THE DETERMINATION OF ACTIVITY COEFFICIENTS AND IONIC CONDUCTIVITIES OF SOME HIGH-CHARGED ELECTROLYTES IN AQUEOUS SOLUTION AT 25°C

By

Kenneth O. Groves

A THESIS

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
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ABSTRACT

Activity coefficients and equivalent conductances have been determined for the electrolytes $K_4[W(CN)_8]\cdot 2H_2O$, $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$, $Pt(pn)_3Cl_4\cdot H_2O$ and $K_2Pt(CN)_4$ in aqueous solutions at 25°C.

The activity coefficients and osmotic coefficients were obtained by isopiestic comparison with aqueous potassium chloride solutions. The values of these coefficients determined for the first three electrolytes listed above were comparable to those previously found for similar electrolytes of the 1-4, 4-1 charge type. The values found indicate that these electrolytes may be extensively associated in solution.

Values of the mean distance of closest approach, $\mathring{a}$, have been determined. The numerical values of these parameters vary considerably depending upon the method of calculation.

The equivalent conductances were also ascertained in the hope of determining values for $\mathring{a}$ independent of the isopiestic method. Such determinations could not be made, however, since deviations from the limiting conductance equation of Onsager were too great. Because of these deviations, present methods of determining limiting ionic conductance values most accurately could not be used. Values for these constants

were determined, however, by simple linear extrapolation of equivalent conductance versus $c^{\frac{1}{2}}$ graphs. These derived values are 114.9 ohm^{-1}, 118.2 ohm^{-1}, 90.15 ohm^{-1}, 81.2 ohm^{-1} for the polyvalent ions $Mo(CN)_8^{-4}$, $W(CN)_8^{-4}$, $Pt(pn)_3^{+4}$ and $Pt(CN)_4^{-2}$, respectively.

Complete evaluation of the conductance behavior of these highly charged species must await further mathematical extensions of the present theory of electrolytic solutions.

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1 - HISTORY

A. Isopiestic Method

The method was first utilized by Bousfield (1, 2) as early as 1913. He introduced the procedure as a method for determining vapor pressure data in order to determine the relative degree of hydration of salts with identical vapor pressures. The method finally adopted after a number of trials of various procedures and apparatus was as follows.

Salts or solutions were placed in separate open vessels in a desiccator which was evacuated to facilitate the exchange of vapor between solutions and maintained at a uniform temperature. Under these conditions equilibrium was reached by the several solutions gaining or losing water until they arrived at the same vapor pressure. The name "isopiestic" was given to these solutions at equilibrium. After equilibrium was reached the containers were weighed, and the amount of water taken up by each salt was recorded. A small quantity of water was then placed in a trough between the vessels containing the solutions and the operation was repeated. In this way Bousfield was able to obtain a series of data for salts in various degrees of hydration and determine approximately the vapor pressure of water above which several pure salts and their hydrates began to take up water.

The vapor pressure data used as a standard for each equilibrium concentration was that of the lithium chloride solution.

Since the accuracy of the vapor pressure data obtained by this method must necessarily depend on the degree of accuracy of the vapor pressure data known for the reference solution, Bousfield (3) began work on determining a standard table for the vapor pressure of aqueous sodium chloride solutions at 18°C and constructed such a table over the whole range of concentrations for this salt.

Sinclair (4) in 1933 attempted to varify the practicability of Bousfield's method for vapor pressure measurements. Using approximately equal concentrations of 1 M potassium chloride solutions, he found that the amount of distillation occurring between the solutions after several days was barely noticeable even when the dishes were floated on mercury to aid temperature equalization.

Sinclair made calculations on the temperature dependence for the distillation of water from one container to the other and concluded that the retardation was due to the thermal resistance between solutions, i.e. although in the evacuated container all surfaces are at the same vapor pressure, they are not necessarily all at the same temperature. Sinclair realized that the times quoted from the work of Bousfield for the equilibrium to be reached between solutions were dependent on the method of introducing the water for each equilibrium run. Bousfield had introduced the water to be distilled in a trough at the bottom of the desiccator. The distillation then involved was from the trough to the solutions over a period of several months, thus avoiding the temperature difference set up between the two solutions by the latent heat of vaporization which occurs when the distillation is directly between the two solutions. Sinclair incorporated the following principles in the design of an apparatus which would reduce the time required for the attainment of equilibrium and make the method practical. He provided good metallic conduction between the solutions in order to reduce retardation of the distillation by thermal resistance. He accelerated the diffusion of solute and the conduction of heat through the solutions, both of which would limit the rate of attainment of equilibrium, by stirring and the use of shallow solutions.

His general procedure consisted of placing silver-plated copper dishes on a copper block into a desiccator. The desiccator was then evacuated and placed on a rocker device in a thermostat. He found that the same set of solutions could be used to make as many as five or six determinations over a range of concentrations varying by about 40 per cent. It was found that the most convenient method for varying concentrations and one which facilitated the attainment of equilibrium most rapidly was by distillation of water from the bottom of the desiccator. In general, results of Sinclair's work with potassium chloride and sucrose solutions indicated that the method was capable of yielding results of high accuracy. His work showed that solutions could be brought rapidly into equilibrium in regard to vapor pressure; and, by taking one solution as a standard, values for vapor pressure lowering could be obtained with an accuracy of 0.3 per cent or less for solutions of concentration above 0.1 M.

In 1934 Sinclair and Robinson (5) published the first paper on the determination of activity coefficients from vapor pressure measurements obtained from the isopiestic method. Although vapor pressure measurements had been utilized previously for the evaluation of activity coefficients, the techniques for determining these vapor pressures were so elaborate and time-consuming that this type of data was seldom used. The principle methods used before that time were molar depression of the freezing point, molar elevation of the boiling point and e.m.f. measurements.

The principle advantage of the isopiestic method is its experimental simplicity. The comparative nature of the method, however, is a disadvantage, in that the vapor pressure - concentration curve of some reference electrolyte must be known with a high degree of accuracy. Hence, Robinson and Sinclair compiled and calculated vapor pressure data of potassium chloride solutions from various reliable sources obtained from as many different methods of determining these values as was known at that time. Among these methods were direct measurement of vapor pressure by Lovelace, et al (6), molar freezing point depression by several different investigators, boiling point elevation by Saxton and Smith (7) and e.m.f. measurements by Smith (8) and Harned (9). From these data they constructed a relative vapor pressure lowering versus concentration curve by weighting the various methods over concentration ranges where they were considered to be the most reliable. These final data were checked against pure sucrose solutions. The general method involves preparing a graph of a function R, defined as

$$R = \frac{P_o - P}{P_o m_2},$$

where P_o = vapor pressure of pure solvent

P = vapor pressure of solution

m_2 = molality of solute dissolved in the solution (sucrose)

against molality of the sucrose solution. The values of $\frac{P_o - P}{P_o}$ at various values of m_2 were determined by isopiestic comparison with potassium chloride solutions. These values were obtained from the smoothed vapor pressure lowering versus molality (potassium chloride) curve.

The graph mentioned above, when extrapolated to infinite dilution, will extrapolate to a constant value of 0.018015, as seen from the following relation

$$R = \frac{Po-P}{P_o m_2} = \frac{X_2}{m_2} = \frac{1}{m_1 + m_2} = \frac{1}{m_1} \text{ as } m_2 \rightarrow 0,$$

using Raoults Law: $P = PoX_1$. The extrapolated value compared favorably with the theoretical value above and led them to the conclusion that the values of R, selected for potassium chloride, were of a high degree of accuracy. This paper was the first effort to correlate the existing data and thus make available a reliable standard reference salt for use in isopiestic measurements.

Having obtained the best vapor pressure data available at that time, Sinclair calculated the activity coefficients of potassium chloride using the graphical integration method of Randall and White (33). This method is discussed below. After obtaining activity coefficients corresponding to the vapor pressures of potassium chloride solutions, the activity coefficients of the other salts were derived by a simplified method.

In 1936 Mason and Gardner (10) adapted the apparatus used by Robinson and Sinclair, utilizing the isopiestic method to determine molecular weights from vapor pressure lowering data. Their apparatus, in general, consisted of a brass vacuum desiccator fitted in such a manner that it could be evacuated. The solutions under investigation were placed in nickel crucibles, and the bottom of the desiccator was covered with standard potassium chloride solution to increase heat transfer between crucibles. That year Mason and Ernst (11) employed the same apparatus, with the exception of the use of glass crucibles instead of nickel crucibles, and obtained the activity coefficients of lanthanum chloride in aqueous solution at 25°C.

In 1938 Mason (12) further modified his apparatus by casting his vacuum desiccator from monel metal which was thought to be more free of pinholes and easier to make vacuum-tight. He also introduced platinum gauze in the bottom of his crucibles and found that this innovation decreased the minimum time to reach equilibrium by one-half. Below 0.5 M he found that the accuracy obtained by using glass weighing bottles as crucibles was decreased rapidly. Therefore, below this concentration he substituted similar bottles made of sterling silver and heavily gold-plated.

In 1938 Scatchard, et al, (13) modified the method of Robinson and Sinclair to give a still greater precision to isopiestic measurements. The actual procedure and apparatus will not be described at this time but will be dealt with in detail in Section 3, Apparatus and Procedures. Scatchard's method was followed closely in determining the isopiestic measurements described in this paper.

B. Conductivity Measurement

One of the fundamental theoretical problems in electrochemistry has been the process of electrical conductance by electrolytic solutions. The earliest studies of the conductivities of solutions were made using large direct currents and resulted in such large electrochemical reactions that these early observers concluded that Ohm's Law was not obeyed by electrolytic solutions. The conductance seemed to be dependent on the e.m.f. If Ohm's Law for metallic conductors was obeyed by electrolytic solutions, then the resistance and, hence, the conductivity, which is the reciprocal of the resistance, should be constant for a given solution. The resistance should be dependent only on the dimensions of the conductor, or in the case of an electrolytic solution the area and distance between the electrodes of the cell used in measuring the resistance of the solution, i.e.

$$R = \frac{\rho L}{A} \text{ ohms},$$

where ρ = specific resistance (a constant)

L = distance between electrodes

A = area of electrodes,

and by definition

$$C = \frac{1}{R} = \frac{kA}{L} \text{ ohms}^{-1},$$

where k = specific conductance.

In 1868 Kohlrausch (14) employed an alternating current of about 1000 cycles per second with a Wheatstone Bridge assembly in order to reduce the effect of polarization and prevent electrochemical reactions. He found that the effect of polarization was decreased still further if the electrodes were coated with a layer of finely divided platinum black. Between 1868 and 1880 Kohlrausch published a long series of careful conductivity investigations. These measurements were made over a range of temperatures, pressures and concentrations.

To reduce his results to a common concentration basis, Kohlrausch defined a function called the "equivalent conductivity",

$$\Lambda = \frac{k}{c^*} 1000 ,$$

where c^* = equivalent per liter.

A quantity, Λ^o, was also defined as the equivalent conductance at infinite dilution. The determination of Λ^o involves an extrapolation of the measured equivalent conductances in dilute solutions to zero concentration. The method used by Kohlrausch for the determination of this quantity was a plot of Λ versus $c^{*\frac{1}{2}}$ which yields a straight line for small values of $c^{*\frac{1}{2}}$. Such an extrapolation is made readily for strong electrolytes but is impossible to make accurately for weak electrolytes because of their tremendous increase in Λ at high dilutions where also the experimental values become more uncertain. It was found that the data were fairly well represented by the empirical equation

$$\Lambda = \Lambda^{o} - k_{c^*} c^{*\frac{1}{2}}$$

where k_{c^*} is an experimental constant. Kohlrausch also observed that Λ^{o} was the sum of two independent terms, one characteristic of the anion and one of the cation

$$\Lambda^{o} = \lambda_{+}^{o} + \lambda_{-}^{o} \quad ,$$

where λ_{+}^{o} and λ_{-}^{o} are the equivalent ionic conductances at infinite dilution. This relation is known as Kohlrausch's Law of the independent migration of ions.

After the work of Kohlrausch and the introduction of alternating current as a method of measuring conductivities, many improvements were made in the bridge design by various investigators. These improvements brought to light many sources of error in the resistance measurements and, hence, cast severe doubts on the accuracy of the results obtained with the various instruments then in common use.

In 1928 Jones (15) and collaberators published the first of a series of eight papers concerned with the problem of eliminating errors from alternating current conductivity measurements. Through these series of publications he has made alternating current conductivity measurements a highly precise and exacting method.

His first paper on the subject contains an experimental and theoretical analysis of the design of the

Wheatstone bridge for measuring resistances with alternating current. Included in this analysis are recommendations on the source of alternating current, amplification to increase the sensitivity of the detector, shielding of bridge components and design of resistance boxes. Of particular interest is his introduction of a new method for grounding the bridge. By using a modification of a method introduced by Wagner (16), which is essentially the introduction of a variable resistance and capacitance in parallel in the ground lead of the bridge, Jones was able to eliminate errors which were as high as a tenth of one per cent in his resistance readings. He suggested that the discovery of this source of error throws some suspicion on all previous measurements of the conductance of solutions. Also of interest is his investigation on the effect that the liquid used for the thermostat had on resistance measurements. Since water, the usual thermostat fluid, is a conductor, an error can be introduced in the measurements due to this conductor being so near the cell. The quantitative considerations of the effects of water as a thermostat fluid were considered too difficult to analyze; however, the use of oil seemed to eliminate most of the error and was recommended for use in all precision measurements.

In a second paper by Jones and Bollinger (17) improvements of some components of the bridge over those introduced in his first paper are described. Among these are suggested improvements in the oscillator and the detector. Shedlovsky (18), a year later, confirmed the importance of Jones' improved bridge design but differed in an opinion on the use of an unscreened bridge. In this paper he has theoretically and experimentally discussed a design for an electrostatically screened bridge for precision work.

A third paper, published by Jones and Bollinger (19), deals with the design of conductance cells. Of more fundamental importance is the fact that this paper repudiates a previous publication by Parker (20), who challenged the fundamental postulate of the Kohlrausch method for the measurement of the conductance of electrolytes, by the observation that "cell constants" are apparently not really constant but vary with the frequency and resistance being measured. Jones attacked the problem of variable cell constants by accurately determining the capacitance in parallel with the resistance box in hopes that this capacitance would depend primarily on the reactance of the cell and, thus, yield some clue as to the nature of the error responsible for the "Parker effect". Analysis of the cell reactance as a function of frequency, resistance and degree of platinization definitely led to the view that the Parker effect at high resistances was due, for the most part, to a faulty design of conductance cells which were in use at that time.

Specifically, the error which caused the Parker effect was due to a series capacitance and resistance shunt built into the cell by constructing the filling tubes and mercury contact tubes parallel and much too close together to the cell proper. Experimental verification of this analysis was carried out varying the construction of the cell. By this method they were able to reduce the error in resistance readings from the Parker effect in their new cells to less than 0.001 per cent. The previous year Shedlovsky (21) also investigated the design of conductance cells as a means of eliminating the undesirable Parker effect. He designed a four-electrode cell to see whether variations of the cell constant would disappear if similar electrodes were included in two arms of the bridge during measurement. He concluded from this arrangement that if the electrode effect was eliminated, then the cell constant was a true constant at various frequencies. Although this cell was not as convenient for routine work, it was suggested that it could be used to calibrate the ordinary two-electrode type.

Shedlovsky (22), following the suggestion of Jones and Bollinger, designed and constructed a cell for high dilution work which was found to be independent of frequency. With very dilute solutions it was found desirable to use a cell of relatively large volume so that increasing concentrations could be built up and successively measured without risk of contamination from atmospheric or other impurities. The cell designed by Shedlovsky differed from those in common use at that time in that the electrodes were taken out of the flask. The leads were thus separated from each other and the space between them was, therefore, filled with the oil of the thermostat. This design was found to eliminate a parasitic current between that part of the leads which was emmersed in the solution. With this cell and an extremely careful technique for the introduction of solutions he was successful in obtaining a consistent accuracy of one or two hundredths of a per cent for the relative conductance values of several univalent salts.

Part of the Parker effect was deduced to be due to polarization. Hence, in 1935 Jones, Bollinger and Christian (23, 24) published two papers concerning platinization of electrodes as a method to minimize the effect of polarization.

The above papers dealt with an analysis of the exact nature of the error due to polarization and the factors upon which polarization may be dependent. Briefly, the following results were found:

1. Polarization resistance is inversely proportional to the square root of the frequency;
2. Polarization causes a capacitance in series with resistance which decreases with increasing frequency;

3. Both polarization capacitance and resistance are dependent upon the metal used for the electrodes and dependent to a lesser degree on the electrolyte and the temperature but independent of the current density and degree of separation of electrodes;

4. Platinization of electrodes from a chloroplatinic acid solution containing a small amount of lead acetate can reduce polarization to a negligible amount. The criterion for the sufficiency of platinization is determined by plotting the resistance versus the square root of frequency. The error due to polarization will be the difference in resistance readings between the highest and lowest frequencies. It was suggested that, if the error thus determined is negligible for the purpose of the measurement, then the platinization is adequate. Jones, Bollinger and Christian also suggest that if the solutions to be measured are acid or alkaline, very dilute, or liable to be influenced catalytically by the platinum, it may be advisable to reduce platinization or even to eliminate it entirely.

Earlier Jones and Bollinger (25) investigated the validity of Ohm's Law for electrolytes. Their interest in this investigation stemmed from a paper by Wien (26) in which he had recorded measurements of the conductance of electrolytes in very strong fields from about 30,000 volts per square centimeter up to about 300,000 volts per square centimeter and concluded that a real increase in conductance with increase in field strength occurs at very high voltages. Likewise, other investigators at that time, namely Taylor and Acree (27), Kraus and Parker (28) and Parker (20), had also reported variations in apparent resistance readings over voltage ranges of the order of 0.2 volts to 10 volts. Some of these reported resistance variations were as high as 0.13 per cent. Hence, Jones and Bollinger undertook to investigate these phenomena to determine if these variations were due to experimental error or an apparent failure of Ohm's Law. The results of these investigations demonstrated that if adequate experimental precautions were taken to avoid errors due to heating, polarization and to secondary effects of inductance and capacitance, there was no measurable variation of the real resistance of electrolytes with variation of the applied voltage throughout the range of voltages and frequencies suitable for use in the Kohlrausch method of measuring electrolytic conductance.

Jones, in collaboration with Bradshaw, next investigated the problem of determining a standard reference solution for the calibration of conductance cells (29). Potassium chloride was chosen as the reference salt because it is easily purified, nonhygroscopic, sufficiently soluble, stable both in solution and in the solid form and nonpoisonous. This salt was first suggested by Kohlrausch and had been used most extensively by latter workers in this field and, hence, prior usage also influenced Jones' decision. He considered the definition of the standard reference of primary importance, noting that several definitions were commonly accepted at that time. The original Kohlrausch definition of gram molecule of potassium chloride per liter of solution at 18°C and a relatively newer definition by Parker and Parker (30) as a gram molecule of potassium chloride per cubic decimeter at 0°C were felt to be objectionable on the grounds that the atomic weight of potassium chloride may be changed from time to time. Hence, he suggested that the definition be stated directly in grams of potassium chloride. He also felt that a definition in terms of volume was objectionable because in practice it was less precise than a definition in terms of weight. A further objection was that both Kohlrausch and Parker had specified their weights in air instead of in vacuo and, hence, introduced some uncertainty because the buoyancy of air is variable from time to time from one laboratory to another.

With the above objections in mind, he defined a standard reference solution of potassium chloride in terms of weight in grams per kilogram of solution corrected to vacuum.

Because Parker's work was considered to be more reliable than the older work of Kohlrausch, Jones decided to retain Parker's standard concentrations but corrected for air buoyancy.

Having decided on a definition, he then determined the specific conductances of standard potassium chloride reference solutions at 0°C, 18°C and 25°C. The conductance cells used in these determinations were previously calibrated by using mercury as the reference substance, since the specific conductance of mercury was known with a high precision.

In regard to a standard reference solution, it is pointed out by Robinson and Stokes (31) that practically all the recent work has been based on the Jones and Bradshaw standards and that these standards should be retained for convenience even if future work shows them to be slightly in error. They also point out that already one change has occurred, in that the international ohm is no longer the recommended unit of resistance, having been replaced by the absolute ohm which is defined in terms of the fundamental units of the c.g.s. electromagnetic system.

The preceeding historical summary on the development of conductance techniques is not a complete account of all work done in this field; however, it is felt that the major contributions have been discussed. The work prior to 1926 has been slighted to some extent, since it is thought that the techniques and instrumentation at this period contained so many systematic errors as to make quantitative results impossible.

