, it is meaningless to speak of its being in the presence of the continuous charge distribution of an ionic atmosphere.

Finally, the Poisson equation applies strictly only to static charge distributions, since it ignores the magnetic interactions produced by moving charges. Hence, difficulties might be expected when the equation is applied to non-equilibrium situations.

C. Potassium Octacyanomolybdate (IV).

Conductance measurements as well as transference number measurements were made on $K_4Mo(CN)_8$ to provide experimental data for comparison with theoretical calculations. The fact that high charge unsymmetrical electrolytes show deviation from the theoretical Onsager conductance equation is not altogether unexpected when one considers the form of the distribution function that is used. This has also been observed in experiments by Grove (130) and Wynveen (134). The equivalent conductance data shown in Figure 12 show a curvature which would appear to introduce considerable error into the value of Λ_0 found by any extrapolation of this curve. The data were also treated by the method of Shedlovsky which allows Λ_0' to be calculated directly from individual values of Λ. The Onsager relation should, of course, be more valid as one approaches infinite dilution. The slope is less steep as shown in Figure 12, but the same intercept of Λ_0 of 188.5 cm^2 ohm^{-1} $equiv.^{-1}$ and λ_0^{-4} of 115.0 is obtained. In comparison, the Owen plot results in a Λ_0 value of 188.0 and λ_0^{-4} of 114.5.

Grove has also determined the value of λ_0^{-4} for $Mo(CN)_8^{-4}$ ion from the conductance measurements of $[N(Me)_4]_4$ $Mo(CN)_8$. Using the simple linear extrapolation of Λ versus $\underline{c}$, he obtained the value of λ_0^{-4} of 114.9 and with an Owen plot the value of 112.5 It can be seen that the simple extrapolation gives good agreement within the limits of accuracy which could be obtained by this procedure. The great variation given by the Owen method indicates that this is not a suitable function for this extrapolation. This deviation may be a function of ion size or mobility. Again it appears that we have no theoretical extrapolation function which can be used generally.

The neglect of higher order terms of the distribution function may introduce considerable error in the theoretical calculations of the conductance behavior of this electrolyte. The higher order terms have a strong dependence on the ion size parameter $\underline{a}$. Since one appreciable difference between K^+ ion and $N(Me)_4^+$ ion is the ionic size, then perhaps a decided factor in the variation of conductance behavior observed is due to the neglect of higher order terms.

We attempted to obtain transference numbers of $K_4Mo(CN)_8$ using the moving boundary method, without success. Each transference run yielded data of good internal precision but they were not reproducible. Solutions freshly prepared were run immediately but no trend could be observed in over thirty determinations. It is possible that the difficulty is due to the decomposition of the $Mo(CN)_8^{-4}$ ion.

Atkinson and co-workers (136) have shown that the 2-1 salts sodium and potassium m-benzenedisulfonate, seem to behave more "normally" than zinc perchlorate. They show curvature at higher concentrations similar to the zinc salt but there is no indication of an upswing at low concentrations. Their data in general do not extend to as low concentrations as the zinc perchlorate data, but our observed upswing begins well above their lowest point. It is interesting to comment in this

connection that Owen and Gurry (14) remark about an effect of similar nature which they encountered in zinc sulfate, "It may be significant, however, that our points of $c \simeq 0.000087$ (molarity) would cause the plots to curve abruptly upward and increase the intercept by about one conductance unit." It would also appear from the data of Atkinson (136) that the 3-1 salts, sodium and potassium 1, 3, 6-naphthalenetrisulfonate, are behaving normally.

The problem with zinc sulfate in common with other 2-2 salts which have been investigated, is the lack of knowledge of how the salt would behave in conductance if it were completely dissociated. A 2-2 electrolyte which would obey the extended theory with reasonable parameters would be a basis for the discussion of association in salts like zinc sulfate. Atkinson (136) reasoned that if the negative-two charge on an ion were separated by a large inert framework the short range interactions of the higher charged ion would be reduced while maintaining the long range properties of the divalent ion. This resulted in the experimental work on the salt copper m-benzenedisulfonate, which appears to show completely dissociated behavior according to our previous criterion for an undissociated electrolyte, i.e., that the conductance curve should approach the limiting law tangent from above.

It would be desirable in the future to examine the behavior of zinc m-benzenedisulfonate. This study should indicate whether the zinc ion is indeed as atypical as we believe it to be.

Combination of the m-benzenedisulfonate anion with a similarly large cation, such as tetramethylammonium ion, might yield interesting information on 1-2 electrolytes. If this should turn out to be a well behaved salt, this would indicate that the trouble with $[N(Me)_4]_4Mo(CN)_8$ lies with the $Mo(CN)_8^{-4}$ ion.

