ACTIVITY COEFFICIENT AND CONDUCTIVITY MEASUREMENTS OF HIGH-CHARGE ELECTROLYTES IN AQUEOUS SOLUTION AT TWENTY-FIVE DEGREES CENTIGRADE

By

Richard A. Wynveen

A THESIS

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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ABSTRACT

Mean activity and osmotic coefficients have been determined at 25° for aqueous solutions of $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$, $K_3Co(CN)_6$, and $[Co(en)_3]_2(SO_4)_3$ by isopiestic comparison with potassium chloride solutions. The salts do not appear to be "strong" 3-1 and 3-2 types and required $\mathring{a}$ values of 3.23, 3.83, 4.01, and 3.43, respectively, to represent the data by means of the Debye-Hückel equation. The results obtained for the 3-1 electrolytes were similar to $Co(en)_3Cl_3$. The solubilities of the $Co(en)_3(NO_3)_3$ and $K_3Co(CN)_6$ were determined to be 0.2749 and 1.311 m, respectively. Measurements were taken over the concentration range from about 0.05 m to the saturated or near saturated solutions.

Conductivity measurements were also made on solutions of the same four electrolytes to about 0.1 N. A decided deviation from the Onsager limiting law was observed. The limiting values obtained were found to be very similar to those obtained by previous workers. The extrapolations were made by the method of Shedlovsky and of Owen. The Shedlovsky procedure gave the higher limiting values, Λ_0. The values of the constants A and B of the extended Onsager equation were determined. A definite cause of the deviations observed must

await extension of the present theories to permit treatment of the high-charge salts studied.

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I. INTRODUCTION

The present work is part of a program involved with a general study of the properties of high-charge type salts in aqueous solution. The main objective is to find salts of high-charge, such as 3-1, 3-2, 4-1, etc., which (1) exhibit little or no tendency to form ion pairs in dilute solution, (2) undergo negligible, if any, hydrolytic action, and (3) are sufficiently soluble so that any theories at higher concentration might be applied.

By means of the preparation of very stable complex salts it should be possible to prepare compounds which actually give ions of charge 3 or 4 in solution. If the cation or anion is large, due to the size and number of coordinated groups, it should be better able to carry this large charge without additional complexation. This means that solvation effects would be smaller owing to the low charge density on these large ion surfaces. Also, if they are sufficiently stable or "inert", hydrolysis would be at a minimum.

The salts studied in this part of the general program are of the 3-1, 3-2, and 1-3 charge types.

Measurement of activity coefficients was suggested by the lack of data on activity coefficients and the effectiveness of measuring them by the isopiestic method.

In addition, it was hoped to be able to determine the distance of closest approach, $\mathring{a}$, from conductivity measurements such as was done by Dye and Spedding (1) for the alkaline-earth and rare-earth salts. In previous tests of this procedure the $\mathring{a}$ values obtained from e.m.f. measurements of mean activity coefficients also gave conductances agreeing with experiment up to 0.008 N. Thus the chance of comparing calculated mean activity coefficients with those obtained experimentally and the availability of the conductivity apparatus dictated measuring a second property, conductivity, of the high-charge salts.

To give a clearer picture of the activity and conductivity theory and calculations, the two properties will be covered separately. For example, the historical treatment of activity coefficients is given first, followed by that for the conductivity; the calculations for mean activity coefficients followed by those for the conductivity, etc. This separation of each section into two parts is adhered to except in cases where a clearer understanding results by considering both properties simultaneously.

The concept of activity in chemical thermodynamics was introduced by G. N. Lewis (2). It was through the substitution of activities for concentrations that the mathematical form of the ideal law was preserved and could be extended to real systems. The activity of a chemical species can be expressed as the product of its concentration and an activity coefficient which measures the deviation of the species from ideal behavior. The numerical value of activity and activity coefficient depends upon the units of concentration employed. For electrolytes the mean activity and mean activity coefficient are used because the activity and activity coefficient of a single ionic species cannot be determined.

Values of activity coefficients can be determined from boiling point elevations, freezing point depressions, e.m.f. measurements using cells with or without liquid junctions, from osmotic coefficients, and vapor pressures.

The activity coefficient is a property determined by measurement of systems in equilibrium. The electrical contance, however, is a property determined by measurements of systems in disturbed states. When an ionizing electrolyte is dissolved in water, the solute consists of electrically charged atoms or groups of atoms, called ions. When an electrical potential is applied between a pair of electrodes in the solution the ions of the electrolyte migrate and a flow of electricity occurs. The specific conductance, L, of a solution is defined as the reciprocal of the solution's specific resistance. The specific resistance is the resistance of 1 $cm.^3$ of a solution between electrodes 1 cm. apart. The specific conductance is a function, therefore, of the same variables as the specific resistance, namely, the nature of the electrolyte, the concentration of the solution, temperature, etc.

The equivalent conductance, Λ, is of more theoretical significance than the specific conductance. It is defined as the conductance of a solution which contains 1 equivalent weight of electrolyte between electrodes 1 cm. apart. The equivalent conductance at infinite dilution, Λ_0, is also an important function in theoretical considerations. It can be defined as the equivalent conductance of a solution which is dilute enough so that further addition of solvent does not affect the conductivity. Its value cannot be measured directly because the concentrations of these dilute solutions are so low that the physical measurements have too high a degree of uncertainty. Its value is obtained by extrapolation of a suitable function of the equivalent conductances and normalities.

This study was undertaken with the purpose of studying the mean activity coefficients and conductivities of four high-charge, complex salts. The salts studied were tris-(ethylenediamine)cobalt(III) nitrate, $Co(en)_3(NO_3)_3$, tris-(propylenediamine)cobalt(III) perchlorate, $Co(pn)_3(ClO_4)_3$, potassium hexacyanocobaltate(III), $K_3Co(CN)_6$, and tris-(ethylenediamine)cobalt(III) sulfate, $[Co(en)_3]_2(SO_4)_3$.

II. HISTORICAL

A. Isopiestic Method

The isopiestic method was introduced in 1918 by W. R. Bousfield (3). He adapted the term "isopiestic" to represent the equilibrium condition resulting after several solutions in a closed container had gained or lost water in order to arrive at the same vapor pressure*. The method was not made practical for accurate determinations of vapor pressures until the work by Sinclair (4) in 1933. At that time the most accurate determinations of vapor pressure were carried out by a method devised by Lovelace, Fraser, and Bahlke (5). Their method involved careful removal of air, a sensitive manometer and attained an accuracy of less than 0.001 mm. The method was, however, much too elaborate for general application.

Sinclair (4), intrigued by the simplicity of the isopiestic method, set out to test its experimental possibilities and found the attainment of equilibrium using the method of Bousfield too slow to be practical. Sinclair (6) and Robinson

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* Isotonic is often used synonymously with isopiestic. It was introduced by Hugo de Vries, who first used an isotonic method in 1882, to define solutions in equilibrium with respect to transfer of the solvent. The term isopiestic, however, seems to have gained the wider acceptance.

and later Scatchard, Hamer, and Wood (7) further improved the method so that vapor pressure measurements would yield activity data with an accuracy comparable with that achieved in the e.m.f. and freezing point methods. The modifications incorporated into the apparatus and procedure to facilitate attainment of equilibrium are as follows. By having good metallic conduction between solutions the retardation of distillation due to thermal resistance between solutions was reduced to a small value. The solutions were held in silver-plated copper dishes, which were then placed in holes bored into a brass block. To prevent fluctuations of temperature, the block was only in contact with its container over a small circular area 5 cm. in diameter, which then acted as an effective thermal buffer. By placing some solution in the crevices between the sample holders (dishes) and the brass block, the distillation rate was greatly increased (due to the reduction of the temperature gradients by substitution of solution for vapor in the gaps). The factors then limiting the rate of attainment of equilibrium were conduction of heat and diffusion of solute through the solution. These factors were minimized by making the solutions shallow and stirring (though not so much as to set up minute heating effects). The solutions were stirred by means of a rocking device situated in the bath. Quantities of the solution were also kept to a minimum, but within weighing accuracy to decrease the amount of water which had to distill. The container was evacuated to remove air which interferred with the distillation. Six drops of water were placed at the bottom to sweep out the air during evacuation and cut down evaporation from the dishes. To control the evaporation and prevent splattering, the air was drawn out very slowly into a bulb of approximately the size of the container, which in turn was connected to the vacuum line. When the pressure reached that of the vapor pressure of water, the vessel was evacuated ten more times to ensure complete removal of air. The isopiestic procedure had one serious drawback. With solutions below 0.1 m, the time required to reach equilibrium was between one and two weeks. Often equilibrium never seemed to be attained. Hence, as a rule the values obtained at low concentrations tended to be somewhat erratic.

In 1943 R. A. Gorden (8) ran a series of measurements on the system KCl-NaCl over the concentration range from 0.03 to 0.10 m and at 25°. He reports that the most serious experimental difficulty is the removal of air from the system. Evidence was adduced that the extreme slowness with which equilibrium is attained in dilute solutions is primarily due to the rate of transportation of solvent in the vapor phase. The procedure adopted to reduce this was to pump the vessel initially down only to 60 mm. pressure and then allow it to rock for 6 hours; it was then pumped to 30 mm. and left overnight; in the morning, a further pumping reduced the pressure to the vapor pressure of water. It was then allowed to rock for 3 periods of 24 hours, at the end of each period the vapor above the solutions was pumped off. In this way he found he could effect a fairly complete degassing of the solutions and thus eliminate the erratic results at low concentrations.

In 1936 Robinson and Jones (9) measured the activity coefficients of some bivalent metal sulfates. The 2-2 charge type was examined since the symmetry was retained and hence rendered the theoretical treatment less complicated. They first calculated the osmotic coefficients, ϕ, of KCl by*

$$\phi = \frac{55.51}{2m} \ln \frac{p_o}{p}$$

from molar vapor pressure lowerings reported by Robinson (10). Since p_o/p is the same for two isopiestic solutions, the osmotic coefficient of the sulfates could be calculated. The activity coefficients were then calculated* by the method of Randall and White (11).

Mason and Ernst (12) used the isopiestic method for the measurement of the vapor pressure of aqueous solutions of lanthanum chloride and hence showed that it was also applicable to 3-1 electrolytes.

* The theory involved in obtaining and using this equation will be postponed until the Theoretical Section.

Due to the uncertainty in the experimental results when the isopiestic method was used below 0.1 m some form of extrapolation was necessary to obtain results from 0.1 m to zero concentration. Robinson and Jones (9) accomplished this by calculating the activity coefficients for concentrations less than 0.1 m from the literature data using the freezing point and e.m.f. measurements. Mason and Ernst (12) overcame the difficulty by using the Debye-Hückel equation (page 29).

In 1938 Mason (13), with revised techniques, extended the method to the determination of the vapor pressures of 6 more 3-1 electrolytes and extended his $LaCl_3$ data to higher concentrations and obtained more accurate data below 0.4 m. The main features included the use of platinum gauze in the solutions to ensure more rapid thermal and distillation equilibrium and a good thermal contact secured by pressing the dishes firmly against the bottom of the brass block while the dishes themselves fit tightly in the holes provided for them in the brass block.