2 - THEORY

The theory involved in the calculation of activity coefficients by the isopiestic method is considered as it was historically developed. It can be divided essentially into two general treatments, one purely thermodynamic and the second based on the modern quantitative theory of electrolytic solutions. The theoretical development that follows will first consider the thermodynamic treatment.

General Thermodynamic Properties of Solutions

A partial molal quantity for any extensive thermodynamic property G is defined by the following expression:

(1) $$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,\, T,\, n_1,\, n_2\, \ldots}\,,$$

where $\bar{G}_1$ refers to the increase in total G when one mole of component 1 is added to an infinite amount of a solution at fixed temperature and pressure and with the number of moles, n_2, n_3 ... , of all other components kept fixed.

If we have a two-component system, we may write any extensive thermodynamic property G at constant temperature and pressure as

(2) $$G = f(n_1,n_2).$$

By using the equation of partial differentiation

(3) $$dG = \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2$$

or from equation (1)

(4) $$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 .$$

Upon integration of the above equation, there is obtained the relationship

(5) $$G = n_1\bar{G}_1 + n_2\bar{G}_2 .$$

This equation can be used to evaluate any extensive property, if we know the amounts and the partial molal quantities of the constituents. If equation (5) is differentiated, then

(6) $$dG = n_1 d\bar{G}_1 + \bar{G}_1 dn_1 + n_2 d\bar{G}_2 + \bar{G}_2 dn_2 ,$$

and if equations (4) and (6) are combined, there results an equation

(7) $$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0,$$

which relates the change in partial molal quantities, $\bar{G}$, at constant temperature and pressure with infinitesimal changes in composition. Thus, for changes in partial molal free energy due to isothermal changes in composition, equation (7) may be written as

(8) $$n_1 d\bar{F}_1 + n_2 d\bar{F}_2 = 0 .$$

The fugacity of a solution constituent is defined as

(9) $$\bar{F}_1 = RT \ln f_1 + B_1(T),$$

where R is the gas constant, T is the absolute temperature and B is a constant for a given substance at a given temperature. This equation defines the quantity, f_1, called the fugacity function. It does not allow for the determination of absolute values of the fugacity since it does not tell how $B_1(T)$ is to be fixed at any particular temperature. Therefore, in order to evaluate the fugacity it must be further specified that the function is defined so that

$$\frac{f}{P} \longrightarrow 1 \quad \text{as} \quad P \longrightarrow 0 \, ,$$

where P is the vapor pressure above the solution. If we consider one constituent of a solution at two different concentrations at the same temperature, equation (9) may be written as

$$\bar{F} - \bar{F}' = RT \ln \frac{f}{f'} \, , \tag{10}$$

where the primed values indicate the initial concentration.

For convenience, a new term is defined called the relative fugacity or activity:

$$a = \frac{f}{f^o} \, , \tag{11}$$

where f is the fugacity in any given state; and f^o is the fugacity in a standard state, at the same temperature.

Equation (10) may, therefore, be written as

$$\bar{F} = \bar{F}^o + RT \ln a \, , \tag{12}$$

assuming the initial state of the solution was the standard state.

The partial molal free energy, $\bar{F}$, has been also called the chemical potential, μ , and, hence, the above equation is perhaps written more often in the form

$$(13) \qquad \mu = \mu^{\circ} + RT \ln a .$$

In the standard state the activity is unity, $a^{\circ} = 1$, while in any other state the activity is given by equation (13). By utilizing the relation expressed in equation (12), we may write equation (8) as

$$(14) \qquad d \ln a_2 = \frac{-N_1}{N_2} d \ln a_1 ,$$

which expresses the activity of the solute, a_2, in terms of the activity of the solvent, a_1. N_1 and N_2 in the above equation represent the concentration of the solvent and solute, respectively, expressed in units of mole fractions.

If we arbitrarily fix the standard state of the solvent as the pure solvent, then the activity of the solvent, a_1, can readily be calculated as

$$(15) \qquad a_1 = \frac{P}{P_0} ,$$

where P is the vapor pressure of the solution; and P_0 is the vapor pressure of the pure solvent.

The above expression arises from the specifications on the fugacity function, i.e.

$$\frac{f}{P} \longrightarrow 1 \quad \text{as} \quad P \longrightarrow 0$$

and the definition of activity, equation (11). Once the activity of one component has been obtained as a function of concentration, the activity of the other component in a binary solution can be calculated from the Gibbs-Duhem equation (equation 14).

The activity of the solute can be obtained from equation (14) by a graphical integration, i.e. plotting N_1/N_2 versus log a_1 and determining the area under the curve.

However, for greatest precision, equation (14) is not used as it now stands. The reason for this is that such a plot as indicated above will tend toward infinity as infinite dilution is approached. Since the infinite dilute area is that region where real solutions approach ideal behavior, this is probably the most important part of the curve. It is also the region of the curve where experimental data cannot easily be obtained.

Activity Coefficients by the Method of Lewis and Randall

Lewis and Randall (32) and Randall and White (33) have developed a special graphical method in order to eliminate this difficulty at infinite dilution.

A function, h, called the divergence function, was invented and defined as

$$h = 55.51 \frac{\ln}{\sqrt{m}} a_1 + 1 , \qquad (16)$$

where m = molality

a_1 = activity of solvent

ν = number of ions dissociated per mole of solute.

The important characteristic of this function is that it will rapidly approach zero at infinite dilution.

Differentiating equation (16) gives

$$dh = \frac{55.51}{m} \, d \ln a_1 - \frac{55.51}{m^2} \ln a_1 \, dm \,, \tag{17}$$

and upon substitution into equation (14), the Gibbs-Duhem relationship, remembering that for an aqueous solution

$$\frac{N_1}{N_2} = \frac{55.51}{\nu \, m} \,,$$

there results an expression

$$d \frac{\ln}{\nu} a_2 = - dh - (h-1) d \ln m \,. \tag{18}$$

Since by definition

$$a\pm = (a_+^{\nu+} + a_-^{\nu-})^{1/\nu}$$

and

$$a_2 = a_+^{\nu+} + a_-^{\nu-} \,,$$

then

$$d \ln a_2 = \nu \, d \ln a\pm \,.$$

Also since

$$m\pm \equiv m(\nu_+^{\nu+} \nu_-^{\nu-})^{1/\nu} \,,$$

then $\ln m\pm = \ln m + \text{constant}$

and $d \ln m\pm = d \ln m$.

Substitution of these two results into equation (18), subtracting d ln $m\pm$ from both sides, integrating, and changing to common logs, yields the desired equation

$$(19) \qquad \log \gamma\pm = \frac{-h}{2.303} - \frac{2}{2.303}\int_{0}^{m} \frac{h}{m^{\frac{1}{2}}}\, dm^{\frac{1}{2}} .$$

The second term can be easily evaluated by plotting $h/m^{\frac{1}{2}}$ versus $m^{\frac{1}{2}}$ and determining the area under the curve.

The advantage of this equation over the original Gibbs-Duhem equation is that although an empiricle extrapolation is necessary, the function $h/m^{\frac{1}{2}}$ will tend toward a finite limit at $m^{\frac{1}{2}} = 0$.

Lewis and Randall have indicated that the plot is so sensitive, even minute defects in the experimental measurements are very noticeable. They have claimed at the time of introduction of this method there was no existing data for dilute solutions of sufficient accuracy to warrant its full application.

The above method of Randall and White was used by Sinclair for determining the activity coefficients of their standard potassium chloride solution from the vapor pressure measurements of these solutions obtained by the isopiestic method.

The Osmotic Coefficient Concept

An alternate derivation of equation (19), which is based on the use of a quantity called the osmotic coefficient, was presented by Bjerrum (34) at about the same time as the method above was outlined by Randall and White. Bjerrum was led to this result by the following reasoning.

In dilute solutions where the solvent is preponderant, the activity coefficient of the solvent, γ_1, is subject to a practical numerical disadvantage, in that it varies only slightly from unity. To obtain a more sensitive measure of the nonideality of solutions in terms of the solvent Bjerrum introduced the concept of the osmotic coefficient. For convenience, two osmotic coefficients were defined. The rational osmotic coefficient, g, in terms of mole fraction of the solvent, was defined as

$$(20) \qquad \mu_1 = \mu_1^{\circ} + g\,RT \ln N_1 \;;$$

and the practical osmotic coefficient, ϕ, in terms of molality of the solute, was defined as

$$(21) \qquad \mu_1 = \mu_1^{\circ} - \phi\,RT \frac{M_1}{1000} \sum m_i \,,$$

where $\sum m_i$ refers to the sum of the molalities of all ions present in solution, and M_1 is the molecular weight of the solvent. This coefficient is equivalent to the van't Hoff factor, i, divided by ν , the number of ions in solution per molecule of solute.

From the definition of the chemical potential in terms of the activity concept (equation 13), it can be seen by comparison with the definition of the practical osmotic coefficient that for a single electrolyte

$$\ln a_1 = -\phi \nu m \frac{M_1}{1000} \quad . \tag{22}$$

This expression relates the activity of the solvent with the practical osmotic coefficient.

It can easily be shown that in dilute solutions ϕ and g are equal, i.e. the two osmotic coefficients are identical.

The immediate importance of the practical osmotic coefficient lies in its relationship to the mean activity coefficient of an electrolyte.

Differentiating equation (22) to obtain d ln a_1 and substituting in the Gibbs-Duhem equation in the form

$$d \ln a_1 = \nu m \frac{M_1}{1000} \, d \ln a_\pm \tag{23}$$

leads to the important relationship first derived by Bjerrum for the relation between the practical osmotic coefficient and the mean activity coefficient

$$d \ln \gamma_\pm = -(1 - \phi) \, d \ln m + d\phi \quad . \tag{24}$$

Examination of this equation after integration will immediately show that if the quantity $(1 - \phi)$ is defined as h, the divergence function of Lewis and Randall, there results an equation identical to that of Randall and White, namely

$$\ln \gamma_{\pm} = -2 \int_{0}^{m} \frac{(1 - \phi)}{m^{\frac{1}{2}}} \, dm^{\frac{1}{2}} - (1 - \phi). \tag{25}$$

The osmotic coefficient is readily adaptable to calculations of activity coefficients derived from isopiestic measurements. The condition for equilibrium of two isopiestic solutions is that the partial molal free energy of the solvent is the same in each solution, or from equation

$$\phi \nu m = \phi_R \nu_R m_R \,, \tag{26}$$

where ϕ, ν, m refer to the experimental electrolyte and ϕ_R, ν_R, m_R refer to the reference electrolyte.

The importance of the above relationship is obvious, for if the osmotic coefficients for a reference substance are known over a range of concentrations, the osmotic coefficients of another electrolyte can be derived from isopiestic measurements without actually determining the vapor pressures.

The preceeding method of Randall and White for determining activity coefficients is a graphical procedure and treats the activity concept wholly as a thermodynamic quantity which is evaluated from observable properties of a solution.

This treatment involves no theory, for the activity is defined in terms of the chemical potential by the expression $\mu = \mu_0 + RT \ln a$; and its experimental determination depends ultimately on this definition.

The main difficulty in the method of Randall and White involves the extrapolation to zero concentration. Since in this region small errors in experimental measurements or in the graphic integration affect the value of the activity coefficient thus calculated, it is desirable to supplement experimental data in this low concentration region with data calculated without recourse to experiment from a theory of electrolytic solutions.

Such a theory has been proposed by Debye and Hückel. Although the theory is severely limited, it is an important advance in understanding the nature of electrolytic solutions.

The Debye-Hückel Theory

The modern quantitative treatment for the investigation of the departure of electrolytic solutions from ideal behavior is mainly due to the work of Debye and Hückel. Their theory is based on the assumption that strong electrolytes are completely dissociated into ions; and observed deviations from ideal behavior are, therefore, thought to arise from electrical interactions between these ions.

This assumption was not original to Debye and Hückel, since many investigators prior to their work were of the view that the behavior of strong electrolytes in dilute solutions could be accounted for by the hypothesis of complete dissociation and an adequate consideration of the effects of interionic attraction. Among the first of these investigators who were of this opinion were Noyes (1904), Sutherland (1906) and Bjerrum (1909). Milner (1912) was the first to devise a mathematical treatment for these ionic interactions; however, it was exceedingly involved and did not give entirely satisfactory results.

General Treatment

The essential concept of the Debye-Hückel theory is that every ion may be considered as being surrounded by an ionic atmosphere of opposite sign.

In general, the theory first involves the formulation of distribution functions for the treatment of an ionic solution in equilibrium. The next step is the calculation of the average electrical potential, ψ, of an ion in solution due to all other ions. This calculation was successfully made by Debye with the use of Poisson's equation borrowed from the science of electrostatics. From the value of ψ, the work necessary to charge the ion reversibly to this potential can be evaluated. This work is considered to be the extra free energy of the solution due to the electrostatic interactions.

The basic assumptions utilized by Debye and Hückel in advancing their theory were:

(a) Only coulombic forces are important in interionic interactions; all other forces are negligible.

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

(c) Ions are regarded as point charges. They, therefore, possess a spherical coulombic field.

(d) The interionic attraction energy is much smaller than the energy of thermal motion.

(e) Strong electrolytes are completely dissociated.

<u>The Distribution Function</u> (35)

As previously stated, the idea underlying the modern theory of electrolytes is that the presence of any particular ion at a given point in the solution will affect the chance of finding any other ion at a nearby point; that is, the space distribution of ions cannot be entirely random.

Let two volume elements dV_1, equaling $dx_1 \cdot dy_1 \cdot dz_1$, and dV_2, equaling $dx_2 \cdot dy_2 \cdot dz_2$, in the solution be located by vectors r_1 and r_2 drawn from an arbitrary origin. The second is located from the first by the vector

$$r_{21} = r_2 - r_1 = -r_{12} \ .$$

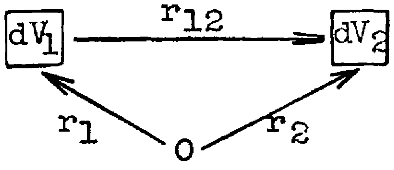


FIGURE 1

It is postulated that the presence of an ion of a given species will affect the ionic concentrations in its vicinity. This is indicated by writing n_{ji} for the time average concentration (ion per cc) of i-ions in the neighborhood of a j-ion in dV_1 and n_{ij} for j-ions in the neighborhood of an i-ion in dV_2. These concentrations will, in general, depend on several variables.

(a) They will depend on the distance r between the i-ion and the point where the concentration of the i-ion is sought, and vice versa;

(b) When forces act on the ion, a particular direction in space is specified; and n_{ji} or n_{ij} will then depend on the direction of r.

From consideration of the volume elements shown in Figure 1, a distribution function can be defined as

$$(27)\quad f_{ji}(r_1, r_{21}) = n_j n_{ji}(r_1, r_{21}) = n_i n_{ij}(r_2, r_{12}) = f_{ij}(r_2, r_{12}).$$

This relationship indicates that f_{ji} is the concentration (ions per cc) of i-ions at a distance r_2, from the j-ion multiplied by n_j, the number of ions per cc of the kind j, located in space by r_1. From the above, it is seen that f_{ji} is the concentration of the i-ions in the atmospheres of n_j ions of the kind j.

In the above function n_j and n_i are known; however, n_{ji} and n_{ij} must be found from further statistical considerations.

From the physical picture created above, every ion can thus be thought of as being associated with an ionic atmosphere of opposite sign. The net charge of the atmosphere will be of equal magnitude to the charge of the ion. In an electrolytic solution, undisturbed by external forces, the field around an ion is the same in all directions and is, therefore, a function of a distance, r, and not the direction. The ionic atmosphere will possess spherical symmetry, and the charge density of the atmosphere will decrease with increasing distance from the central ion. For a solution in which the ions are in equilibrium, it is assumed that the Maxwell-Boltzmann distribution function for particles in a field of varying potential energy is applicable.

Utilization of this distribution function will give the concentration of an ion in the neighborhood of another ion as

$$n_{ji} = n_i \, e^{-\psi_j e_i/kT} \tag{28}$$

and

$$n_{ij} = n_j \, e^{-\psi_i e_j/kT} ,$$

where n_i and n_j are the total number of i and j ions, respectively, in a unit volume of solution, e_i or e_j is the charge on the i or j-ion, respectively, ψ_j or ψ_i is the time average of the electrical potential in the center of the volume element, k is the Boltzmann constant, and T is the absolute temperature.

The product $\psi_j e_i$ in the exponential function of the above relationship is equivalent to the potential energy of the central ion, which in this specific case is an i-ion. This potential energy is equal to the work required in charging the i-ion in a field of potential ψ_j. This reasoning is based on the assumption that the average force acting on the i-ion is given by the potential of the j-ion. This is equivalent to assuming a linear superposition of the fields.

These distribution functions are an average value for the concentrations of the i and j-ions diminished by the Boltzmann factor. The Boltzmann factor is a relationship between the coulombic tendency to bring unlike charges together and the thermal tendency to mix all ions regardless of sign.

Determination of the Potential Function

From electric field theory we know that a system of electrostatic charges gives rise to an electrostatic potential.

An ion of charge e_i in a liquid of dielectric constant D possesses an electrical potential e_i/Dr at a distance r from the ion.

In a solution containing an electrolyte, ionic atmospheres are formed, and the fields of the ions derivable from the potential are assumed to superpose. The potential due to the ion and its atmosphere is defined as ψ.

In a medium containing electrical charges subject to coulombic forces, the relationship between the charge density, ρ, and the potential is given by Poisson's equation as

(29) $$\nabla^2\psi = \frac{-4\pi\rho}{D} .$$

In terms of spherical coordinates this equation may be written as

$$\frac{1}{r^2}\frac{\partial\left(r^2\frac{\partial\psi}{\partial r}\right)}{\partial r} = \frac{-4\pi\rho}{D} .$$

Because of the symmetry properties of the specialized point charge problem, the terms involving $\partial\psi_j/\partial\phi$ and $\partial\psi_j/\partial\theta$ are equal to zero.

The above equation states that at any point in the medium located by three space coordinates (r_1, ϕ_1, θ_1), the total outward flux of the force at this point is proportional to the charge density at this point.

The charge density at some point in the electrolytic medium, i.e. in the unit volume located at a distance r from the central ion, can be formulated as

$$\rho = \sum_{i=1}^{s} e\ z_i n_{ji} .$$

Upon substitution for n_{ji} according to the Maxwell-Boltzmann distribution function and expanding the two exponential series in the above expression and assuming that the magnitude of $\left[e_i\psi_j/kT\right]^2$ and higher terms are negligible compared to unity, there results

$$\rho_j = \frac{-\,e^2\psi_j}{kT} \sum_{i=1}^{s} n_i z_i^2 \,, \tag{33}$$

where n_i and z_i represent the number (per unit volume) and valence of ions of the i type. The summation is taken over all kinds of ions in solution. In the above formulation we have arbitrarily chosen the central ion to be the j-ion.

The above assumption is valid only when the potential energy $z_i e\psi_j$ of the i-ion is small compared to its thermal energy. This is true for ions in dilute solution, where the central j-ion is separated by large distances from all other ions in solution. However, in concentrated solutions the ions are more closely packed, and this approximation is not valid.

In a sense, we have abandoned the Boltzmann distribution when we make this approximation; and in its place we have substituted a linear distribution function

$$n_{ji} = n_i \left(1 - \frac{e_i\psi_j}{kT}\right) \tag{33a}$$

This above assumption is very important in evaluating the Debye-Hückel expression for ions of higher unsymmetrical charge type in solution. However, it is necessary in order to validate the previous assumption of superposition of electric fields for ions in solution. This latter assumption requires that ionic potentials be additive. Since the ionic potential is directly proportional to the charge density of an ion according to Poisson's equation, then a two-fold increase in the charge density necessitates a two-fold increase in ionic potential. This requirement could not be met if the Boltzmann distribution function is retained in an exponential form. In fact, this requirement can only be met if a linear distribution function is used.

In converting the Boltzmann distribution to a linear function it is assumed that higher terms than of the order of one are negligible. This will introduce an error on the magnitude of $\left[e_i\psi_j/kT\right]^2$ in the final calculations.

For ions of symmetrical valence type $z_i = z_j$ and $n_i = n_j$, this error is not introduced since all even powers of ψ vanish in expanding the Boltzmann function. This factor accounts for the superior quantitative agreement found between experiment and theory with these types of electrolytes.

