1959

Some physical and chemical properties of scandium and the rare earths

Maynard Allyn Hiller

Iowa State University

SOME PHYSICAL AND CHEMICAL PROPERTIES

OF SCANDIUM AND THE RARE EARTHS

by

Maynard Allyn Hiller

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1959

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GENERAL INTRODUCTION

The Debye-Hückel concept of electrolytic solutions has been successful in explaining the deviations from ideal behavior of extremely dilute solution (1). Simplifying assumptions in both the model and the mathematics employed in the theory limit applicability of the equations to solutions of relatively low concentration.

There is a need for experimental evidence derived from electrochemical measurements such as conductance, and transference, in order to correlate the various properties of solutions with their dependence on concentration. For several years, the personnel of the Ames Laboratory have been engaged in such measurements on the rare-earth salts.

Spedding, Porter and Wright (2, 3, 4) started the investigations by measuring conductances, transference numbers, and activity coefficients by means of e.m.f.'s of concentration cells with transference for some of the rare-earth chlorides. Continuing the study, Yaffe (5) measured the same three properties for some of the bromides; Dye (6) measured more of the chlorides; Jaffe (7) determined the solubilities, conductances, and densities for some of the sulfates, as well as conductances and transference numbers for some of the perchlorates and nitrates (8). The most recent investigators in the field were Heiser (9) who worked on conductances, transference

numbers, and activity coefficients from isopiestic comparisons for more of the nitrates and Saeger (10) who currently is engaged in conductance measurements on very concentrated solutions of several of the chlorides.

As a part of the overall program, Ayers (11) obtained densities and partial molal volumes by a magnetic float method. Atkinson (12) measured molal compressibilities by ultrasonic interferometry and obtained an idea of the degree of hydration from these data.

Calorimetric measurements of heats of solution of rare-earth metals and salts in water and hydrochloric acid were carried out by Miller (13, 14), Flynn (15, 16), Naumann (17), and Eberts (18).

The rare earths are ideally suited for electrochemical measurements since they are moderately basic and show little tendency to hydrolyze or to form complexes with strongly acid anions.

The rare-earth elements together with yttrium are particularly valuable for studies of electrolytic solutions for another reason. In the rare-earth series, the inner $4f$ shell of electrons is being filled while the outer electron shells are, for the most part, filled to the same degree for the entire series. The inclusion of yttrium allows one to observe the effect of removing whole shells of electrons, thus changing the effective nuclear field strength.

Scandium shares the distinction with the rare earths and yttrium of being another member of the group having completed outer shells while also possessing incomplete inner shells. The three valency electrons, common to all, are tied up with the negative ions when the salts ionize. It is the leading element in the first transition series. However, electrochemical data for aqueous scandium solutions are not as easy to interpret as rare-earth data since scandium is weakly basic and its solutions exhibit extensive hydrolysis.

When a supply of very pure scandium oxide became available as a result of methods developed at the Ames Laboratory (19), it was decided to add to the collection of thermodynamic and electrochemical data which had been accumulated for the rare earths and yttrium by measuring some of the same properties for scandium.

It was the intent of this thesis, then, to measure the conductance of some of the simple scandium salts, the transference numbers with the necessary accompanying partial molal volumes and densities, the stability constants with several organic chelating agents, and the solubility of some of the simple salts. It was known that the hydrolysis and subsequent polymerization of scandium would complicate any attempt to interpret electrochemical data quantitatively. Primarily then, the work included in this thesis on conductance and

transference measurements was intended to be mainly a pre-
liminary survey of the field.

The measurement of the stability constants of scandium
chelates led to the measurement of constants for the rare-
earth complexes formed with two new chelating agents. This
work was performed as an alternate route to the determination
of the scandium stability constants, as well as to allow a
comparison of the behavior of scandium with that of the rare
earths.

Thus, this thesis includes work which is, at present,
only a preliminary investigation in the electrochemical field
(conductances and transference numbers of aqueous scandium
solutions) as well as other work which is of fundamental im-
portance in the separation of the rare earths (measurement of
the stability constants of complexes of scandium, yttrium, and
the rare earths with 1,2-bis-[2-di(carboxymethyl)aminoethoxy]
ethane and 2,2'-bis-[di(carboxymethyl)amino] diethyl ether.
The stability constants for the scandium complexes with
ethylenediamine-N,N,N',N'-tetraacetic acid, N'-(hydroxyethyl)-
ethylenediamine-N,N,N'-triacetic acid, 1,2-diaminocyclohexane-
N,N,N',N'-tetraacetic acid, and (carboxymethyl)-bis-[2-di-
(carboxymethyl)aminoethyl] amine were also measured.

EVOLUTION OF, AND INTRODUCTION TO, THE

IONIC INTERACTION THEORY

It was recognized by the early workers in solution chem-
istry that measurement of colligative properties of electro-
lytes such as boiling point elevation, freezing point depres-
sion, and osmotic pressure showed a definite deviation from
ideal behavior. The number of particles in solution was
greater than indicated by the molecular formula of the solute.

Modern electrolytic solution theory assumes solutions of
electrolytes contain charged entities, commonly referred to as
ions, which are in exact electrical balance. Arrhenius first
advanced such an idea in 1887 (20). He assumed that the con-
centration dependence of such properties as equivalent con-
ductance was due to incomplete dissociation and proposed that
α, the degree of dissociation, was given by

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

where Λ_0 is the equivalent conductance at infinite dilution.
Ionic mobility was assumed to be independent of concentration.

Some parts of the Arrhenius' theory began to be disproved
after 1900. Much data pointed toward the idea of complete
dissociation and the observed variation of the transference

number with concentration cast doubts on the assumption of mobility being independent of concentration.

Modern thinking advances the idea that little association occurs in solutions of strong electrolytes. This concept is proved correct by the striking success of the Debye-Hückel theory in predicting behavior of strong electrolytes in dilute aqueous solutions.

van't Hoff (21) introduced an empirical factor, i, into the gas law equation when applied to the osmotic pressure of electrolytic solutions. This enabled him to fit the equation to the data exactly. The van't Hoff factor was found to be equal to the ratio of the number of molecular particles actually present to the number which would have been in solution had no dissociation occurred. The degree of dissociation as calculated from van't Hoff's factor and the Arrhenius theory agreed very well for weak electrolytes. This supported the idea of ionic dissociation.

The concept of incomplete dissociation did not, however, explain the behavior of strong electrolytes. The proposal naturally followed, then, that strong electrolytes were completely dissociated in aqueous solutions. If the solution of a strong electrolyte were looked upon as a collection of small charged spheres in a medium of given dielectric constant, the deviations from ideal behavior could be looked upon as due to the interactions of these charged spheres.

The effect of coulombic forces on the ions in solution was recognized by Van Laar (22) who pointed out that coulombic forces between the ions should produce anomalous effects in osmotic pressure, conductance, and other properties.

In 1904, Noyes (23) studied the spectra of solutions of colored strong electrolytes. His conclusions were that the salts were completely dissociated even in concentrated solutions.

Sutherland (24), in 1907, made an attempt at calculating the magnitude of the effect of the coulombic forces on the properties of an ionic solution. His calculations were only approximate but did show that coulombic forces between ions could produce the observed decrease in conductance with concentration.

Hertz (25) and Ghosh (26) attempted the mathematical treatment of interionic attraction, but the basis of their treatments proved to be inadequate. Milner (27), however, developed a mathematical theory which was essentially correct. He treated the problem by statistical methods and graphical solutions, but the mathematics proved to be too cumbersome to be practical. He was able to show, however, that at low concentrations, the deviations from ideal behavior should be proportional to the square root of the concentration.

In 1923, Debye and Hückel (1) developed a method for the integration of Milner's equations which resulted in simplifi-

cation of the method and led to very successful interpretations of conductances, activity coefficients, transference numbers, and various partial molar quantities. The basic assumption for their work had been previously proposed by Bjerrum in 1909 (28). He suggested that typical strong electrolytes are completely dissociated in dilute aqueous solutions and deviation of the properties of such solutions from ideality are due to the electrostatic field of force due to the ionic charges. The magnitude of such deviations is determined primarily by concentrations and charges of the ions.

Some of the people who have concerned themselves with the statistical basis of the Debye-Huckel theory are Kramers (29), Fowler (30), Fowler and Guggenheim (31), Onsager (32), Kirkwood (33), and Halpern (34).

The important assumptions of the Debye-Huckel theory were:

1. All deviations from ideal behavior in moderately dilute solutions of electrolytes may be attributed to the coulombic interactions of the charged ions. Because electrical charges of unlike sign attract and those of like sign repel, a given ion will be surrounded by an ionic atmosphere in which there are, on the average, more ions of an opposite sign than those of like sign.

2. The solvent medium is assumed to be continuous with a constant dielectric constant.

3. The time-average charge distribution is such that the Boltzmann distribution factor is applicable to the ions.

4. The Poisson equation is valid for systems of ions in a solvent.

5. The solution of the potential equation is effected by expansion of the Boltzmann exponential expression and, since the net electrostatic potential in the atmosphere of any ion is small, the series converges rapidly and higher terms may be neglected. The solution of the equation gives the electrostatic potential in the neighborhood of the reference ion.

The development of the theory will not be included here since Glasstone (35) and Harned and Owen (36) develop the theory in great detail in their monumental texts.

Suffice it to say that expressions for the activity coefficient, conductance, and transference number arise from the theory and have been shown on numerous occasions in the past to render a true picture of the experimental data at infinite dilutions.

CONDUCTANCES

Introduction and Theory

Conductance of electrolytic solutions is due to movement
of the ions under the influence of an impressed electric
field. Each individual ion carries a characteristic portion
of the current.

A few fundamental definitions of quantities dealing with
conductance measurements are:

1. The resistance, R, of a conductor is that property
   which converts electrical energy to heat. The re-
   sistance of a homogeneous medium of uniform cross-
   sectional area is:

$$R = \Gamma \frac{1}{A}$$

   where A is the cross-sectional area, 1 is the length,
   and Γ is the specific resistance. The specific
   resistance is the resistance between two opposite
   sides of a unit cube of the substance.

2. The conductance, K, of a conductor is equal to the
   reciprocal of the resistance, R.

3. The specific conductance, L, is equal to the
   reciprocal of the specific resistance, $1/\Gamma$,

and is a characteristic property of the conductor.

4. The equivalent conductance, Λ, is related to the specific conductance, L, by

$$\Lambda = \frac{1000\ L}{C}$$

where C is the concentration in equivalents per liter. The equivalent conductance is the conductance of a solution containing one gram equivalent per liter when measured with parallel electrodes one centimeter apart. The equivalent conductance is made up of contributions from each ion such that

$$\Lambda = \sum_{j=1}^{s} \lambda_j \ .$$

λ_j is related to the mobility of the ion, u_j, by the relationship

$$\lambda_j = 96,500\ u_j \ .$$

The mobility of an ion, u_j, is its velocity under a potential gradient of one volt per centimeter.

An isolated ion has a definite mobility, u_j^o, in the absence of all other ions which is characteristic of the ion at constant temperature, pressure, and solvent, and depends on the ionic size and the tendency of the ion to carry solvent molecules with it through the solution.

Theoretical treatments of conductances allow the mobility at infinite dilution to be an empirical constant which can be determined from experimental data at infinite dilution.

Experimentally the mobility of an ion is found to be a function of concentration. Onsager (37) treated this phenomenon by applying an extension of the interionic attraction theory to conductance and obtained an expression for the equivalent conductance of an ionic constituent in a binary electrolyte.

$$\lambda = \lambda_o - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} \omega \lambda_o + \frac{28.94 \, z_1}{\eta (DT)^{1/2}}\right] \left[(z_+ + z_-)C\right]^{1/2}$$

where C is the concentration in equivalents of solute per liter, D is the dielectric constant, η is the viscosity of the solvent, and T is the absolute temperature.

$$\omega = z_+ \, z_- \, \frac{2 \, q}{1 + (q)^{1/2}}$$

and

$$q = \frac{Z_+ \, Z_-(\, \lambda_o^+ \, + \, \lambda_o^-)}{(Z_+ + Z_-)(Z_+ \, \lambda_o^- + Z_- \, \lambda_o^+)}$$

where λ_o^+ and λ_o^- are the limiting equivalent conductances, and Z_+ and Z_- are the valences of the positive and negative ions, respectively.

The first bracketed term of the equation for the equivalent conductance of an ionic constituent in a binary electrolyte accounts for the time of relaxation effect and the second for the electrophoretic effect. Onsager postulated these two effects to account for the influence of the ionic atmosphere on the motion of the central ion. The basic ideas behind the two effects are:

1. The time of relaxation effect occurs since, around a selected ion, the atmosphere has spherical symmetry. When the ion is suddenly moved, the ionic atmosphere tends to move with it but is not able to adjust to the new position instantaneously. This results in an asymmetrical atmosphere, or dipole, with the central ion, which will exert an electrostatic attraction in the opposite direction to which the ion is moving. This, of course, results in a partial cancellation of the field, and hence, a slowing down of the ion's movement. For a

steadily moving ion, a permanent distortion is effected.