The activity coefficients of a large number of compounds have been determined by the isopiestic method. Of special interest is the application of the isopiestic procedure to complex salts similar to the ones considered in the present study. Robinson (14) applied the procedure to $K_4Fe(CN)_6$ and Brubaker (15,16) reported his findings on four additional complex salts of the 4-1, 1-4, and 3-1 charge type. There still remains, however, a definite lack of information on the mean activity coefficients at high concentrations for other similar salts.

B. Conductivity

The study of the phenomena exhibited by chemical substances when they are subjected to the action of electrical forces began in 1776 with Cavendish. He measured the conductivities of aqueous solutions of chemical compounds (17). In his apparatus the solution whose resistance was to be compared was contained in a long tube with movable wire electrodes inserted at each end. One set of electrodes from two such tubes were connected with the outside of a Nairne battery of Leyden jars, while the other electrodes were connected each to a separately insulated piece of tinfoil. Cavendish charged all the jars of the battery together to a known degree of electrification and shorted first one of the pieces of tinfoil through his body, then the other. By adjusting the lengths of the liquid columns, he was able to judge when he received a shock of the same intensity from each, and thus was able to compare the resistances of the two electrolytes.

The branch of chemistry which deals with the electrical conductivity of solutions can actually be said to have originated when a distinction was drawn between metallic conduction and electrolytic conduction.

One of the most noteworthy of the early investigators is Kohlrausch. He made an extensive study of the variation of the conductivity of electrically conducting solutions with concentration and temperature, and discovered that the specific conductivity, L, changed with concentration. By expressing the concentration, N, in terms of gram-equivalents per 1,000 cm^3 he was able to measure the equivalent conductance of the solution, which is defined as

$$\Lambda = \frac{1000\ L}{N} \tag{2}$$

Kohlrausch (18) then proceeded to show that in dilute solutions, the conductivities of strong electrolytes could be expressed empirically by the equation

$$\Lambda = \Lambda^{o} - k(N)^{\frac{1}{2}} \tag{3}$$

known as the square root law. It is also due to Kohlrausch that we have the law of independent ionic mobilities (19),

$$\Lambda^{o} = \lambda_{+}^{o} - \lambda_{-}^{o} \tag{4}$$

Here λ_{-}^{o} and λ_{+}^{o} represent the contributions to the limiting value of the equivalent conductivity due, respectively, to the anion and cation of the electrolyte.

In 1923, Debye and Hückel (20,21), gave an analysis of the specific distribution principle which enabled them to calculate the conductivity of solutions.

The resistance of an electrolytic solution is most frequently determined by means of some form of Wheatstone bridge circuit, one arm of which is a conductivity cell containing the solution. In the earliest measurements direct current was employed, but this caused the results to be erratic because of the so-called "polarization" due to gases liberated at the electrodes. Following the suggestion of F. Kohlrausch (22), a rapidly alternating current is now generally used. The direction of the current is reversed about a thousand times per second, so that the "polarizations" produced by successive pulses counteract one another. Kohlrausch did his experiments on the conductivity of electrolytes using a simple slide-wire bridge, an induction coil as a source of current to minimize the polarization, and a telephone to find the point of balance. The telephone replaced the galvanometer originally used as the detector.

Since the initial development of the a.c. conductivity bridge, many technical advances have been made in bridge design, and in the source of and method of detection of the a.c. signal. To give a complete review of the subject would require a lengthy treatise. However, certain points in the development will be considered, especially those in a series of papers by G. Jones and co-workers.

In 1928 Jones (23) published the first paper of the series.

It consisted of an experimental and theoretical study of the principles of design of the Wheatstone bridge for use with alternating current. It was pointed out in this paper that the use of water as a thermostat liquid for electrical conductivity gave erroneous results, since the presence of a conductor (i.e., water) near the cell caused an error in the value of the resistance being measured. Although the reasons for the errors were not all known, use of oil as the thermostat liquid gave results independent of grounding, value of resistance being measured, specific conductivity of the bath liquid, and frequency.

In 1929, Jones and co-worker (24) reported on some improvements in the oscillator and detector. Their studies included the variation of resistance and polarization with voltages, amplification, and bridge pickup. Their modifications made use of lower voltages to reduce heating effects of the current in the cell which, however, reduced the sensitivity. To correct this they improved the step-up ratio of the amplifier. This in turn resulted in increased disturbances, such as tube noise, electric circuit hum, etc. To counteract these disturbances they used wave filters, which consisted of a variable inductor and a variable condenser in parallel with the telephone detector.

In 1923, Parker (25) stated that he had experimental proof that "cell constants" were not really constant but vary with the resistance being measured. In 1930, Shedlovsky (26) undertook to design, build, and test a new form of cell which could be used to check the variation in "cell constant" when the nature or concentration of the measured solution was varied. (i.e., variation in magnitude of resistance). His cell consisted of four electrodes which were free from errors due to effects at the electrode which caused changes in the "cell constant". Thus cells with two electrodes could be compared with the four electrode cell. In 1931, Jones and Bollinger (27) also undertook the study of cell design to investigate the variation of cell constant with resistance. Jones termed this phenomenon the "Parker Effect" to distinguish it from polarization. The fact that the "Parker Effect", a function of bridge design generally being used at that time, was unobserved or at least unreported caused Jones to state that suspicion was thrown on all previous conductivity measurements of electrolytes in which the Kohlrausch bridge method had been used. Harned and Owen (28) summarized the behavior somewhat as follows:

> "The capacitance of the cell is ordinarily compensated by a variable condenser in the opposite bridge arm, but Jones and Bollinger showed that if the leads to the electrodes are not widely separated from certain parts of the cell which contain solution, there is produced a capacitance by-path of such a nature that compensation is not practicable."

It was shown that this fault in cell design would produce an error which must vary with the specific resistance of the solution. This offered a ready explanation for the observation that the cell constants of certain cells show a slight variation with the conductivity of the solution. To ascertain this point Jones and Bollinger went through a proof which is much too elaborate to be given in detail, but involved a variation of phase angle, frequency, resistance, degree of platinization and size of electrodes. It was in this study that the modern day bridge design had its foundation.

Ohm's Law is defined as

$$E = IR \qquad 5$$

where E is the potential applied across the ends of a conductor, I the current, and R the resistance of the conductor. The unit of the resistance is thus determined by choice of the units of potential and current. If E is measured in volts and I in coulombs per second, i.e., amperes, then R is in absolute ohms. Ohm found that R is directly proportional to the length, l, of a uniform, homogeneous conductor and inversely proportional to the cross section, A, so that,

$$R = \sigma \frac{l}{A}. \qquad 6$$

The proportionality factor σ is defined as the specific resistance of the given conductor in ohm cm. (and represents the resistance of a conductor of 1 cm. length and 1 cm.^{2} cross section).

The reciprocal $1/\sigma = L$ is termed the specific conductance of the conductor; its dimensions are ohm^{-1}cm.$^{-1}$, (and its numerical value is equal to the length in cm. of a conductor of unit cross section which has a resistance of one ohm).

These relations are valid for electronic conductors if it is assumed that constant conditions exist, particularly with regard to temperature. In examining the applicability of Ohm's Law to electrolytes, it was found that the current which passes thru an electrolyte solution is directly proportional to the applied e.m.f., and thus Ohm's Law is obeyed. The validity of Ohm's Law for electrolytes indicates that the mobility and charge of ions are independent of the strength of the applied electric field.

Two sets of conditions are known, however, when deviations from Ohm's Law occur. Debye and Falkenhagen, (29) showed that if the frequency of the alternating current used in measuring resistances is so high that the period of oscillation of the ion is comparable with the time required for the formation of the ion-atmosphere, the "period of relaxation" effect will begin to diminish and the mobility of the ion increases with increasing frequency.

The second set of conditions under which Ohm's Law fails to hold was investigated by Wien (30). Wien showed experimentally that at a sufficiently high field strength (3,000 to 300,000 v./cm.) the conductivity was also observed to increase. The explanation is that the velocities of the ions become so high, with these large fields, that the ionic atmospheres are left behind entirely, and the ions move independently.

In 1931, Jones and Bollinger (31) published their fourth paper on the measurement of the conductance of electrolytes, with emphasis on the validity of Ohm's Law for electrolytes. They demonstrated that if adequate experimental precautions are taken to avoid errors due to heating, to 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 voltage and frequency suitable for use in the Kohlrausch method of measuring electrical conductivity and, hence, Ohm's Law applies.

The relation between the measured resistance across the terminals of a conductivity cell and the specific conductivity of the solution depends upon the geometry of the cell. To avoid the necessity of constructing cells of uniform and accurately known dimensions, a cell constant, k, was incorporated and is calculated by the equation

$$L = k/R \qquad 7$$

from the measured value of R when the cell contains a standard solution of known specific conductivity, L. After Kohlrausch developed his method of measuring conductance of solutions by an a.c. bridge, he (32) determined the specific conductance of standard KCl solutions by mechanically determining the cross sectional area, a, and length, l, of two cells ($k = l/a$ in cm^{-1}). There was, however, some ambiguity in the manner in which Kohlrausch described the composition of his standard solutions. Parker and Parker (33) in order to eliminate an inconsistency in units, proposed a new concentration unit, the demal. A demal, (written 1D), solution was defined as one containing a gram molecule of salt dissolved in one cubic diameter of solution at 0°.

Jones and Bradshaw (34), using the latest principles in bridge and cell design, made new absolute measurements of the specific conductivity of standard KCl solutions and these are the standards generally accepted today.

An analysis of the errors due to polarization and the factors upon which polarization depends was reported in a paper on the galvanic polarization by alternating current published in 1935 by Jones and Christian (35). With the use of a conductivity cell having a movable electrode and micrometer caliper to control and measure the separation, they came to the following conclusions. First, polarization resistance is inversely proportional to the square root of the frequency;

2) polarization causes a capacitance in series with the resistance which decreases with increasing frequency; 3) both polarization resistance and polarization capacitance are greatly dependent on the metal used for the electrodes and dependent to a lesser extent on the electrolyte and temperature, but independent of the current density and separation of the electrodes and uninfluenced by another superimposed current of a different frequency.

Although Kohlrausch (18) discovered that errors due to polarization can be minimized by platinizing the electrodes, Jones and Bollinger developed a convenient and reliable quantitative test for the quality and sufficiency of the platinization. During this study they gave proof of Warburg's law, that polarization resistance is inversely proportional to the square root of the frequency within the audio range. A test of the effectiveness of the platinization could be based on this law,

$$R_s = R_t + K/(\omega)^{\frac{1}{2}} \qquad 8$$

where R_s is the measured or apparent resistance of the cell and R_t is the true resistance of the electrolyte solution with errors due to polarization eliminated. Therefore, if the measured resistance, R_s, is plotted against the reciprocal of the square root of the frequency, $(\omega)^{-\frac{1}{2}}$, a straight line should be obtained, provided the other causes for variation of resistance with frequency have been eliminated. The intercept of this line on the axis of the resistance should give the true resistance. The difference between the apparent resistance and the true resistance as thus determined gives the error due to polarization. This depends upon the frequency, quality of the platinization and possibly on other factors. If the error as thus determined is insignificant the platinization is adequate and no correction needs to be applied to the measured resistance to give the true resistance. The platinizing solution used by Jones and Bollinger was composed of 0.025 N HCl containing 0.3% by weight $PtCl_2$ and 0.025% of lead acetate. The lead acetate was found to improve the quality of the platinization.