If the value of ψ_j, as formulated by equation (33), is substituted into Poisson's equation, there is obtained the relationship

(34) $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_j}{\partial r}\right) = K^2\psi_j ,$$

where

(34a) $$K = \left[\left(\frac{4\pi e^2}{DkT}\sum_{i=1}^{s} n_i z_i^2\right)\right]^{\frac{1}{2}} .$$

The above differential equation has the general solution

(35) $$\psi_j = \frac{Ae^{-Kr}}{r} + \frac{Be^{Kr}}{r}$$

but from definition $\psi_j \rightarrow 0$ as $r \rightarrow \infty$ and, therefore, B must be equal to zero; and the solution becomes $\psi_j = \frac{Ae^{-Kr}}{r}$. The constant A can readily be evaluated (31) and is of the form

(37) $$A = \frac{ze}{D} \frac{e^{K\mathring{a}}}{1 + K\mathring{a}} \text{ ,}$$

where $\mathring{a}$ represents the minimum distance of approach of any ion to the central ion. Thus, the total potential of the central ion can be expressed as

(38) $$\psi_j = \frac{ze}{D} \frac{e^{K\mathring{a}}}{1 + K\mathring{a}} \frac{e^{-Kr}}{r} \text{ .}$$

For an isolated ion in a medium of dielectric constant D, the potential at a distance r from the central j-ion would be

$$\psi_j{}' = \frac{ze}{Dr} \text{ .}$$

If the principle of linear superposition of fields is valid for ions in solution, the actual potential of the central ion would consist of the sums of $\psi_j{}'$, the potential of the isolated j-ion, and $\psi_j{}''$, the potential of the j-ion, due to the surrounding ions. This being the case, then the total potential function ψ_j as given by equation (38) can be divided into two parts:

$$\psi_j{}' = \frac{z_j e}{Dr} \tag{39}$$

and

$$\psi_j{}'' = \frac{z_j e}{Dr}\left[\frac{e^{K\mathring{a}}}{1 + K\mathring{a}} \quad e^{-Kr} - 1\right].$$

The above formulation of $\psi_j{}''$ gives that part of the potential of the central j-ion due to the surrounding ions for any distance r from the central ion. However, at a distance of $r = \mathring{a}$ no other ions can penetrate and the potential $\psi_j{}''$ is, therefore, constant for all $r < \mathring{a}$ and equal to its value at $r = \mathring{a}$

$$\psi_j{}'' = - \frac{z_j e}{D} \cdot \frac{K}{1 + K\mathring{a}} . \tag{40}$$

Determination of the Work Required to Charge an Ion to a Potential ψ_j

The free energy of a solution containing ions may be considered to be made up of two parts

$$F = F(\text{ideal}) + F(\text{elec}),$$

where F(ideal) is the free energy of an ideal solution at the same concentration as the ionic solution, and F(elec) is the free energy due to the electrical interaction of the ions.

Upon differentiating with respect to n_j, the total number of ions of the j-th kind at constant temperature and pressure, there is obtained

$$\frac{\partial F}{\partial n_j} = \frac{\partial F(\text{ideal})}{\partial n_j} + \frac{\partial F(\text{elec})}{\partial n_j}$$

or

(41) $$\mu_j = \mu_j(\text{ideal}) + \mu_j(\text{elec}) ,$$

where μ_j is the chemical potential of the j-th ion and by definition is

(13) $$\mu_j = \mu_j^{\circ} + kT \ln a_j .$$

The activity, a_j, can be defined as the product $X_j f_j$ where X_j = the mole fraction of j-th ions and f_j is a correction factor known as the activity coefficient, which is a characteristic function of a j-th ion in the given solution. Hence, equation (13) may be written as

(42) $$\mu_j = \mu_j^{\circ} + kT \ln X_j + kT \ln f_j .$$

For an ideal solution in which there is no electrical interaction between ions

$$\mu_j(\text{ideal}) = \mu_j^{\circ} + kT \ln X_j .$$

Therefore, upon comparison with equation (41)

(43) $$\mu_j(\text{elec}) = \frac{\partial F(\text{elec})}{\partial n_j} = kT \ln f_j .$$

From a knowledge of the electrical potential on the surface of an ion due to its ionic atmosphere, it is possible to calculate the work required to charge the ion to this extra potential due to electrical interactions between the ions.

Ignoring the possible small volume change in the charging process, this work can be identified with the electrical free energy of solution.

$$W(\text{elec}) = \Delta F(\text{elec})$$

The work required to charge the ions to this extra potential may be formulated as

$$W(\text{elec}) = \Delta F(\text{elec}) = \sum_{j=1}^{n_j} \int_0^{z_j e} \psi_j(e_j)de \; . \tag{44}$$

The charging process may be considered in several ways; however, the simplest method was devised by Guntelburg (36).

In this method the charging process is brought about by adding the discharged ion j to an assembly of the remaining ions in solution which already have their full charges and then gradually increasing the charge of j from zero to $z_j e$. By substituting $\psi_j(e_j)$ as expressed by equation (38) into the above equation and performing the indicated operations an expression is obtained for the activity coefficient f_j in terms of known or derivable quantities, i.e.

$$\log f_j = - \frac{N z_i^2 e^2 \; B \mu^{\frac{1}{2}}}{2(2.303)DRT} \quad \frac{1}{1+\overset{\circ}{a}B\mu^{\frac{1}{2}}} \tag{45}$$

where

$$B = \frac{2^{3/2} N \pi^{\frac{1}{2}} e}{(1000 \; DRT)^{\frac{1}{2}}}$$

$$\mu = \tfrac{1}{2}\sum_{i=1}^{s} c_i z_i^2$$

$$\overset{\circ}{a} = a \times 10^{-8}\text{cm or } \overset{\circ}{a} \text{ angstrom units} \; .$$

Since it is not possible by any experimental method to evaluate the activity coefficient of a single ionic species, the Debye-Hückel equation cannot be tested in the above form. However, it is possible to derive an expression for the mean activity coefficient, this being the quantity that is obtained experimentally.

For the general case of an electrolyte, $M_{\nu^+}A_{\nu^-}$, which dissociates in the following manner

$$M_{\nu^+}A_{\nu^-} = \nu_+ M^+ + \nu_- A^- ,$$

a mean activity coefficient, $f_\pm$ may be defined as

(46) $$f_\pm = (f_+^{\nu_+} + f_-^{\nu_-})^{1/\nu}$$

where

$$\nu = \nu_+ + \nu_-$$

From this definition of $f_\pm$ in terms of f_+ and f_-, the Debye-Hückel equation can be written as

(47) $$\log f_\pm = \frac{-Az_+z_-\mu^{\frac{1}{2}}}{1 + \mathring{a}B\mu^{\frac{1}{2}}}$$

where

$$A = \frac{1.823 \times 10^6}{(DT)^{3/2}}$$

$$B = \frac{35.57}{(DT)^{\frac{1}{2}}}$$

Activity Coefficients by the Method of Smith

A largely analytical method based on the Debye-Hückel theory was introduced by Smith (37). He formulated the

Debye-Hückel equation in terms of the osmotic coefficient. This was done by utilizing equation (24), the relation between osmotic coefficient and activity coefficient derived by Bjerrum, in the form of

$$(48) \qquad d \ln \gamma_{\pm} = \frac{1}{m} d \left\{ m(1 - \phi) \right\}$$

and the expression for the Debye-Hückel extended law in the form

$$(49) \qquad \log \gamma_{\pm} = \frac{- S_{m(f)} m^{\frac{1}{2}}}{1 + A'_m m^{\frac{1}{2}}} ,$$

where $S_{m(f)} = z_+ z_- A \, d_o^{\frac{1}{2}}$,

$A'm = \mathring{a} B \, d_o^{\frac{1}{2}}$,

d_o = density of the solvent.

Substitution of equation (48) into equation (49) will yield

$$(50) \qquad d\left\{ m(1 - \phi) \right\} = \frac{k m^{\frac{1}{2}} dm}{2(1 + A'_m m^{\frac{1}{2}})^2}$$

where $k = 2.303 \, S_{m(f)}$.

Integration of equation (50) gives

$$(51) \quad 1 - \phi = \frac{k m^{\frac{1}{2}}}{3} \left\{ \frac{3}{A'^3_m m^{3/2}} \left[1 + A'_m m^{\frac{1}{2}} - 2 \ln (1 + A'_m m^{\frac{1}{2}} - \frac{1}{1 + A'_m m^{\frac{1}{2}}} \right] \right\}$$

or $$(52) \qquad 1 - \phi = \frac{k m^{\frac{1}{2}}}{3} \sigma .$$

The function σ, defined by equation (51), can be expanded to the form

$$(53) \qquad \sigma = \sum_{n=1}^{\infty} \frac{3n}{n+2} \left(-A'_m m^{\frac{1}{2}}\right)^{n-1} ,$$

and substituting the value for k into equation (52) yields

$$(54) \qquad 1 - \phi = 0.7676\, S_{m(f)} \sigma m^{\frac{1}{2}} .$$

Smith used the above equation plus an added term, Bm/2, to represent the data at high concentrations:

$$(55) \qquad 1 - \phi = 0.7676\, S_{m(f)} \sigma m^{\frac{1}{2}} + \tfrac{1}{2} Bm.$$

This expression was used to represent experimental values of $(1 - \phi)$ as a function of concentration.

The first term of equation (55) has been shown to be derivable from the Debye-Huckel theory, but the second term is an empirical correction in which the constant B is chosen to fit the experimental results in the more concentrated solutions.

The experimental values of ϕ, calculated from isopiestic measurements, equation (26) may be smoothed by plotting the deviation, $\Delta\phi$, defined by

$$(56) \qquad \Delta\phi = -(1 - \phi) + 0.7676\, S_{m(f)} \sigma m^{\frac{1}{2}} + \tfrac{1}{2} Bm$$

against m or $m^{\frac{1}{2}}$. Numerical values of A'_m and B are chosen so that the deviation is not large at any concentration.

Substituting $(1 - \phi)$, as defined in the above equation for the deviation function, into Bjerrum's equation,

equation (24), and integrating we obtain

$$(57)\quad \ln \gamma_{\pm} = \frac{-\,2.303\, S_{m(f)}\, m^{\frac{1}{2}}}{1 + A'_m\, m^{\frac{1}{2}}} - Bm + \int_0^m \frac{\Delta\Phi}{m}\, dm + \Delta\Phi\,.$$

The two terms containing $\Delta\Phi$ are evaluated graphically.

Extension of the Method of Lewis and White in Dilute Solutions

From equation (25), which is identical to that of Lewis and White, but in terms of the osmotic coefficient, we can complete the plot of $1 - \Phi/m^{\frac{1}{2}}$ versus $m^{\frac{1}{2}}$ from about 0.1 m to infinite dilution by using the Debye-Hückel extended equation in the form

$$(58)\qquad \frac{(1 - \Phi)}{m^{\frac{1}{2}}} = 0.7676\, S_{m(f)}\, \sigma\,.$$

However, in order to use the above equation, it is necessary to evaluate A'_m in order to calculate σ. A'_m was defined as

$$A'_m = \mathring{a} B'\, d^{\frac{1}{2}}\,.$$

Since $\mathring{a}$ is usually unknown, a value of A'_m is selected by trial which will make equation (58) fit the experimental data at the lowest concentration. Using this value for A'_m the above equation will then allow the calculation of values for $(1 - \Phi)/m^{\frac{1}{2}}$ in that region where experimental values cannot be obtained accurately.

The Onsager Conductance Equation

The interionic attraction theory was also applied by Debye and Hückel (38) to the electric conductivity of solutions.

A more exact mathematical treatment was later developed by Onsager and Fuoss (35). The theory presented here will follow closely the quantitative treatment developed by Onsager and Fuoss.

The fundamental physical concepts upon which the mathematical theory was developed are as follows.

If an ion is moved through the solution by means of an external field, it will tend to move away from its atmosphere. However, the displaced ion will still attract the lagging atmosphere which will continue to form around the ion as it moves. The formation of the ionic atmosphere will take a certain time. This finite time is termed the time of relaxation of the ionic atmosphere. Thus, because of this finite time, the density in front of the ion will be somewhat smaller than the equilibrium value, while behind the ion it will not yet have fallen to its equilibrium value. Hence, during motion there will always be a somewhat greater electrical density behind the ion than in front of it. This will result in an asymmetrical charge distribution superimposed upon the original symmetrical ionic atmosphere. Since the ion and its atmosphere are always of opposite charge, there results a force which tends to oppose the motion of the ion. This effect has been termed the asymmetry effect.

A second effect which opposes the motion of an ion under the influence of an external field is the electrophoretic effect. This phenomenon arises in the following way. When an ion or its associated solvent molecules move in a solution under the influence of an applied potential, there is an opposing force which tends to move the ionic atmosphere and its associated solvent molecules in a direction opposite to that of the ion. Hence, the ion is not moving relative to a stationary solvent but relative to a solvent streaming in the opposite direction. This effect will be concentration dependent since the distance between the ions is of importance.

The problem of conductance was treated by Onsager as a problem of ions migrating in a general homogeneous field of forces; that is, external forces k_i, k_j (per ion) acting on ions of species i and j, respectively, and a balancing force k_o

$$n_o k_o = - n_i k_i - n_j k_j \tag{59}$$

acting on the molecules of the solvent.

He has shown through thermodynamic arguments that this system of forces is equivalent to an arbitrary combination of a homogeneous electric field $E = - \nabla \Psi$ and uniform concentration gradients $\nabla n_i, \nabla n_j$, subject to the restriction of electrical neutrality

$$e_i \nabla n_i + e_j \nabla n_j \equiv (n_i e_i + n_j e_j) = \cdot \nabla (0) = 0 \text{ ,}$$

the same as those caused by the system of forces k_o, k_i, k_j.

Electrophoretic Effect

The electrophoretic effect is due to a volume force operating in the liquid that surrounds an ion. If the average concentration of j-ions is n_j, the average applied force on the ions contained in a unit volume of solution is

$$n_i k_i + n_j k_j = n_\sigma k_\sigma ,$$

where σ indicates summation. This force is transferred to the n_o solvent molecules per unit volume of solution, and the equilibrium condition can be written

$$n_\sigma k_\sigma + n_o k_o = 0 .$$

The force acting on the ions in an element of volume dV near a j-ion is $n_{j\sigma} k_\sigma$ dV because the presence of a j-ion changes the average concentration of i-ions in dV by electrostatic interaction. The force on the solvent remains $n_o k_o$ dV, and the net force acting on dV is

$$(60) \qquad (n_{j\sigma} k_\sigma + n_o k_o) dV = (n_{j\sigma} - n_\sigma) k_\sigma dV$$

in spherical coordinates (j-ion at origin), $dV = r^2 dr d\Omega$ so that the force acting on a spherical shell of solution at a distance r from the central ion is

$$(64) \qquad F = 4\pi r^2 (n_{j\sigma} - n_\sigma) k_\sigma dr .$$

The force is uniformly distributed over the shell and is in the direction of the applied force k. This distribution of forces is the same as that acting on a solid sphere of radius r moving through a liquid of viscosity η. Therefore, Stokes' Law is applicable:

$$v = \frac{F}{6\pi \eta r}, \tag{62}$$

and a force F, applied as above, will cause all points in the interior of the spherical shell to move with the same velocity, v.

In order to calculate the force density, the quantity $(n_{j\sigma} - n_\sigma)$, must be obtained as a function of r.

This quantity can be evaluated from the expanded Boltzmann distribution function in terms of Debye's ionic potentials. Having obtained this quantity, and using Stokes' Law, the total velocity of the entire ionic atmosphere can be formulated as

$$v_j = -\frac{2}{3} \frac{e_j e_\sigma n_\sigma k_\sigma}{DkT\, K(1 + K\mathring{a})}. \tag{63}$$

For an electrical force where $k_j = Xe_i$ and $K\mathring{a}$ is small (dilute solutions), substitution of the definition of K, equation (34a) in the above expression yields

$$v_j = -\frac{Xe_j K}{6\pi\eta}, \tag{64}$$

which is the formulation for velocity of the medium in a direction opposite to the motion of the central j-ion under an external force Xe_j.

The Equations of Motion

The factors that cause the ions to move can be reduced to three: (a) forces on the ions, (b) thermal (random) motion, and (c) flow of solution. The forces which influence the ions may be external (outside electrical field), and internal (concentration gradients and electrostatic forces due to the presence of the ions themselves). If the mobility of an ion is w_i, then a force, K_i, acting upon it will produce a velocity equal to $K_i w_i$. Mobility as used above is defined as reciprocal of the frictional resistance of the medium on the moving ion; $w_i = 1/\rho$, where ρ is the coefficient of friction. This definition comes about from the fact that an object moving through a continuous medium encounters a retarding force which is proportional to its velocity, the proportionality constant being equal to ρ .

If the diffusion constant for an ion is taken to be kTw, then a concentration gradient ∇f will produce a current strength $-kT\, w \nabla f$. Since this current is equal to vf (velocity x concentration), the diffusion velocity is $-kT\, w \nabla \ln f$. If we neglect any actual flow of solution, then we can formulate the total velocity, v_{ji} and v_{ij} at a point located by r_2 and r_1, respectively, as

$$v_{ji} = w_i(K_{ji} - kT \nabla_2 \ln f_{ji}), \tag{65}$$

and, similarly

$$v_{ij} = w_j(K_{ij} - kT \nabla_1 \ln f_{ij}).$$

The Time Rate of Change of the Distribution Function

The time rate of change of the distribution function was obtained by Onsager by determining the difference between the influx and outflow of ions for any pair of faces for an imaginary six-dimensional element of volume. The treatment is essentially the same as that used in describing the kinematics of moving fluids. From this treatment there is developed an equation of continuity,

$$(66)\quad -\frac{\partial f}{\partial t}(r_1, r_{21}) = \nabla_1 \cdot (f_{ij} v_{ij}) + \nabla_2 \cdot (f_{ji} v_{ji}) = -\frac{\partial f}{\partial t}(r_2, r_{12}),$$

where v_{ji} = the velocity of an i-ion in the neighborhood of a j-ion,

$$v_{ji} = v_{ji}\,(r_1, r_{21}).$$

Similarly,

$$v_{ij} = v_{ij}\,(r_2, r_{12})$$

and the quantities f_{ij} and f_{ji} are defined by equation (27).

Perturbation of Ionic Atmospheres

When a force acts upon a solution of an electrolyte, there will exist a preferred direction and both the distribution function and the ionic potentials will become asymmetric. Therefore, it is possible to write

$$(67)\quad \begin{aligned} \psi_j &= \psi'_j(r_1, r_{21}) + \psi^o_j\,(r) \\ f_{ji} &= f'_{ji}(r_1, r_{21}) + f^o_{ji}(r)\,, \end{aligned}$$

where the primed terms represent the small changes brought about by the perturbation (perturbation terms).

If it is assumed that the applied forces are small, then the perturbation terms will be proportional to the force.

The asymmetric addition to the potential ψ'_j is related to f'_{ji} by the Poisson equation

$$\nabla^2 \psi'_j = \frac{-4\pi}{D} \sum_i \frac{f'_{ji} e_i}{n_j} .$$

Since the perturbing force sets up an irreversible process in solution, the distribution is no longer given by the Boltzmann equation. Therefore, the general condition, equation (73), must apply since v_{ji} no longer gives an average of zero. If a linear superposition of the potentials and charge densities is assumed for the asymmetric addition terms, it is possible to compute the field due to two ions. For the total force K_{ji} acting on an i-ion in the vicinity of a j-ion we have

(68) $K_{ji} = k_i - e_i \nabla_2 \psi'_i\,(0) - e_i \nabla_2 \psi_j(r_1, r_{21})$,

where k_i is the applied external force, $-e_i \nabla_2 \psi'_i\,(0)$ is the force on the i-ion due to the i-ion's own atmosphere (the potential at the point occupied by the i-ion, $r = 0$), and $-e_i \nabla_2 \psi_j(r_1, r_{21})$ is the force on the i-ion due to the potential of the j-ion and its atmosphere (with the j-ion taken as the origin).

If one substitutes the total force, K_{ji}, as expressed above, into the equation of motion (equation 65), multiplies by f_{ji}, and takes the divergence, then

$$(69)\quad \nabla_2(f_{ji}v_{ji}) = \nabla_2\cdot \Big[w_i(f_{ji}k_i - e_i f_{ji}\nabla_2 \psi'(0) - e_i f_{ji}\nabla_2 \psi_j - kT\nabla_2 f_{ji})\Big] .$$

The applied force k_i is constant and, therefore, the term $\nabla_2\cdot k_i = 0$ when the above expression is expanded. According to Debye and Hückel the potential of an undisturbed ion and its atmosphere is $\psi^o_i = \frac{e_i}{D}\frac{e^{-Kr}}{r}$.

Hence, the term in the above expression involving $\nabla_2 \psi'_i(0)$ may be neglected since it is of the order of e_i^2 while the other terms are of the order e_i. The f_{ji} in the $-e_i f_{ji}\nabla_2\psi_j$ term can be replaced by $n_j n_i$ since $f_{ji} - n_j n_i \sim e_i$, according to the expanded Boltzmann distribution function, and the term already has a coefficient of e_i.