2. The electrophoretic effect arises as a consequence of the ionic atmosphere that surrounds the ion. When a potential gradient is impressed across a solution, a given ion tends to move with a certain velocity in the direction of the field, superimposed on the thermal motion. This velocity is related to the ion's limiting mobility. However, the ionic atmosphere, being of opposite charge, will tend to move in a direction opposite to that taken by the ion. This motion imparts energy to the solvent molecules through which the central ion is moving and the net velocity of the central ion is less than would be expected if the solvent molecules were stationary.

History of the Method

Several reviews of the history of conductance measurements (38, 39, 40) are available in the literature.

Kohlrausch (41) made what were probably the first accurate measurements of electrolytic conductances in 1868.

Measurements of conductance were made prior to Kohlrausch's work but they employed D. C. methods such as were

used to measure the resistance of solids (42, 43, 44). Such methods allowed the formation of concentration gradients in the neighborhoods of the electrodes which resulted in polarization and non-reproducibility, and, as a result, these early experiments gave erratic data.

Kohlrausch used an alternating current of 1000 cycles per second and measured the resistances on a modified Wheatstone bridge, using a telephone receiver as a null indicator. He viewed the reaction at the electrodes as the adsorption of oxygen and hydrogen which would redissolve in the solution if the polarity were reversed (45, 46). The effective capacitance of the cell was compensated by connecting a condenser in parallel with the resistance on the other arm of the bridge (47). To aid the reversible adsorption of hydrogen and oxygen at the electrodes, he plated the platinum electrodes with platinum black (48) in order to increase their surface. In addition, the cell was designed so that the measured resistance would be high since Kohlrausch and Holborn (49, p. 10) found polarization effects were negligible if the resistance was greater than fifty divided by the area of the electrodes. The cell constant was obtained by actual measurement of the cell dimensions (50). After determining the cell constant, seven standard reference solutions were prepared as secondary standards and their conductances measured. He also realized the importance of temperature

control to accurate conductance measurements (51). The work was so carefully done that the data on potassium chloride are accepted as standard even today.

Improvements in conductance measurements since Kohlrausch's first work have been limited to better design of equipment rather than basic changes in methods of measurement. In 1913, Washburn and Bell (52) used a high-frequency generator as a current source and Washburn (53), in 1912, investigated the design of cells and characteristics of telephone receivers and other null indicators.

Taylor and Acree (54) made a study of alternating current sources in 1916. They found that a pure sine wave current was desirable to prevent unsymmetrical electrolysis at the electrodes and to annul the influence of harmonics in the detector. They also found that the resistance of solutions is independent of the voltage providing the voltage is low enough to avoid heating effects in the cells.

In 1919, Hall and Adams (55) were the first to use an electronic oscillator as a current source and also an amplifier to increase the sensitivity of the measurements.

Some of the people who concerned themselves with conductivity bridge design were Washburn and Bell (52), Taylor and Acree (54), Jones and Josephs (56), Jones and Bollinger (57, 58, 59), Shedlovsky (60, 61), and Jones and Christian (62).

A description of the conductance equipment available from Leeds and Northrup Co. has been published by Dike (63).

Use of an amplifier between the bridge and detector was introduced by Hall and Adams in 1919 (55). In 1929, Jones and Bollinger (57) made a study of amplification problems.

The telephone receiver has been the classic null detector for several years. In 1917 Washburn and Parker (64) made some studies concerning the sensitivity of the telephone receiver. In 1952 Spedding, Porter, and Wright (2) replaced the telephone receiver with an oscilloscope and thereby increased the sensitivity of the measurements immensely.

Taylor and Acree (54) experimented with the design of cells. They observed that the cell behaved as if it were a resistance in series with a condenser when used with alternating current. They found that the cell capacitance could be balanced out by use of a condenser in parallel or in series with the variable resistance arm of the bridge, or with an inductance in series with the cell. Resistance of solutions decreased slightly with an increase in frequency of the current used. Small, bright electrodes enhanced this effect and large, platinized ones inhibited it. Taylor and Acree reasoned that the ratio of resistances for any given solution in two cells, or of two solutions in any cell, must be constant. Experimentally they found this to be true for platinized electrodes. When they determined the ratio of

resistances of two solutions in a cell with platinized electrodes and the ratio for the same two solutions in a cell with bright electrodes, they found a 2% discrepancy at 60 cycles. The discrepancy varied inversely with frequency and was least when results were extrapolated to infinite frequency by use of the formula

$$R_{\text{infinite frequency}} = R - \frac{K'}{f}$$

where R is the measured resistance, f is the frequency in cycles per second, and K' is a constant.

In 1916 Washburn (53) presented an extensive study on the theory and design of conductivity cells. He obtained formulas for the optimum area and separation of the electrodes as functions of bridge component resistances, specific conductance of the solution being measured, accuracy desired, and other factors. In general, the lower the specific conductance being measured, the larger the electrode areas should be.

Potassium chloride is probably the best known standard for the calibration of conductivity cells. Kohlrausch (50) measured his cell dimensions physically and then measured potassium chloride as a secondary standard. Parker and Parker (65) redetermined the specific conductance of potassium chloride solutions and eliminated an inconsistency in units

by defining a demal (written 1 D) solution as one containing one gram molecule of salt dissolved in one cubic decimeter of solution at 0°. This defined the volume for the standard solution in the same units as the cell dimensions.

Jones and Bradshaw (66) made new absolute measurements of the specific conductivity on solutions of the same composition as used by Parker and Parker, and Jones and Prendergast (67) reinvestigated the solutions used by Kohlrausch. The values of Jones are currently accepted as the best standards available at 0°, 18°, and 25° C. but the values vary only very slightly from those of Kohlrausch and Parker and Parker. Jones and Prendergast (67) used pure mercury as a primary standard at 0° C. The constants for several cells were obtained and the specific conductivity of concentrated sulfuric acid was measured so that it could be used as a secondary standard.

Complete cell calibration must provide for the Parker effect (68) which is the variation of the cell constant with the measured resistance. Parker believed this effect was due to adsorption at the electrodes. Shedlovsky (69) and Jones and Bollinger (58) correctly attributed this effect to capacitance between the cell leads.

For temperature control, any arrangement which would hold the temperature to $\pm$ 0.01^o C. was found to be suitable. Jones and Josephs (56) point out that water is a conductor,

in comparison to mineral oil, and since the glass cell walls can act as a dielectric in a condenser, current may be permitted to flow in the water outside the cell. This, of course, would introduce an error and, hence, mineral oil is recommended as a bath medium.

Thus, for accurate measurement of conductivities one should observe the following precautions:

1. Use a fairly high frequency (preferably above 500 cycles per second) since data at low resistances (high concentrations) were found to be effected mainly by polarization phenomena and use of high frequencies lowers polarization capacitance (58).

2. Use cells having horizontal solution compartments with vertical filling tubes and vertical cell lead compartments placed as far apart as possible to minimize cell capacitive effects. The cell should also be as long as possible since a shorter cell will have a relatively greater polarization error with the same solution than a longer one (58).

3. The electrodes should be heavily platinized to lower cell capacitance and minimize variation of resistance with frequency (54). The electrode areas should also be as large as is practical since, again, polarization capacitance is minimized by increasing electrode areas and, in general, the lower the

specific conductance being measured, the larger the electrode areas should be for greatest accuracy (53, 58).

4. Use a capacitance in parallel or in series with the variable resistance arm of the bridge or an inductance in series with the cell to nullify cell capacitive effects.

5. Use a low-voltage alternating current source to avoid electrolysis at the electrodes and to avoid heating in the cell.

6. The bridge should be shielded from stray magnetic fields and the oscillator should be situated a respectable distance from the bridge and cells.

7. An oil bath fitted with a temperature control capable of ± 0.01° C. is desirable.

8. The cells should be calibrated taking the Parker effect into account and then should be used only in the region where their calibration was most accurate.

9. Use of an amplifier between the bridge and the detector is recommended as well as an oscilloscope as a null indicator.

Experimental

Preparation of materials

The scandium used in this research was prepared as the oxide by applying the techniques of solvent extraction and ion exchange as developed at the Ames Laboratory (70) in the treatment of thortveitite ore.

The thortveitite ore, $(Sc, rare earths)_2-Si_2O_7$, was ground to a powder, ball-milled, mixed with excess ammonium bifluoride, and heated overnight at $375-400^\circ$ C. in a platinum boat. A slow stream of air removed the gaseous products. The reaction may be represented as

$$M_2O_3 \cdot SiO_2 + 10 \ NH_4HF_2 \longrightarrow 2 \ MF_3 + SiF_4 + 10 \ HF +$$

$$10 \ NH_3 + 5 \ H_2O \ .$$
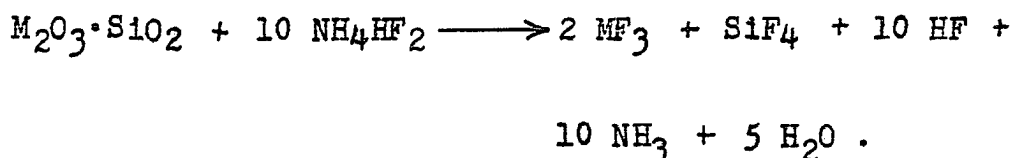
The resulting fluoride mixture was mixed with excess calcium metal and reduced by heating in a tantalum crucible in an inert atmosphere at 1400° C. The reaction was

$$2 \ MF_3 + 3 \ Ca \longrightarrow 3 \ CaF_2 + 2 \ M \ .$$
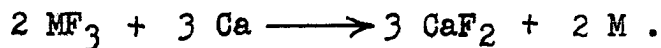
The scandium-rare earth metal buttons prepared as just outlined were dissolved in hydrochloric acid, the solution

swamped with ammonium thiocyanate, and extracted with diethyl ether according to the procedure of Fischer and Bock (71). After evaporating the ether, the residues were ignited at 800° C. The resulting oxide was then converted to the chloride, loaded on Dowex 50-X8 hydrogen form cation-exchange columns, and eluted with 0.018 M N'-(hydroxyethyl)ethylene-diamine-N,N,N'-triacetic acid buffered to a pH of 7.4-7.6 with NH₄OH. The material was recovered in consecutive samples as the oxide by boiling the solution dry, destroying the organic matter with nitric acid, and igniting at 800° C.

The oxide was further purified by one or two precipitations as the oxalate. This insured removal of iron which interferes in the solvent extraction and ion-exchange purifications probably because of poor kinetics. The purity of the resulting oxide as used in preparing the nitrate, chloride, and perchlorate was as listed in Table 1.

The salt solutions were prepared by dissolving the oxide, with heating, in the respective reagent-grade acids. Because scandium oxide is not very basic, the pH of the solutions resulting from the dissolution was usually about one or below. For this reason, a procedure for elevating the pH without introducing extraneous cations or anions was used (72). The solution that was desired was one that would result if a pure sample of the anhydrous salt were placed in water and allowed to come to equilibrium

Table 1. Purity of the scandium oxide

| Impurity[a]	Analysis[b]
Lu	$\lesssim 0.005$
Yb	$\lesssim 0.005$
Tm	$\lesssim 0.005$
Er	$\lesssim 0.005$
Y	d. < 0.01
Ca	very weak
Na	very weak
Be	very weak
Si	trace
Fe	very faint trace
Cu	very faint trace
Hf	very faint trace
Sn	very faint trace
Mg	very faint trace
Zn	not detected
Ti	not detected
Zr	not detected
Pb	not detected
Al	not detected

[a]The spectrum was examined for thirty-one other common elements as well as the other rare earths, but none were detected. The ones listed above are those most commonly associated with scandium.

[b]All analyses were made by emission spectrography. $\lesssim$ means the element if present was below the 0.005 limit and d < means detected but less than.

$$Sc^{+3} + H_2O \rightleftharpoons Sc(OH)^{+2} + H^+.$$

While in the case of the chloride, the anhydrous salt
could have been prepared and then dissolved, it is simpler
to titrate the solution to the equivalence point. To obtain
such a titration curve, the pH must be above the equivalence
pH at the start of the titration.