A great number of conductance studies have been reported. Of special interest are those on salts similar to the ones in the present series. James and Monk (37) reported on the conductivities of several 1-3 and 3-3 hexacyano complex salts. In 1951, they (38) reported on the conductivities of some complex cobalt chlorides and sulfates. Since the limiting values of the chloride and sulfate were known to a high degree of accuracy, this permitted the evaluation of the limiting values for the complex ions. In both cases the results were obtained over a narrow concentration range, thus limiting their usefulness. The Owen (39) method of extrapolation was used to obtain the limiting values and dissociation constants were calculated to explain the results obtained.

In the present study some of the same salts were studied, but to much higher concentrations, and additional salts were also examined.

III. THEORETICAL

In their general treatment of electrolytic solutions Harned and Owen (40) present a detailed discussion of the fundamental theories and basic experimental methods involved in studying electrolytic solutions. Robinson and Stokes (41) also present a general treatment of this subject, but in less detail. The present section will give a brief resumé of the theories and thermodynamic background required to study the two properties with which this thesis is concerned. Further amplification of this section can be found in the two preceeding references.

The modern quantitative theory of electrolyte solutions is based on the concept of the forces acting on the ions due to the presence of the ions themselves and external forces. In its higher refinements the sizes of the ions and interactions with solvent molecules are also considered. The theory was founded by Debye and Hückel (20) in 1923. They developed a theory for quantitatively predicting the deviations from ideality of dilute electrolyte solutions by making use of the basic assumptions that: (a) all deviations of dilute electrolytic solutions result from the electrostatic interactions between ions; (b) strong electrolytes are completely dissociated into ions in dilute solution; (c) each ion can be treated as a point charge; and (d) the dielectric constant of the solution is the same as that of the solvent. The fundamental idea, underlying the deductions, is that as a consequence of the electrical attraction between ions of opposite charge, there are, on the average, more ions of unlike sign than of like sign in the neighborhood of any ion. Every ion may, therefore, be regarded as being surrounded by a centrally symmetric ionic atmosphere having a resultant charge whose sign is opposite to that of the ion itself.

The essential feature is the calculation of the electrical potential, Ψ, at a point in the solution in terms of the concentration and charges of the ions and the properties of the solvent. This was done by combining the Poisson equation (a general expression of Coulomb's law of force between charged bodies) of electrostatic theory with a statistical distribution formula to formulate a "distribution function" which gives the probability of finding a particle in a given position relative to another particle.

Using the Poisson equation expressed in the special form for the spherically symmetrical case, the electrical potential Ψ at a distance r from a given spherical central ion-j is given as

$$\frac{1}{r^2}\frac{d}{dr}\left(\frac{r^2 d\Psi_j}{dr}\right) = -\frac{4\pi}{D}\rho_j \qquad 9$$

where D is the dielectric constant of the solvent, ρ_j is the charge density and the subscript j is attached to ρ and Ψ to point out that the moving j-ion is the center of the coordinate system.

Debye and Hückel assumed the Boltzmann distribution law, according to which, since the electrical potential energy of an i-ion is $z_i \epsilon \Psi_j$, the average local concentration n_i' of the i-ions at the point in question is

$$n_i' = n_i \exp\left(\frac{-z_i \epsilon \Psi_j}{kT}\right) \qquad 10$$

where n_i is the number of ions of species i per cm^{-3}, z_i the charge on the i-ion, ϵ the charge on the electron, k the Boltzmann constant, and T the absolute temperature. Since each i-ion carries a charge $z_i \epsilon$, the net charge density is, summing for all ionic species

$$\rho_j = \sum_i n_i z_i \epsilon \exp\left(\frac{-z_i \epsilon \Psi_j}{kT}\right) \qquad 11$$

By expanding the right-hand side of equation (11) into an exponential series and considering only solutions so dilute that ions will rarely be very close together (i.e., $z_i \epsilon \Psi_j \ll kT$) all terms of higher order than the second can be omitted. The first term of the expanded form also vanishes since the solution is electrically neutral, meaning

$$\sum_i n_i z_i = 0 \qquad 12$$

Thus only the term linear in Ψ is left and equation (11) reduces to

$$\rho_j = -\sum_i \frac{n_i z_i^2 \epsilon^2 \Psi_j}{kT} \tag{13}$$

By substituting the expression just obtained for ρ_j into equation (9) one obtains the Poisson-Boltzmann equation

$$\frac{d}{dr}\left(r^2 \frac{d\Psi_j}{dr}\right) = \kappa^2 r^2 \Psi_j \tag{14}$$

where

$$\kappa^2 \equiv \frac{4\pi\epsilon^2}{DkT} \sum_i n_i z_i^2 \tag{15}$$

Equation (14) can be solved by substituting $u = \Psi_j r$ giving

$$\frac{d^2u}{dr^2} = \kappa^2 u \tag{16}$$

so that

$$u = Ae^{-\kappa r} - Be^{\kappa r} \tag{17}$$

or

$$\Psi_j = \frac{Ae^{-\kappa r}}{r} - \frac{Be^{\kappa r}}{r} \tag{18}$$

A and B are constants and determined by applying the appropriate boundary conditions, namely that (a) $\Psi_j = 0$ when $r = \infty$;

(b) both Ψ_j and $d\Psi_j/dr$ must be continuous at $r = a$, where a is the distance of closest approach of the other ions to the central ion j. The solution of equation (18) under these boundary conditions is

$$\Psi_j = \frac{z_j\epsilon}{Dr} \cdot \frac{\exp\left[\kappa(a - r)\right]}{1 + \kappa a} \qquad 19$$

This equation represents the Debye-Hückel expression for the time average potential at a distance r from the j-ion of valence z_j and in absence of any external force.

At $r = a$, the potential, given by equation (19) after expansion and neglecting higher terms, becomes

Failure to see where comes in

$$\Psi_j = \frac{z_j\epsilon}{Da} \cdot \frac{1}{1 + \kappa a} = \Psi_o - \Psi_j^* \qquad 20$$

where

$$\Psi_o = \frac{z_j\epsilon}{Da} \qquad 21$$

and

$$\Psi_j^* = \frac{-z_j\epsilon}{D} \cdot \frac{\kappa}{1 + \kappa a} \qquad 22$$

Here Ψ_o is simply the potential at a distance $r = a$ due to the charge $z_j\epsilon$ in a medium of dielectric constant D and Ψ_j^* is the potential due to the ionic atmosphere.

Knowing Ψ_j we can calculate the work that must be expended to charge the ions reversibly to the potential ψ_j, and this work will be the free energy due to electrostatic interactions. The extra electric free energy is simply related to the ionic activity coefficient, since both are measures of the deviation from ideality. Thus for a single given j-ion the extra free energy is equal to the additional electrical work required to charge the j-ion, due to the presence of its ion-atmosphere, to the required potential ψ_j^*. Hence

$$\Delta F = w = kT \ln f_j = \int_0^{z_j} \psi_j^* d(z_j \epsilon) \qquad 23$$

Substituting equation (22) into equation (23) and integrating yields

$$-kT \ln f_j = - \frac{z_j^2 \epsilon^2}{2D} \cdot \frac{\kappa}{1 + \kappa a} \qquad 24$$

The quantity κ was defined in equation (15) as

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_i n_i z_i^2 \qquad 15$$

and has the dimensions of reciprocal length. The relationship between the concentration n_i (ions per cc.) and c_i, the concentration of an ion in mols per liter of solution, is expressed by

$$c_i = \frac{1000 \; n_i}{N} \qquad 25$$

where N is Avogadro's number. Consequently, by defining the "ional" concentration as

$$\Gamma = \sum_{i} c_i z_i^2 \qquad 26$$

or in the important special case of solutions containing only a single electrolyte, which dissociates into only 2 kinds of ions

$$\Gamma = c \sum_{i} \nu_j z_j^2 \qquad 27$$

then

$$\kappa = \left(\frac{4\pi\epsilon^2 N \Gamma}{1000 DkT} \right)^{\frac{1}{2}} \qquad 28$$

Although there is no way of measuring the individual activity coefficients, it is nevertheless convenient to have the expression for the activity coefficient of an electrolyte in terms of the ions into which it dissociates. For the general case of an electrolyte $A_{\nu_+}B_{\nu_-}$ dissociating into ν_+ cations and ν_- anions, the mean rational activity coefficient may be defined

$$f_\pm \equiv f^{1/\nu} \equiv \left(f_+^{\nu_+} f_-^{\nu_-} \right)^{1/\nu} = \left(\frac{a_{c\pm}}{c_\pm} \right)^{1/\nu} \qquad 29$$

with

$$\nu = \nu_+ + \nu_- \qquad 30$$

and the mean ionic activity defined by

$$a_{\pm} \equiv (a_{+}^{\nu_{+}} a_{-}^{\nu_{-}})^{1/\nu} = a^{1/\nu} \qquad 31$$

and the mean ionic concentration defined by

$$c_{\pm} \equiv (c_{+}^{\nu_{+}} c_{-}^{\nu_{-}})^{1/\nu} = c^{1/\nu} \qquad 32$$

Thus by combining equations (24), (28), and (29) and changing into common logarithms the expression for calculating mean activity coefficients in dilute solutions is obtained.

$$\log f_{\pm} = - \frac{S(f)(c)^{\frac{1}{2}}}{1 + A'(c)^{\frac{1}{2}}} \qquad 33$$

where

$$S(f) = \frac{2.303}{\nu}\left(\sum_{1}^{2} \nu_j z_j^2\right)^{3/2} \epsilon^2 \kappa \qquad 34$$

and is the Debye-Hückel limiting slope and

$$A' = \frac{\mathring{a} \kappa 10^{-8}}{(c)^{\frac{1}{2}}} \qquad 35$$

where $\mathring{a}$ is the distance of closest approach expressed in Ångstrom units. Harned and Owen (42) have calculated the numerical values of S(f) and $A'/\mathring{a}$ for aqueous solutions at 25° for different salt types.

So far, the fundamental theory necessary for treatment of the ionic atmosphere has been considered and applied to the calculation of the limiting law for the variation of activity coefficients. By addition of further concepts, such as application of the general equation for continuity to irreversible processes, it is possible to formulate exact equations for computing the electrostatic contribution of Coulomb's forces to conductance of dilute electrolyte solutions. The development of the theory is due to Debye and Hückel (21), Falkenhagen (29), and Onsager (43).