Since $\nabla_2 n_j n_i$ is zero, then this term will reduce to $\nabla_2\cdot e_i w_i n_j n_i \nabla_2 \psi_j$. Upon making these reductions, the above equation reduces to

$$(70)\quad \nabla_2(f_{ji}v_{ji}) = w_i(k_i\cdot \nabla_2 f_{ji}) - e_i w_i n_j n_i \nabla_2\cdot\nabla_2\psi_j - w_i kT\nabla_2\cdot\nabla_2 f_{ji}.$$

Similarly,

$$\nabla_1(f_{ij}v_{ij}) = w_j(k_j\cdot\nabla_1 f_{ij}) - e_j w_j n_j n_i\nabla_1\cdot\nabla_1\psi_i - w_j kT\nabla_1\cdot\nabla_1 f_{ij} .$$

If one substitutes the perturbation terms for f_{ji}, f_{ij}, ψ_i and ψ_j in these equations, noting that for $k_i = 0$ or $k_j = 0$, $v_{ji} = 0$ or $v_{ij} = 0$, the steady state terms f^o and ψ^o must cancel one another. And, if one substitutes these resulting expressions into the general equation of continuity, there is obtained a final equation of continuity specialized to suit the problem of irreversible processes in electrolytic solutions, namely

$$\begin{aligned} (71)\quad -\frac{\partial f_{ji}(r_1,\ r_{21})}{\partial t} &= \frac{\partial f_{ij}(r_2,\ r_{12})}{\partial t} = w_i(k_i \cdot \nabla_2 f_{ji}) \\ &+ w_j(k_j \cdot \nabla_1 f_{ij}) - e_i w_i n_j n_i \nabla_2 \cdot \nabla_2 \psi'_j - e_j w_j n_i n_j \nabla_1 \cdot \nabla_1 \psi'_i \\ &- w_i kT \nabla_2 \cdot \nabla_2 f'_{ji} - w_j kT \nabla_1 \cdot \nabla_1 f'_{ij} \ . \end{aligned}$$

As mentioned earlier since the external forces are of a small enough magnitude, i.e. the electrolyte is in an alternating field of such a low frequency, the charge distribution in the ionic atmosphere at any moment will correspond to the instantaneous velocity of the ion. For such a specialized case, it is possible to approximate f in the first two terms of equation (71), by f^o. Likewise, because the external force is constant, then f_{ji} and f_{ij} do not vary with time and

$$-\frac{\partial f_{ji}}{\partial t}(r_1,\ r_{21}) = 0 \ .$$

The Asymmetry Effect

This effect can be evaluated with the aid of the general equation of continuity, specialized for the case of a stationary field (constant external force)

$$(72)\quad w_i(k_i \cdot \nabla_2 f^o{}_{ji}) + w_j(k_j \cdot \nabla_1 f^o{}_{ij}) - e_i w_i n_j n_i \nabla_2 \cdot \nabla_2 \psi'_j$$

$$- e_j w_j n_i n_j \nabla_1 \cdot \nabla_1 \psi'_i$$

$$- w_i kT \nabla_2 \cdot \nabla_2 f'_{ji} - w_j kT \nabla_1 \cdot \nabla_1 f'_{ij} = 0 .$$

The first two terms of this equation contain the perturbing factor k, and the last four represent the asymmetric contributions to potential and distribution thereby produced.

From consideration of the symmetry conditions, $r_{12} = - r_{21}$, and from the definition

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \quad \text{or} \quad \nabla = \frac{\partial}{\partial x} ,$$

considering only the rate of change along the direction of the applied external force, it is possible to reduce the above equation to

$$(73)\quad (w_i k_i - w_j k_j)\frac{\partial f^o{}_{ji}}{\partial x} - e_i w_i n_i n_j \nabla_2 \cdot \nabla_2 \psi'_j + e_j w_j n_i n_j \nabla_1 \cdot \nabla_1 \psi'_i$$

$$- (w_i + w_j) kT \nabla_2 \cdot \nabla_2 f'_{ji} = 0 .$$

For the specialized problem of a single electrolyte which yields two ions, i and j, in a stationary field, the general procedure for the calculation of the asymmetric addition to the potential of the ion is obtained in the following manner. By means of the Poisson equation

$$\nabla^2 \psi'_j = -\frac{4\pi}{D} \sum_i \frac{e_i}{n_j} f'_{ji}$$

The asymmetric addition to the distribution function may be eliminated from equation (73). Also, by means of equation (27), which defines the steady state distribution function, we can eliminate f^o_{ji} from this equation. If k_i and k_j are replaced by Xe_i and Xe_j, where X is the X-component of the external field, and since $\psi'_i = \psi'_j$ from the condition of electrical neutrality of solutions the above equation will reduce to

$$(74) \quad (\nabla \cdot \nabla)^2 \psi'_i - K_j^2 \nabla \cdot \nabla \psi'_j = \Omega K_j^2 \frac{\partial}{\partial x} \left(\frac{e}{r}^{-Kr}\right),$$

where

$$K_j^2 = q^* K^2$$

$$q^* = \frac{e_j w_j - e_i w_i}{(e_j - e_i)(w_j + w_i)}$$

and

$$\Omega = \frac{X e_j e_i}{DkT} \quad .$$

Integration of this equation yields

$$\psi'_j = \frac{\Omega K^2{}_j x}{K^2 - K^2{}_j} \left\{ -\left(\frac{K - K}{3}{}_j\right) + \left(\frac{K^2 - K^2}{8}{}_j\right) r - \dots \right\}.$$

From this result the field strength (the divergence of the potential) ΔX_j at the central ion j (r = 0) due to the perturbation of the atmosphere is

$$(75) \qquad \Delta X_j = \frac{e_j e_i}{3DkT} \left(\frac{q^*}{1 + q^*}\right) KX \quad .$$

General Equation for the Conductance of an Electrolyte which Dissociates into Two Kinds of Ions

From this calculation of the effect on the potential of the central ion by an asymmetric atmosphere superimposed on the original symmetrical atmosphere and the effect of electrophoreses on the velocity of the central ion, a general formulation can now be derived to represent the conductance of an electrolytic solution.

The total field acting on the central ion is $X + \Delta X_j$ and because of the electrophoretic effect, the velocity of the ion in the x-direction will be less than $e_j w_j (X + \Delta X_j)$. It will, in fact, be

(76) $$v_j = X\left(e_j w_j + \frac{\Delta X_j e_j w_j}{X} - \frac{e_j K}{6\pi\eta}\right) ,$$

upon introduction of the previously calculated counter-current velocity Δv_j. The mobility, u_j, is the velocity of the ion under a potential gradient of unity, i.e. one volt per centimeter.

(77) $$u_j = \frac{|v_j|}{X} ,$$

or in practical units, volts,

$$\bar{u}_j = \frac{1}{300}\left[|e_j| w_j + \frac{\Delta X_j}{X} e_j w_j - \frac{|e_j| K}{6\pi\eta} \right].$$

In the limit of low concentration, the interactions between ions may be neglected and the mobility will depend only upon the resistance offered by the solvent. Thus, the mobility of an ion at infinite dilution in practical units can be formulated as

$$\bar{u}_j^{o} = \frac{|e_j|\, w_j}{300} .$$

The ionic conductance, λ_j, is proportional to the ionic mobility, $\bar{u}_j$. The proportionality constant is equal to F, the Faraday

$$\lambda_j = F\, \bar{u}_j .$$

If these above equations and K, as defined in equation (34a), are substituted for the mobility $\bar{u}_j$, there is obtained

$$\lambda_j = \lambda_j^{o} + \frac{\Delta X_j}{X}\, \lambda_j^{o} - \frac{29.16\, |Z_j|\, \Gamma^{\frac{1}{2}}}{\eta\, (DT)^{\frac{1}{2}}} . \tag{78}$$

This equation can be simplified by introducing the value of $\Delta X_j/X$ derived for the asymmetric potential, equation (75), and evaluating the constants. Likewise, an identical equation may be derived for the i-ion. Addition of the two resulting expressions will give an expression representing the conductance of both kinds of ions in the electrolyte

$$\Lambda = \Lambda^{o} - S\, \Gamma^{\frac{1}{2}}, \tag{79}$$

where

$$S = \frac{1.981 \times 10^{6}}{(DT)^{3/2}} \left(\frac{q^{*}}{1 + q^{*}}\right) Z_1 Z_2 \Lambda^{o} + \frac{29.16(|Z_1| + |Z_2|)}{\eta\, (DT)^{\frac{1}{2}}} \tag{80}$$

and

$$q^{*} = \frac{Z_1 Z_2}{(|Z_1| + |Z_2|)} \; \frac{\lambda_1^{o} + \lambda_2^{o}}{(|Z_2|\, \lambda_1^{o} + |Z_1|\, \lambda_2^{o})} . \tag{81}$$

This can be written in terms of molar concentrations, since

$$\Gamma = c\left[\nu_i z_i^2 + \nu_j z_j^2\right].$$

For the special case of the conductance of an electrolyte in an aqueous solution at 25°C, the resulting expression is

$$\Lambda = \Lambda^{\circ} - (\alpha^* + \beta^* \Lambda^{\circ})\, c^{\frac{1}{2}}\,, \tag{82}$$

where

$$\alpha^* = 0.2289\, w'Q$$

$$\beta^* = 60.19\, w^*$$

and

$$Q = \frac{q^*}{0.2929(1 + q^{*\frac{1}{2}})}$$

$$w' = |Z_1 Z_2|\left(|Z_1 Z_2| \frac{\nu}{2}\right)^{\frac{1}{2}}$$

$$w^* = \left(\frac{|Z_1| + |Z_2|}{2}\right)\left(\frac{\nu\, |Z_1 Z_2|}{2}\right)^{\frac{1}{2}}$$

q^* is as defined by equation (81).

3 - APPARATUS AND PROCEDURE

I. Preparation of Compounds

A. Preparation of Potassium Tetracyanoplatinate (II), $K_2Pt(CN)_4$ (39).

Preparation of Hexachloroplatinic (IV) Acid Hexahydrate: Platinum metal is dissolved in aqua regia and evaporated to dryness upon a hot plate. The residue thus obtained is dissolved in hydrochloric acid and evaporated to dryness three times to insure complete removal of the nitric acid, after which it is dissolved in water and filtered. The filtrate is evaporated on a hot plate, and the last traces of water are removed by drying over sulfuric acid in a vacuum. The product thus obtained is the red-brown hexachloroplatinic (IV) acid 6-hydrate, $H_2PtCl_6 \cdot 6H_2O$.

Preparation of Platinum (II) Chloride, $PtCl_2$ (40): 10.6 grams of $H_2PtCl_6 \cdot 6H_2O$ is dissolved in 50 milliliters of water. 1.07 grams of solid hydrazine dihydrochloride are added in small portions to the solution. There is an effervescence with each addition. The total time of addition is approximately five minutes. The resulting cherry red solution is warmed until bubbling stops, filtered and evaporated to dryness on the steam bath. The chocolate brown residue is dried for twelve hours at 112°C and then pulverized, after which it is dried for four more hours at 150°C. These drying operations remove the hydrogen chloride. Unreduced platinum (IV) chloride and the remaining traces of H_2PtCl_6 are removed by warming the solid on a steam bath with 10 milliliters of water and decanting through a filter. This decantation is repeated four times, and the product is poured on the filter with the last extract. It is then washed with a few milliliters of cold water and dried at 110°C for two hours.

Preparation of Potassium Tetracyanoplatinum (II), $K_2Pt(CN)_4$: The $PtCl_2$ is added slowly over a long period of time to a cold concentrated solution of potassium cyanide. Since there is a violent reaction at the surface of the reaction mixture which may cause some spattering, the $PtCl_2$ is added in small portions. The reaction mixture is heated to boiling and filtered. The solution is then placed in an ice bath. At this temperature yellow, needle-shaped crystals of $K_2Pt(CN)_4 \cdot 2H_2O$ are formed. The salt thus obtained is purified by repeated recrystallization from an aqueous medium. The crystals are collected on a filter and dried over phosphorous pentoxide in vacuo. The desired product is the white dehydrated $K_2Pt(CN)_4$.

B. Preparation of Tris(1,2-propylenediamine)platinum (IV) Chloride Monohydrate, $Pt(pn)_3Cl_4 \cdot H_2O$ (41).

A solution of 10 grams $H_2PtCl_6 \cdot 6H_2O$, prepared as described above, in 50 milliliters of absolute ethyl alcohol is made. Ten grams of 1,2-propylenediamine monohydrate is added to the above solution which has been placed in an ice bath. At this point a yellow precipitate of $C_3H_6(NH_3)_2PtCl_6$ appears. The reaction mixture is then placed on a steam bath for approximately one-half hour. Next, the solution is removed and cooled. It is then filtered and the precipitate is washed with a mixture of 50 per cent ethyl alcohol-50 per cent ethyl ether and then with pure ethyl ether. The product is dissolved in water and recrystallized. Several recrystallizations are necessary in order to obtain the pure product. A yellow colored impurity of much greater solubility than the desired product concentrates in the filtrate after each recrystallization. The desired product is pure white and is colorless upon dissolution. The salt is slightly soluble in water and also slightly soluble in absolute ethyl alcohol. It is dried at room temperature and is not hygroscopic.

C. Preparation of Tetramethylammonium Octacyanomolybdate(IV) Dihydrate, $[N(CH_3)_4]_4Mo(CN)_8 \cdot 2H_2O$.

Preparation of Potassium Octacyanomolybdate (IV) Dihydrate, $K_4[Mo(CN)_8] \cdot 2H_2O$ (42): Fifty grams of molybdenum (VI) oxide, MoO_3, is dissolved in a solution of 40 grams of potassium hydroxide in 100 milliliters of water. To this solution, 250 milliliters of hydrochloric acid is added and placed on a steam bath. A concentrated solution of potassium thiocyanate is added slowly with constant stirring. The resulting deep red solution is diluted with 300 milliliters of water and left on the bath for two hours, with constant stirring. The solution is filtered while warm, and pyridine is added until a yellow solid begins to separate. The mixture is placed in an ice bath until the red oily product has settled out and becomes very viscous. The supernatant liquid is decanted, and the product is washed twice with water.

The oily pyridine compound is treated with 200 grams of potassium cyanide in 300 milliliters of water. The pyridine compound dissolves, giving first a green and finally a yellow-brown solution. The solution is heated on a water bath with constant stirring for one-half hour. A black residue is filtered from the solution and the filtrate is evaporated until its volume is reduced approximately 50 per cent. The solution is cooled and the crystals are collected on a filter.

The crude product is dissolved in a minimum amount of water at 70°C. Activated charcoal is added to the solution and filtered. Ethyl alcohol is added to the filtrate until a yellow crystalline solid separates. Three such recrystallizations will yield a 100 per cent pure product. The product is analyzed by oxidation to Mo^{+5} by a standard cerium sulfate solution with tris(o-phenanthroline) iron (II) ion as indicator.

Preparation of Tetramethylammonium Octacyanomolybdate (IV) Dihydrate, $[N(CH_3)_4]_4Mo(CN)_8 \cdot 2H_2O$: A weighed amount of $K_4[Mo(CN)_8]$ is dissolved in the least amount of water at room temperature. A calculated amount of silver nitrate is added to the solution with constant stirring. The precipitated $Ag_4[Mo(CN)_8] \cdot 2H_2O$ is filtered and rapidly dried. A weighed amount of this salt is added to a solution of tetramethylammonium bromide, $N(CH_3)_4Br$, from which silver bromide separates. The solution is filtered through an asbestos filter. The filtrate consists of a solution of $[N(CH_3)_4]_4 Mo(CN)_8 \cdot 2H_2O$. This product is separated with the addition of absolute ethyl alcohol, filtered and dried in a desiccator over barium oxide.

D. Preparation of Potassium Octacyanotungstate (IV) Dihydrate, $K_4[W(CN)_8] \cdot 2H_2O$.

Preparation of Potassium Tungstate, K_2WO_4: Water is added to 200 grams of potassium carbonate until it just dissolves at approximately 40°C. Tungsten (VI) oxide, WO_3, is added in small portions. Each addition is made after the previously added portion has completely dissolved. The addition of WO_3 is stopped when the milky white precipitate first formed no longer dissolves after three to four minutes. During the addition the temperature is gradually raised to just below 100°C. Care is taken near the boiling point since at that temperature carbon dioxide is evolved violently. The solution is then cooled in an ice bath, yielding white crystalline K_2WO_4. This product is filtered and recrystallized. Recrystallization is necessary because the product retains potassium carbonate very tenaciously.

Preparation of Potassium Hexachloro-μ-trichloroditungstate (III), $K_3W_2Cl_9$ (43): A slurry of 50 grams of K_2WO_4 in 20 milliliters of water is prepared. The slurry is added with vigorous agitation to one liter of concentrated hydrochloric acid which has been heated to approximately 90°C. After the addition of the slurry, the solution of K_2WO_4 in concentrated hydrochloric acid is cooled to 70°C and saturated with anhydrous hydrogen chloride.

Thirty grams of metallic tin are added to the solution, and the solution is allowed to stand at room temperature for approximately one and a half hours. The solution goes through the following color changes: dark blue, red violet, and finally green-brown. When the solution reaches the red violet stage, the rate of reduction may be increased by warming the reaction mixture to approximately 45°C. The solution is cooled to 0°C and saturated with anhydrous hydrochloric acid for approximately three and a half hours.

It is then left for two days at 0°C, yielding a light green crystalline product. This product is purified by dissolving this precipitate in water and precipitating by the addition of a saturated solution of potassium thiocyanate.

Preparation of Potassium Octacyanotungstate (IV) Dihydrate, $K_4[W(CN)_8]\cdot 2H_2O$ (44, 45): A solution of 20 grams of $K_3(W_2Cl_9)$ in 150 milliliters of water on a water bath is gradually mixed with 65 grams of pulverized potassium cyanide. The solution becomes red in color and is evaporated for about one and a half hours on the water bath. The potassium chloride precipitated during evaporation is filtered off while the solution is still hot and the precipitated potassium chloride is washed with cold water. To this, a concentrated cadmium sulfate solution is added and digested with weak acetic acid upon a water bath. Dirty yellow crystals of $Cd_2[W(CN)_8]\cdot 2H_2O$ are precipitated. This product is filtered and dissolved in concentrated NH_4OH. The yellow $[Cd(NH_3)_4]_2\ W(CN)_8\cdot 2H_2O$ separates when this solution is saturated with gaseous NH_3. This product is filtered and converted to $Cd_2[W(CN)_8]\cdot 2H_2O$ by the addition of one to two per cent sulfuric acid. This product is converted to $K_4[W(CN)_8]\cdot 2H_2O$ by reacting it with a calculated amount of potassium carbonate. The $K_4[W(CN)_8]\cdot 2H_2O$ is precipitated by the addition of absolute ethyl alcohol.

II. Isopiestic Measurements

The apparatus used was very similar to that used by Scatchard and Wood (13). A detailed description of the actual construction is given in a paper by Brubaker, et al (46). An exception to the apparatus described in the above paper is that platinum crucibles and covers were used instead of gold-plated copper crucibles.

The general procedure is as follows: The platinum crucibles were dried and weighed. Four crucibles were used for each run, two containing the reference salt, potassium chloride, and two containing the salt whose osmotic coefficients were to be determined. The salts were weighed directly in the crucibles for all weights larger than 0.1 grams. For weights smaller than 0.1 gram, standard potassium chloride solutions were prepared of various molalities. The desired amount of solution was introduced into the crucibles from a weight burette, the exact weight being determined by the difference in weight of the burette before and after introduction. The molecular weights of the salts to be run were of such a magnitude that at least 0.1 gram could be weighed directly into the crucibles for even the lowest concentrations. The preparation of standard solutions of these compounds was deemed undesirable because of the possibility of a photochemical reaction occurring during the storage of these solutions.

For all runs in which the dry salt was weighed directly into the crucibles at least 1 milliliter of water was added. The crucibles containing the solutions were then placed into the vacuum bomb. Five drops of water were added to the bottom of the bomb to compensate for water vapor lost during evacuation and to displace air from the interior of the bomb. The bomb was then closed and evacuated through a glass bulb of approximately the same volume as the bomb. This procedure was used to control the evacuation and thus prevented possible bumping spattering of the solutions inside the bomb at reduced pressures. The bombs were evacuated until the pressure read on a monometer, included in the evacuation system, corresponded to the vapor pressure of water at room temperature. At this point the bomb was evacuated through the bulb ten more times to insure complete removal of air within the bomb and to allow any oxygen adsorbed in the water of the solutions to diffuse out and be removed. The last ten evacuations were done slowly over a period of approximately one hour.