Hydroxide form Dowex 1-X8 anion resin was prepared by
passage of carbonate-free base over a column of it until no
more chloride was detected in the effluent solution. The
carbonate-free base was prepared by the procedure of Powell
and Hiller (73). Addition of this hydroxide-form resin to
the scandium solutions raises the pH since the equilibrium
for the reactions

$$\bar{R}OH + A^- \rightleftharpoons \bar{R}A + OH^-$$

$$M^{+n} + OH^- \rightleftharpoons MOH^{(n-1)+}$$
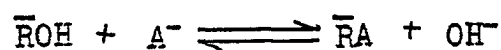
favors the right hand side where $\bar{R}$ is the insoluble resin
cation, M is the salt cation, and A is the anion of the
desired salt. Titration of an aliquot with the acid corre-
sponding to the anion of the salt then gives

$$\text{MOH}^{(n-1)+} + (n-1)\,A^- \rightleftharpoons M^{+n} + n\,A^- + H_2O .$$
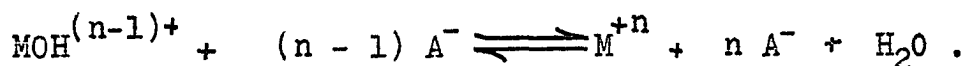
A Beckman, model G, pH meter was used and the equivalence pH read from a graph of Δ pH/ Δ milliliter vs. the average number of milliliters of acid used. The aliquot was returned to the stock solution which was then adjusted to the indicated equivalence pH and boiled to help break up any colloidal material suspended in solution. The nitrate, however, could not be boiled since the basic nitrate would precipitate upon boiling. Therefore, it was heated for two days with heat lamps while keeping below the boiling point. The solutions were then cooled and, after redilution to the same total volume they occupied before boiling, their pH was checked. If it had changed, the titration procedure was repeated until the pH remained constant after boiling. Solutions prepared in this manner were stable indefinitely.

The resulting stock solution was then analyzed by evaporating aliquots under a heat lamp and treating the solid chloride and perchlorate residues with a few drops of concentrated nitric acid to avoid formation of oxy-compounds which might not ignite easily to the oxide. Weighing as the oxide, Sc_2O_3, followed ignition at 800° C.

The scandium chloride stock solution was analyzed for chloride ion gravimetrically by precipitating the silver

salt, filtering on sintered glass filters, drying at 120° C., and weighing as silver chloride. The results showed an empirical formula of $ScCl_{3.008}$. Thus, it was felt that the titration-curve method was adequate for the preparation of equivalent solutions.

An average of fifteen dilutions were made from each stock solution using Normax or calibrated glassware and conductivity water. The conductivity water was made by redistilling ordinary distilled water over potassium permanganate and sodium hydroxide in a block tin Barnsted conductivity still.

The potassium chloride solutions for determination of the cell constants of the conductance cells were made up by weight from twice-recrystallized reagent grade potassium chloride which was fused in a platinum boat in a nitrogen atmosphere according to the method of Pinching and Bates (74). The data of Parker and Parker (65) were used in this research since, even though their data is not recognized as the most precise, they did their work over a much wider temperature range. A value for the specific conductance of potassium chloride at 35° C. was needed and, since the data of Parker and Parker covered the range 0° to 30° in 5° intervals, and the plot was nearly linear, an extrapolation was made to obtain a value at 35° C.

Apparatus

The bridge used in this research was obtained from the Leeds and Northrup Company, Philadelphia, Pennsylvania. It was a research model conductivity bridge, catalog number 4666, as described by Dike (63).

Alternating current of 500, 1000, and 2000 cycles per second was provided by a Leeds and Northrup audio-frequency electronic oscillator, catalog number 9842.

The signal from the bridge was amplified by a Leeds and Northrup audio-frequency, narrow-band amplifier, catalog number 9847, which could be tuned to the same frequency as the oscillator.

A cathode-ray oscillograph, type 274-A, manufactured by the Allen B. DuMont Laboratories, Inc. was used as a detector. The horizontal section of the oscilloscope was blocked out so a vertical line was produced when the conductance bridge was out of balance and a spot when the bridge was balanced. The electronic circuit diagram is shown in Figure 1 and the block diagram of the equipment in Figure 2.

The conductance cells used in this research were of the general form recommended by Jones and Bollinger (58) from their cell design studies. A set of three cells having widely different cell constants were used so that the specific conductance of a solution could be cross checked with at
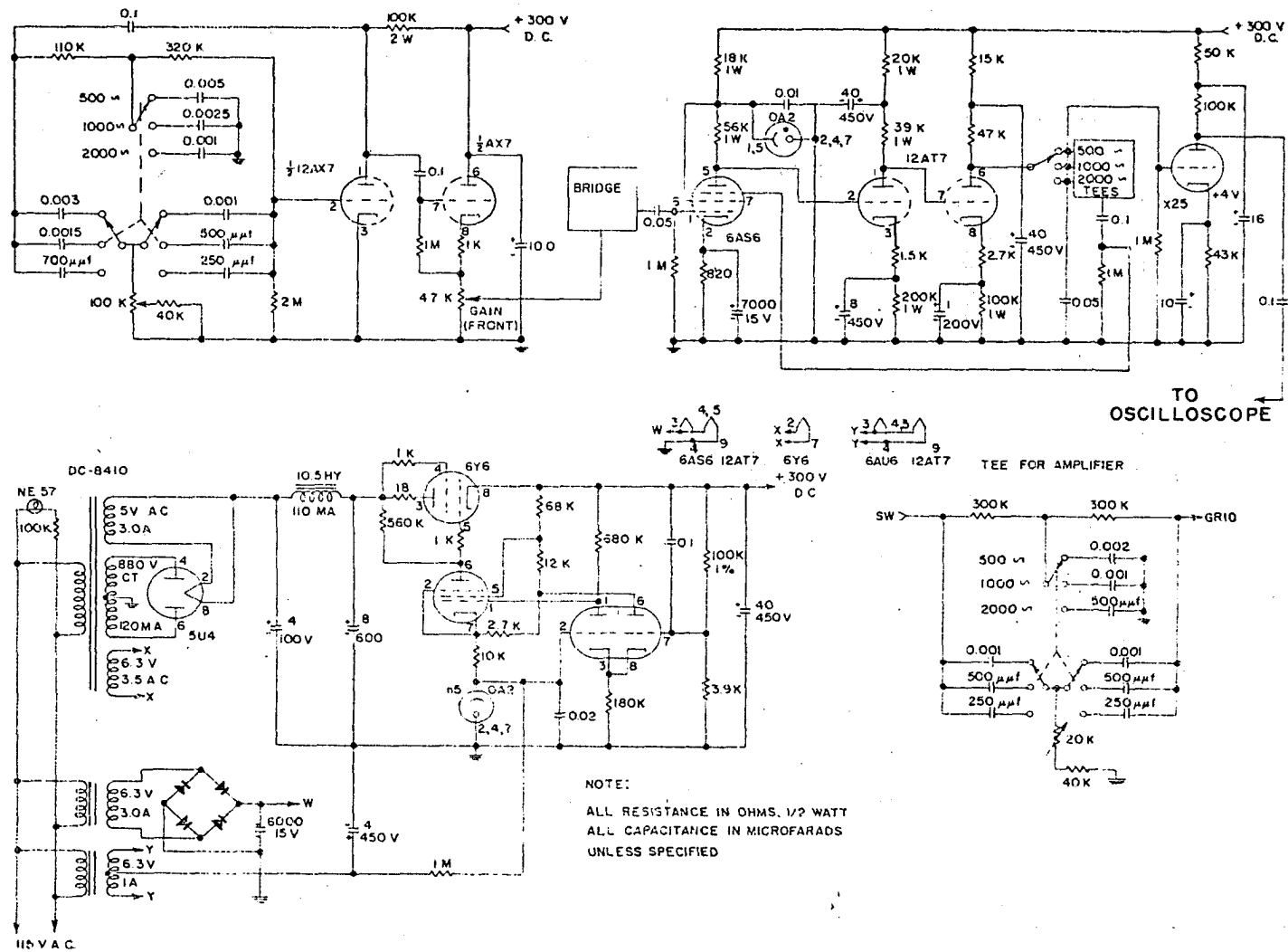
Figure 1.   The electronic circuit for the oscillator and amplifier used
in the conductance measurements

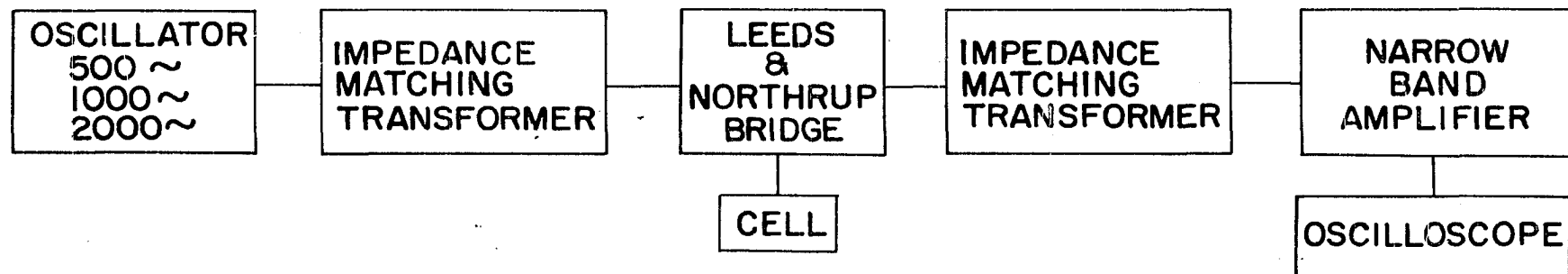| OSCILLATOR 500 ~ 1000~ 2000~ | IMPEDANCE MATCHING TRANSFORMER | LEEDS & NORTHRUP BRIDGE | IMPEDANCE MATCHING TRANSFORMER | NARROW BAND AMPLIFIER |

CELL

OSCILLOSCOPE

Figure 2. Block diagram of the equipment used in conductance measurements

least two cells and so that appropriate cells could be used
to keep the measured resistance within the optimum range of
the bridge. The cells were also obtained from Leeds and
Northrup (catalog numbers 4911, 4914, and 4915). The elec-
trodes of all cells were adequately platinized as shown by
agreement of measurements at 1000 and 2000 cycles per second.
The so-called low cell had a cylindrical vertical chamber
about 3 cm. in diameter by 6 cm. in height with rectangular
electrodes hugging opposite sides and having about a 12 square
cm. area. The medium cell had a cylindrical horizontal cham-
ber about 2 1/2 cm. in diameter by 7 cm. long with circular
electrodes about 1 3/4 cm. in diameter sealed in opposite
ends. The high cell had three separate, circular, bubble-
like compartments about 2 1/4 cm. in diameter by 1 cm. thick,
the center one opening to the filler tube, the two end ones
containing the electrodes which were about 1 3/4 cm. in di-
ameter as well as air escape tubes to facilitate filling.
The three compartments were joined by a tube about 3 cm. long
with an inside diameter of about 1/2 cm. The cell was thus
about 9 cm. long.

The constant temperature baths were controlled by micro-
set mercury thermoregulators coupled with electronic relays
made by Precision Scientific Company, Chicago, Illinois,
catalog numbers 62541 and 62690. The relays operated 250
watt infrared heat lamps which provided heat to the baths,

and the coolant pump in the case of the 15° C. bath. The 35° C. bath required no cooling facilities, the 25° C. bath was cooled by a cold finger having tap water circulated through it, and the 15° C. bath was cooled by pumping 5° C. water through a copper cooling coil buried in the bath. A second relay between the thermoregulator relay and the centrifugal coolant pump caused the operation of the pump and the infrared bulb to alternate. The 5° C. cooling water was supplied by a refrigeration unit manufactured by the Lehigh Manufacturing Company, Lancaster, Pennsylvania. The cells, when immersed in the baths, were shielded from the infrared lamps by a metal plate, blackened on the side toward the lamp, and immersed across the center of the bath. The bath temperatures were checked periodically against a narrow-range thermometer which was calibrated by the National Bureau of Standards. The temperatures were held to within $\pm$ 0.02° C.

All the baths were stirred with laboratory stirrers and were filled with mineral oil to minimize capacitance effects.

Connection of the cells to the bridge was made by means of platinum wire leads dipping into mercury compartments which were, in turn, in contact with the electrode leads. This arrangement facilitated connection and disconnection.

Procedure

The conductivity cells were thoroughly cleaned with sulfuric acid-potassium dichromate cleaning solution and then very thoroughly rinsed with distilled water and soaked in several changes of conductivity water. Their cell constants were determined at several concentrations of standard potassium chloride solutions. The cell constant was plotted versus the measured resistance for each cell at each temperature as shown in Figure 3. When measuring the scandium solutions the appropriate cell constant was read from the plot and used at each resistance.