It will be remembered that Kohlrausch showed that, in dilute solutions, the conductivities of strong electrolytes could be expressed empirically by the equation

$$\Lambda = \Lambda_0 - k(N)^{\frac{1}{2}} \qquad 3$$

This equation was also obtained for dilute solutions from the ion atmosphere theory, by Debye and Hückel. The reason why it applies only to the limiting case of very dilute solutions is apparent from the assumptions which must be made in deducing it. Debye and Hückel first showed that, as a consequence of the ion atmosphere which form around any ion, this ion is subject to two retarding influences when it moves in an electric field (21). First, whenever the ions of an electrolyte are subjected to an electrical field disturbance, the central ion moves relative to its ionic atmosphere and hence the latter no longer possess a symmetrical structure, i.e., there is a change in the charge density. This is known as the dissymmetry effect. If the disturbing force is suddenly removed, the ionic atmosphere will tend to revert to its normal equilibrium condition with a certain velocity. The finite time required for change from the disturbed to the normal condition is called the "time of relaxation".

The second electrical action that lowers the mobility of the ions is called the electrophoretic effect. It arises in the following manner; the ions comprising the atmosphere around a given central ion are also under the influence of the applied field and hence are also moving and, on the average, in the opposite direction. Also, since they are solvated, they tend to drag along with them their associated solvent molecules, which results in a net flow of solvent in the direction opposite to the motion of any given solvated central ion. The central ion is thus forced to move against this countercurrent, which accounts for its lower mobility.

A limiting law has been calculated for conductance of electrolytes using methods similar to those used in obtaining the limiting law for activity coefficients. However, the conductivity limiting law is a result of the two effects which slow down ion mobilities, i.e., relaxation and electrophoretic effects.

The limiting law for the relaxation effect was first developed by Debye and Hückel (21) but treated more successfully by Onsager (43), using an incomplete expression for potential and assuming point charges. Falkenhagen and coworkers (44) extended and modified the theory in order to make allowances for the finite sizes of the ions.

The computation of the concentration-dependent electrophoretic effects also requires the use of the distribution function, but in this case with a disturbed symmetry. The Boltzmann distribution, or a similar distribution, is again assumed and Stokes' law for the motion of a sphere in a viscous fluid is then applied. Its application arises in the calculation of the velocity of the counter-current which the central ion experiences due to the electric force applied. It is assumed that the entire charge, $(-z_i\epsilon)$ of an ionic atmosphere is found at a distance $1/\kappa$ from the central ion and is distributed on a spherical shell of the radius $1/\kappa$.

By combining the two effects, the final velocities can be calculated. The velocity of the ion under a potential gradient of unity gives the ionic mobility, which, when multiplied by Faraday's constant, F, gives the ionic conductance. Since

$$\Lambda = \lambda_+ + \lambda_- \qquad 36$$

the limiting law expression may be formulated. In its final form the limiting law (for the conductance of electrolytes dissociating into two kinds of ions in fields of low frequency and magnitude) may be written

$$\Lambda = \Lambda_o - S_{(\Lambda)}(N)^{\frac{1}{2}} \qquad 37$$

where

$$S_{(\Lambda)} = \alpha^* \Lambda_o + \beta^* \qquad 38$$

and represent the limiting slope. For aqueous solutions at 25^o the constants are defined as follows (45),

$$\alpha^* = .2289w'Q \qquad 39$$

and

$$\beta^* = 60.19w^* \qquad 40$$

The factors w', w^*, and Q are valence factors and defined by

$$w' = |z_1z_2|(|z_1z_2|\nu/2)^{\frac{1}{2}} \qquad 41$$

$$w^* = \left(\frac{|z_1| + |z_2|}{2}\right)\left(\frac{\nu|z_1z_2|}{2}\right)^{\frac{1}{2}} \qquad 42$$

and

$$Q = \frac{q^*}{0.2929[1 + (q^*)^{\frac{1}{2}}]} \qquad 43$$

The parameter q^* which appears in the definition of Q is given by

$$q^* = \frac{|z_1z_2|(\lambda_1^o + \lambda_2^o)}{(|z_1| + |z_2|)(|z_2|\lambda_1^o + |z_1|\lambda_2^o)} \qquad 44$$

The Onsager conductance equation is one means of comparing theory with experimental results. Several extensions have been used for extending the range in which the Onsager equation can be used. One such extension considers the introduction of finite dissociation constants to interpret the conductance of electrolytes which fall below the limiting law in dilute solution (46). The reciprocal of the ionization constant of the associated ion pair is given by

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{z_1 z_2 \epsilon^2}{DkT}\right)^3 Q(b) \qquad 45$$

Q(b) is an integral in terms of the function b, where b is given by

$$b = \epsilon^2/aDkT \qquad 46$$

Values of Q(b) have been computed by Bjerrum and by Fuoss (47). However, it was pointed out by Kraus (48) that all negative deviations from Onsagers equation can not be ascribed to ion association.

Another extension is based upon estimating the effects of the mathematical simplifications used in deriving the law and correcting by the addition of two terms of order higher than $(c)^{\frac{1}{2}}$. Assuming complete dissociation, Onsager and Fuoss(49) and Fuoss (50) have shown that such terms appear as follows

$$\Lambda = \Lambda^{\circ} - (\Lambda^{\circ}\alpha^{*} + \beta^{*})(N)^{\frac{1}{2}} + AN \log N + BN \qquad 47$$

where the constants A and B are semi-empirical and only in the case of symmetrical valence types has much success been found for their theoretical explanation (51). Rearrangement of equation (47) to read

$$\left[\frac{\Lambda + (\alpha^{*}\Lambda^{o} + \beta^{*})(N)^{\frac{1}{2}} - \Lambda^{o}}{N}\right] = A \log N + B \qquad 48$$

shows that a plot of the bracketed terms against log N permits evaluation of the constants A and B. A plot such as this is known as an Owen (39) plot and is used to obtain the value of Λ^{o} when ordinary extrapolation procedures do not yield sufficient precision. A preliminary value of Λ^{o} is selected from a rough extrapolation of Λ _versus_ $(N)^{\frac{1}{2}}$. This value is then used to calculate $\Lambda + (\alpha^{*}\Lambda^{o} + \beta^{*})(N)^{\frac{1}{2}}$ which remain constant while the selection of a Λ^{o} to best fit the Owen plot is found. This final value of Λ^{o} is then used to calculate more accurate values of $\Lambda + (\alpha^{*}\Lambda^{o} + \beta^{*})(N)^{\frac{1}{2}}$ and the procedure repeated until a value of Λ^{o} is obtained which will express the data by equation (48) to the maximum concentration and yet within the limits of experimental error.

The third possibility for extending the Onsager conductance equation is by purely empirical extensions. A summary of these and other conductance equations can be found in reference (52).

The activity, a, of a pure chemical solute in a solution may be given a general definition by the equation

$$\bar{F}_i - \bar{F}_i{}^{o} = RT \ln a_i \qquad 49$$

where $\bar{F}_i$ refers to the increase in total free energy, F, when one mole of component i is added to an infinite amount of solution at fixed temperature, pressure, and with the number of moles, $n_1, n_2, \ldots n(i-1)$, of all other components kept fixed. $\bar{F}_i{}^{o}$ is the partial molal free energy in some arbitrary state.

Before the activity can be given a definite numerical value the standard state must be clearly and unambiguously defined. For electrolyte solutions, the standard state of the solvent is the pure solvent at the same temperature and pressure as the solution. For electrolytes, however, the pure solute is not a very practical choice, since it is often a solid with properties very different from those of solutions. For electrolytes, the standard state is a hypothetical solution at unit concentration and at the temperature and pressure of the solution (i.e., 25°C. and one atmosphere), and has the property that the mean ionic activity coefficient approaches unity when the concentration is reduced to zero.

To obtain a more sensitive measure of the non-ideality of solutions in terms of the solvent, Bjerrum (53) intreduced the concept of osmotic coefficients. He defined the practical osmotic coefficient, ϕ, for an electrolyte dissociating into ν ions as

$$\bar{F}_1 - \bar{F}_1^{\circ} = -\phi RT\nu mM_1/1000 \qquad 50$$

where the subscript 1 refers to the solvent and M_1 is the molecular weight of the solvent. Combining equations (49) and (50) yields

$$\ln a_1 = -\phi\nu mM_1/1000 \qquad 51$$

The activity of the solvent can be expressed as

$$a_1 = p_1/p_o \qquad 52$$

where p_1 is the vapor pressure of the solution and p_o that for the pure solvent. Strictly speaking, the ratio p_1/p_o should be replaced by the ratio of fugacities, f_1/f_o. However, since the vapor pressure of electrolyte solutions and solvent are of similiar magnitude, the deviation of p_1 from f_1 and p_o from f_o are equal to within an amount less than experimental error in measuring pressures. After solutions of two different salts have been allowed to equilibrate through the vapor phase, an isopiestic condition exists in which

$$a_{1(m)} = a_{1(mR)} \qquad 53$$

where a_1 is the solvent activity and m is the molality of the solution under investigation and m_R is the molality of a reference solution in which the activity or osmotic coefficient is known as a function of concentration. Thus for isopiestic solutions one obtains

$$\phi = \frac{\phi_R \nu_R m_R}{\nu m} \qquad 54$$

which permits the calculation of osmotic coefficient of a solution in terms of the corresponding property of the reference solution.

The method of graphical integration given by Lewis and Randall (54) or the following expression obtained by Randall and White (11)

$$\log \gamma_\pm = - \frac{(1-\phi)}{2.303} - \frac{2}{2.303} \int_0^m \frac{(1 - \phi)}{(m)^{\frac{1}{2}}} d(m)^{\frac{1}{2}} \qquad 55$$

permits evaluation of activity coefficient from osmotic coefficients.

Since the lower concentration limit for which data can be obtained by the isopiestic method is around 0.1m, some form of the Debye-Hückel equation must be used to extend the $(1 - \phi)/(m)^{\frac{1}{2}}$ versus $(m)^{\frac{1}{2}}$ plot to infinite dilution. One method, developed by Scatchard (55) involves calculating the osmotic coefficient from the expression

$$(1 - \phi)_{calc.} = 0.7676 S_m(f)\sigma_m(m)^{\frac{1}{2}} + \tfrac{1}{2}Bm - (\Delta\phi)_{smoothed} \qquad 56$$

where the $(\Delta\phi)_{smoothed}$ is obtained by the method of Scatchard and Prentiss (56), which was used in treating freezing point data, and represents a smoothing of the experimental data. Here the $S_m(f)$ is defined by

$$S_m(f) \equiv S_{(f)}(d_o)^{\frac{1}{2}} \qquad 57$$

where $S_{(f)}$ was given in equation (34) and d_o is the density of water. The constant σ_m is a function of A' (equation 35), with the numerical values available in tabulated form (57). The $\frac{1}{2}Bm$ term is equal to the slope of a $\left\{\left[(1 - \phi)/(m)^{\frac{1}{2}}\right]_{obsd.} - \left[(1 - \phi)/(m)^{\frac{1}{2}}\right]_{calc.}\right\}$ against $(m)^{\frac{1}{2}}$ plot and is used to represent the data at higher concentrations. Numerical values of B and A_m' $(\equiv A'(d_o)^{\frac{1}{2}})$ are chosen so that the deviation, $\Delta\phi$, is not large at any concentration. A value of A_m' is selected by trial which permits the equation

$$(1 - \phi)/(m)^{\frac{1}{2}} = 0.7676 S_m(f)\sigma_m \qquad 58$$

to give the best fit of the experimental data at the lowest concentrations.