The evacuated bomb was then placed in a constant temperature bath controlling at $24.978 \pm 0.005^{\circ}C$. The time required to reach equilibrium varied, depending upon concentration of the solutions. Solutions whose molality ranged from 0.5 $\underline{m}$ to 1.2 $\underline{m}$ were allowed to remain in the bath for 48 hours. Solutions below 0.5 $\underline{m}$ in concentration were kept in the bath from one to two weeks. After an appropriate length of time the bomb was removed from the bath, opened, and the crucibles were capped and weighed. Equilibrium was considered reached when the calculated molal concentrations were found to agree within three parts per thousand between duplicate samples.

After each run a small amount of water was added to each crucible which was then placed back into the bomb and the entire process was repeated. Thus, in many cases, one sample weighing was sufficient for two or three equilibrium values. This process of diluting and redetermining equilibrium concentrations was found to be feasible until approximately 4 milliliters of water had been added. Larger amounts of solvent than this greatly increased the time to reach equilibrium, and this process was no longer practicable.

III. Conductance Measurements

A. The A. C. Bridge and Resistance Measurements:

The resistance measurements were taken with an alternating current conductance bridge. The bridge design is essentially the same as that given by Jones and Bollinger (17, 19). The basic circuit is sketched below.

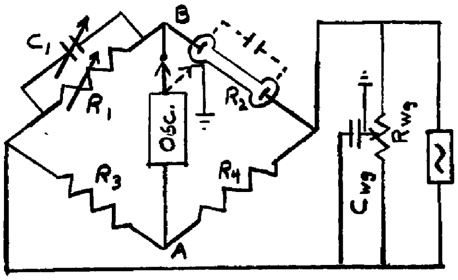


FIGURE 2

The condition of balance for the alternating current bridge is as follows:

In terms of alternating current, Ohm's Law will take the form of $V = IZ$, where Z is the impedance of the circuit. Z^2 is equal to $R^2 + X^2$, where R and X are the resistance and reactance of the circuit, respectively. The condition of balance, i.e. when there is no flow of current through the detector, will be

$$\frac{I_1 Z_1}{I_2 Z_2} = \frac{I_3 Z_3}{I_4 Z_4} .$$

Since there is no flow of current between points A and B, then I_1 must equal I_2 and I_3 must equal I_4, so that

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4} .$$

It can be shown that, if the resistances are also to be balanced, it is necessary that

$$\frac{X_1}{R_1} = \frac{X_2}{R_2} \quad \text{and} \quad \frac{X_3}{R_3} = \frac{X_4}{R_4} ,$$

which simply means that not only the amplitudes of the voltage at points A and B must be equal but the voltages must also be exactly in phase with each other at these points.

The reactance, X, of the circuit depends on the frequency as well as the capacitances and inductances in the circuit. Hence, the reactance is kept deliberately small in all portions of the bridge; and, in particular, the inductive reactance is kept as small as possible by preparing the ratio arms R_3 and R_4 as identical as possible in resistance and construction.

In the other bridge arm R_1 and R_2, the reactance is maintained small by connecting a variable capacitor C_1 in parallel with R_1 which, upon adjusting, will allow the ratio of $\frac{X_1}{R_1}$ to be equal to the ratio $\frac{X_2}{R_2}$, where X_2 is the parallel capacitive reactance inherent in all conductance cells.

The parallel R_{wg}, C_{wg} combination included in the ground leads shown in Figure 2 is called the Wagner ground. This special method of grounding assures the detector to be at ground level and prevents a possible charging current for any capacitance which may be set up unavoidably between detector and ground. Such a current would upset the proper balance of the bridge and prevent a sharp null-point to be observed.

The oscillator used for this work was designed to give five different audio frequencies over the range of 400 cycles/sec. to 5000 cycles/sec., and the detector used was an oscilloscope. The complete bridge system used was constructed by students of the Physical Chemistry Department under the direction of J. L. Dye. The schematic electrical circuit and details of construction for this system have been included in a paper by Faber (47).

The general operational procedure for taking resistance readings with the above system was as follows:

The cell was introduced into the bridge (R_2-C_2 in Figure 2), and the bridge was balanced by adjusting the variable resistance and capacitance R_1 and C_1, respectively. This is done with switch S, in the position of the full line indicated in Figure 2. The switch S is then changed to the ground position indicated by the dotted line. The variable capacitance and resistance C_{wg} and R_{wg} were then adjusted to give a minimum signal on the oscilloscope. Switch S is then returned to the full line position and balance is again obtained by varying R_1 and C_1. These steps are repeated until there is no adjustment required when switch S is varied between ground potential and the potential at B. The resistance reading for R_1 is then recorded and the entire procedure is repeated at a different frequency. The frequency dependence of R_1 is explained in detail in the section dealing with polarization of electrodes.

B. The Conductance Cells:

The conductance cells used for low concentration readings were constructed from a one-liter erlenmeyer flask and a Leeds and Northrup type A conductance cell. The cell was designed by J. L. Dye and is similar to that used by Daggett, et al (48). It differs from the above-mentioned cell in that a side arm is included which may be opened or closed by a stopcock, and an air outlet has been included in the cap which is also controlled by a stopcock. These modifications were incorporated so that the conductance water could be introduced into the cell directly from the distillation apparatus.

C. Platinization of Electrodes:

In order to eliminate polarization effects by the alternating current, the electrodes of the conductance cells are coated with a layer of finely divided platinum black. The platinization is carried out by electrolysis of a solution containing about 3 per cent chloroplatinic acid and 0.02 per cent lead acetate. The lead acetate seems to facilitate the depositing of the platinum black in a finely divided, adherent form. The platinizing current is about 20 amperes and the polarity is reversed every 10 seconds for about 40 seconds.

The effect of platinization can be seen in the variation of resistance with frequency. As was previously mentioned, the resistance variation is a linear function of the reciprocal of the square root of the frequency. When this variation of resistance from the lowest frequency, 400 cycles/sec., to the extrapolated value at ∞ cycles/sec. was greater than 8-10 ohms, the electrodes were replatinized; and the cell constant was recalculated.

D. Constant Temperature Bath:

During resistance measurements the cell is emmersed in a constant temperature bath set at 25.00 ±0.015°C. Transformer oil is used as the fluid. Water is unsuitable since there is danger of current leakage leading to errors in the resistance measurements.

E. Preparation of Conductance Water:

Distilled water, due to the presence of dissolved impurities, is not suitable for conductance measurements for very dilute solutions. Many of the impurities may influence the ionization or may even become involved in chemical combination with the electrolyte being studied. Therefore, it is not just a simple matter of subtracting the conductance of the water used from the total conductance observed. The procedure for the preparation of conductance water was essentially that used by Vogel and Jeffery (49). This procedure is as follows: A solution of approximately 15 grams of sodium hydroxide and 15 grams of potassium permanganate is prepared from four liters of demineralized water. The water is then distilled from this solution through a glass packed colume and collected in a flask. The water thus obtained is then transferred to another distillation apparatus through which a current of nitrogen is continuously flowing. The water is distilled into a flask still under a nitrogen atmosphere from which it may be transferred directly to the conductance cell by means of a Teflon tube. Such a transfer is made by closing of the nitrogen outlet on the storage flask and allowing the nitrogen to force the water from the flask to the cell. The water prepared in the above fashion has a specific conductance of approximately 0.6×10^{-6} $ohm^{-1}cm^{-1}$ at 25°C. Variations in the above conductance value may occur usually depending on the time of storage before transfer. The major impurity in the above water is dissolved carbon dioxide.

F. General Procedure:

All glassware in which the solutions to be run were contained were cleaned with soap and water. They were then rinsed from 10 to 20 times with warm distilled water and finally steamed with conductivity water. After the steaming process the glassware was drained of all remaining water and dried in an oven at 120°C.

Solution concentrations were first determined from weight measurements. For concentrations higher than 0.01 N the dry salt was weighed directly into a 100-milliliter volumetric flask. Water was then added up to the mark and the total weight was then determined. Lower concentrations were then prepared by transferring various weights of the original stock solution to volumetric flasks which were then diluted to a total volume of 100 milliliters. The solutions thus prepared were then transferred directly from the flasks to the cell for measurement of resistance. For concentrations below 0.01 N a stock solution was prepared as indicated above and then transferred to a weight burette.

The alternating current bridge used is limited to accurate resistance readings from 30,000 ohms to 2000 ohms. Therefore, in order to cover the concentration range from 0 to 0.1 N, it is necessary to use a cell with a small cell constant for the most dilute solutions and cells with higher cell constants for the more concentrated solutions.

In general, three cells were used for the resistance measurements. One of the cells which has been designated as E-2 is used for concentrations ranging from 0.1×10^{-3} N to 2.5×16^{-3} N. It has a cell constant of approximately 0.3 cm^{-1}. A second cell designated as E-3 is used over the range 2.5×10^{-3} N to 10×10^{-3} N and has a cell constant of approximately 1.0 cm^{-1}. The third cell designated as E-1 is used for concentrations greater than 0.01 N. Its cell constant is approximately 30 cm^{-1}.

For measuring resistances of dilute solutions one of the erlenmeyer type cells, E-2 or E-3, was used. The cell was first drained of any water it contained and then dried at 120°C for three hours. The dry cell was cooled and a small amount of Dow Corning High Vacuum Grease was applied to the stopcocks and the ground glass cap joint. It was weighed and the conductance water was introduced into the flask directly from the distillation apparatus by increasing the nitrogen pressure. The conductance water should not be too warm or vapor condensation will occur inside the cap of the cell and will remain throughout the run. The cell and water were weighed to determine the amount of water. The cell was then rotated gently in order to mix thoroughly any impurities which might have remained in the conductance cell even after cleaning. Care was taken not to allow the water to touch any greased joints. The cell was then placed in the oil bath and allowed to reach temperature equilibrium. Twenty minutes was sufficient in most cases. During this time the resistance of a standard resistance, which was previously emmersed, in the oil bath was determined. The standard resistance was then connected in parallel with the cell and the total resistance of the parallel combination was obtained. This value was determined at the lowest frequency, 400 cycles/sec. The cell was then removed from the bath and the water was again mixed thoroughly and the cell was replaced in the bath. The cell was allowed to reach temperature equilibrium and the resistance was again determined. These processes were repeated until there was no change in resistance upon mixing. When a constant value is thus obtained, the resistance readings were then recorded throughout the entire frequency range. By this method the resistance of the water can be determined using the relation,

$$R_{H_2O} = \frac{R_{std}R_{total}}{R_{std}-R_{total}} .$$

Having obtained the value for the resistance of the water, the cell is removed from the bath and a line leading from a nitrogen cylinder was attached to the side arm of the cell. With the nitrogen flowing the stopcocks of the cell were opened, and the cap was then removed. A small amount of the solution whose conductance was to be determined was then added from a weight burette. The cap was replaced, stopcock closed and the cell was removed from the nitrogen line and replaced in the bath after mixing thoroughly. Thus, by the addition of successive small quantities of the electrolyte the concentration is gradually built up and the resistance at each concentration is measured as previously explained.

For the higher concentrations, above 0.01 N, the cell E-1 was used. The stock solutions, prepared as previously indicated, were added directly to the cell from the volumetric flasks in which they were prepared. Before addition, however, the cell was rinsed with the solution to be run. After its resistance was measured, a new portion of the same solution was added and the resistance was redetermined.

G. Determination of the Densities of Solutions:

The solutions whose conductances were determined had been prepared in terms of molal concentration units. Since the conductance relations are formulated in molar or normal concentration units, it was necessary to determine the density of the more concentrated solutions. The density determinations were made with a pycnometer, the volume of which was determined in the following way. The pycnometer was filled with conductance water and immersed in a constant temperature bath at 25 ± 0.05°C. The contents were allowed to reach equilibrium, the overflow cap was removed and any excess water wiped off. The cap was replaced and the pycnometer was wiped dry and weighed. The recorded weight was corrected to the weight of water in vacuo, and the volume was calculated using the density of water in vacuo.

After calibration, the density of several of the solutions prepared for high concentration conductance calculations was determined as above. A graph of molality versus density was constructed, and the densities could be determined graphically at any concentration (Appendix III).

H. Determination of the Cell Constant:

The cell constant was determined in the following way. A standard solution of potassium chloride was prepared of such concentration that several readings could be taken over the resistance range from 20,000 ohms to 2,000 ohms. The additions were made, and the readings were taken according to the method previously described. The equivalent conductance for each concentration was calculated with the aid of the equation

$$\Lambda = \Lambda^{o} - S \quad c^{*\frac{1}{2}} + A \ c^{*} \log c^{*} + B \ c^{*} ,$$

where $\Lambda^{o} = 149.87$

$A = 31.8$

$B = 144$

c^{*} = concentration of solute in terms of normality.

The above constants were taken from Harned and Owen (54). Upon determining the equivalent conductance, the cell constant was determined by using the relations

$$\Lambda = \frac{L}{c^{*}} \quad \text{and} \quad LR = k,$$

where L = the specific conductance

R = the observed resistance

k = cell constant.

The average of a minimum of five concentrations were used with a maximum allowable deviation of ± 0.05 per cent.

4 - RESULTS AND DISCUSSION

It was the purpose of this project to prepare high-charged electrolytes, specifically the 4-1, 1-4 or 4-2 type. Not only was the charge type important but the investigation of their behavior in aqueous solution necessitated that they be of rather high solubility and unreactive with respect to the solvent. This last restriction severely limits the possible electrolytes to be investigated to those of the coordination type compounds. This comes about due to the fact that a high charge carried upon a small ion usually creates a high enough charge density to distort the water dipole past its breaking point. Thus, the ion may enter into chemical combination with the oxygen of the solvent to form oxide or hydroxide containing ions. This principle of relieving the charge density on the central ion is inherent in coordination type compounds except that it is brought about without a solvent interaction.

In coordination compounds the high charge on the central ion is relieved by rearrangement of the electronic levels due to the close proximity of the surrounding ligands with the possible formation of dative-pi bonds. The surrounding ligands also sufficiently screen the central ion so that the solvent molecules cannot approach closely enough for possible interactions. Thus, the central ion of a coordination compound can exist with a high charge but may have a low enough charge density to remain in the solvent without any strong interactions such as hydrolysis. However, it is quite possible that the ligand may react with the solvent or even be replaced in the coordination sphere by the solvent. Because of this, the choice of ligand is of great importance.

It was thought that the best starting point for stable 4-1 electrolytes would be with the platinum (IV) amine complexes. Initial interest centered upon chelate type ligands. The chelate compound is that type of coordination compound in which the central ion is jointed to two or more donor groups of a single molecule or ion. Qualitative observations of these compounds have shown them to be of exceptionally high stability in many cases. In general, it has been found that the greater the number of points of attachment of each ligand to the central metal ion, the greater the stability of the complex.

Spike and Parry (50) have done some quantitative work on the chelate effect and have found that the chelate effect for nontransition metal ions is almost entirely an entropy effect, but that for transition metals it is in part an enthalpy effect. The entropy effect simply means that if equal concentrations of a monodintate ligand (coordinates at one point) and a bidintate (coordinates at two points) were used for a reaction with a particular metal ion, there would be twice the chance for reaction with the bidintate ligand than the monodintate. The enthalpy effect observed for transition metal ions is considered to be due to a gain in crystal field stabilization energy which is not observed for the nontransition metals. The crystal field stabilization energy is an increase in bonding energy brought about by the preferential filling of certain d orbitals with the electrons of the metal. In particular, those orbitals directed away from the electrostatic field of the ligands are lowered energetically and, thus, would contain the metal electrons while those orbitals directed at the ligands will tend to be of a much higher energy and void of electrons. Such an arrangement will result in a much more stable system than a system in which the electrons have a random distribution, which would be the case for the normally degenerate d levels. For nontransition metals the d levels are either completely empty or completely full. In these circumstances the d levels are only slightly affected by the ligand fields; and, thus, there would be no crystal field stabilization affect.

The attempted synthesis of some platinum-amine complexes of the chelate type has been previously reported (51). These were the tris-substituted coordination compounds

2,2'-bipyridine(bipy), phenanthroline(phen) and the hexa-substituted pyridine(py) with the platinum (IV) ion.

However, none of the above compounds were isolated. Recently Martin and Waind (52) have described the ultraviolet and visible absorption spectra of the tris-(bipyridine) complexes of rhodium, cobalt and iridium. Of particular interest is that they report the absorption bands for the rhodium complex at 240 mμ, 305 mμ, 318 mμ, 490 mμ and 530 mμ (the last two bands have been assigned as characteristic of the metal ion). The highly colored filtrate from the reaction mixture of $PtCl_4$ and molten bipyridine, as previously reported, gives absorption bands at 287 mμ, 297 mμ, 320 mμ, 487 mμ and 527 mμ. Such close agreement between these absorption spectra may well indicate that it is possible to form the tris-(bipyridine)platinum (IV) complex in solution but that decomposition to lower substituted complexes may occur during the crystallization process.

Initial interest centered on these particular amines not only for the suspected stability due to the chelate effect with the bipyridine and phenanthroline molecules but also for the possible gain in stability through formation of coordinate double bonds in resonance with the aromatic rings.

It was decided to prepare a 4-2 electrolyte from a metathetical reaction of silver sulfate and tris-(ethylenediamine) platinum (IV) chloride or tris-(1,2-propylenediamine)platinum (IV) chloride. Both chlorides had been previously prepared.

The tris-(1,2-propylenediamine)platinum (IV) sulfate was formed and identified. However, this compound was found to be unsuitable for study since an apparent hydrolytic reaction occurs in solution by the formation of an insoluble brown residue when an aqueous solution of this salt is allowed to stand for one to two days. This hydrolytic reaction was noticed to occur even in the absence of light.

The preparation of tris-(ethylenediamine)platinum (IV) sulfate was attempted; however, it was never obtained. In every case the product was a mixture of an insoluble brown residue and a soluble white compound. This mixture could not be separated as it was formed with each recrystallization procedure. Since the hydrolytic phenomena is not observed with solutions of the chlorides of these complexes, it is suspected that the sulfate ion may be competing with the amine molecule as a chelating agent. This explanation seems doubtful in view of the fact that the tris-(ethylenediamine) cobalt (III) sulfate can be formed and is quite stable in solution. However, the higher charge on the platinum ion may be a deciding factor in the difference of stability of the complexes.

It was decided to obtain isopiestic measurements for the tris-(1,2-propylenediamine)platinum (IV) chloride in an effort to clear up the inconsistency observed in the å, the distance of closest approach, values obtained from isopiestic measurements with the tris-(ethylenediamine)platinum (IV) chloride and the tris-(ethylenediamine)platinum (IV) perchlorate (53, 60).

Since the solubility of the 1,2-propylenediamine complex was extremely low, an attempt was made to prepare the tris-(1,3-propylenediamine) complex in the hope of obtaining a more soluble compound. The reaction was run identically to the 1,2-propylenediamine reaction. The product isolated, however, was not the tris-(propylenediamine)platinum (IV) but, instead, the bis-(propylenediamine)platinum (II) chloride.

The 1-4 type complexes prepared were the $K_4[W(CN)_8]$ and $[N(Me_4)]_4Mo(CN)_8$. The activity coefficients had been determined for the $K_4[Mo(CN)_8]$; however, it was felt that the effect of a large cation on its solution properties would be of interest.

These compounds are known to be photosensitive and, therefore, the physical measurements were made as soon as possible after standard solutions were prepared. While handling these solutions, they were kept away from fluorescent lights. Of particular interest is that conductance measurements made with these electrolytes after cleaning the electrodes with aqua regia showed a definite time dependency. This time dependency was not in evidence before cleaning and the conductance data reported below were obtained at this time. A similar time dependency during conductance measurements of the electrolyte $K_4Fe(CN)_6$ has been reported. However, these compounds must be stable toward hydrolytic reactions as evidenced by the reproducibility of conductance and isopiestic data.

Treatment of Isopiestic Data

Activity coefficients were calculated by either the method of Smith or the method of Randall and White.

Calculations based on Smith's method involving the relation

$$\ln \gamma_{\pm} = - \frac{2.303\ S_{m(f)} m^{\frac{1}{2}}}{1 + A'_m\ m^{\frac{1}{2}}} - Bm + \int_0^m \frac{\Delta\phi}{m}\, dm + \Delta\phi \qquad (57)$$

where $\Delta\phi = -(1 - \phi)_{obs} + 0.7676\ S_{m(f)} \sigma_m\ m^{\frac{1}{2}} + \frac{1}{2}Bm$

were made first since this method was considered to have a more theoretical significance than the relation of Randall and White.

The osmotic coefficients obtained from the isopiestic method were first plotted as a function of $m^{\frac{1}{2}}$. These graphs served two purposes. First, they were used to give indications of whether or not equilibrium had been obtained in all samples, since this function is very sensitive to experimental error. Secondly, they were used to smooth out experimental error in the osmotic coefficient determinations. A smooth curve was drawn through the experimentally determined points; and using such a curve, the osmotic coefficients were determined as a function of molality.