The resistance of the conductivity water used in making up the samples was also measured using the low and medium cells by shunting 30,000 ohms in parallel with the cell. Since the true specific conductivity, L_T, is found by

$$L_T = \frac{k}{R} - L_{H_2O} = L_m - L_{H_2O}$$

where L_m is the measured specific conductivity, the conductivity of the water must be known to get, k, the cell constant but L_m cannot be obtained without knowing the cell constant. Thus, the cell constants were obtained by successive approximations.
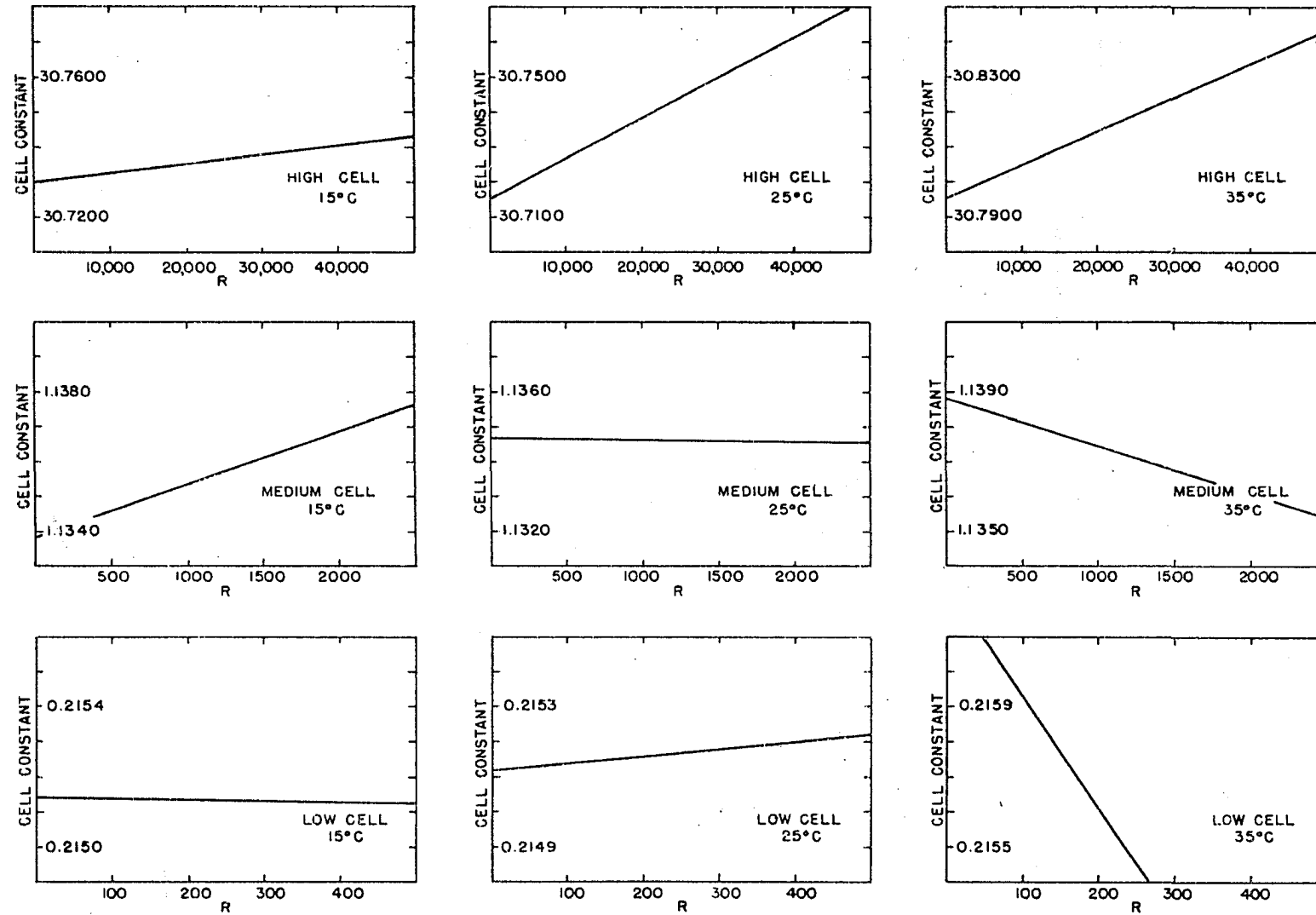
Figure 3. Variation of cell constant with measured resistance for the high, medium, and low cells at 15°, 25°, and 35° C.

Readings on the potassium chloride standards as well as the scandium solutions were taken at 1000 and 2000 cycles per second and with two cells for each concentration. It was found to be unnecessary to correct the data to infinite frequency. The Taylor and Acree ratio (54) was also checked and the consistency of the cells found to be within experimental error and the limit of accuracy of dilution of the solutions.

To avoid errors due to soaking out of salt absorbed at the electrodes, the lowest concentration solution was measured first, followed by ones of higher concentration. The cell was always rinsed at least four times with the solution to be measured.

The cells and their contents were found to come to temperature equilibrium in about 30 to 45 minutes after immersion in the bath. At least 45 minutes was allowed before readings were taken. Completeness of temperature equilibration could be followed by observation of the drift in resistance readings. An effort was made in all cases to read the resistance as soon as possible after throwing the switch to connect the cell into the circuit. In this way, heating effects in the cell were negligible.

Results

The data obtained from the measurements on the solutions were the resistances of the solutions, R. The calculations

used to obtain the equivalent conductances of the solutions were

$$L_s = (k/R) - L_{H_2O} - L_H^+$$

and

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

where L_s is the specific conductance of the solution due to the solute only, k is the cell constant taking the Parker effect into account, R is the measured resistance in ohms, L_{H_2O} is the specific conductance of the water used in preparing the solutions, L_H^+ is the specific conductance of the hydrogen ion in the solution minus the specific conductance of the hydrogen ion in the water used to prepare the solutions, and C is the concentration of the solution in equivalents per liter.

The specific conductance of the hydrogen ion in the solution was calculated from its approximate concentration difference between solution and solvent as measured with a Beckman model G pH meter. The Onsager equation for the ionic specific conductivity

$$\lambda = \lambda_o - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} \omega \lambda_o + \frac{28.94 \, Z_1}{\eta \, (DT)^{1/2}}\right] \left[(Z_+ + Z_-)C\right]^{1/2}$$

was used to calculate λ_{H^+} where

$$\omega = Z_+ \, Z_- \, \frac{2 \, q}{1 + (q)^{1/2}}$$

and

$$q = \frac{Z_+ \, Z_- (\lambda_o^+ + \lambda_o^-)}{(Z_+ + Z_-)(Z_+ \lambda_o^- + Z_- \lambda_o^+)} \quad .$$

For uni-univalent salts or monobasic acids such as nitric, hydrochloric, and perchloric, $q = 1/2$ since Z_+ and Z_- are both one. This in turn makes $\omega = 0.5857$. Thus, the Onsager equation for all temperatures reduces to

$$\lambda = \lambda_o - \left[\frac{0.57592 \times 10^6 \, \lambda_o}{(DT)^{3/2}} + \frac{28.94}{\eta \, (DT)^{1/2}}\right] C^{1/2}$$

where C is the concentration in equivalents of solute per liter and D, T, η and λ_o vary with temperature. The values for D, η, and T are given in Table 2.

The values for λ_o^+ used in the Onsager equation were taken from Harned and Owen (36, p. 234). The values at each

Table 2. Values of the dielectric constant, viscosity, and
temperature used in the Onsager equation

Property	15° C.	25° C.	35° C.
Dielectric constant, D, in Debye units	82.23[a]	78.54[a]	75.04[a]
Viscosity, η, in poise x 10^3	11.404[b]	8.949[c]	7.225[b]
Absolute temperature, $T°$ K.	288.16	298.16	308.16

[a]Reference 36, p. 161.

[b]Reference 75, p. 1632.

[c]Reference 97, p. 57.

temperature for hydrogen ion were 300.73 at 15° C., 349.80 at
25° C., and 396.91 at 35° C. Substitution of these values
gave

$$\lambda_{H^+} = 300.73 - 31.6042 \ c^{1/2} \text{ at 15° C.,}$$

$$\lambda_{H^+} = 349.80 - 35.0827 \ c^{1/2} \text{ at 25° C., and}$$

$$\lambda_{H^+} = 396.91 - 38.7345 \ c^{1/2} \text{ at 35° C. for monobasic}$$

acids.

The λ_{H^+} values calculated from the above were then convert-
ed to specific conductivities by

$$L_{H^+} = \frac{C_{H^+} \, \lambda_{H^+}}{1000} \, .$$

Subtraction of L_{H^+} and L_{H_2O} from the measured specific conductivities gave specific conductivities for the solute only, L_s, which were then converted to equivalent conductivities by

$$\Lambda = \frac{1000 \, L_s}{C_{ScX_3}} \, .$$

The corrected and uncorrected equivalent conductivity data for the three scandium salts are given in Tables 3-8 and the corresponding curves are included as Figures 4-9. The curves in all cases immediately follow the table corresponding to them.

It will be noticed that the pH's used in correcting the conductivity data were measured at 25° C. The hydrogen ion concentrations from these pH's were corrected for temperature and substituted in the Onsager equation to obtain the specific conductances. Essentially the equivalent conductance correction resulting from these specific conductances was the same whether it was 15°, 25°, or 35° C. This is because the hydrogen ion concentrations were all below 0.004 M and the densities of hydrochloric, nitric, or perchloric acid

Table 3. Equivalent conductances of scandium chloride solutions, uncorrected for hydrogen ion conductivity

Normality[a]			Equivalent conductance		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.0001165	0.0001163	0.0001159	143.5	178.7	229.9
0.0002331	0.0002326	0.0002318	136.9	168.5	218.8
0.0004663	0.0004653	0.0004637	129.4	161.8	205.9
0.0009325	0.0009305	0.0009275	121.3	154.3	195.6
0.001865	0.001861	0.001855	114.9	148.6	186.1
0.003730	0.003723	0.003710	108.7	139.4	173.3
0.007460	0.007445	0.007420	102.6	131.1	162.5
0.01492	0.01489	0.01484	96.08	120.7	150.9
0.02984	0.02977	0.02969	89.65	112.7	139.7
0.05968	0.05955	0.05936	83.49	104.8	129.1
0.1194	0.1191	0.1187	77.29	96.91	118.7
0.2388	0.2382	0.2375	71.24	89.10	108.7
0.4775	0.4764	0.4749	64.74	80.74	98.08

[a]The densities used in calculating the normalities at other than 25° C. can be found in the section of this thesis which deals with densities.
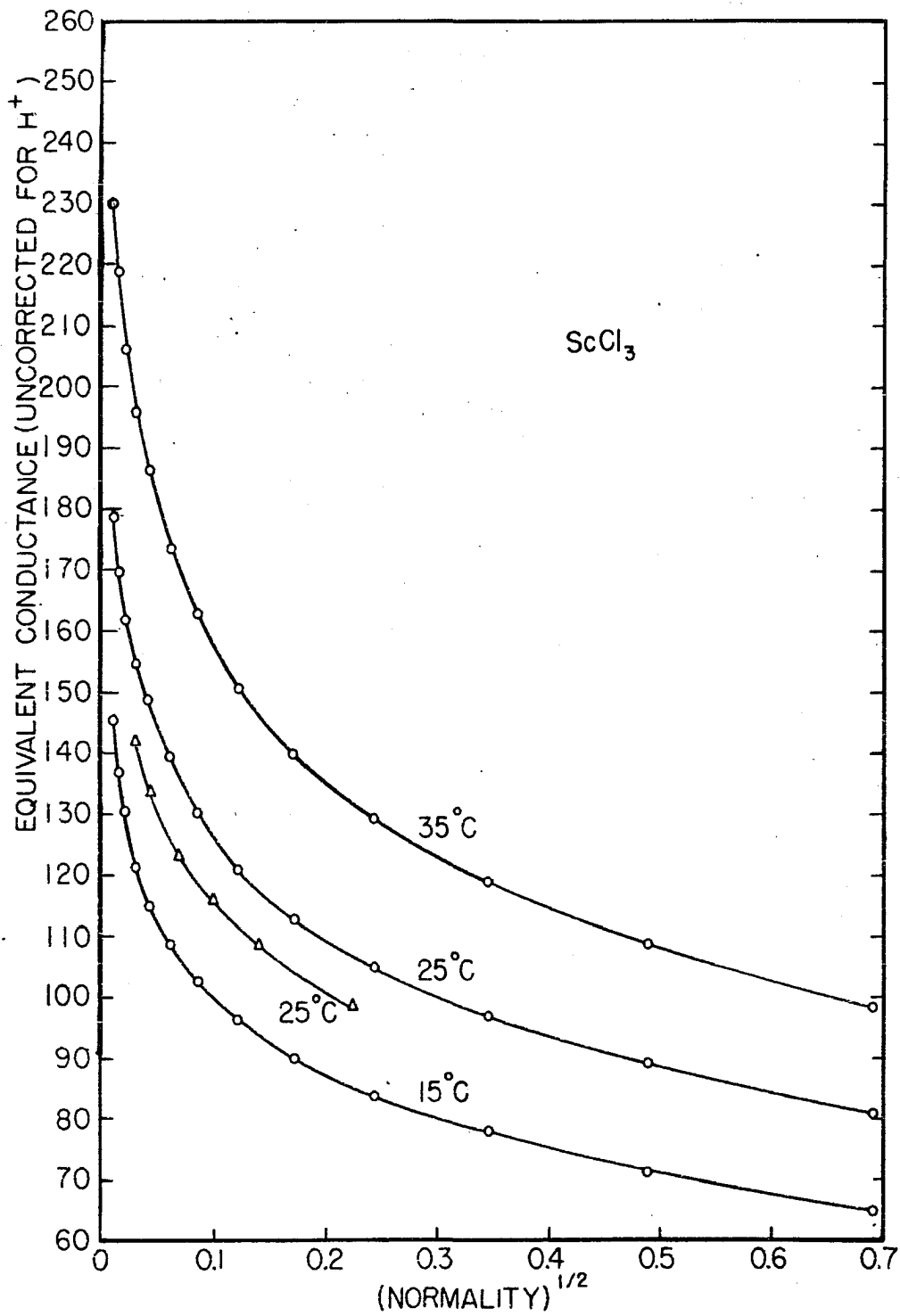
Figure 4. Equivalent conductance of scandium chloride, uncorrected for hydrogen ion conductivity, at 15°, 25°, and 35° C.