SUMMARY

An outline of the history of the method of conductance and transference number measurements, as well as a history of the interionic attraction theory of electrolytic solutions is presented.

As a test of the theoretical expressions which have been developed for the description of the conductance phenomenon, an attempt was made to fit the conductance data of zinc sulfate. Three parameters are involved, one of which is the equivalent conductance of zinc sulfate. To reduce the number of arbitrary parameters, the equivalent ionic conductance of zinc ion was sought by an independent measurement of the equivalent conductance of aqueous zinc perchlorate. The conductance of this salt was found to deviate markedly from the Onsager equation even in dilute solution. Attempts made to explain this behavior on the basis of ion-pairing, hydrolysis and purely electrostatic interactions were entirely unsatisfactory.

As a further test of the theory the transference number of zinc sulfate in water as a function of concentration was measured by the moving boundary method at 25°C.

The conductance data for zinc sulfate can be adequately fit by either the Fuoss-Onsager theory including ion association or by including terms of the electrophoretic equation which are usually neglected. The former treatment also gives a fairly suitable limiting form for transference numbers. However, when the limiting ionic conductance for zinc ion from measurements on zinc perchlorate is used, it is much too high for either theory to describe the behavior adequately.

We conclude that zinc salts do not form typical dilute solutions but that, perhaps due to the covalent bonding tendencies of the zinc ion, there are deviations from any theory which is based on the assumption of hard, non-polarizable ions.

While the primary objective of determining λ_0 for zinc ion thus could not be achieved, the new phenomenon observed will require a new approach to this conductance problem. It also indicates that not all electrolytes can be treated in the conventional fashion.

In addition to these considerations, the equivalent conductance of potassium octacyanomolybdate (IV) was determined. Large deviations from the limiting equation of Onsager occur, so that the limiting ionic conductance could not be accurately determined by the methods now available. We attempted to obtain the transference number of this salt from the moving boundary method. No reproducible transference number could be determined. It was concluded from examination of much self-consistent data that perhaps some immediate decomposition was occurring even in freshly prepared solutions.

REFERENCES

(1) P. Debye and E. Hückel, Physik Z., 24, 185 (1923).

(2) L. Onsager, ibid., 28, 227 (1927).

(3) L. Onsager and R. M. Fuoss, J. Phys. Chem., 36, 2689 (1932).

(4) N. Bjerrum, Kgl. Danske Vikensk. Selskab., Math-fys., Medd. 7, No. 9 (1926).

(5) R. M. Fuoss, J.Am.Chem. Soc., 79, 3301 (1957).

(6) R. M. Fuoss and C. A. Kraus, ibid., 79, 3304 (1957).

(7) R. M. Fuoss, ibid., 81, 2659 (1959).

(8) L. Onsager and R. M. Fuoss, Proc. Nat. Acad. Sci., 41, 274 (1955).

(9) Ibid., 41, 1010 (1955).

(10) Ibid., J. Phys. Chem., 61, 668 (1957).

(11) Ibid., 62, 1339 (1958).

(12) J. L. Dye and F. H. Spedding, J. Am. Chem. Soc,, 76, 888 (1954).

(13) D. J. Karl, Ph. D. Thesis, Michigan State University (1960).

(14) B. B. Owen and R. W. Gurry, J. Am. Chem. Soc., 60, 3074 (1938).

(15) I. L. Jenkins and C. B. Monk, ibid., 72, 2695 (1950).

(16) J. H. Jones, ibid., 67, 855 (1945).

(17) E. P. Purser and R. H. Stokes, ibid., 73, 5650 (1951).

(18) R. Gold, Ph. D. Thesis, New York University (1954); Dissertation Abstr. 15, 998 (1955).

(19) E. N. Horsford, Ann. Physik., 70, 238 (1847).

(20) G. Wiedmann, ibid., 99, 177 (1856).

(21) W. Schmidt, ibid., 107, 539 (1859).

(22) F. Kohlrausch and L. Holborn, Leitvermogen der Elektrolyte, Teubner, Leipsig (1898).

(23) F. Kohlrausch, Wied. Ann., 6, 145 (1879).

(24) Ibid., 26, 123, 161 (1885).

(25) G. Jones and R. C. Joseph, J. Am.Chem.Soc., 50, 1049 (1928).

(26) G. Jones and G. M. Bollinger, ibid., 51, 2407 (1929).

(27) Ibid., 53, 1207 (1931).

(28) Ibid., 57, 280 (1935).

(29) K. Wagner, Elektrotechnische Zeitschrift, 32, 1001 (1911).

(30) M. Wien, Ann. Physik., 85, 795 (1928).

(31) W. A. Taylor and S. F. Acree, J. Am. Chem. Soc., 38, 2416 (1916).