The Debye-Hückel relationship as a function of the osmotic coefficient and with a linear term to represent data for higher concentrations can be written as

$$\frac{1 - \Phi}{m^{\frac{1}{2}}} = 0.7676\ S_m(f)\sigma_m + \tfrac{1}{2}Bm^{\frac{1}{2}}.$$

The term $\frac{1 - \Phi}{m^{\frac{1}{2}}}$ was plotted as a function of $m^{\frac{1}{2}}$. Since σ is a function of an arbitrary parameter $\mathring{a}$, it is first adjusted until the value for $\frac{1 - \Phi}{m^{\frac{1}{2}}}$, calculated from the above relationship, agrees with the experimentally determined value of $\frac{1 - \Phi}{m^{\frac{1}{2}}}$ at the lowest experimental concentration. Having determined an approximate value for this parameter, calculated values of $\frac{1 - \Phi}{m^{\frac{1}{2}}}$ were plotted as a function of $m^{\frac{1}{2}}$. The difference in $\frac{1 - \Phi}{m^{\frac{1}{2}}}$'s between these curves was plotted as a function of $m^{\frac{1}{2}}$. This graph should be a straight line with a slope of $\frac{1}{2}B$, if the linear term $\frac{1}{2}Bm$ is a suitable function to represent experimental data at higher concentrations. Having obtained a value for the function B, the value of $\mathring{a}$ was then varied until osmotic coefficients calculated from equation 57 show the smallest deviation from the experimentally determined coefficients. Once the values for these parameters were known, then the activity coefficients could be determined directly from equation 57. The integral in equation 57 was evaluated by determining the area under the curve of a graph of $\Delta\phi/m$ versus m (Figure 3).

All of the electrolytes investigated in this paper could be treated by this method up to a concentration of approximately 0.2 m. However, this represents such a small portion of the total experimental concentration range for most of these electrolytes that the method of Randall and White was used for the determination of the activity coefficients for all of the electrolytes reported here except $Pt(pn)_3Cl_4 \cdot H_2O$.

The method of Smith could be used successfully throughout the experimental concentration range for this electrolyte. Values for the parameters $\overset{\circ}{a}$ and B derived from this method are given in Table I.

TABLE I

Parameters for Equation 57

Electrolyte	B	$\overset{\circ}{a}$ (angstroms)
*$K_4W(CN)_8$	2.40	7.09
*$[N(Me)_4]_4Mo(CN)_8$	2.52	4.85
$Pt(pn)_3Cl_4$	4.24	8.11
*$K_2Pt(CN)_4$	1.36	7.18

*Valid for a limited concentration range only.

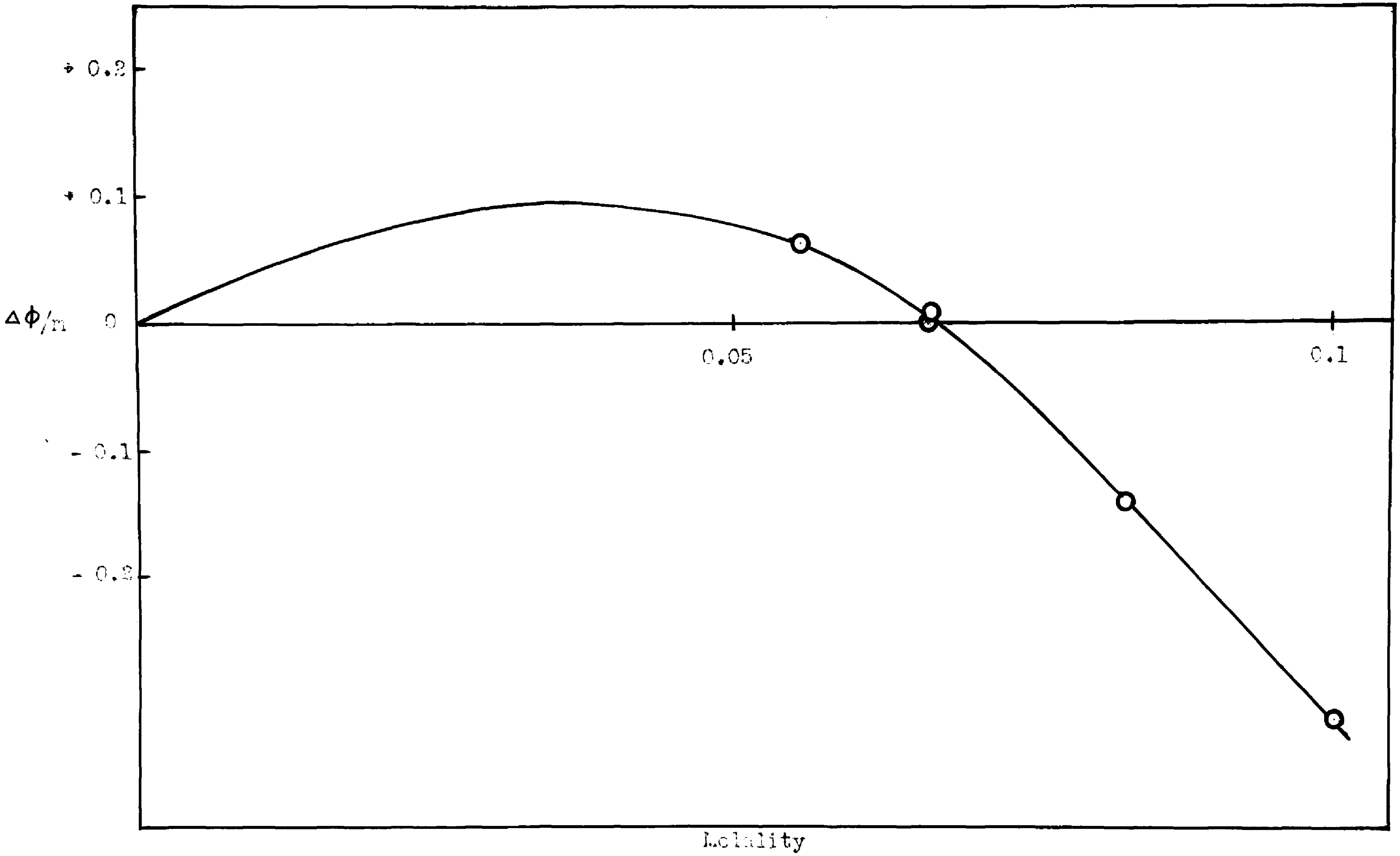


FIGURE 3

Graphical Procedure for Evaluating the Integral $\int_0^m (\Delta\phi/m)\,dm$ for $Pt(pn)_3Cl_4 \cdot H_2O$

A comparison of observed and calculated osmotic coefficients for $Pt(pn)_3Cl_4 \cdot H_2O$ are tabulated below.

TABLE II

Isopiestic Molalities, Observed and
Calculated Osmotic Coefficients of
$Pt(pn)_3Cl_4 \cdot H_2O$

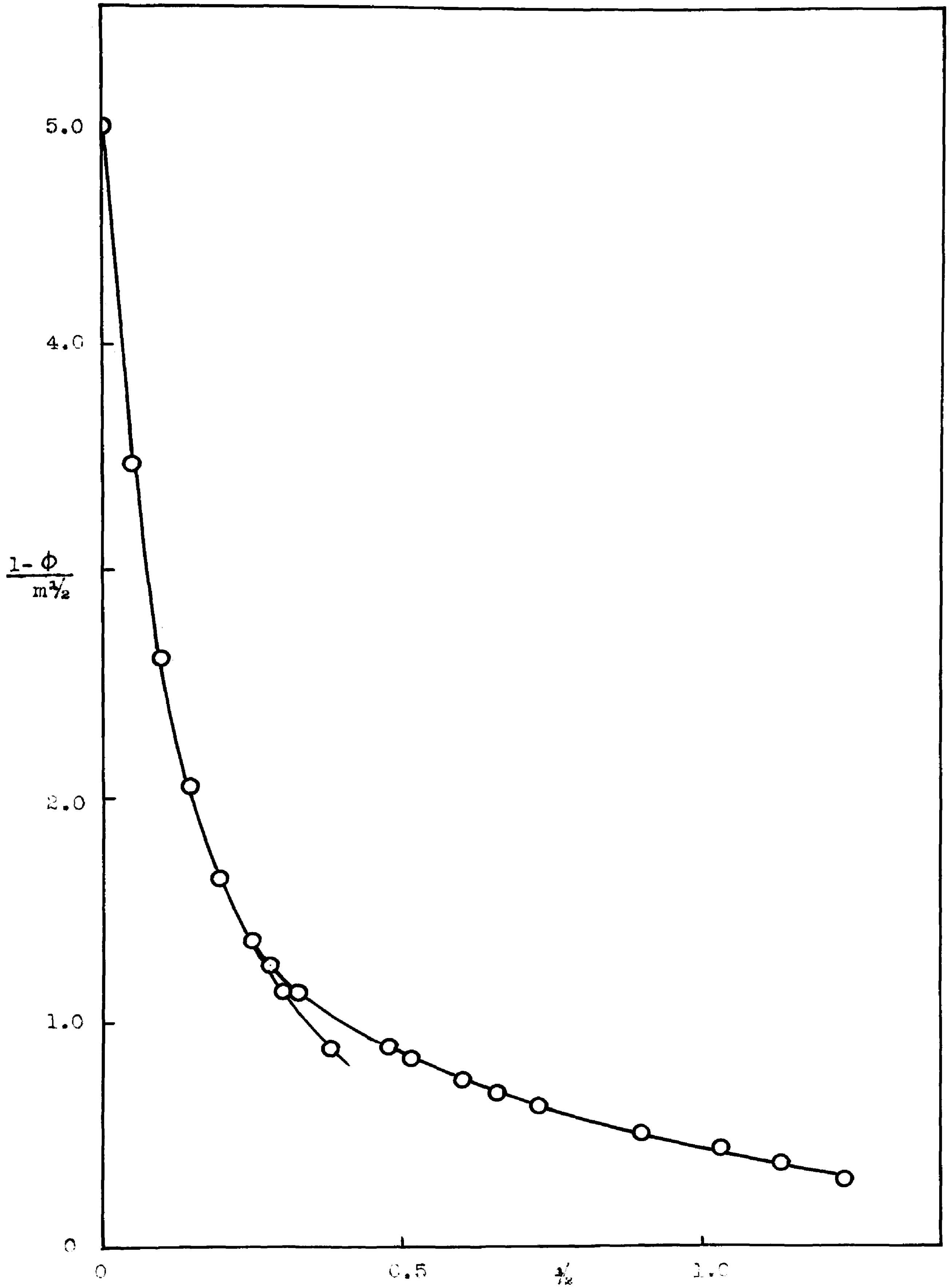
Molality	Φ_{calc}	Φ_{obs}
0.0556	0.6755	0.6719
0.0665	0.6548	0.6546
0.0678	0.6523	0.6517
0.0831	0.6233	0.6350
0.1047	0.5865	0.6191

Values for smoothed activity and osmotic coefficients for this electrolyte as a function of concentration are listed in Table III.

In the method of Randall and White the relation

$$(58) \quad \ln \gamma_{\pm} = -(1 - \Phi) - 2 \int_0^m \left(\frac{1 - \Phi}{m^{\frac{1}{2}}}\right) d\, m^{\frac{1}{2}}$$

is used. The first term in the above relation can be obtained graphically at any concentration from the graphs of $1 - \Phi$ versus $m^{\frac{1}{2}}$. The second term is evaluated by determining the area under the curve of a graph of $\frac{1 - \Phi}{m^{\frac{1}{2}}}$ versus $m^{\frac{1}{2}}$, consisting of the experimentally determined values of $\frac{1 - \Phi}{m^{\frac{1}{2}}}$ down to the lowest concentration (upper portion of the curve in Figures 4 to 6) and the calculated values of



Graphical Procedure for Evaluating the Integral $_0\int^m (1-\phi/m^{1/2})\,dm^{1/2}$ in the Determination of $\gamma_\pm$ for the Electrolyte $K_4[W(CN)_8]\cdot 2H_2O$

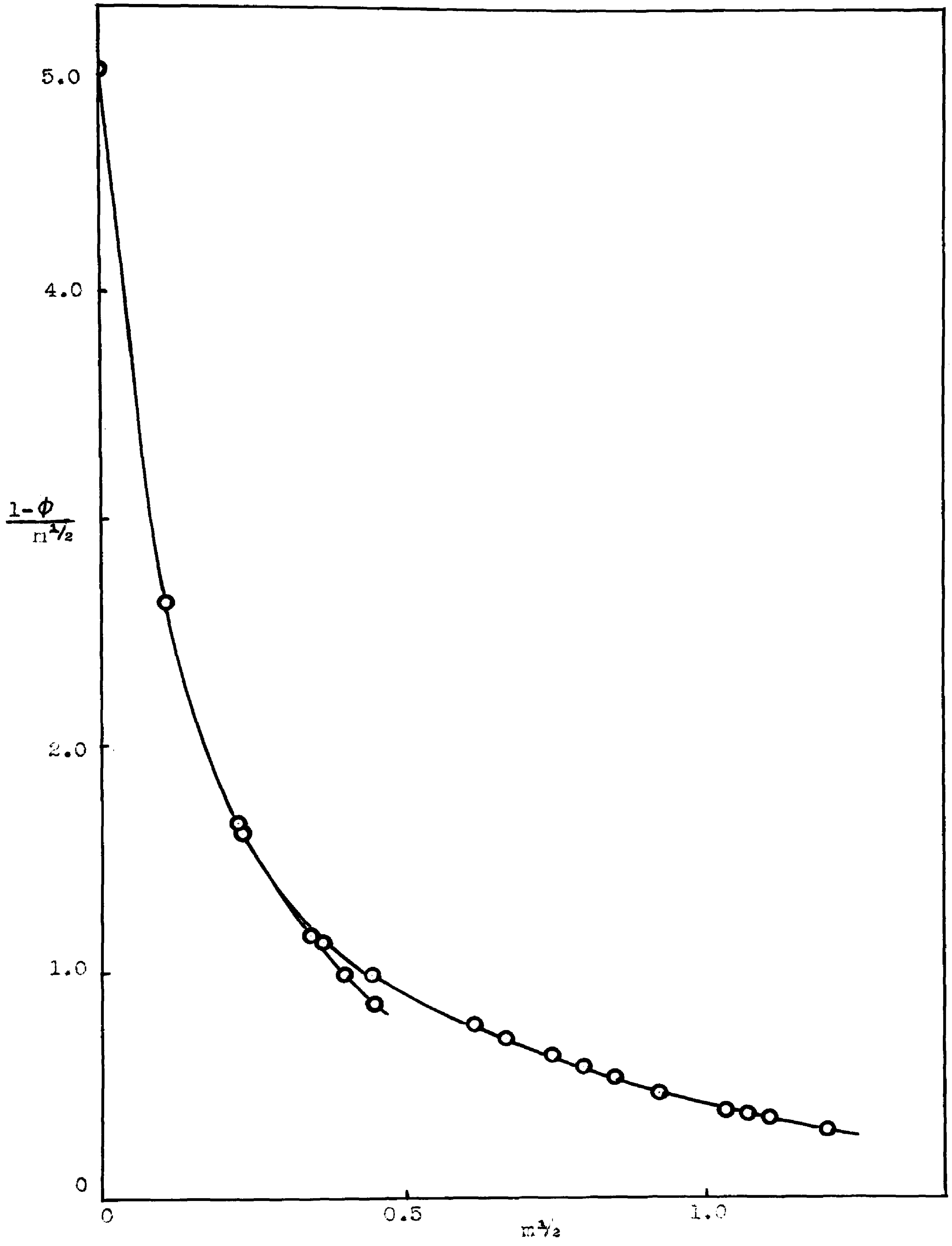


FIGURE 5

Graphical Procedure for Evaluating the Integral $_0\int^m (1-\Phi/m^{1/2})dm^{1/2}$ in the Determination of $\gamma_\pm$ for the Electrolyte $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$

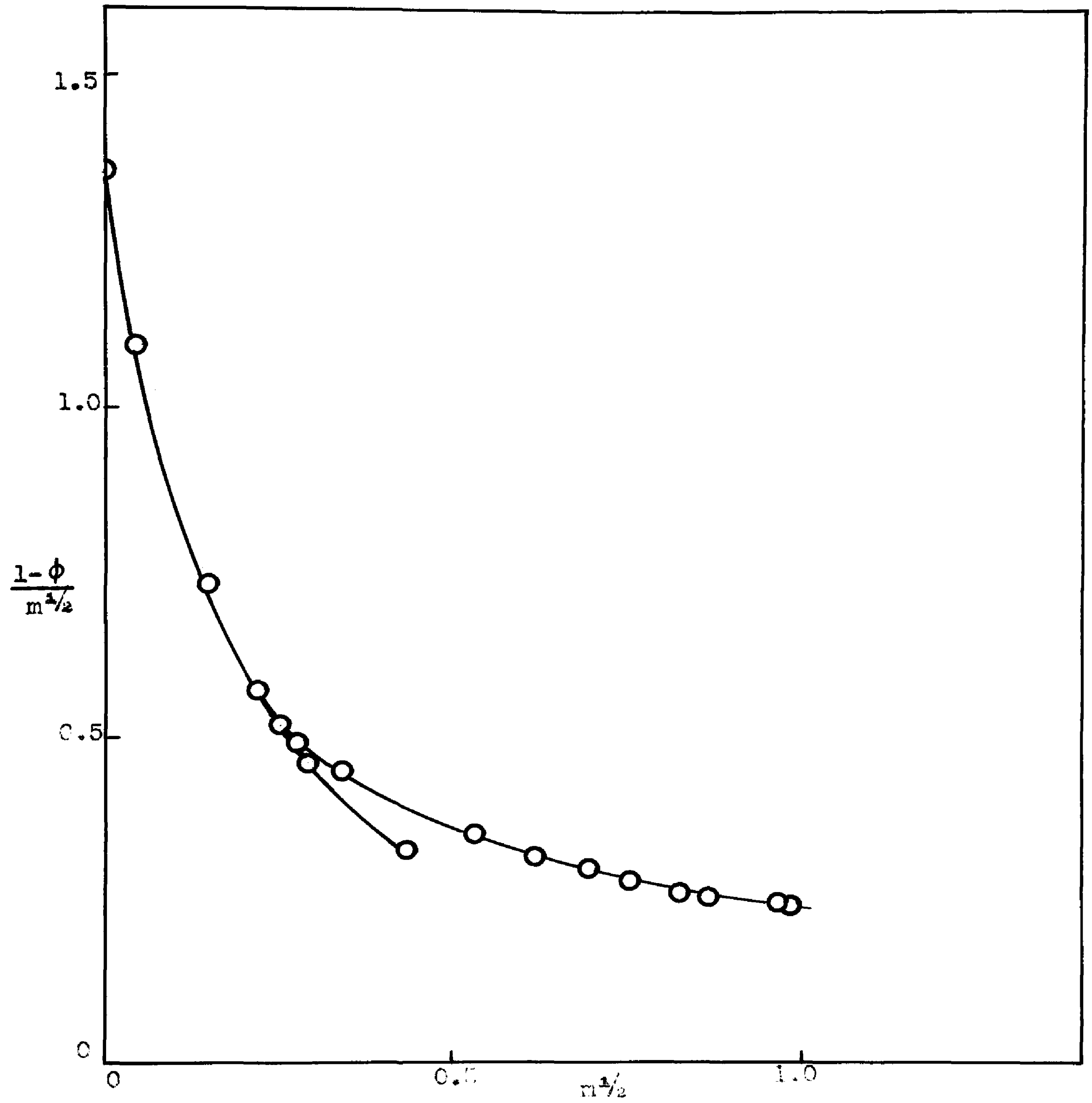


FIGURE 6

Graphical Procedure for Evaluating the Integral $_0\int^m (1-\phi/m^{1/2})dm^{1/2}$ in the Determination of γ_t for the Electrolyte $K_2Pt(CN)_4$

TABLE III

Smoothed Activity and Osmotic Coefficients at 25°C

	$K_4[W(CN)_8]$		$[N(Me)_4]_4Mo(CN)_8$	
m	$\gamma_\pm$	Φ	$\gamma_\pm$	Φ
0.01	0.419	0.854	0.359	0.753
0.025	0.295	0.768	0.252	0.685
0.050	0.216	0.683	0.184	0.638
0.075	0.180	0.651	0.155	0.612
0.10	0.159	0.632	0.136	0.596
0.25	0.111	0.572	0.0859	0.542
0.50	0.0808	0.541	0.0612	0.524
0.75	0.0653	0.536	0.0515	0.551
1.00	0.0578	0.548	0.0468	0.581
1.10	0.0537	0.555	0.0451	0.592
1.25	0.0515	0.571	0.0440	0.610
1.44			0.0426	0.631
1.50	0.0478	0.604		

TABLE III, continued -

	$Pt(pn)_3Cl_4$		$K_2Pt(CN)_4$	
m	$\gamma_\pm$	Φ	$\gamma_\pm$	Φ
0.01	0.429	0.786	0.756	0.937
0.025	0.330	0.737	0.672	0.907
0.050	0.258	0.683	0.612	0.882
0.075	0.213	0.643	0.573	0.867
0.10	0.177	0.621	0.545	0.857
0.25			0.470	0.823
0.50			0.402	0.795
0.75			0.365	0.782
1.00			0.337	0.768

$\frac{1 - \Phi}{m^{\frac{1}{2}}}$ from this point to infinite dilution (lower portion of the curve in Figures 4 to 6). This area is determined by graphical integration procedures. The values of the activity coefficients determined by this procedure, along with smoothed osmotic coefficients at various concentrations, are given in Table III.