Table 4. Equivalent conductances of scandium chloride
solutions, corrected for hydrogen ion conductivity

pH[a]	Normality[b]			Equivalent conductivity[a]		
	15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
4.67	0.0001165	0.0001163	0.0001159	88.18	118.9	159.1
4.52	0.0002331	0.0002326	0.0002318	98.64	131.5	168.5
4.38	0.0004663	0.0004653	0.0004637	98.54	131.2	170.5
4.11	0.0009325	0.0009305	0.0009275	96.53	127.7	163.2
3.90	0.001865	0.001861	0.001855	94.69	125.0	158.0
3.71	0.003730	0.003723	0.003710	92.95	121.1	152.4
3.54	0.007460	0.007445	0.007420	90.30	117.7	147.3
3.43	0.01942	0.01489	0.01484	87.20	113.4	141.0
3.17	0.02984	0.02977	0.02969	83.50	107.3	133.0
3.09	0.05968	0.05955	0.05936	79.35	100.4	123.6
2.78	0.1194	0.1191	0.1187	73.16	92.24	113.2
2.60	0.2388	0.2382	0.2375	68.10	85.42	104.4
2.39	0.4775	0.4764	0.4749	62.19	77.88	94.74

[a]Two batches of conductivity water were used on these
samples, one had a pH of 6.75, the other 6.05. To obtain the
correct L_{H^+} values and L_{H_2O} values, synthetic mixtures of the
two batches were made to exactly duplicate the composition
found in the respective scandium samples but, of course, with-
out the scandium salt. Measurement of the pH and conductivities
of these samples enabled true values of L_{H_2O} and L_{H^+} to be de-
termined so they could be used in correcting the equivalent
conductivity. A further comment regarding the pH measurement
is to be found in the text immediately following the presenta-
tion of the tables and curves dealing with conductivities.

[b]The densities used in calculating the normalities at
other than 25° C. can be found in the section of this thesis
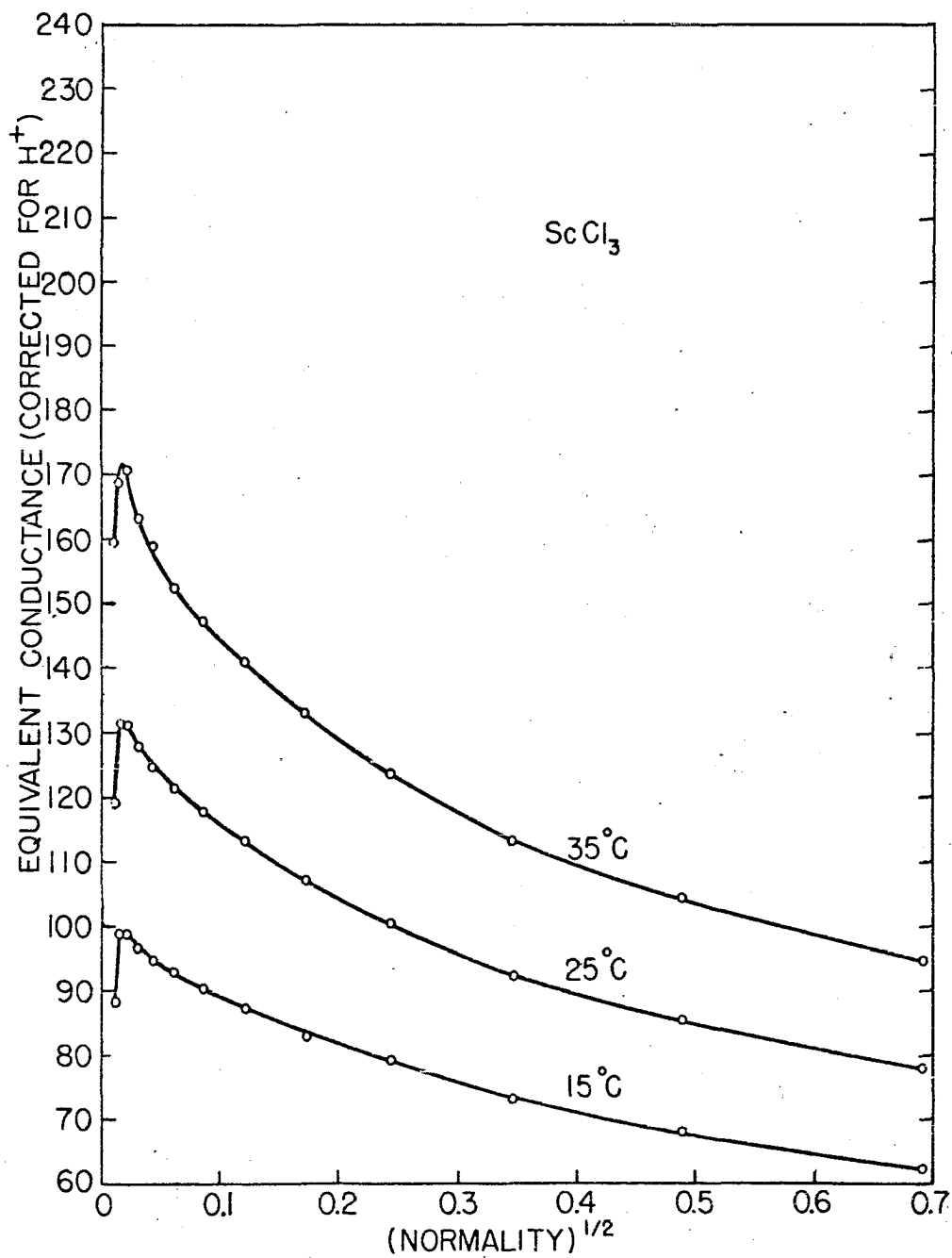which deals with densities.

Figure 5. Equivalent conductance of scandium chloride, corrected for hydrogen ion conductivity, at 15°, 25°, and 35°C.

Table 5. Equivalent conductances of scandium nitrate
          solutions, uncorrected for hydrogen ion
          conductivity

Normality[a]			Equivalent conductivity		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.0002947	0.0002940	0.0002930	118.6	154.2	191.7
0.0005895	0.0005880	0.0005860	113.7	146.5	182.8
0.001179	0.001176	0.001172	108.6	139.4	175.1
0.002359	0.002353	0.002344	103.2	131.9	164.7
0.004718	0.004705	0.004688	97.04	123.3	152.9
0.009435	0.009411	0.009375	90.90	115.4	142.7
0.01887	0.01882	0.01875	84.55	106.8	131.6
0.03773	0.03764	0.03750	78.34	98.59	120.9
0.07547	0.07528	0.07501	72.00	90.59	110.5
0.1509	0.1506	0.1500	65.70	81.99	99.84
0.3019	0.3011	0.3000	59.14	73.50	88.85
0.6037	0.6023	0.6001	51.67	63.94	76.94

[a]The densities used in calculating the normalities at
other than 25° C. can be found in the section of this thesis
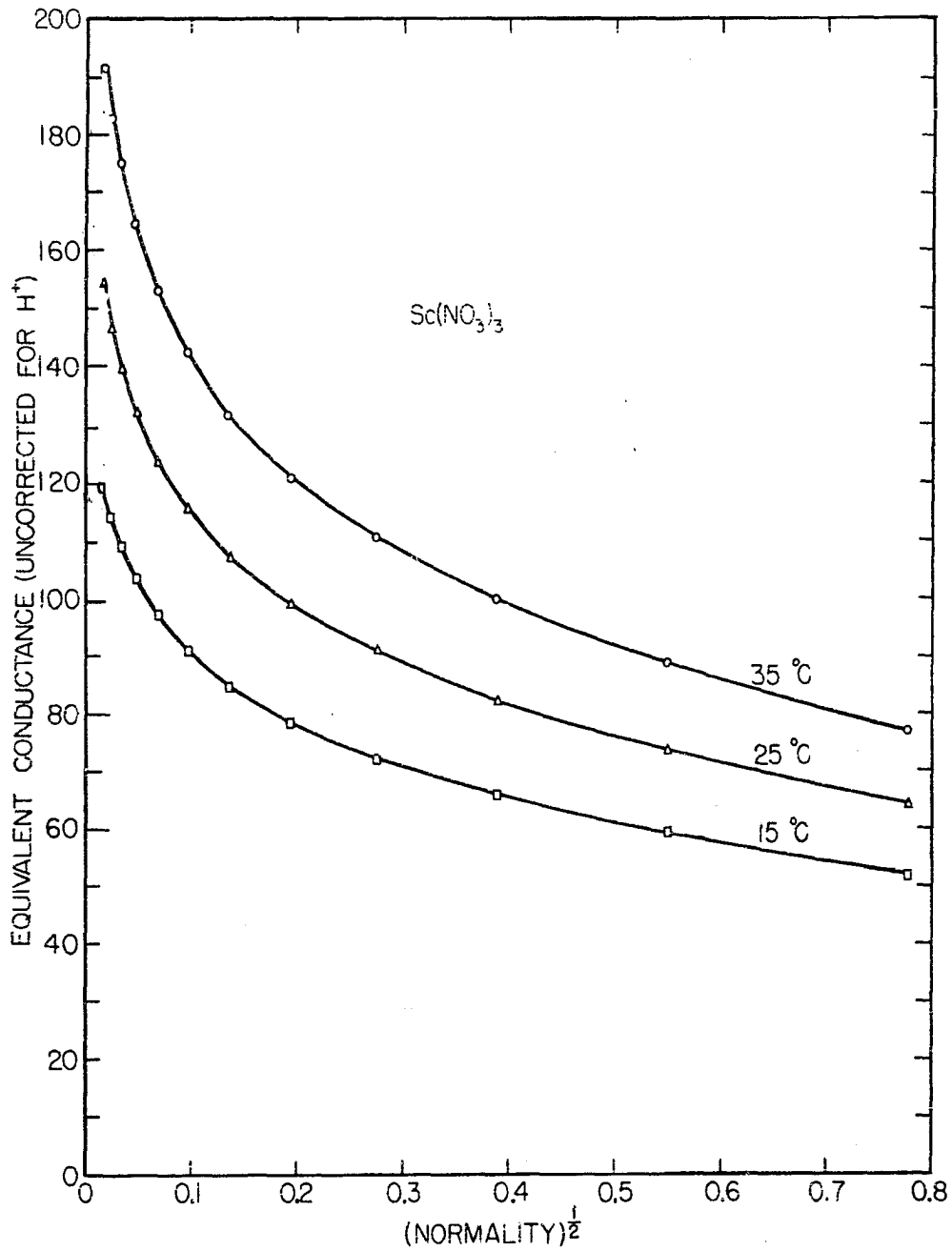which deals with densities.

Figure 6. Equivalent conductance of scandium nitrate,
uncorrected for hydrogen ion conductivity,
at 15°, 25°, and 35° C.

Table 6. Equivalent conductances of scandium nitrate solutions, corrected for hydrogen ion conductivity

pH[a]	Normality[b]			Equivalent conductivity		
	15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
4.33	0.0002947	0.0002940	0.0002930	72.58	100.2	130.5
4.18	0.0005895	0.0005880	0.0005860	81.07	108.6	139.8
3.99	0.001179	0.001176	0.001172	83.06	109.8	141.2
3.81	0.002359	0.002353	0.002344	83.60	109.2	138.8
3.65	0.004718	0.004705	0.004688	82.89	106.9	134.2
3.48	0.009435	0.009411	0.009375	80.43	103.2	128.8
3.30	0.01887	0.01882	0.01875	76.61	97.55	121.1
3.16	0.03773	0.03764	0.03750	72.85	92.19	113.6
2.98	0.07547	0.07528	0.07501	67.84	85.75	105.0
2.79	0.1509	0.1506	0.1500	62.49	78.25	95.57
2.50	0.3019	0.3011	0.3000	56.02	69.85	84.69
2.23	0.6037	0.6023	0.6001	48.76	60.55	73.08

[a]The pH of the conductivity water used in these dilutions was 5.69.