So long as the osmotic coefficients can be calculated by equation (56) and the deviations are small, the activity coefficients can then be calculated by the method which Smith (58) used in treating solutions of sodium chloride at their boiling point, namely,

$$\ln \gamma_{\pm} = -\frac{2.303 S_m(f)(m)^{\frac{1}{2}}}{1 + A_m'(m)^{\frac{1}{2}}} - Bm + \int_0^m \frac{\Delta\phi}{m}dm + \Delta\phi \qquad 59$$

The two terms containing $\Delta\phi$ are evaluated graphically. If the $\Delta\phi$ term is not small or if it is applicable over too narrow a concentration range to warrant its use, the method of calculating the osmotic coefficients is not used. The activity coefficients are then calculated by graphical integration of equation (55) with the experimental plot extended to infinite dilution by means of equation (58).

IV. EXPERIMENTAL

A. Raw Materials: The following is a list of the reagents used in this work.

Ammonium Carbonate, $(NH_4)_2CO_3$, Fischer Scientific, C.P. Reagent
Ammonium Chloride, NH_4Cl, Merck Reagent Grade
Ammonium Hydroxide, NH_4OH, Mallinckrodt Analytical Reagent
Barium Chloride, $BaCl_2 \cdot 2H_2O$, "Baker's Analyzed" Reagent
Cobaltous Chloride, $CoCl_2 \cdot 6H_2O$, Mallinckrodt Analytical Reagent
Cobaltous Nitrate, $Co(NO_3)_2 \cdot 6H_2O$, Mallinckrodt Analytical Reagent
Calcium Chloride, $CaCl_2$, Mallinckrodt Analytical Reagent
p-Dioxane, $\underbrace{OCH_2CH_2OCH_2CH_2}$, Eastman Organic Chemicals, Practical
Ethylenediamine, $NH_2CH_2CH_2NH_2$, Eastman Organic Chemicals
Hydrochloric Acid, HCl, "Baker's Analyzed" Reagent
Nitric Acid, HNO_3, "Baker's Analyzed" Reagent
Perchloric Acid, 70% $HClO_4$, Mallinckradt Analytical Reagent
Phosphorous Pentoxide, P_2O_5, Mallinckrodt Analytical Reagent
Potassium Chloride, KCl, Mallinckradt Analytical Reagent
Potassium Cyanide, KCN, Mallinckradt Analytical Reagent
Potassium Hydroxide, KOH, Fischer Scientific, C.P. Reagent
Potassium Permanganate, $KMnO_4$, Mallinckradt Analytical Reagent
Propylenediamine, $CH_3CHNH_2CH_2NH_2$, Eastman Organic Chemicals
Silver Nitrate, $AgNO_3$, "Baker's Analyzed" Reagent
Sodium Bisulfite, $NaHSO_3$, Mallinckradt Analytical Reagent
Sodium Hydroxide, $NaOH$, Mallinckradt Analytical Reagent
Sulfuric Acid, H_2SO_4, "Baker's Analyzed" Reagent

In addition to the above, distilled (or conductivity) water and C.P. grade ethanol and acetone were employed.

C. Preparation of Compounds:

Potassium hexacyanocobaltate(III) was prepared according to the procedure as given in Inorganic Syntheses (59). Two methods of purification were used, and conductivity results from each were found identical. One method was repeated fractional precipitation with dioxane from conductivity water and the precipitate dried in a vacuum desiccator over P_2O_5. The second, was recrystallization three times from conductivity water and then the precipitate was stored over anhydrous $CaCl_2$. The anhydrous form results with either method and was the form used in this work.

Tris(propylenediamine)cobalt(III) perchlorate was prepared by a quantitative metathesis reaction between $Co(pn)_3Cl_3$ and $AgClO_4$ in aqueous solution. The $Co(pn)_3Cl_3$ was prepared by the method used by Jenkins and Monk (38). The anhydrous propylenediamine used was made from 70% propylenediamine by the method of Rollinson and Bailar (60). The silver perchlorate was prepared by reacting an excess of Ag_2O, nitrate free, with 0.1M $HClO_4$. The resulting $AgClO_4$ solution was separated from the excess Ag_2O by filtration, diluted, and analyzed by AgCl precipitation. An aqueous solution of the complex chloride was then quantitatively titrated with $AgClO_4$, making sure no more than one or two drops excess were added. The AgCl was filtered off after digestion on a steam bath for one hour. The resulting $Co(pn)_3(ClO_4)_3$ solution was then concentrated by evaporation and the $Co(pn)_3(ClO_4)_3 \cdot H_2O$ precipitated by addition of ethyl alcohol. The salt was recrystallized a minimum of three times from conductivity water and dried in a vacuum oven at 90° until the anhydrous form resulted.

Tris(ethylenediamine)cobalt(III) nitrate was prepared by a quantitative metathesis reaction between $Co(en)_3Cl_3$ and $AgNO_3$. The $Co(en)_3Cl_3$ was prepared according to the procedure found in Inorganic Syntheses (61). The metathesis reaction was carried out as above using $AgNO_3$ in place of the $AgClO_4$. The $Co(en)_3(NO_3)_3$ was recovered by evaporation of the filtrate and was dried until the anhydrous form resulted.

Tris(ethylenediamine)cobalt(III) sulfate was prepared from $Co(en)_3Cl_3$ and H_2SO_4 using the method described by Meyer and Grohler (62). $Co(en)_3Cl_3$ was dissolved with stirring in ice-cold concentrated H_2SO_4. The mixture was then placed in a vacuum desiccator for 24 hours over concentrated H_2SO_4. A beaker of KOH pellets was also present to remove the escaping HCl. The solution was then cooled with ice and ice-cold ethyl alcohol was added. The precipitate which formed was filtered and dissolved in 20% ice-cold H_2SO_4 and again precipitated with ice-cold ethyl alcohol. After filtrating, the precipitate was dissolved in water. Addition of ethyl alcohol caused an oil to form which crystallized after being rubbed with a glass stirring rod. The tetrahydrate form resulted.

C. Apparatus and Procedure:

1. Isopiestic measurements: The apparatus and procedure used has been described by Brubaker (16,63).

Duplicate samples of two solutions were run together, one being the reference salt, KCl, and the other the salt under investigation. When duplicate samples agreed to within three parts per thousand in molality, the salts were considered at equilibrium. The constant temperature bath was controlled at 24.978 ± 0.005°C.

2. Conductance Measurements: The resistance measurements were made with an A. C. bridge essentially of the design of Jones and Bollinger (24,28). The actual bridge was designed by Thompson and Rogers (64). The oscillator used permitted resistance values to be taken at five frequencies over the range 400 cycles per sec. to 5,000 cycles per sec. An oscilloscope was used to determine the balance point. Before each run the value of a standard resistance was checked to ensure that the bridge was functioning properly.

The cells were held at a constant temperature of 25.00 ± 0.015°C. in an oil bath. A group of three cells, with cell constants of about 0.3 cm^{-1}, 1.0 cm^{-1} and 30 cm^{-1}, were used to cover the concentration range $1 \times 10^{-4}N$ to $3 \times 10^{-1}N$. For the higher concentrations a Leeds and Northrup type B conductance cell (cell constant about 30 cm^{-1}) was used. The other two cells were similar to the erlenmeyer type described by Daggrett, Bair, and Kraus (65). A Leeds and Northrup type A conductance cell was sealed to a 500 ml. erlenmeyer flask which had the added feature (introduced by Dye) of two stopcocks. One stopcock was attached to the cap, and the other to an added side-arm. This permitted the introduction of carbon dioxide free conductivity water directly from the distilling apparatus under a pressure of nitrogen. Also, a steady stream of nitrogen was permitted to flow through the cell when the top was removed for making additions to the solution. The cell constants were determined using aqueous potassium chloride solutions (66).

The electrodes were lightly platinized using a current of about 20 milliamps. for 40 seconds, with the polarity reversed every 10 seconds. When the variation of resistance with frequency over the range 400-5000 c.p.s. (equation 8) was greater than approximately 8 ohms, the electrodes were re-cleaned with fuming nitric acid, replatinized and the cell constant redetermined.

The conductivity water was prepared by the method described by Vogel (67). First, water in equilibrium with the carbon dioxide in the atmosphere was prepared by distillation from an alkaline potassium permanganate solution of demineralized water. This was then redistilled in a distillation apparatus through which nitrogen was flowing. The water prepared in this way had a specific conductivity of approximately 0.6×10^{-6} $\text{ohm}^{-1}\text{cm}^{-1}$.

For the dilute solutions the erlenmeyer type cells were used. The water was forced into the weighed empty cell by means of nitrogen pressure. After reweighing the cell and water, the exact weight of water was calculated. The cell plus water then placed in the thermostat to permit determination of solvent conductance. Then successive portions of a stock solution were added. The contents of the cell were then thoroughly mixed and the cell replaced in the bath. The attainment of temperature equilibrium was indicated when successive resistance readings checked to within 0.01%. The resistance values were then recorded. The cell was removed from the bath and contents remixed. The contents were again allowed to reach temperature equilibrium and the resistance values rechecked. Remixing of the solution continued until the successive readings checked to within 0.01%.

For the higher concentrations the stock solutions were added directly to the Leeds and Northrup type B conductance cell after the cell had been rinsed several times with the solution. The resistances were recorded after equilibrium was reached and the procedure repeated for new portions of the solution in order to check the rinsing procedure.

Densities of solutions of the compounds were also measured in order to be able to transfer molality data to volume concentration. They were determined at 25°C. with a pycnometer and are represented by the equation

$$d = Am + 0.99707 \qquad 60$$

The values of A for the various electrolytes are found in Table I.

TABLE I

VALUES OF THE CONSTANT A OF EQUATION 60

Electrolyte	A
$Co(en)_3(NO_3)_3$	.1945
$Co(pn)_3(ClO_4)_3$	.2558
$K_3Co(CN)_6$	.1862
$[Co(en)_3]_2(SO_4)_3$	.3740

V. RESULTS AND DISCUSSION

A. Isopiestic

The experimental results are given in Table II as molalities of the isopiestic solutions and the corresponding osmotic coefficients, which were calculated from equation (54) using known values of potassium chloride solutions. From the experimental results given in Table II the activity coefficients given in Table III were calculated using one of two methods. The first method tried in all cases was that employed by Smith (58) for treating sodium chloride solutions at their boiling points.

$$\ln \gamma_{\pm} = -\frac{2.303 S_m (f)(m)^{\frac{1}{2}}}{1 + A_m (m)^{\frac{1}{2}}} - Bm + \int_0^m \frac{\Delta\phi}{m} dm + \Delta\phi \qquad 59$$

The application of this method depends upon the calculation of osmotic coefficients using the expression

$$(1 - \phi)_{\text{calc.}} = 0.7676 S_m (f) \sigma_m (m)^{\frac{1}{2}} - \tfrac{1}{2}Bm - (\Delta\phi)_{\text{smoothed}} \qquad 56$$

This represents the Debye-Hückel expression for osmotic coefficients with a linear term of $\frac{1}{2}Bm$ to represent the data at higher concentration (55).