The numerical value of $\mathring{a}$ is determined by adjusting the function σ in equation 58 until a calculated value of $1 - \Phi$ becomes identical with the experimentally determined value of $1 - \Phi$ at the lowest experimental concentrations. Values of $\mathring{a}$ determined by this method are given below.

TABLE IV

Values for $\mathring{a}$ Determined by the Method of Randall and White

Electrolyte	$\mathring{a}$ (angstroms)
$K_4W(CN)_8$	4.81
$[N(Me)_4]_4Mo(CN)_8$	4.25
$Pt(pn)_3Cl_4$	5.17
$K_2Pt(CN)_4$	6.20

Discussion of Isopiestic Measurements

Of the methods used to determine activity coefficients the procedure of Smith is preferred. Although this method was not used in three of the four cases described in this paper, it has been shown (53) that activity coefficients calculated by either method will differ by less than 1 per cent. Thus, the actual method used for these calculations does not seem to be too significant.

Perhaps the greatest difference between these methods lies in the evaluation of the parameter $\overset{\circ}{a}$. This is easily seen by comparing the values for this parameter derived from both methods as listed in Tables I and IV.

The reason for these variations is quite obvious if we briefly compare the two methods. From the method of Randall and White the values for $\overset{\circ}{a}$ are derived by determining that value which will allow the experimental data at the lowest concentrations to be calculated directly from the Debye-Hückel equation. This procedure is in obvious error since the Debye-Hückel relationship cannot be expected to be valid due to the inherent limitations imposed in its derivation at even the lowest experimental concentrations. The method of Smith, however, takes these limitations into account. By this method the deviation between experimental and calculated data is assumed to be a linear function. The magnitude of this linear function is determined graphically from the experimental data; and the parameter $\overset{\circ}{a}$ is then adjusted so that calculated data, through use of the Debye-Hückel relationship plus the linear function, can be determined which will give the smallest deviation from the experimental data at any particular concentration.

Admittedly, the method gives considerable weight to the numerical contribution of the linear function at even the lowest experimental concentrations, but nevertheless it considers the obvious fact that the Debye-Hückel relationship cannot be used alone at these concentrations. Some inherent difficulties of the method are:

(a) the linear function is determined graphically from those portions of the $1 - \phi$ versus $m^{\frac{1}{2}}$ curves which have a considerable curvature and, thereby, impart a substantial uncertainty in the exact magnitude of the linear function;

(b) the deviations at these concentrations may be other than linear.

Although it would appear that the linear function approximation may be a poor one, nevertheless, it must be considered better than none at all.

These above limitations are only applicable to the evaluation of the $\overset{\circ}{a}$ term and not to activity coefficient calculations since any deviation due to the curvature or nonlinear terms are corrected for by introduction of the $\Delta\phi$ function described on page 87.

One obvious argument in favor of Smith's method is the larger $\overset{\circ}{a}$ values determined from this method. Consideration of molecular dimensions and hydrated ionic radii leads to $\overset{\circ}{a}$ values from 8 - 10 Å for the 4-1, 1-4 electrolytes studied depending on the degree of hydration. Fairly good agreement with these magnitudes is indicated in Table I.

Figure 7 illustrates the relative magnitudes of the activity coefficients determined for these electrolytes.

In general, there is very little variation between the numerical values for the activity coefficients of these 1-4, 4-1 type of electrolytes.

In every case the activity coefficients are higher than one would calculate by using the Debye-Hückel relationship alone. This can be explained with the aid of Bjerrum's concept of ion-pair formation. However, a detailed mathematical investigation on the effect of neglecting the higher order terms in the linear expansion of the Boltzmann distribution function may be a more satisfactory approach. A brief comparison of these two approaches is made a little later under the discussion of conductance data (page 116).

From the activity coefficients determined, the electrolyte $K_2Pt(CN)_4$ does not behave as a typical 1-2 electrolyte but rather intermediate between a 1-1 and a 1-2 electrolyte. The explanation for this behavior undoubtedly lies in its square planer structure. Perhaps this is either due to extensive solvent interaction at the apex of an octehedron, consisting of the cyanide molecules and paired 5d electrons, or to extensive ion - ion interaction at these apexes.

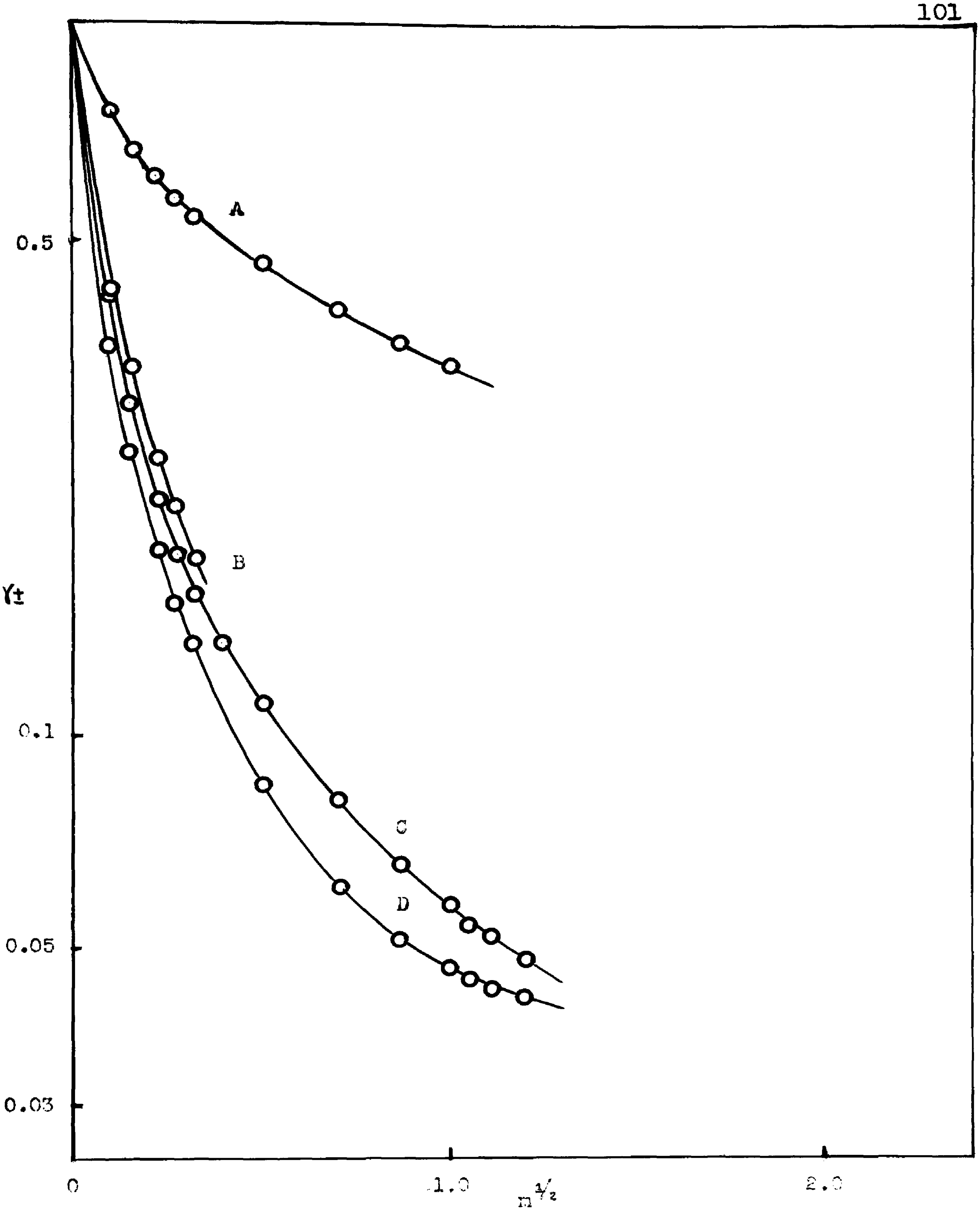


FIGURE 7

$\gamma_\pm$ versus $m^{1/2}$ for A-$K_2Pt(CN)_4$, B-$Pt(pn)_3Cl_4 \cdot H_2O$, C-$K_4[W(CN)_8] \cdot 2H_2O$, D-$[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$

Determination of Ionic Conductances

It was considered desirable to determine the conductance of these electrolytes whose activity coefficients had been determined, since it is possible to evaluate the mean distance of closest approach, $\mathring{a}$, from such data (56, 57). In this way, the value of $\mathring{a}$ obtained from isopiestic measurements could be substantiated by a method independent of the isopiestic method.

The equivalent conductance data obtained from resistance measurements were initially plotted as a function of $c^{\frac{1}{2}}$. This treatment follows from consideration of Onsager's relation for the conductance of strong electrolytes, which the electrolytes investigated in this paper were assumed to be,

$$\Lambda = \Lambda^{\circ} - S\ c^{\frac{1}{2}}.$$

Such a graphical procedure is known to yield a straight line plot in the most dilute regions for lower charged strong electrolytes. However, for these electrolytes a slight curvature was noticed throughout the region of the lowest experimental concentrations. Although the curvature in many cases was not too great, the slopes of these curves were quite large as they approached infinite dilution; and a simple linear extrapolation to infinite dilution would appear to introduce a considerable error in the value of Λ° found by this procedure.

Values of Λ^o obtained by this procedure are listed below.

TABLE V

Values for Limiting Conductance
Determined by Linear Extrapolation
of Λ versus $c^{\frac{1}{2}}$ Curves

Electrolyte	Λ^o ohm^{-1}
$K_4[W(CN)_8]\cdot 2H_2O$	191.7
$[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$	157.5
$Pt(pn)_3Cl_4\cdot H_2O$	166.5
$K_2Pt(CN)_4$	154.7

The data were then treated by the method of Shedlovsky (13), involving the rearrangement of Onsager's conductance equation so that Λ^o may be calculated directly from individual values of Λ .

The reasoning behind this method is that although Onsager's relation would not be expected to hold at higher concentrations, it should become more valid as infinite dilution is approached. Thus, a variable $\Lambda^{o\prime}$, defined by

$$\Lambda^{o\prime} = \Lambda + S\,c^{\frac{1}{2}},$$

should approach a constant value of Λ^o for the most dilute solutions. However, it is necessary to have a value of Λ^o in order to evaluate the constant S. For this purpose, as a first approximation, the values of the Λ^o obtained from a linear extrapolation of the Λ versus $c^{\frac{1}{2}}$ curve were used.

Graphs of $\Lambda^{o\prime}$ versus c^* were prepared, Figure 8[1]. These curves appear to become linear for the most dilute experimental values; however, the slopes of these curves are even greater than the slopes of the Λ versus $c^{*\frac{1}{2}}$ curves; and, hence, an even greater error would be introduced in the determination of Λ^o by a linear extrapolation procedure.

Failure of the above two methods in finding a suitable extrapolation procedure for evaluating a Λ^o led to the use of a method by Owen (55) which had been previously used by various investigators who have dealt with higher charged electrolytes. This method is based upon empirical extensions of the simple Onsager equation of the form

$$\Lambda = \Lambda^o - S\ c^{*\frac{1}{2}} + Ac^* \log c^* + Bc^*,$$

where A and B are empirical constants to be determined. The above equation can be rearranged into the form

$$\frac{\Lambda^{o\prime} - \Lambda^o}{c^*} = A \log c^* + B.$$

This equation represents an equation for a straight line of slope A and intercept B. This form of the equation can be used to determine a Λ^o without a graphical extrapolation procedure. By this method $\frac{\Lambda^{o\prime} - \Lambda^o}{c^*}$ is plotted as a function of $\log c^*$. The values for Λ^o, obtained from the

---

[1] Graphs of the function $\Lambda^{o\prime}$ versus c^* have been plotted as $(\Lambda^o - \Lambda^{o\prime})$ versus c^*. This has been done in order to compare the relative deviations from Onsager's limiting slopes between the various electrolytes studied. The abscissa has been graduated in terms of c^* to conform to previously published data of this type (66).

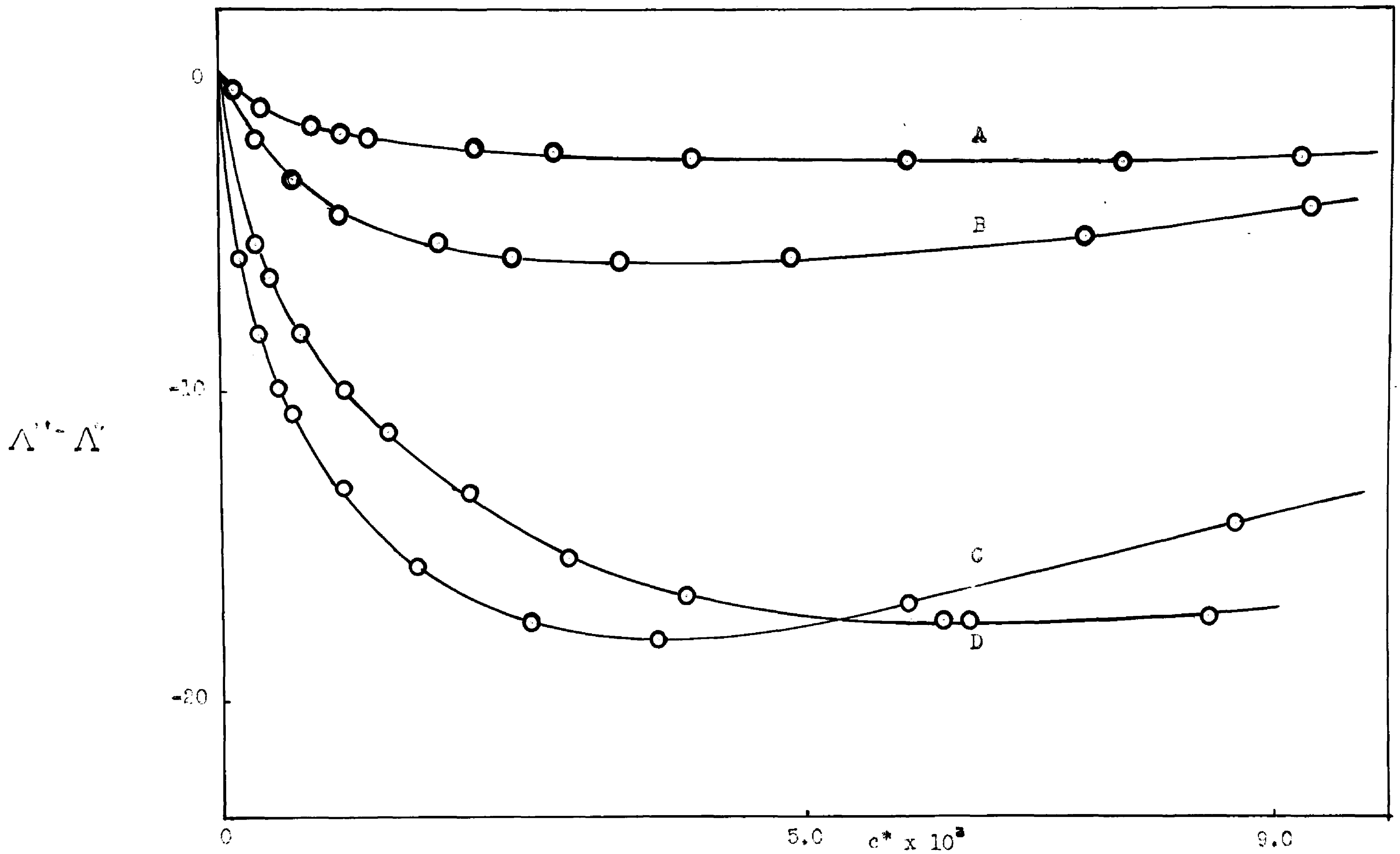


FIGURE 8

Variation of $\Lambda^{\circ\prime}$ with Concentration for Various Electrolytes in Aqueous Solution at 25°C; A-$K_2Pt(CN)_4$, B-$K_4[W(CN)_8]\cdot 2H_2O$, C-$Pt(pn)_2Cl_4\cdot H_2O$, D-$[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$

linear extrapolation of the curve Λ versus $c^{*\frac{1}{2}}$, were again used as a first approximation. Since these values for Λ^{o} did not yield a straight line, then Λ^{o} was lowered accordingly until a straight line function was obtained (Figure 9). Values for Λ^{o} and the arbitrary constants A and B, derived from Figure 9 , are listed in Table VI. The radii of circles shown in Figure 9 represent an error of ± 0.1 ohm^{-1} in $\Lambda^{o\prime}$ which roughly corresponds to a ± 0.05 per cent experimental error.

TABLE VI

Parameters of the Empirically
Extended Onsager Equation

Electrolyte	A	B	Λ^{o}
$K_4[W(CN)_8]\cdot 2H_2O$	4762	9952	191.2
$[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$	6312	11440	157.4
$Pt(pn)_3Cl_4\cdot H_2O$	14626	32301	164.7
$K_2Pt(CN)_4$	2232	4880	154.6

Discussion of Conductance Measurements

Due to the large deviations from the limiting Onsager slopes which appear to be typical of these highly charged electrolytes, the method of Dye and Spedding for determining $\mathring{a}$ values was found to be unsuitable. The method was tried for $K_4[W(CN)_8]\cdot 2H_2O$ which shows the smallest deviation, and the results indicated a value of $\mathring{a}$ too small to have a physical meaning.

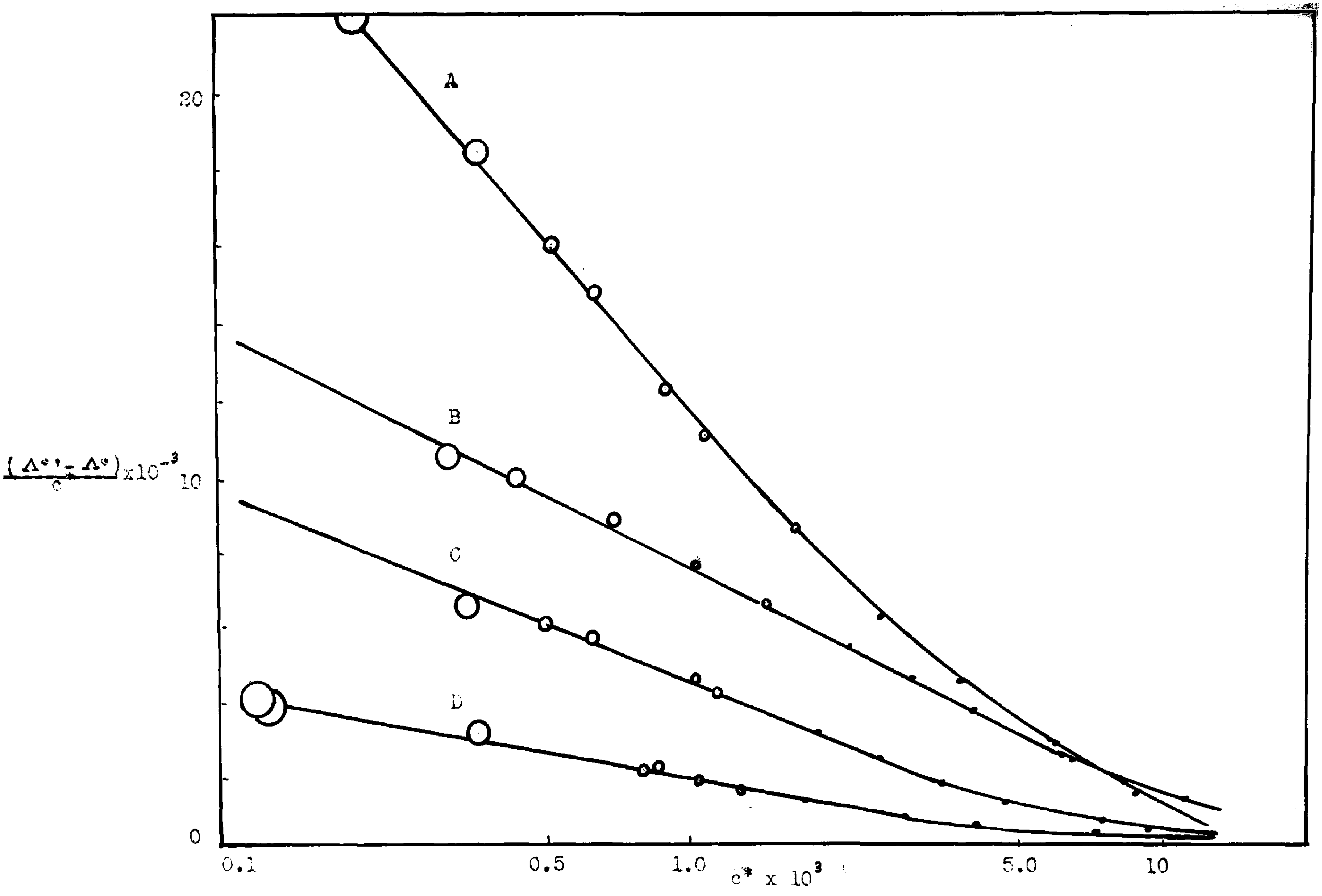


FIGURE 9

Graphical Evaluation of the Parameters in the Empirically Extended Onsager Equation for Various Electrolytes; A-$Pt(pn)_3Cl_4 \cdot H_2O$, B-$[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$, C-$K_4[W(CN)_8] \cdot 2H_2O$, D-$K_2Pt(CN)_4$

Comparison of the results for the evaluation of the limiting conductance, Λ^{o}, for the electrolytes studied by:

(a) simple linear extrapolation of a graph of Λ versus $c^{*\frac{1}{2}}$, Λ^{o}_{1};

(b) by application of the empirically extended Onsager equation, Λ^{o}_{2}, is tabulated below.