[b]The densities used in calculating the normalities at other than 25° C. can be found in the section of this thesis which deals with densities.
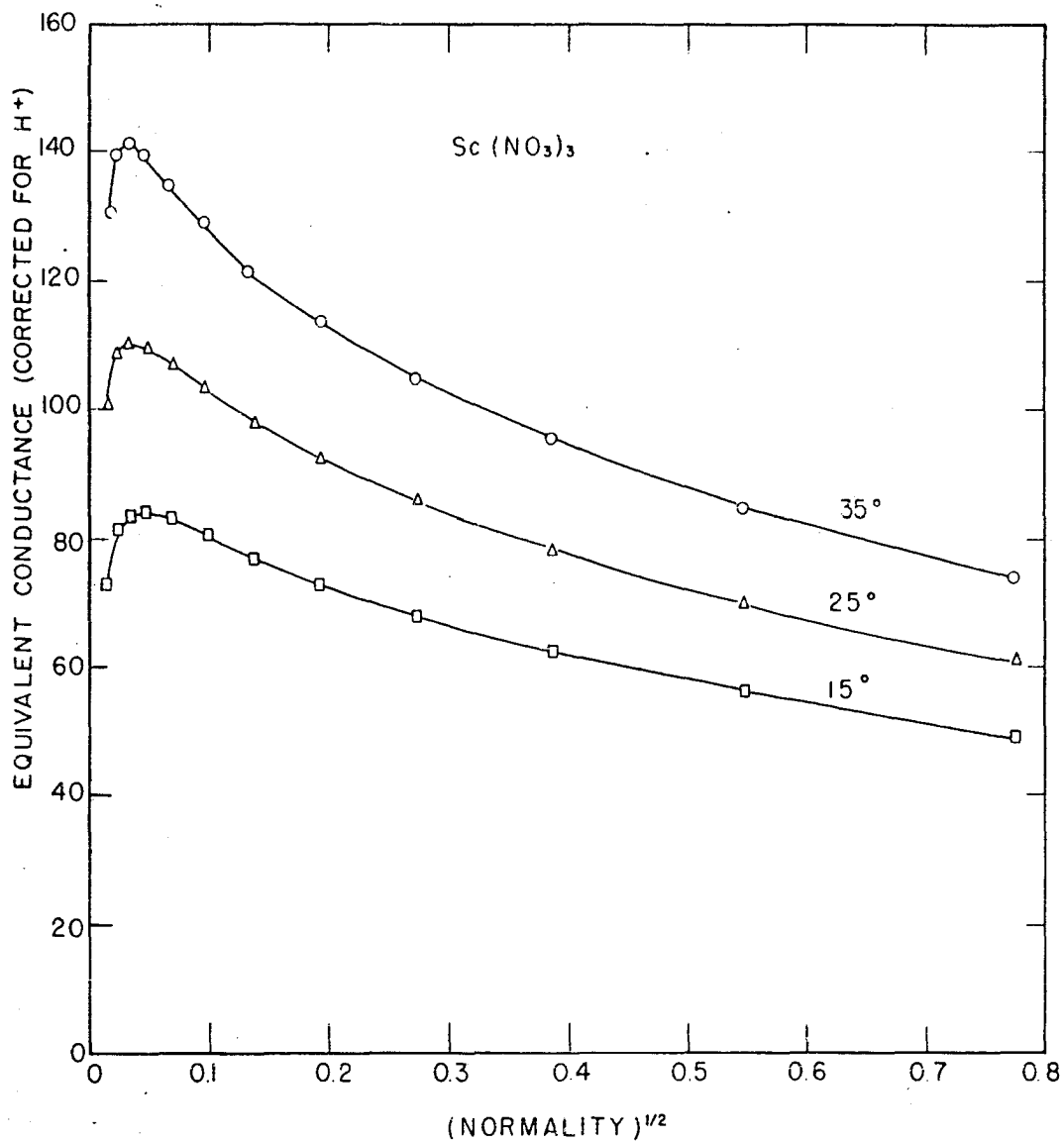
Figure 7. Equivalent conductance of scandium nitrate,
uncorrected for hydrogen ion conductivity, at
15°, 25°, and 35° C.

Table 7.   Equivalent conductances of scandium perchlorate
           solutions, uncorrected for hydrogen ion
           conductivity

Normality[a]			Equivalent conductivity		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.0001193	0.0001193	0.0001185	137.0	176.1	216.7
0.0002386	0.0002385	0.0002371	129.3	166.6	207.3
0.0004773	0.0004770	0.0004743	123.4	159.4	198.7
0.0009545	0.0009540	0.0009485	115.7	150.1	187.9
0.001909	0.001908	0.001897	108.3	139.5	175.3
0.003818	0.003807	0.003795	102.0	131.2	163.5
0.007635	0.007613	0.007590	96.28	123.3	153.1
0.01518	0.01523	0.01518	90.50	115.2	142.4
0.03036	0.03045	0.03036	84.91	107.7	132.6
0.06072	0.06091	0.06072	79.58	100.6	123.5
0.1214	0.1218	0.1214	74.71	94.15	115.3
0.2428	0.2436	0.2428	69.66	87.37	106.7

[a]The densities used in calculating the normalities at
other than 25° C. can be found in the section of this thesis
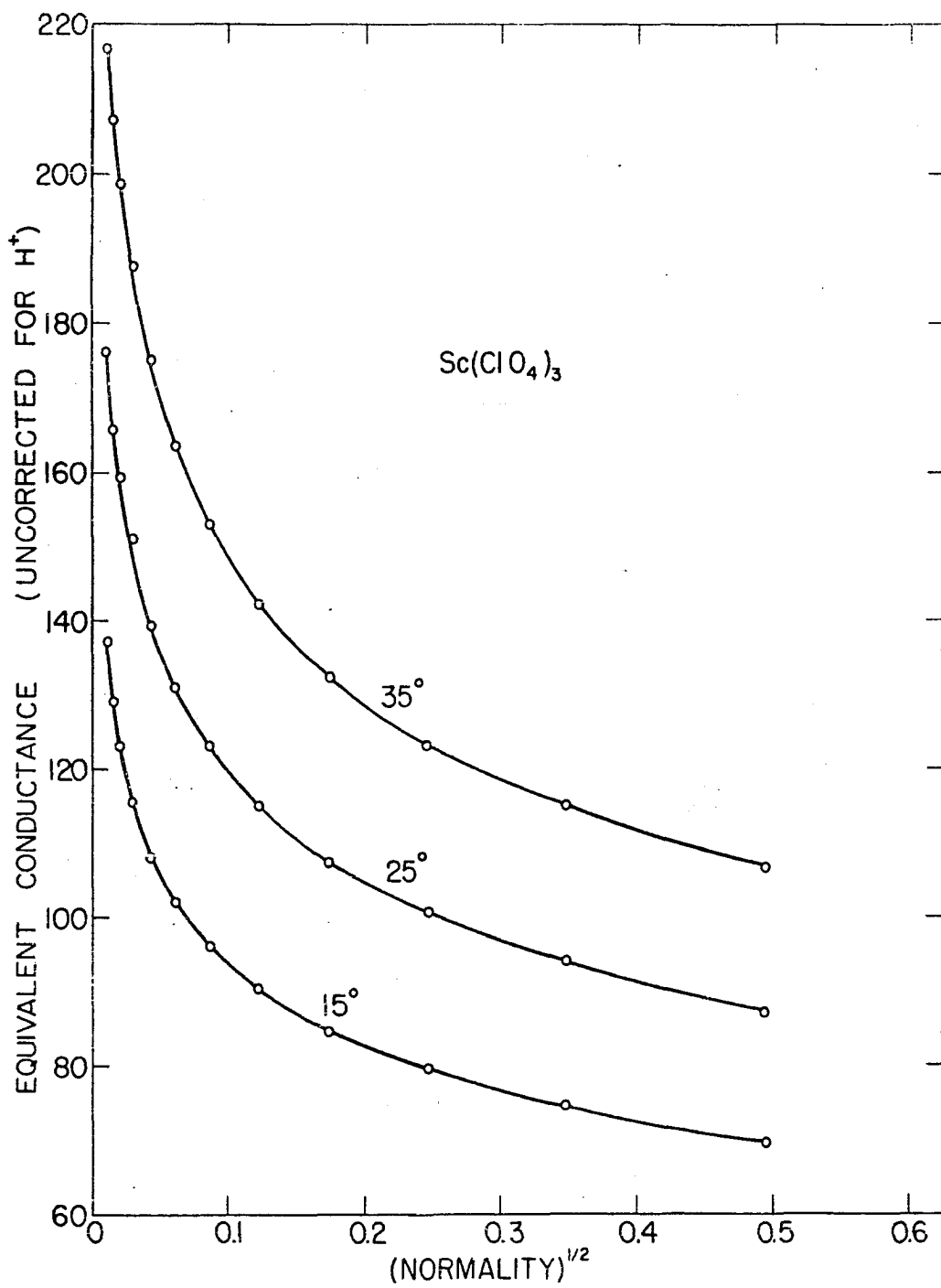which deals with densities.

Figure 8. Equivalent conductance of scandium perchlorate
solutions, uncorrected for hydrogen ion
conductivity, at 15°, 25°, and 35° C.

Table 8. Equivalent conductances of scandium perchlorate
solutions, corrected for hydrogen ion conduc-
tivity

pH[a]	Normality[b]			Equivalent conductivity		
	15° C.	25° C.	35° C.	15°C.	25° C.	35° C.
4.73	0.001193	0.0001193	0.0001185	94.07	126.1	160.0
4.46	0.0002386	0.0002385	0.0002371	87.64	118.1	152.0
4.21	0.0004773	0.0004770	0.0004743	85.48	115.3	148.6
4.05	0.0009545	0.0009540	0.0009485	88.32	118.1	151.6
3.88	0.001909	0.001908	0.001897	87.84	116.6	148.5
3.73	0.003818	0.003807	0.003795	87.49	114.3	144.2
3.58	0.007635	0.007613	0.007590	85.00	110.8	138.9
3.38	0.01518	0.01523	0.01518	82.34	106.3	131.6
3.23	0.03036	0.03045	0.03036	79.14	101.0	124.9
3.07	0.06072	0.06091	0.06072	75.41	95.76	117.9
2.88	0.1214	0.1218	0.1214	71.48	90.38	111.0
2.61	0.2428	0.2436	0.2428	66.66	83.87	102.7

[a]The pH of the conductivity water used in these dilutions
was 5.77.