In the actual solutions there exist interactions other than those considered by Debye and Hückel in deriving the

TABLE II

ISOPIESTIC MOLALITIES AND OSMOTIC COEFFICIENTS OF ELECTROLYTES AT 25°

$Co(en)_3(NO_3)_3$		$Co(pn)_3(ClO_4)_3$	
$m_{av.}$	$\phi_{obsd.}$	$m_{av.}$	$\phi_{obsd.}$
0.03055	0.6918	0.05747	0.6693
.05267	.6789	.06898	.6603
.08276	.6468	.09056	.6424
.1266	.6241	.1117	.6270
.1349	.6098	.1336	.6098
.1574	.5952	.1548	.5984
.1853	.5795	.1659	.5894
.2587	.5410	.2027	.5719
.2612	.5408	.2243	.5629
.2749	.5361	.2502	.5523
		.2578	.5464
		.2612	.5498

TABLE II, continued

$K_3Co(CN)_6$		$[Co(en)_3]_2(SO_4)_3$	
$m_{av.}$	$\phi_{obsd.}$	$m_{av.}$	$\phi_{obsd.}$
0.03035	0.7479	0.08160	0.2613
0.07393	.7075	.1453	.2417
0.1508	.6926	.1489	.2379
0.2730	.6819	.2407	.2027
0.4571	.6768	.3504	.1705
0.5828	.6768	.4580	.1705
0.6775	.6804	.5004	.1681
0.7309	.6857	.6190	.1641
0.7667	.6876	.8993	.1862
0.8172	.6918	1.003	.1993
0.8497	.6924	1.064	.2043
0.9507	.7007	1.252	.2259
1.026	.7063	1.298	.2310
1.082	.7116	1.429	.2499
1.217	.7258	1.536	.2622
1.223	.7305	1.800	.2979
1.235	.7331	1.844	.3050
1.306	.7421		
1.311	.7425		

TABLE III

MEAN ACTIVITY COEFFICIENTS AND SMOOTHED OSMOTIC COEFFICIENTS OF ELECTROLYTES AT 25°

	$Co(en)_3(NO_3)_3$		$Co(pn)_3(ClO_4)_3$	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.01	0.505	0.7980	0.513	0.7967
.03	.357	.7185	.368	.7156
.05	.296	.6832	.305	.6787
.07	.258	.6592	.266	.6563
.10	.222	.6338	.228	.6351
.15	.184	.5995	.189	.6003
.20	.158	.5709	.163	.5740
.25	.140	.5465	.145	.5527
.2612			.141	.5498
.2749(satd.)	.133	.5361		

TABLE III, continued

	$K_3Co(CN)_6$		$[Co(en)_3]_2(SO_4)_3$	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.01	0.522	0.9126	0.152	0.4787
.03	.385	.7487	.0654	.3418
.05	.323	.7116	.0440	.2943
.07	.293	.7089	.0339	.2761
.10	.260	.6968	.0256	.2569
.15	.228	.6902	.0186	.2393
.20	.207	.6838	.0146	.2219
.25	.193	.6830	.0120	.2040
.30	.181	.6801	.0102	.1872
.50	.153	.6758	.00648	.1685
.75	.135	.6887	.00462	.1686
1.00	.127	.7055	.00381	.2100
1.20	.123	.7284	.00337	.2291
1.30	.122	.7424	.00320	.2385
1.311(satd.)	.122	.7425		
1.50			.00294	.2625
1.75			.00272	.2962
1.844			.00265	.3047

limiting expression, (e.g., short range interactions between ions and solvent molecules). Thus by including a term linear in concentration, a more theoretically significant result is obtained in which the parameter $\mathring{a}$ is not forced to take some of the responsibilities of the linear term.

By adjusting the values of $\mathring{a}$ and B to fit the experimental curve, expressions could be obtained which would give a better fit over a smaller concentration range, or a poorer fit over a greater range. The values of $\mathring{a}$ and B which were found to fit best the experimental data over the widest concentration range and with reasonable accuracy, are given in Table IV.

TABLE IV

VALUES OF THE PARAMETERS $\mathring{a}$ AND B USED IN THE SMITH METHOD

Electrolyte	B	$\mathring{a}$
$Co(en)_3(NO_3)_3$	(0.480)	(3.45)
$Co(pn)_3(ClO_4)_3$	0.971	3.83
$K_3Co(CN)_6$	(0.131)	(4.13)
$[Co(en)_3]_2(SO_4)_3$	(0.792)	(3.61)

The values for three salts are in parentheses to point out the fact that the method was not found to reproduce the experimental data with sufficient accuracy over a concentration range large enough to warrant its use. A comparison of the observed osmotic coefficients for $Co(pn)_3(ClO_4)_3$ and those calculated from equation (56) are tabulated in Table V.

TABLE V

ISOPIESTIC MOLALITIES, OBSERVED AND CALCULATED OSMOTIC COEFFICIENTS OF $Co(pn)_3(ClO_4)_3$

$m_{av.}$	$\phi_{obsd.}$	$\phi_{calc.}$
0.05747	0.6693	0.6778
.06898	.6603	.6633
.09056	.6424	.6418
.1117	.6270	.6259
.1336	.6098	.6099
.1548	.5984	.5973
.1659	.5894	.5910
.2027	.4719	.5718
.2243	.5629	.5616
.2503	.5523	.5498
.2578	.5464	.5466
.2612	.5498	.5450

When the Smith method was found unsuitable, the second method, that of Randall and White (11), was applied. In this case the activity coefficients are determined by graphical integration of the equation

$$\ln \gamma_{\pm} = -(1 - \phi) - 2\int_0^m \left(\frac{1 - \phi}{m^{\frac{1}{2}}}\right) dm^{\frac{1}{2}} \qquad 61$$

The extension of the function $(1 - \phi)/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ to infinite dilution was carried out by means of the Debye-Hückel equation and required that the parameter $\mathring{a}$ have the values recorded in Table VI.

TABLE VI

VALUES FOR $\mathring{a}$ DETERMINED BY THE METHOD OF RANDALL AND WHITE

Electrolyte	$\mathring{a}$
$Co(en)_3(NO_3)_3$	3.23
$Co(pn)_3(ClO_4)_3$	(3.16)
$K_3Co(CN)_6$	4.01
$[Co(en)_3]_2(SO_4)_3$	3.43

The value for the $Co(pn)_3(ClO_4)_3$ is in parenthesis to show that it would be the value required if the Randall and White method had been applied.

It was found in both the present study and in that by Brubaker (16) that the activity coefficients calculated by either method differed by only about one per cent.

A comparison of the $\mathring{a}$ values obtained by the two different methods shows that the method of Randall and White yields the lower values. This is to be expected, since the linear term was obtained from the deviation between experimental and calculated data. The $\mathring{a}$ was then increased to permit the $\frac{1}{2}Bm$ term to be added and have the resulting expression still fit the experimental data.

The linear term alone appears to be insufficient to account for the deviations from the Debye-Hückel expression and a better reproduction of the data could possibly have been obtained by introducing further arbitrary terms in higher powers of concentration so that the $\Delta\phi$ would remain small at the higher concentrations.

The limiting value for $(1 - \phi)/m^{\frac{1}{2}}$ is given by the Debye-Hückel theory as 2.868 for 1-3 and 3-1 valence type electrolytes and 9.069 for the 3-2 type. Since the objections to the theory in finite concentrations vanish as m approaches zero, these limiting values of $(1 - \phi)/m^{\frac{1}{2}}$ should not be subject to errors greater than those found in the experimental techniques used to evaluate the various constants found in the limiting expression, such as the dielectric constant of water, etc.

A fundamental equation of the Debye-Hückel theory was shown to be

$$\rho_j = \sum_i n_i z_i \epsilon \exp\left(-z_j \epsilon_j \Psi_j / kT\right) \qquad 11$$

The higher order terms neglected by the approximation

$$\exp\left(-\epsilon_j \Psi_j / kT\right) \simeq 1 - \epsilon_j \Psi_j / kT \qquad 62$$

are functions of the valences of the ions, and while nearly negligible for 1-1 electrolytes, increase markedly in magnitude when the charge on the ions increases. The exact determination of the effect of extended terms of equation (11) is very difficult, since it is obscured by other factors present (68). On the basis of a complicated mathematical treatment presented by Gronwall, LaMer, and Sandved (69) and the simpler ion-association theory of Bjerrum, large deviations from the Debye-Hückel first approximation are to be expected for polyvalent electrolytes. By considering the electrolytes in view of Bjerrum's theory we see that if r, the minimum distance of approach of two ions of opposite sign, is greater than $b = \epsilon^2 |z_1 z_2|/2DkT$, then the probability of ionic association is negligible. For 3-1 and 3-2 electrolytes, b equals 10.5 and 21 Å, respectively. Since these values are much greater than $\mathring{a}$ for the electrolytes studied (Tables IV and VI) considerable ionic association of the Bjerrum type could be said to exist. In any case, the $\mathring{a}$ values are small and do not approach the values to be expected from crystallographic radii.

The concentrations of the saturated solutions of the $Co(en)_3(NO_3)_3 \cdot H_2O$ and $K_3Co(CN)_6$ were found to be 0.2749 and 1.311 m, respectively. The conversion of the undissolved $Co(pn)_3(ClO_4)_3$ to the monohydrate in equilibrium with the saturated solution was slow and its solubility was not determined, but is estimated to be .27 m. The highest concentration employed for the $[Co(en)_3]_2(SO_4)_3$ was limited by amount which could be weighed conveniently into the dishes.

The logarithms of the activity coefficients given in Table III are plotted in Figure 1, along with the values obtained by Brubaker (16) for $Co(en)_3Cl_3$. By definition, $\gamma_\pm$ is unity at infinite dilution for all electrolytes. In any case, $\gamma_\pm$ decreases rapidly with increasing molality at low values of m. The steepness of this initial drop, however, varies with the valence type of the electrolyte as is exemplified by the 3-2 salt behavior. The activity coefficients of the $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$ and $Co(en)_3Cl_3$ are all within about 2% of each other and are represented by one curve until approximately .09 m. Although the activity coefficient data does not show the present 3-1 salts to be very "strong" electrolytes, they are very similiar to the values obtained for the $Co(en)_3Cl_3$. Data such as this would seem to indicate the possibility of estimating the activity coefficients of similiar size and charge type complexes.