Electrolyte	Λ^{o}_{1}	Λ^{o}_{2}
$K_4[W(CN)_8]\cdot 2H_2O$	191.7	191.2
$[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$	159.8	157.4
$Pt(pn)_3Cl_4\cdot H_2O$	166.5	164.7
$K_2Pt(CN)_4$	154.7	154.6

The extremely large difference in the Λ^{o}'s obtained by these two methods, especially in the case of $[N(Me)_4]_4Mo(CN)_8$ and $Pt(pn)_3Cl_4$, leaves considerable doubt in the applicability of Owen's method to highly charged electrolytes. The justification for the application of this method to the above electrolytic types was based on prior usage (55).

In one of his original papers (35) on the mathematical derivation of the conductance equation, Onsager stated that more exact computations, which were not attempted at that time because of the mathematical complications involved, would lead to expressions of the type

$$\Lambda = \Lambda^{o} - S\,c^{*\frac{1}{2}} + Ac^{*}\log c^{*} + Bc^{*} \quad \ldots \quad .$$

Specifically, in the derivation of the general equation of continuity terms of higher order than linear in the charge of the reference electrolyte were dropped (page 53). These neglected terms give rise to terms of order c^* and also to transcendental terms which, upon expansion, lead to terms of $c^* \log c^*$ and higher powers of c^* in the conductance equation.

The transcendental term when expanded is a function of $K\overset{o}{a}$ where K is as previously defined (equation 34a) and $\overset{o}{a}$ is the mean closest distance of approach parameter obtained from experiment. Recently Fuoss (59) has pointed out that the expansion representing the transcendental term is only valid for values of $K\overset{o}{a}$ numerically less than 0.2. A rough calculation of $K\overset{o}{a}$ for electrolytes of the 4-1 or 1-4 type shows that for an $\overset{o}{a}$ value of 5, which is the lowest average value for the electrolytes studied in this paper obtained from isopiestic measurements, the limiting concentration at which the $c^* \log c^*$ term would be expected to be valid is approximately 2.5×10^{-3} $\underline{N}$. For an $\overset{o}{a}$ value of approximately 10 which should be a more accurate estimate considering the size of the ions involved in this investigation, the limiting concentration for the validity of using the $c^* \log c^*$ terms would be decreased to approximately 0.7×10^{-3} $\underline{N}$.

From these considerations it must necessarily be concluded that there is no theoretical significance in adapting the extended Onsager equation of Shedlovsky to the electrolytes investigated in this paper. Thus, values of Λ^o derived from this method are considered to be of little theoretical significance. This can be emphasized by considering the values of λ^o_- for the $Mo(CN)_8^{-4}$ ion obtained from conductance measurements of $[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$ and $K_4[Mo(CN)_8]$ and comparing those derived from Owen's method and those derived from the simple linear extrapolation procedure.

Derived values of λ^o_- for the $Mo(CN)_8^{-4}$ ion from conductance measurements of $[N(Me)_4]_4Mo(CN)_8$ are 114.9 ohm^{-1} and 112.5 ohm^{-1} for the linear extrapolation and Owen's method, respectively. The value for the ionic conductance of $N(Me)_4^+$ and K^+ have been taken as 44.9 ohm^{-1} and 73.5 ohm^{-1}, respectively (67). Derived values for the same ion using conductance determinations of $K_4Mo(CN)_8$ by Faber (47) are 115.0 ohm^{-1} and 114.5 ohm^{-1} for the linear extrapolation and Owen's method, respectively. It can be seen that the simple linear extrapolation gives very good results with reproducibility well within the limits of the accuracy which can be obtained by this procedure. On the other hand, the large variation in the values derived from Owen's method is much too great to be due to experimental procedures and, in fact, appears to be a function of the ionic size or mobility of the species of opposite charge in the electrolytic solution.

The large deviations from the Onsager limiting slopes, as evidenced by the deep minima observed in Figure 8, can most probably, in part, be explained to a large degree of association or ion-pair formation, particularly in the case of the 4-1 or 1-4 type of electrolytes.

The concept of ion-pair formation is generally described in terms of Bjerrum's equations of ion pairing (66). Bjerrum's treatment of ionic pairing involves the determination of a probability function for the formation of ion pairs under the influence of coulombic forces. In his formulation of the probability function he has used the complete exponential Boltzmann distribution function in which the potential energy term included in this function has the form of a simple coulombic potential.

This resulting probability function has the property of possessing a minimum at a distance q, such that

$$r\,(\text{min}) = q = \frac{e^2|z_1 z_2|}{2DkT}.$$

Bjerrum has then assumed that two ions at a distance $r < q > \mathring{a}$ are associated. Further application of this probability function results in a formulation of the reciprocal of the ionization constant of the associated ion-pair as

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1 z_2|e^2}{DkT}\right)^3 Q(b),$$

where Q(b) is an integral, in terms of the function b, and whose upper limit depends on the magnitude of the parameter

$\mathring{a}$. The value of the function b is given by

$$b = \frac{|z_1 z_2|^{\;2}}{\mathring{a}\ DkT}\ .$$

Values of Q(b) have been tabulated as a function of b (66). Application of this method to the 4-1 or 1-4 type of electrolytes investigated by Brubaker (53, 60) and in this paper using the value of $\mathring{a}$ for each electrolyte as calculated from the isopiestic method, will yield values for the dissociation constant, K, for the reaction

$$[M^{4}A^{-}]^{+3} \rightleftharpoons M^{4} + A^{-}$$

as listed below in Table VII.

TABLE VII

Ion-Pair Dissociation Constants for 1-4, 4-1 Electrolytes Derived from Bjerrum's Method

Electrolyte	$\mathring{a}$	K
$Pt(en)_3Cl_4$[1]	3.61	338
$K_4Mo(CN)_8 \cdot 2H_2O$[1]	4.33	219
$[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$	4.25	230
$K_4[W(CN)_8] \cdot 2H_2O$	4.80	175
$Pt(pn)_3Cl_4 \cdot H_2O$	5.17	155
$K_4Fe(CN)_6$		176[2]
		237[3]

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[1] Obtained by Brubaker from isopiestic measurements.

[2] The value of K for this substance was estimated by Davies (62) from conductance data of Jones and Jelen.

[3] This value for K was derived from spectrophotometric studies (63).

The usefulness of the absolute values of K tabulated above are doubtful since the validity of the method employed depends strongly on the accuracy of the values of å used in the calculations of K. However, as an order of magnitude result, they appear to be of some value in light of the rather close agreement obtained between these values and the spectrophotometric studies of $K_4Fe(CN)_6$. In particular, there is little reason to believe that the degree of association should vary to any great extent among the complex cyanides listed in Table VII, since they all have almost identical charge to size ratios.

Thus, if we can consider the degrees of association calculated above as reasonable, there is brought to light a discrepancy in the observed conductance data and subsequent treatment of such. This discrepancy is the relative deviation from Onsager's limiting slope between $K_4Mo(CN)_8$ and $[N(Me)_4]_4Mo(CN)_8$ as observed in Figure 8[1]. It should be mentioned, however, that comparison of conductance data for unsymmetrical electrolytes necessitates not only knowledge

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[1] The actual curve of $\Lambda^\circ - \Lambda^{\circ\prime}$ for $K_4Mo(CN)_8$ is not shown; however, data from the work of Faber (47) indicate it is almost identical to that obtained for $K_4W(CN)_8$. Likewise, a curve of this function from data obtained from work done by Jones and Jelen (64) for $K_4Fe(CN)_6$ is also almost identical. In each case, however, there is a shift to lower concentrations in the observed minimum point.

of the degree of association but also the mobility of the ion-pair formed. This is not the case for symmetrical electrolytes for which the ion-pair formed is a nonconducting species.

Here again, it is considered extremely unlikely that the mobility could vary to any great extent between the species $M(Me)_4Mo(CN)_8^{-3}$ and $KMo(CN)_8^{-3}$.

With this reasoning that the mobility of the ion pairs are almost the same and assuming an almost identical degree of association, it is considered highly unlikely that the large deviations from Onsager's limiting slope, which is found for these electrolytic types, can be entirely explained on the basis of Bjerrum's ion-pair concept.

It must necessarily be concluded that a large share of these deviations are due to the failure of Onsager's equations to describe accurately the conductance behavior for electrolytes of this high a charge type. Most certainly, the mathematical simplifications used in deriving the Onsager limiting equations are a contributing factor in the observed deviations indicated in this paper.

All authors in the field of electrolytic conductance agree that by neglecting the higher order terms of the distribution function, particularly in the case of high-valence type electrolytes, a considerable error is introduced in the theoretical calculations of the conductance behavior of these electrolytes. Essentially Bjerrum's theory of ion-pair formation is an attempt to reduce the magnitude of this error. This is done by using the pair-wise Boltzmann distribution function for distances less than q and the linear expanded distribution function at distances greater than q. Actually, one calculates the number of ions within the distance q to å; and because of their close proximity and high interaction terms, they are considered effectively removed from solution as conducting ions. If the electrolyte is symmetrical, both of the interacting ions are effectively removed from the solution. By subtracting these calculated concentrations of ion pairs from the total concentration and then applying Onsager's limiting equations, one has effectively superimposed the complete distribution function over the linear function and has a more correct prediction of the behavior of the conducting species. However, as it was previously pointed out, in the case of unsymmetrical electrolytes such a procedure is not applicable since the ion-pair formed is also a conducting species and must necessarily contribute to the total conductance behavior of the electrolyte.

Of considerable interest, along this line, is the effect of the linear approximation of the Boltzmann distribution function involved in the derivation of the electrophoretic effect which has been recently emphasized by Dye (56).

He has used the complete exponential distribution function instead of the linear function approximation (page 49) in evaluating this correction term.

This procedure may be considered inconsistent since the linear approximation was used in the derivation of the Debye potential which Dye has used in the complete Boltzmann distribution function. Nevertheless, recent calculations made by him (68) show qualitatively that the complete exponential function follows the Bjerrum distribution at close distances to the central ion (in the region of ion-pair formation) and approaches the linear distribution function at farther distances. Although the function does not quantitatively agree with Bjerrum's function, it lies intermediate between it and the linear function and definitely seems to indicate that a large part of the effect normally considered as due to ion-pair formation must be attributed to the neglect of higher order terms. He has shown that for 4-1, 1-4 type electrolytes the neglected higher order terms have a magnitude of approximately 1.3 to 1.7, the value of the correction term calculated from the linear distribution function over a range 4×10^{-4} N to 0.01 N for an electrolyte of $\mathring{a}$ equal to 4. However, of particular interest to this argument is the strong dependence of the higher order terms upon the ion size parameter $\mathring{a}$. Since the ionic size seems to be the only appreciable difference between the $N(Me)_4^+$ and K^+ ions, then perhaps a decided factor in the variation of the conductance behavior observed for the octacyanomolybdates of these ions are higher order neglected terms.

The evaluation of the effects of neglecting some of these higher order terms in the derivation of asymmetry effect for 1-1 electrolytes has recently been reported (58). However, the general treatment of this effect is extremely complicated and has not been attempted for higher valency type electrolytes.

SUMMARY

Activity coefficients and equivalent conductances have been determined for the electrolytes $K_4[W(CN)_8]\cdot 2H_2O$, $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$, $Pt(pn)_3Cl_4\cdot H_2O$ and $K_2Pt(CN)_4$ in aqueous solutions at 25°C.

The activity coefficients and osmotic coefficients were obtained by isopiestic comparison with aqueous potassium chloride solutions. The values of these coefficients determined for the first three electrolytes listed above were comparable to those previously found for similar electrolytes of the 1-4, 4-1 charge type. The values found indicate that these electrolytes may be extensively associated in solution.

Values of the mean distance of closest approach, $\mathring{a}$, have been determined. The numerical values of these parameters vary considerably depending upon the method of calculation.

The equivalent conductances were also ascertained in the hope of determining values for $\mathring{a}$ independent of the isopiestic method. Such determinations could not be made, however, since deviations from the limiting conductance equation of Onsager were too great. Because of these deviations, present methods of determining limiting ionic conductance values most accurately could not be used. Values for these constants were determined, however, by simple linear extrapolation of equivalent conductance versus $c^{*\frac{1}{2}}$ graphs. These derived values are 114.9 ohm^{-1}, 118.2 ohm^{-1}, 90.15 ohm^{-1}, 81.2 ohm^{-1} for the polyvalent ions $Mo(CN)_8^{-4}$, $W(CN)_8^{-4}$, $Pt(pn)_3^{+4}$ and $Pt(CN)_4^{-2}$, respectively.

Complete evaluation of the conductance behavior of these highly charged species must await further mathematical extensions of the present theory of electrolytic solutions.

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APPENDIX I

ISOPIESTIC MEASUREMENTS

A. Observed osmotic coefficients of $K_4[W(CN)_8]\cdot 2H_2O$ at 25°C calculated from the relation $\Phi_{obs} = 0.4 \frac{m_{KCl}}{m} \Phi_{KCl}$

Molality $K_4[W(CN)_8]\cdot 2H_2O$	Molality KCl	Φ $K_4[W(CN)_8]\cdot 2H_2O$
0.0659	0.1176	0.6588
0.0773	0.1369	0.6517
0.1081	0.1859	0.6288
0.1096	0.1870	0.6238
0.2238	0.3593	0.5803
0.2624	0.4130	0.5678
0.3550	0.5456	0.5533
0.3950	0.6069	0.5523
0.4320	0.6609	0.5497
0.4912	0.7406	0.5414
0.5249	0.7917	0.5417
0.5996	0.8924	0.5347
0.8023	1.2010	0.5376
1.0630	1.6143	0.5510
1.2856	2.0166	0.5744
1.5452	2.5445	0.6109

B. Observed osmotic coefficients of $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$ at 25°C calculated from the relation $\Phi_{obs} = 0.4 \frac{m_{KCl}}{m} \Phi_{KCl}$

Molality $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$	Molality KCl	Φ $[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$
0.0544	0.0906	0.6218
0.1039	0.1656	0.5843
0.2003	0.3080	0.5571
0.3806	0.5502	0.5201
0.4478	0.6516	0.5228
0.4551	0.6579	0.5193
0.5505	0.8129	0.5304
0.6390	0.9565	0.5383
0.7241	1.1035	0.5489
0.8510	1.3265	0.5625
1.0751	1.7521	0.5917
1.1505	1.8874	0.5987
1.2355	2.0681	0.6138
1.3384	2.2497	0.6192
1.4588	2.4791	0.6299

C. Observed osmotic coefficients of $K_2Pt(CN)_4$ at 25°C calculated from the relation $\Phi_{obs} = 0.67 \frac{m_{KCl}}{m} \Phi_{KCl}$

Molality $K_2Pt(CN)_4$	Molality KCl	$\Phi_{K_2Pt(CN)_4}$
0.0592	0.0831	0.8745
0.0725	0.1023	0.8697
0.1145	0.1592	0.8494
0.2706	0.3683	0.8189
0.3524	0.4786	0.8146
0.3704	0.5009	0.8108
0.4722	0.6298	0.7980
0.5494	0.7316	0.7962
0.6631	0.8742	0.7892
0.7277	0.9530	0.7841
0.7613	0.9864	0.7759
0.9150	1.1737	0.7699
0.9481	1.2137	0.7686

D. Observed Csmotic Coefficients of $Pt(pn)_3Cl_4 \cdot H_2O$ at 25°C Calculated from the Relation $\phi_{obs} = 0.4 \frac{m_{KCl}}{m}$ KCl

Molality $Pt(pn)_3Cl_4 \cdot H_2O$	Molality KCl	ϕ $Pt(pn)_3Cl_4 \cdot H_2O$
0.0556	0.1007	0.6719
0.0665	0.1179	0.6546
0.0678	0.1197	0.6517
0.0831	0.1435	0.6350
0.1047	0.1771	0.6191

APPENDIX II

CONDUCTANCE MEASUREMENTS

A. Equivalent conductance of $K_4[W(CN)_8]\cdot 2H_2O$ in aqueous solution at 25°C.

Concentration ($\underline{c}^{*} \times 10^{3}$)	Equivalent Conductance (Λ)
0.33052	180.790
0.4945	178.159
0.62008	176.419
1.02520	172.039
1.13040	171.231
1.8984	165.877
2.5052	162.514
3.4308	158.412
4.6416	153.313
4.8724	153.434
7.4252	146.695
9.3191	142.870
10.52	142.091
20.68	130.218
44.48	117.968
90.40	107.606
191.84	97.315
401.16	90.547

B. Equivalent conductance of $[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$ in aqueous solution at 25°C.

Concentration ($\underline{c}^* \times 10^3$)	Equivalent Conductance (Λ)
0.3078	146.474
0.4288	144.042
0.6881	139.843
1.0007	136.121
1.0681	135.149
1.4437	131.318
2.1498	125.638
2.985	119.923
3.9924	114.913
6.2040	107.063
6.4376	106.558
8.4879	101.289
11.0926	96.064
12.04	93.500
27.35	76.821
56.20	65.671
106.5	56.042
208.4	47.042

C. Equivalent conductance of $K_2Pt(CN)_4$ in aqueous solution at 25° C.

Concentration ($\underline{c}^* \times 10^3$)	Equivalent Conductance (Λ)
0.1202	152.545
0.1283	152.501
0.3551	150.825
0.3930	150.509
0.7551	149.076
0.7927	148.973
1.0509	148.110
1.2740	147.529
1.7572	146.505
2.1874	145.685
2.8680	144.543
4.0492	142.866
4.2714	142.112
5.8924	140.660
7.2275	139.192
9.220	138.069
16.448	133.943
24.160	131.357
89.380	119.865

D. Equivalent conductance of $Pt(Pn)_3Cl_4 \cdot H_2O$ in aqueous solution at 25°C.

Concentration ($\underline{c}^* \times 10^3$)	Equivalent Conductance (Λ)
0.19205	154.814
0.33799	150.495
0.35367	150.490
0.51092	147.311
0.62696	145.234
0.63168	145.205
0.88432	141.774
1.0676	139.657
1.6810	133.657
2.6719	127.506
3.7531	122.910
5.929	117.550
8.732	113.385
19.218	101.690
27.344	95.549
54.044	84.168

APPENDIX III

DENSITIES OF SOLUTIONS

The density of all of the electrolytes studied in this paper have been determined at 25°C as a function of concentration. These densities are related to molal concentration units, m, by the linear expression

$$\rho = Am + 0.99707.$$

The values of A for the various electrolytes are listed below.

DENSITY AS A FUNCTION OF MOLALITY

Electrolyte	A
$K_4[W(CN)_8]\cdot 2H_2O$	0.3784
$[N(Me)_4]_4Mo(CN)_8\cdot 2H_2O$	0.1080
$Pt(pn)_3Cl_4\cdot H_2O$	0.3155
$K_2Pt(CN)_4$	0.2514