[b]The densities used in calculating the normalities at
other than 25° C. can be found in the section of this thesis
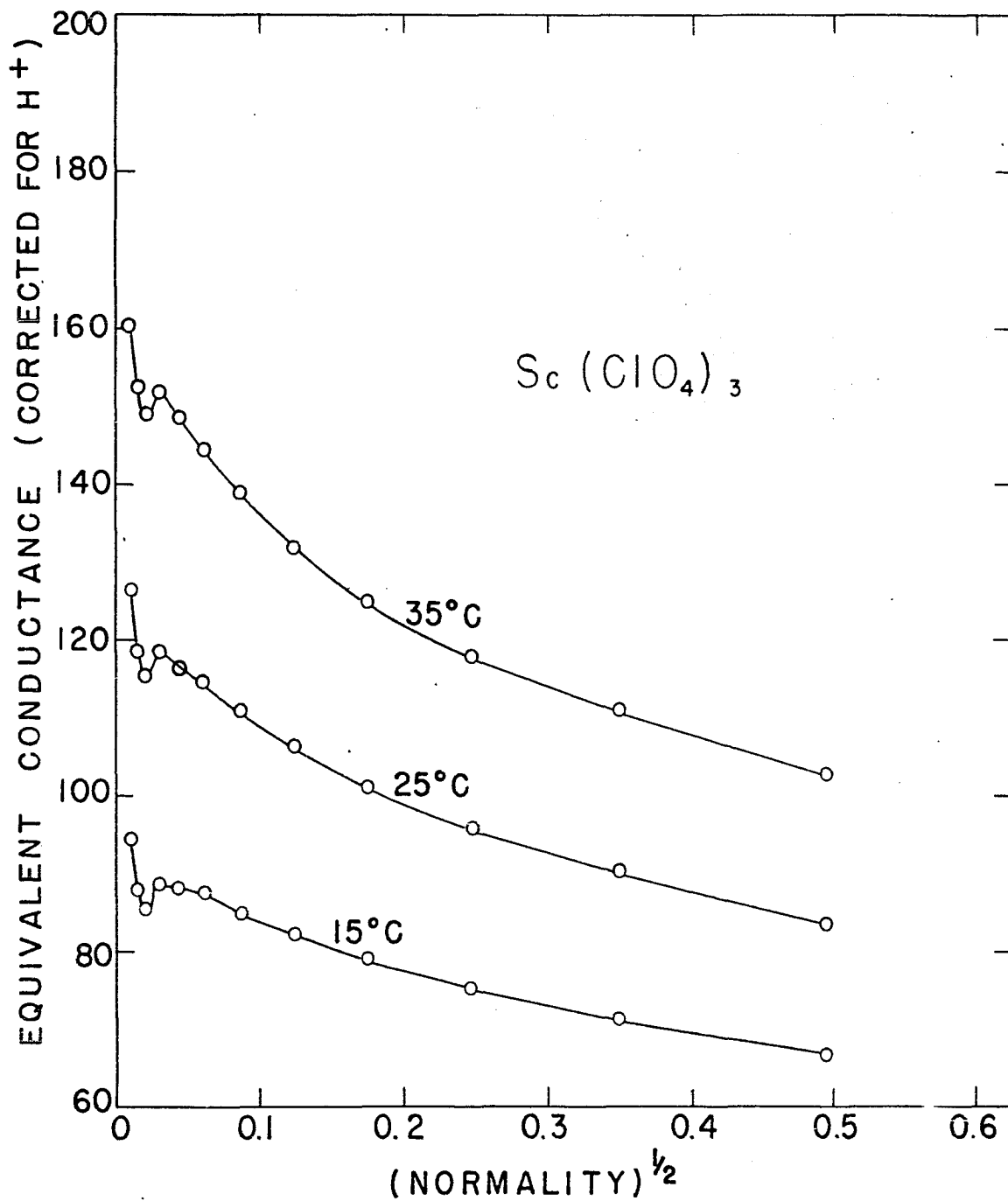dealing with densities.

Figure 9. Equivalent conductance of scandium perchlorate solutions, corrected for hydrogen ion conductivity, at 15°, 25°, and 35° C.

solutions at this molarity do not change very much with a 10° temperature change.

The analysis for nitrate, done by reduction to ammonia with Devarda's alloy and subsequent titration, showed only 2.76 nitrates per scandium in the scandium solutions. It was also noted that the error in analysis was about 3%. The solutions were, of course, prepared exactly as were the perchlorates and chlorides and should have been at their equivalence point as shown by the titration curves. Nevertheless, this discrepancy injects a degree of uncertainty regarding the validity of the nitrate data. Since the nitrate showed such a discrepancy, it was decided to check the perchlorate. An analysis was done gravimetrically using tetraphenylarsonium chloride and gave an empirical formula of $Sc(ClO_4)_{2.94}$.

As has been mentioned before, the calculation of the normalities at 15° C. and 35° C. from the normality as measured at 25° C. involves the use of density data for the scandium solutions. Since normality is defined as

$$N_{25^\circ\,C.} = G.\ E.\ W./liter\ of\ solution\ at\ 25^\circ\ C.$$

then division by the density (D = grams of solution/milliliter) and by 1000 to change liters to milliliters gives the units

$$\text{(G. E. W./liter of solution)} \left(\frac{\text{milliliter}}{\text{grams of solution}} \right) \left(\frac{1}{1000} \right)$$

$$= \text{G. E. W./gram of solution at } 25^{\circ} \text{ C.}$$

To convert this to G. E. W./liter at t° C. which is actually the normality, $N_{t^{\circ} \text{ C.}}$, one multiplies by the density at t° C. and by 1000 to reconvert to a liter basis. The final form is then

$$N_{25^{\circ} \text{ C.}} \, (D_{t^{\circ} \text{ C.}}/D_{25^{\circ} \text{ C.}}) = N_{t^{\circ} \text{ C.}} \, .$$

Since the density data is also needed to calculate the partial molal volumes, which are needed as corrections on the transference numbers, the section on densities immediately follows the conductance section and precedes the transference number section of this thesis.

Bodlander's data on scandium chloride conductivities presented in Figure 4, actually agrees fairly well with the data corrected for hydrogen ion conductivity gathered in this research. The discrepancy could arise from Bodlander not having pure scandium, not adjusting her solutions to the equivalence point, or from the measuring equipment, it being not so highly advanced in design in 1915 as it is today.

An attempt was made to extrapolate the conductivity data to infinite dilution by use of Onsager's limiting law for the case of a single electrolyte dissociating into two kinds of ions

$$\Lambda = \lambda_1 + \lambda_2 = \Lambda_0 - S_{(\Lambda)} \Gamma^{1/2}$$

where Γ is the ionic strength, $1/2 \sum c_i (z_+ + z_-)^{1/2}$ and Λ_0 is the equivalent conductance at infinite dilution. $S_{(\Lambda)}$ is the limiting slope and can be expressed by

$$S_{(\Lambda)} = A \Lambda_0 + B$$

which then gives

$$\Lambda_0 = [A \Lambda_0 + B] \Gamma^{1/2} .$$

A is equal to $\omega (1.981 \times 10^6)/(DT)^{3/2}$ where $\omega = (|z_+| |z_-|)(2q)/(1 + q^{1/2})$ and

$$q = \left[\frac{|z_+| |z_-|}{(|z_+| + |z_-|)} \right] \left[\frac{\lambda_+ + \lambda_-}{|z_+| \lambda_- + |z_-| \lambda_+} \right] .$$

B is equal to $\dfrac{29.16(|z_+| + |z_-|)}{\eta (DT)^{1/2}}$.

Since $\Lambda_o = \lambda_+^o + \lambda_-^o$, if one now substitutes $\Lambda_o - \lambda_-^o$ for λ_+^o and defines y as equal to $q/(1 + q^{1/2})$, then for 3 - 1 electrolytes

$$y = \frac{0.75 \Lambda_o/(\Lambda_o + 2 \lambda_-^o)}{1 + \left[0.75 \Lambda_o/(\Lambda_o + 2 \lambda_-^o)\right]^{1/2}}$$

and by use of the values of D, T, and η given in Table 2, and the λ_-^o values given in Table 9, equations relating Λ and Λ_o for the chloride, nitrate, and perchlorate salts at 15°, 25°, and 35° C. were developed. The resulting equation for aqueous solutions of 3 - 1 electrolytes at 15° C. has the form

$$\Lambda_o = \Lambda + \left[132.719 + 3.2619 \, y \, \Lambda_o\right] c^{1/2} .$$

At 25° C.

$$\Lambda_o = \Lambda + \left[170.318 + 3.3138 \, y \, \Lambda_o\right] c^{1/2}$$

and at 35° C.

$$\Lambda_o = \Lambda + \left[213.130 + 3.3798 \, y \, \Lambda_o\right] c^{1/2} .$$

Table 9. Values of Λ^o for chloride, nitrate, and perchlorate ions at 15°, 25°, and 35° C.

Temperature	Ion		
	Chloride	Nitrate	Perchlorate
15	61.41[a]	58.60[b]	55.00[b]
25	76.34[c]	71.42[d]	67.32[e]
35	92.21[a]	84.25[b]	80.00[b]

[a]Reference 76, p. 454.

[b]These values were extrapolated from data presented in Reference 76, p. 454.

[c]Reference 78, p. 40.

[d]Reference 79.

[e]Reference 77.

At each experimental concentration the measured values of Λ were used to calculate Λ_o, the calculated values being given the symbol Λ_o'. Since the expression could not be solved explicitly for Λ_o', values for Λ_o' at each approximation had to be obtained by successive approximations. The calculations were carried out by use of the I. B. M. 650 computer. The values of Λ_o' so derived are shown in Tables 10-13 with accompanying Figures 10-13.

Table 10. Equivalent conductance at infinite dilution
for scandium chloride at 15°, 25°, and 35° C.,
uncorrected for hydrogen ion conductivity

Normality			Calculated Λ_o'		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.00005806	0.00005806	0.00005806	157.7	195.3	243.4
0.0001165	0.0001163	0.0001159	146.3	179.1	234.4
0.0002331	0.0002326	0.0002318	140.6	173.2	224.9
0.0004663	0.0004653	0.0004637	134.6	168.4	214.3
0.0009325	0.009305	0.0009275	128.4	164.4	207.4
0.001865	0.001861	0.001855	124.7	161.4	201.0
0.003730	0.003723	0.003710	122.5	157.2	195.9
0.007460	0.007445	0.007420	122.1	156.3	194.3
0.01492	0.01489	0.01484	124.0	156.3	196.1
0.02984	0.02977	0.02969	130.0	164.6	205.5

The method of calculating Λ_o' used here is a modification of the method used by Shedlovsky (81).

Discussion of Data

The troubles experienced in trying to get any quantitative ideas from the measured conductances stem from the fact
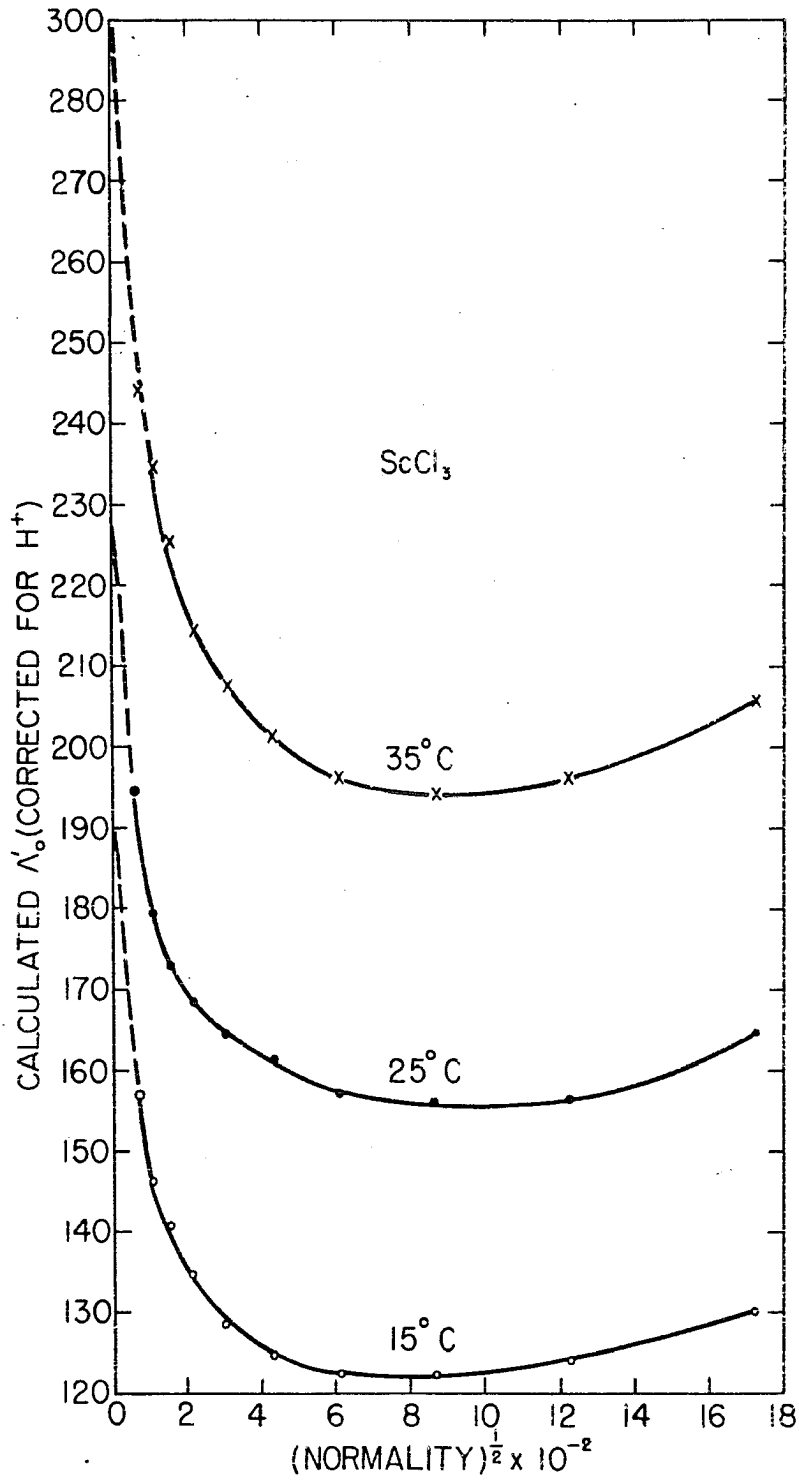
Figure 10. Equivalent conductance at infinite
dilution for scandium chloride at 15°,
25°, and 35° C., uncorrected for
hydrogen ion conductivity