(32) C. A. Kraus and H. C. Parker, ibid., 44, 2438 (1922).

(33) H. C. Parker, ibid., 45, 1370 (1923).

(34) T. Shedlovsky, ibid., 52, 1806 (1930).

(35) G. Jones and G. M. Bollinger, ibid., 53, 411 (1931).

(36) T. Shedlovsky, ibid., 54, 1411 (1932).

(37) G. Jones and S. M. Christian, ibid., 57, 272 (1935).

(38) G. Jones and G. M. Bollinger, ibid., 57, 280 (1935).

(39) G. Jones and B. C. Bradshaw, ibid., 55, 1780 (1933).

(40) G. Jones and M. J. Prendergast, ibid., 59, 731 (1937).

(41) J. F. Daniell, Phil. Trans., 129, 97 (1839).

(42) Ibid., 130, 209 (1840).

(43) N. Hittorf, Ann. Physik. ser. 2, 89 (1853); ibid., 98, 1 (1856); ibid., 103, 1 (1858); ibid., 106, 337 (1859); ibid., 106, 513 (1859).

(44) W. Hittorf, Z. physik. Chem., 39, 612 (1901); ibid., 43, 239 (1903).

(45) G. Kortum and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. 1, Elsevier Publishing Co., New York, N. Y. (1951).

(46) J. W. McBain, Proc. Washington Acad. Sci., 9, 1 (1907).

(47) A. A. Noyes and K. G. Falk, J. Am. Chem. Soc., 33, 1436 (1911).

(48) G. Jones and M. Dole, ibid., 51, 1073 (1929).

(49) D. A. MacInnes and M. Dole, ibid., 53, 1357 (1931).

(50) G. Jones and B. C. Bradshaw, ibid., 54, 138 (1932).

(51) B. J. Steel and R. H. Stokes, J. phys. Chem., 62, 450 (1958).

(52) H. von Helmholtz, Ann. Physik. ser. 3, 3, 201 (1878).

(53) W. T. Pearce and L. Mortimer, J. Am. Chem. Soc., 40, 518 (1918).

(54) D. A. MacInnes and J. A. Beattie, ibid., 42, 1117 (1920).

(55) D. A. MacInnes and K. Parker, ibid., 37, 1445 (1915).

(56) B. B. Owen, ibid., 61, 1393 (1939).

(57) O. Lodge, Brit. Assn. Advancement Sci. Rep., 389 (1886).

(58) W. C. D. Whetham, Phil. Trans. 184A, 337 (1893).

(59) Ibid., Z. physik. Chem., 11, 220 (1893).

(60) N. Nernst, Z. Elektrochem., 3, 308 (1897).

(61) H. Masson, Phil. Trans., 192A, 331 (1899).

(62) F. Kohlrausch, Ann. Physik., 62, 209 (1897).

(63) D. A. MacInnes and I. A. Cowperthwaite, Proc. Nat. Scad. Sci. 15, 18 (1929).

(64) D. A. MacInnes and L. G. Longsworth, Chem. Rev., 11, 171 (1932).

(65) D. A. MacInnes and E. R. Smith, J. Am. Chem. Soc., 45, 2246 (1923).

(66) Ibid., 46, 1398 (1924).

(67) J. L. Dye, Ph. D. Thesis, Iowa State College, (1953).

(68) B. D. Steele, J. Am. Chem. Soc., 79, 414 (1901).

(69) Ibid., Phil. Trans., 198 A, 105 (1902).

(70) E. G. Franklin and H. P. Cady, J. Am. Chem. Soc., 26, 499 (1904).

(71) R. B. Denison and B. D. Steele, Phil. Trans., 205, 449 (1906).

(72) Ibid., Z. physik. Chem., 57, 110 (1906).

(73) D. A. MacInnes and T. B. Brighton, J. Am. Chem. Soc., 47, 994 (1925).

(74) F. H. Spedding, P. E. Parter and J. M. Wright, ibid., 74 2055 (1952); ibid., 74, 2778 (1952).

(75) G. N. Lewis, ibid., 32, 862 (1910).

(76) E. E. Smith, Bur. Standards J. Research, 8, 457 (1932).

(77) D. A. MacInnes "Principles of Electrochemistry." Reinhold Publishing Corp., New York, N.Y. (1939)

(78) L. G. Longsworth, J. Am. Chem. Soc., 54, 2741 (1932).

(79) S. A. Arhennius, Z. physik. Chem., 1, 631 (1887).

(80) D. A. MacInnes and T. Shedlovsky, J. Am. Chem. Soc., 54, 1429 (1932).

(81) T. Shedlovsky, A. S. Brown and D. A. MacInnes, Trans. Electrochem. Soc., 66, 165 (1934).