With the $[Co(en)_3]_2(SO_4)_3$ the extrapolation is somewhat uncertain, but the results are of the right order of magnitude with other 3-2 electrolytes, such as $Al_2(SO_4)_3$ and $In_2(SO_4)_3$ (70).

B. Conductivity

In addition to the isopiestic measurements of activity coefficients it seemed desirable to try to determine the

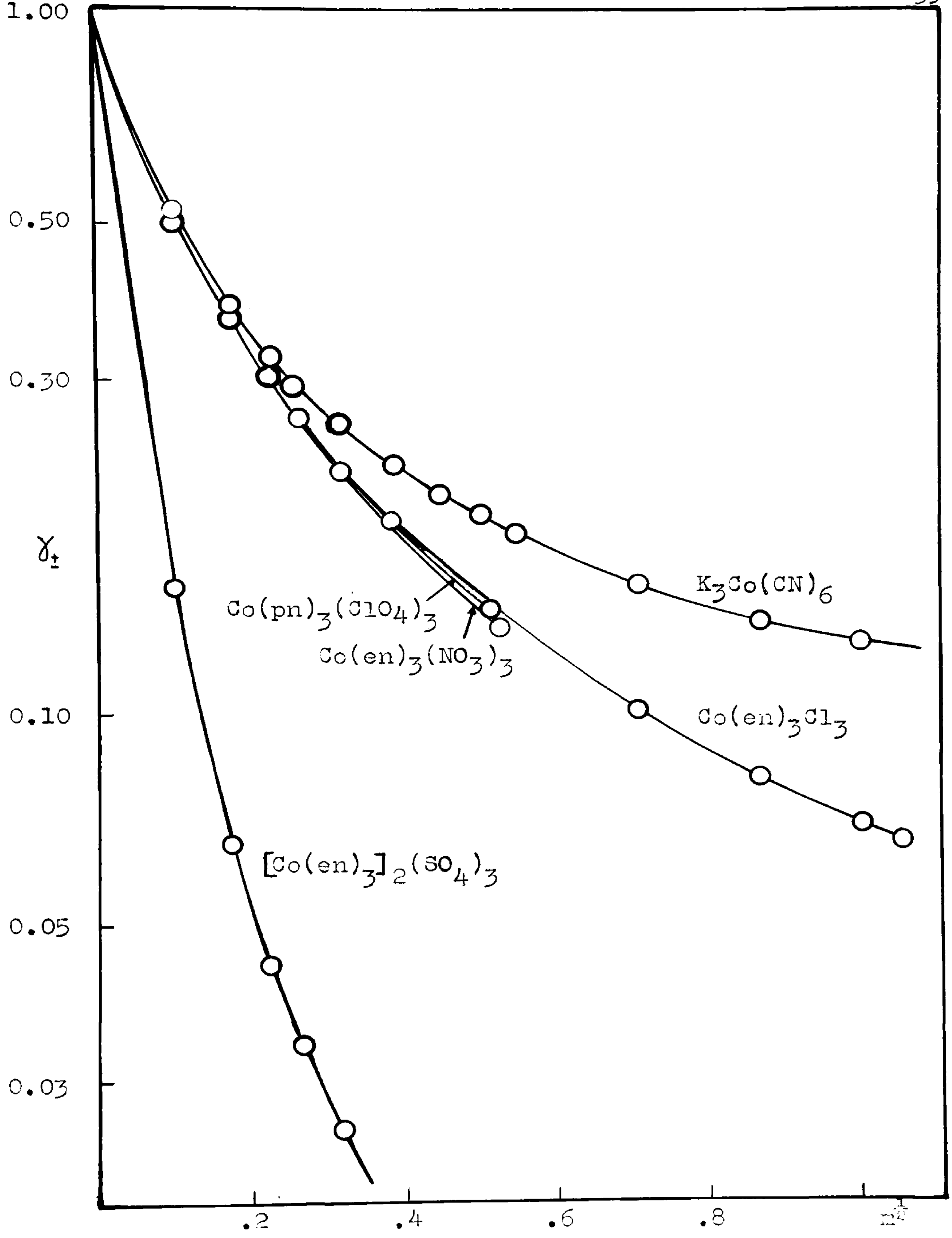

1.00
0.50
0.30
0.10
0.05
0.03
$\gamma_\pm$
.2
.4
.6
.8
$m^{\frac{1}{2}}$
$K_3Co(CN)_6$
$Co(pn)_3(ClO_4)_3$
$Co(en)_3(NO_3)_3$
$Co(en)_3Cl_3$
$[Co(en)_3]_2(SO_4)_3$

FIGURE 1

distance of closest approach parameter, å, from conductivity measurements, as was done by Dye and Spedding (1) for the alkaline earth and rare earth salts. This would have enabled one to substantiate the values of å by a second and independent method.

From the experimental results given in Table VII, the values of Λ_0' were calculated by the method of Shedlovsky (71).

$$\Lambda_0' = \Lambda - S_{(\Lambda)} N^{\frac{1}{2}} \qquad 63$$

The extrapolation to infinite dilution of the Λ_0' values as a function of the square root of the normality, can then be used as an indication of the applicability of the Onsager limiting law since the theory is being followed when the slope of the curve is zero. It was found, however, that for all the salts studied the slope was not zero, but had a decided upswing. The upswing, from the curve minimum to the limiting value, was observed to vary from a maximum of about 42.2 conductance units with the $[Co(en)_3]_2(SO_4)_3$ to a minimum of 1.24 for the $K_3Co(CN)_6$. Although the technique of Dye and Spedding can handle a slight upswing, the magnitude of the deviations found with the present salts did not permit the å parameter to be calculated by this method.

The observed values of the limiting equivalent conductance obtained by the Shedlovsky method are given in Table VIII. The value for the sulfate is in parentheses to show that the

TABLE VII

EQUIVALENT CONDUCTANCES OF ELECTROLYTES AT 25°

$Co(en)_3(NO_3)_3$

$N \times 10^3$	Λ	$N \times 10^3$	Λ	$N \times 10^3$	Λ
0.17248	141.87	1.3817	133.80	3.2964	127.49
.32775	140.23	1.6524	132.61	5.3353	123.15
.50322	138.78	1.8254	132.01	6.2610	121.65
.55665	138.36	1.8907	131.79	9.9483	117.20
.79662	136.99	2.2708	130.28	29.627	102.19
1.0990	135.18	2.6028	129.42	78.432	88.285
1.2053	134.60	3.1044	128.05	211.58	74.213
1.2057	134.60	3.2343	127.66	288.89	69.812

$Co(pn)_3(ClO_4)_3$

$N \times 10^3$	Λ	$N \times 10^3$	Λ	$N \times 10^3$	Λ
0.098169	129.05	0.84051	122.78	4.3566	112.77
.18140	127.88	0.86718	122.69	5.5635	110.79
.29019	126.61	0.98445	122.32	7.0419	108.49
.30363	126.44	2.1662	117.86	8.8596	106.18
.31845	126.40	3.3393	114.75	19.289	98.637
.43830	125.26	3.3528	114.78	27.267	94.587
.51138	124.74				

TABLE VII, continued

$K_3Co(CN)_6$

$\text{Nx}10^3$	Λ	$\text{Nx}10^3$	Λ	$\text{Nx}10^3$	Λ
0.51600	164.81	1.7722	158.17	6.4080	148.34
0.66384	163.76	1.8225	158.10	12.663	141.93
0.67491	163.58	2.1315	157.09	19.294	135.38
0.86460	162.55	3.1473	154.06	28.882	130.24
0.97386	161.79	3.2655	153.55	119.36	113.30
1.0824	161.37	3.7839	152.79	210.09	107.40
1.1288	161.01	4.3572	151.36	299.27	103.91
1.4242	159.73				

$[Co(en)_3]_2(SO_4)_3$

$\text{Nx}10^3$	Λ	$\text{Nx}10^3$	Λ	$\text{Nx}10^3$	Λ
0.23889	136.05	5.6155	67.467	26.707	44.161
0.81565	108.82	6.0890	65.566	44.457	38.577
1.4727	94.901	6.6255	64.628	153.10	27.920
2.3912	84.133	14.898	51.560	337.91	23.130
3.8719	74.356				

limiting value was selected by adding the limiting values for the two ions rather than by extrapolation.

TABLE VIII

LIMITING EQUIVALENT CONDUCTANCES OBTAINED BY THE SHEDLOVSKY METHOD

Electrolyte	Λ_o
$Co(en)_3(NO_3)_3$	146.24 ± 0.07
$Co(pn)_3(ClO_4)_3$	132.47 ± 0.06
$K_3Co(CN)_6$	172.59 ± 0.09
$[Co(en)_3]_2(SO_4)_3$	(154.80)

This was considered more accurate in view of the steep slope observed and characteristic of 3-2 salts in general.

The Owen method of extrapolation was then applied with the hope that this extrapolation procedure would give a more accurate limiting value. The use of this method was also suggested by the fact that the values of the limiting ionic conductivities of the complex cobaltic ions reported in the literature had been calculated by means of the Owen method. The values of Λ_o and the constants A and B obtained, when this procedure was used, are found in Table IX. No value for the sulfate is given since the method is not sufficiently sensitive to warrant its use.

From the limiting conductivities of the nitrate, perchlorate, potassium and sulfate ions, the limiting ionic

TABLE IX

PARAMETERS OF THE SEMI-EMPIRICALLY EXTENDED ONSAGER EQUATION AT 25°

Electrolyte	A	B	Λ_o
$Co(en)_3(NO_3)_3$	1,586	3,248	146.12 ± 0.07
$Co(pn)_3(ClO_4)_3$	4,679	12,400	132.40 ± 0.06
$K_3Co(CN)_6$	1,293	2,914	172.52 ± 0.09

conductivities of the complex cobaltic ions may be obtained with a high degree of accuracy. The results have been tabulated in Table X in order to permit a comparison of the limiting ionic conductivities obtained in the present study with the Shedlovsky and Owen methods, as well as the values previously reported by other workers. From the table it can be seen that higher limiting values are obtained when the Shedlovsky method is used. In either case, the two methods give results within the experimental error of 0.05% for all ions.