(82) J. J. van Laar, Z. physik. Chem., 18 245 (1895).

(83) A. A. Noyes and J. Coolidge, J. Am. Chem. Soc., 26, 167 (1904)

(84) H. Jahn, Z. physik. Chem., 33, 545 (1900).

(85) W. Sutherland, Phil. Mag., 3, 161 (1902); ibid., 7, 1 (1906).

(86) G. N. Lewis, Z. physik. Chem., 70, 214 (1910).

(87) G. N. Lewis and N. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y. (1923).

(88) W. Sutherland, Phil. Mag., 14, 1 (1907).

(89) S. R. Milner, ibid., 23, 551 (1912); ibid., 25, 742 (1913).

(90) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, New York, (1950).

(91) H. Muller, Physik. Z. 28, 324 (1927); ibid., 29, 27 (1928).

(92) T. H. Gronwall, V. K. LaMer and K. Sandved, ibid., 29, 358 (1928).

(93) C. W. Davies and J. C. Jones, Proc. Roy. Soc., 195A, 116 (1948).

(94) J. C. Jones, J. Chem. Soc., 1094 (1950).

(95) H. S. Dunsmore and J. C. Jones, ibid., 2925 (1951).

(96) C. A. Kraus and R. M. Fuoss, J. Am. Chem. Soc., 55, 21 (1933); ibid., 55, 1019 (1933).

(97) R. M. Fuoss, ibid., 80, 5059 (1958).

(98) P. Debye and E. Hückel, Physik. Z. 24, 305 (1923).

(99) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers Inc., New York, N. Y. (1959).

(100) Reference 90, page 23.

(101) H. Falkenhagen and G. Kelbg, Z. Elektrochem., 58, 653 (1954).

(102) Reference 10, equation 4.7, page 671

(103) Reference 99, Chapter 14, page 173.

(104) Reference 99, page 195.

(105) T. Shedlovsky, J. Am. Chem. Soc., 54, 1405 (1932).

(106) H. Falkenhagen and M. Dole, Z. physik. Chem., 6, 159 (1929); ibid., 30, 611 (1929).

(107) H. Falkenhagen, Physik. Z. 32, 365, 745 (1931).

(108) A. Einstein, Ann. Phys., 19, 289 (1906).

(109) W. S. Wilson, Dissertation, Yale University, (1936).

(110) L. Onsager, J. Chem. Phys., 2, 599 (1934).

(111) I.. A. Cowperthwaite and V. K. LaMer, J. Am. Chem. Soc., 53, 4333 (1931).

(112) G. Scatchard and S. S. Prentiss, ibid., 55, 4355 (1933).

(113) G. D. Pinching and R. G. Bates, J. Research, Natl. Bur. Standards, 37, 311 (1946).

(114) D. E. Fowler, W. V. Loebensyein, P. B. Paul and C. A. Kraus, J. Am. Chem. Soc., 62, 1140 (1940).

(115) L. F. Audrieth, "Inorganic Synthesis," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y. (1950), pp. 160-162.

(116) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N.Y. (1940).

(117) H. B. Thompson and M. T. Rogers, Rev. Sci. Instru., 27, 1079 (1956).

(118) H. M. Daggett, E. J. Blair and C. A. Kraus, J. Am. Chem. Soc., 73, 799 (1951).

(119) "Lange's Handbook of Chemistry" Handbook Publishers Inc., Sandusky, Ohio, (1946).

(120) Reference 90, p. 556.

(121) Reference 90, p. 151.

(122) Reference 90, p. 587.

(123) T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc., 56 1066 (1934).

(124) I. M. Kolthoff and T. Kameda, ibid., 53, 832 (1931).

(125) W. J. Moore, "Physical Chemistry," Prentice Hall Inc., New York, N. Y. (1950).

(126) D. A. MacInnes, J. Franklin Inst., 225, 661 (1938).

(127) International Critical Tables of Numerical Data, Vol. III, National Academy of Sciences, p. 51 (1928).

(128) B. B. Owen and H. Zeldes, J. Chem. Phys., 18, 1083 (1950).

(129) I. J. Jenkins and C. B. Monk, J. Chem. Soc., 68, (1951).

(130) K. O. Groves, Ph. D. Thesis, Michigan State University (1959).

(131) C. W. Davies, Trans. Faraday Soc., 23, 351 (1927).

(132) Reference 90, p. 35.

(133) Reference 90, p. 83.

(134) R. A. Wynveen, Ph. D. Thesis, Michigan State University (1959).

(135) J. E. Lind Jr., J. J. Zwolenik and R. M. Fuoss, J. Am. Chem. Soc., 81, 1557 (1959).

(136) G. Atkinson, M. Yokoi and C. J. Hallada, ibid., 83, 1570 (1961).