From the data in Table X it can be seen that the variation in the limiting conductivities of the complex cobaltic ions is that which would be expected, i.e., as the size increases, the mobility becomes less (74). The larger mobility of the $Co(CN)_6^{-3}$ and $Co(en)_3^{+3}$ ions (approximately 100 and 75 units, respectively) compared with those of the rare earth trivalent ions (close to 70), would seem to indicate that in

TABLE X

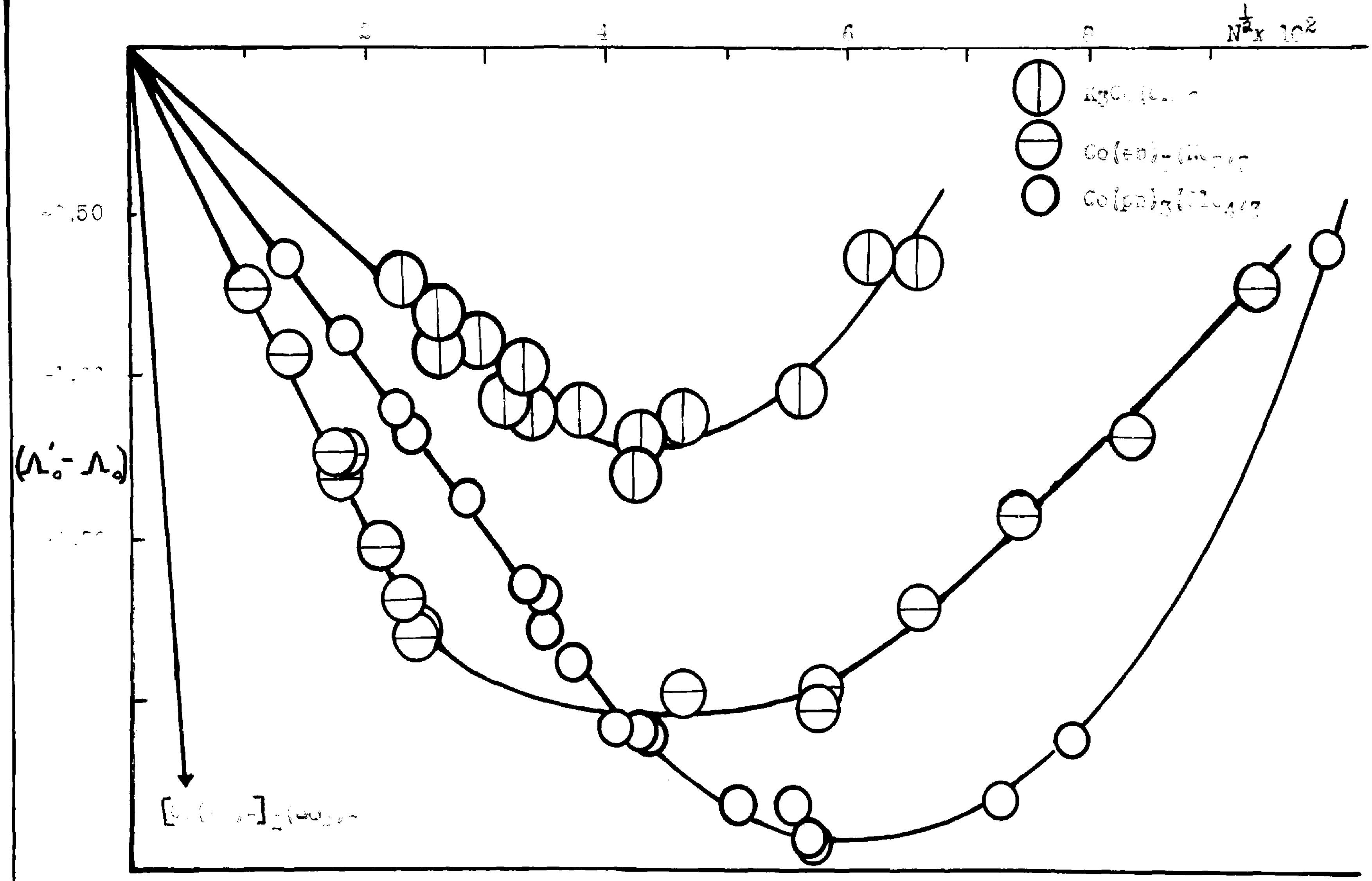
LIMITING EQUIVALENT CONDUCTIVITIES AT 25°

	Present		Literature	
Ion	Shedlovsky	Owen	Value	Ref.
$Co(en)_3^{+3}$	74.80 ± 0.07	74.68 ± 0.07	74.7*	(38)
$Co(pn)_3^{+3}$	65.11 ± 0.06	65.06 ± 0.06	65.06*	(38)
$Co(CN)_6^{-3}$	99.07 ± 0.09	99.00 ± 0.09	98.9*	(37)
NO_3^{-1}	Literature value was used		71.44	(72)
ClO_4^{-1}	Literature value was used		67.36	(73)
K^{+1}	Literature value was used		~~80.00~~	(72)
SO_4^{-2}	Literature value was used		~~73.52~~	(72)

* estimated by the Owen method.

these ions the first layer of water molecules is replaced by the cyanide and ethylenediamine groups, respectively, and hence water molecules do not appear to attach themselves to these foreign groups as readily as to other water molecules. With large spherical ions one would expect solution effects to be much smaller owing to the lower charge densities on their surfaces, a condition more favorable to a higher mobility.

The deviations of the observed conductivities is shown in Figure 2. It is a plot of $\Lambda_o' - \Lambda_o$ versus $(N)^{\frac{1}{2}}$, where Λ_o' is the value obtained from equation (63) and Λ_o is the limiting value obtained by extrapolation in the Shedlovsky


2
4
6
8
$N^{\frac{1}{2}}$x 10^2
.50
$(\Lambda_0' - \Lambda_0)$
Co(en)
Co(pn)

[illegible]

[illegible]

method. When the Shedlovsky values are replaced by those obtained from the Owen method, the curves do not pass thru zero, but the general shape is the same. The value for $[Co(en)_3]_2(SO_4)_3$ has such a large deviation that when it is plotted the axis requires compressing to such an extent that all sensitivity is lost. For this reason, only the beginning of the sulfate curve is shown.

An explanation of the differences between experimental conductivities and the theoretical Onsager equation has been discussed by numerous workers in terms of incomplete dissociation. For example, James, Jenkins, and Monk (37,38) have calculated dissociation constants for the dissociation of ions of; (a) the type MX^{+2} into ions of the type M^{+3} and X^{-1}, (b) the type MY^{+1} into ions of the type M^{+3} and Y^{-2}, and (c) the type ZM^{-2} into ions of the type Z^{+1} and M^{-3}. Several of the values obtained for the dissociation constants, K, are given in Table XI. Two of the values given are for salts that were also studied in the present work, while the others are very similar to the remaining salts. It has been common practice, especially for spectrophotometric work, to regard the perchlorate of polyvalent cations as exempt from the difficulties which arise when other salts, more susceptible to ion-pair formation, are used. However, it should be noted that spectrophotometric evidence has been found, by Herdt and Berestecki (75), for $CeClO_4^{+2}$ ions in $Ce(ClO_4)_3$ solutions.

TABLE XI

DISSOCIATION CONSTANTS OF COMPLEX IONS IN WATER ESTIMATED FROM CONDUCTANCE DATA AT 25°

Ion-pair	$K \times 10^3$	Ref.
$Co(NH_3)_6Cl^{+2}$	33.4	(38)
$Co(en)_3Cl^{+2}$	18.8	(38)
$Co(pn)_3Cl^{+2}$	25.0	(38)
$Co(NH_3)_6SO_4^{+1}$	27.7	(38)
$Co(en)_3(SO_4)^{+1}$	3.55	(38)
$KCo(CN)_6^{-2}$	59.0	(37)

Thus, although the K values given in Table XI are for the chlorides, the perchlorate and nitrate of the appropriate cation might be expected to yield values within the same order of magnitude. From the magnitude of K for these salts, it would appear that dissociation is far from complete in solutions of this type of high valence electrolyte. However, the evaluation of K can be done in one of several ways. One method is the arbitrary selection of some conductance curve to represent a hypothetical completely dissociated electrolyte (43,76). All deviations of the electrolyte under consideration from the hypothetical salt are then considered as resulting from incomplete dissociation. However, the difficulty of selecting an experimental curve as a standard is greatly magnified in the case of high-charge salts.

Another approach is that of Fuoss (77) and Shedlovsky (78), where K and Λ_0 are simultaneously evaluated by a suitable extrapolation to infinite dilution. Both methods have the common dissadvantage, however, that some knowledge of the activity coefficient of the electrolyte as a function of the concentration is required. The $\gamma_\pm$ would be known for the salts under investigation, but the values of the activity coefficients for the ion-pairs would have to be estimated. The two largest approximations, however, are; (a) the selection of a mobility for the ion-pair with the aid of assumptions of uncertain validity, e.g., that the ion-pair and the trivalent ion are similar in size, shape, and solvation, and (b) the selection of a standard curve to represent the completely dissociated electrolyte.

It is interesting to note that Harned and Hudson (79) found these assumptions to be inadequate to explain the mobilities calculated from their diffusion studies of the ion-pairs formed in zinc and magnesium sulfate solution. It might also be added that large differences in the values of the dissociation constants are often found when different methods are used to evaluate them. A case in point is the $[Co(NH_3)_6]SO_4^{+1}$ for which Bale, Davies, and Monk (80) found $K = 11.3 \times 10^{-4}$ by spectrophotometric means, whereas Jenkins and Monk (Table XI) obtained $K = 2.77 \times 10^{-4}$ from conductivity measurements.

At the present time it is impossible to state definitely whether the observed values approach the limiting slope from below due to the presence of an incompletely dissociated electrolyte or whether the theoretical calculation of the limiting slope is presently inadequate to handle the high-charge type salts studied. Part of the failure of the Onsager equation comes from the mathematical simplifications used in deriving the limiting law. Bjerrum's method of ion-association represents one way to reduce the magnitude of error in the limiting law. Although the Owen method is based upon the assumption of complete dissociation, it is difficult to distinguish between the effects of ion-pairs, postulated in the estimation of K, and the higher electrostatic terms represented by AN log N and BN. Until A and B are evaluated theoretically and/or the selection of a standard conductivity curve is made less arbitrary in the calculation of K, there seems to be no ideal method available to explain the deviations found with high-charge type salts. Empirical extensions of various theoretical equations can be found to represent the experimental data, but are dangerous when applied as extrapolation procedures due to the weight given to the empirical parameters.

The main problem seems to be to distinguish, at concentrations beyond the Onsager range, between effects of interionic forces, viscosity, and incomplete dissociation, bearing in mind that further disturbing influences may eventually demand consideration.

VI. SUMMARY

The activity coefficients and conductivities of aqueous solutions of four high-charge electrolytes have been determined. The electrolytes studied were $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$, $K_3Co(CN)_6$, and $[Co(en)_3]_2(SO_4)_3$.

The activity coefficient data does not show the salts to be "strong". The highest values observed for the activity coefficients were for the $K_3Co(CN)_6$. The values obtained for the 3-1 salts were very similar to those previously obtained for $Co(en)_3Cl_3$. Data such as this would indicate the possibility of estimating the activity coefficients of similar size and charge type complexes. The values obtained for the 3-2 sulfate were lower than other 3-2 salts.

The conductivities do not follow Onsager's limiting equation as expected. Whether the upswing observed in the Shedlovdky Λ_0' plot is a result of ion-pair formation or inadequacy of the present theories to cope with unsymmetrical high-charge types is still unknown.

The values of the limiting conductivities obtained for the complex cobaltic ions are 74.80, 65.11, and 99.07 ohm^{-1} cm^{-1}, for the $Co(en)_3^{+3}$, $Co(pn)_3^{+3}$, and $Co(CN)_6^{-3}$ ions, respectively. These values correspond with those obtained for the limiting values by other workers.

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