Table 11. Equivalent conductance at infinite dilution for scandium chloride at 15°, 25°, and 35° C., corrected for hydrogen ion conductivity

Normality			Calculated Λ_0'		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.00005825	0.00005815	0.00005795	85.07	112.3	147.4
0.0001165	0.0001163	0.0001159	90.29	121.7	162.8
0.0002331	0.0002326	0.0002318	101.7	135.6	173.8
0.0004663	0.0004653	0.0004637	103.0	137.1	178.1
0.0009325	0.0009305	0.0009275	102.8	136.0	173.8
0.001865	0.001861	0.001855	103.6	136.7	172.9
0.003730	0.003723	0.003710	105.7	137.7	173.5
0.007460	0.007440	0.007420	108.5	141.5	177.5
0.01492	0.01489	0.01484	113.8	147.9	184.6
0.02984	0.02977	0.02969	122.5	157.9	197.1

that scandium is drastically hydrolyzed in aqueous solution. In 1953 and 1954 Kilpatrick and Pokras (82), working with scandium perchlorate solutions, calculated the hydrolysis constants from their e.m.f. data. In 1956 Biedermann, Kilpatrick, Pokras, and Sillén (83) recalculated Kilpatrick's and Pokras' original data using general methods for polynuclear complexes.
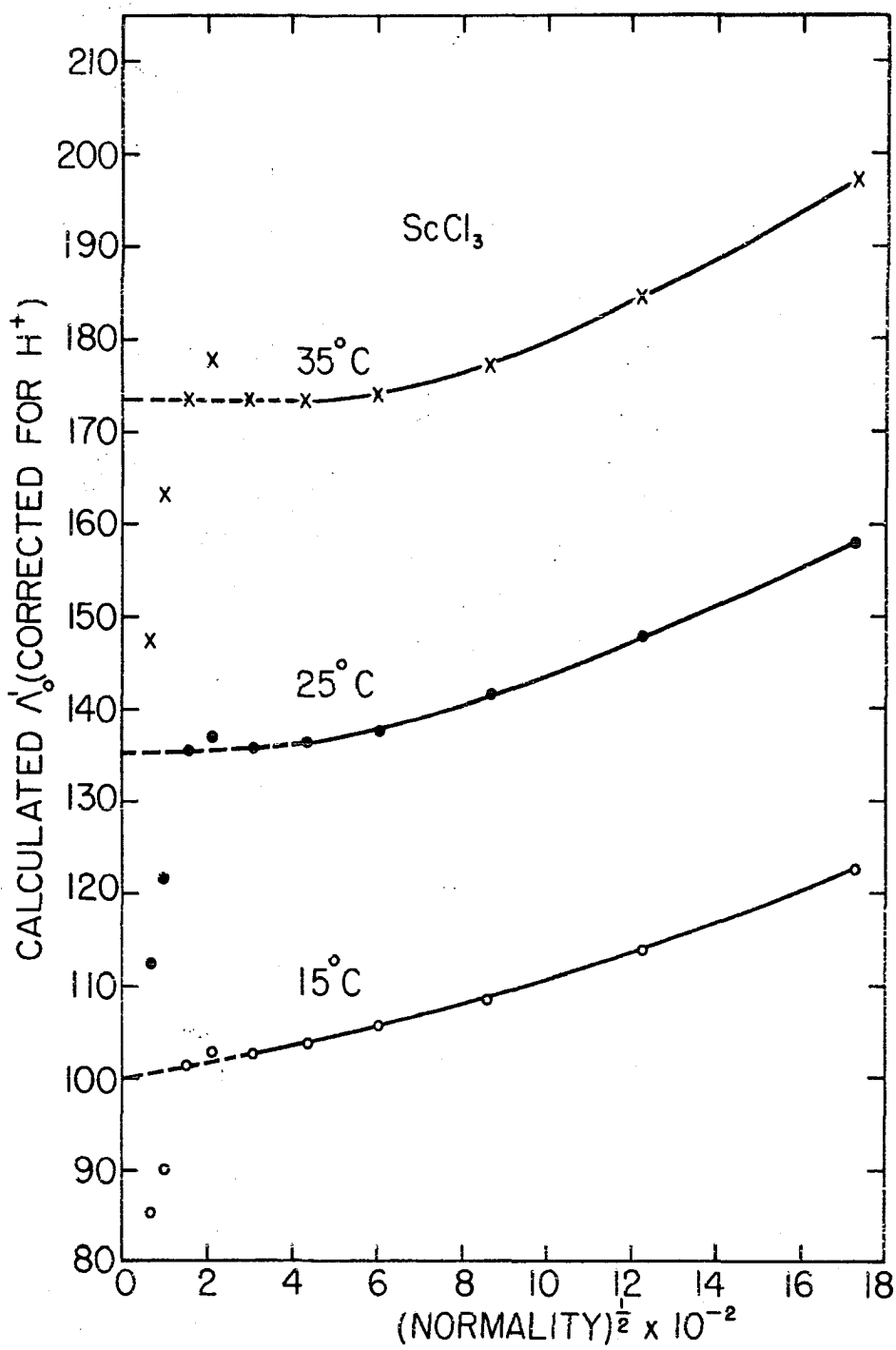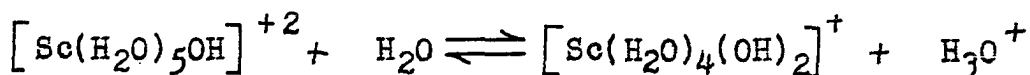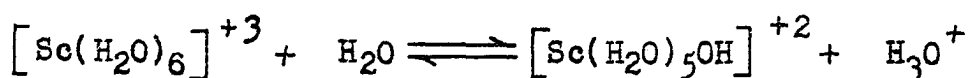
Figure 11. Equivalent conductance at infinite dilution
for scandium chloride at 15°, 25°, and 35° C.,
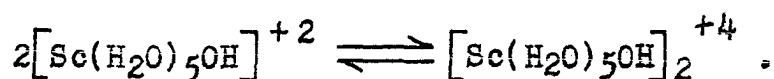corrected for hydrogen ion conductivity

Table 12.   Equivalent conductance at infinite dilution for
scandium nitrate at 15°, 25°, and 35° C., corrected
for hydrogen ion conductivity

Normality			Calculated $\Lambda_o^!$		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.00003685	0.00003675	0.00003663	43.71	57.78	77.85
0.00007370	0.00007350	0.00007325	61.17	82.68	107.1
0.0001474	0.0001470	0.0001465	67.90	93.24	121.5
0.0002947	0.002940	0.0002930	75.64	104.3	135.8
0.0005895	0.0005880	0.0005860	85.67	114.7	147.7
0.001179	0.001176	0.001172	89.70	118.5	152.4
0.002359	0.002353	0.002344	93.14	121.7	154.8
0.004718	0.004705	0.004688	96.63	124.8	157.0
0.009435	0.009411	0.009375	100.2	128.9	161.5

The data showed that the following reactions take place

$$\left[Sc(H_2O)_6\right]^{+3} + H_2O \rightleftharpoons \left[Sc(H_2O)_5OH\right]^{+2} + H_3O^{+}$$

$$\left[Sc(H_2O)_5OH\right]^{+2} + H_2O \rightleftharpoons \left[Sc(H_2O)_4(OH)_2\right]^{+} + H_3O^{+}$$

and

$$2\left[Sc(H_2O)_5OH\right]^{+2} \rightleftharpoons \left[Sc(H_2O)_5OH\right]_2^{+4} .$$
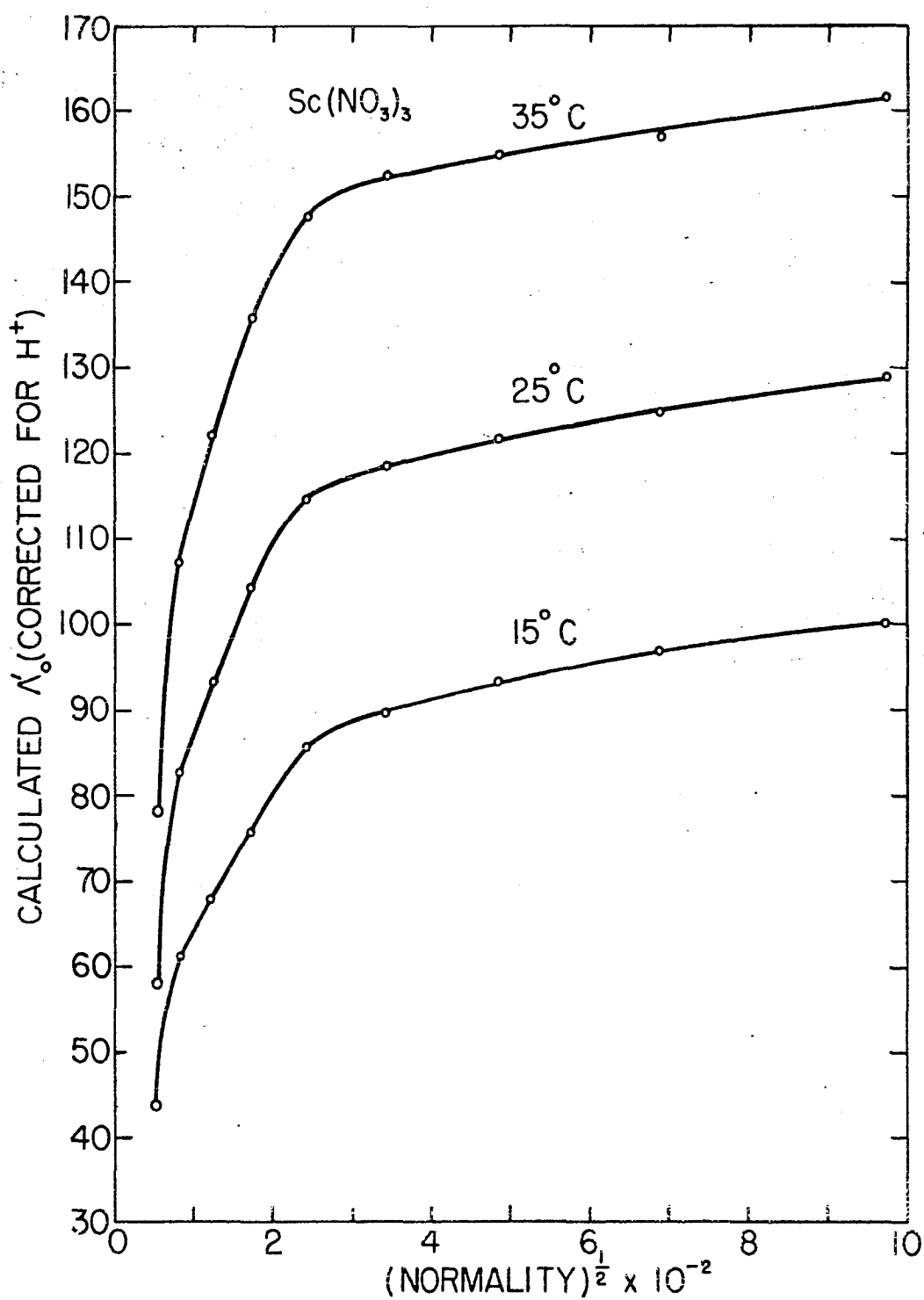
Figure 12. Equivalent conductance at infinite dilution
for scandium nitrate at 15°, 25°, and 35° C.,
corrected for hydrogen ion conductivity

Table 13. Equivalent conductance at infinite dilution for scandium perchlorate at 15°, 25°, and 35° C., corrected for hydrogen ion conductivity

Normality			Calculated $\Lambda_o^{'}$		
15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
0.00002985	0.00002975	0.00002965	79.46	114.4	143.3
0.00005970	0.00005950	0.00005930	80.52	112.0	139.5
0.0001194	0.0001190	0.0001186	96.27	129.1	163.8
0.0002387	0.0002380	0.0002372	90.66	122.1	152.2
0.0004773	0.0004760	0.0004743	89.75	121.0	155.9
0.0009545	0.0009520	0.0009485	94.50	126.4	162.1
0.001909	0.001904	0.001897	96.67	127.3	163.4
0.003818	0.003808	0.003795	99.20	130.2	165.5
0.007635	0.007615	0.007590	103.27	134.7	169.3
0.01527	0.01523	0.01518	108.91	140.9	175.5

The formation of the monohydroxy species and its polymerization seem to be the dominant reactions. The recalculation of the data assuming "core plus links" complexes of the general formula $\left[Sc\ (OH)_2Sc \right]_n^{+(3+n)}$ showed that at least the complexes with n equal to 1 and 2, $Sc_2(OH)_2^{+4}$ and $Sc_3(OH)_4^{+5}$, must exist. Existence of higher complexes was also indicated.
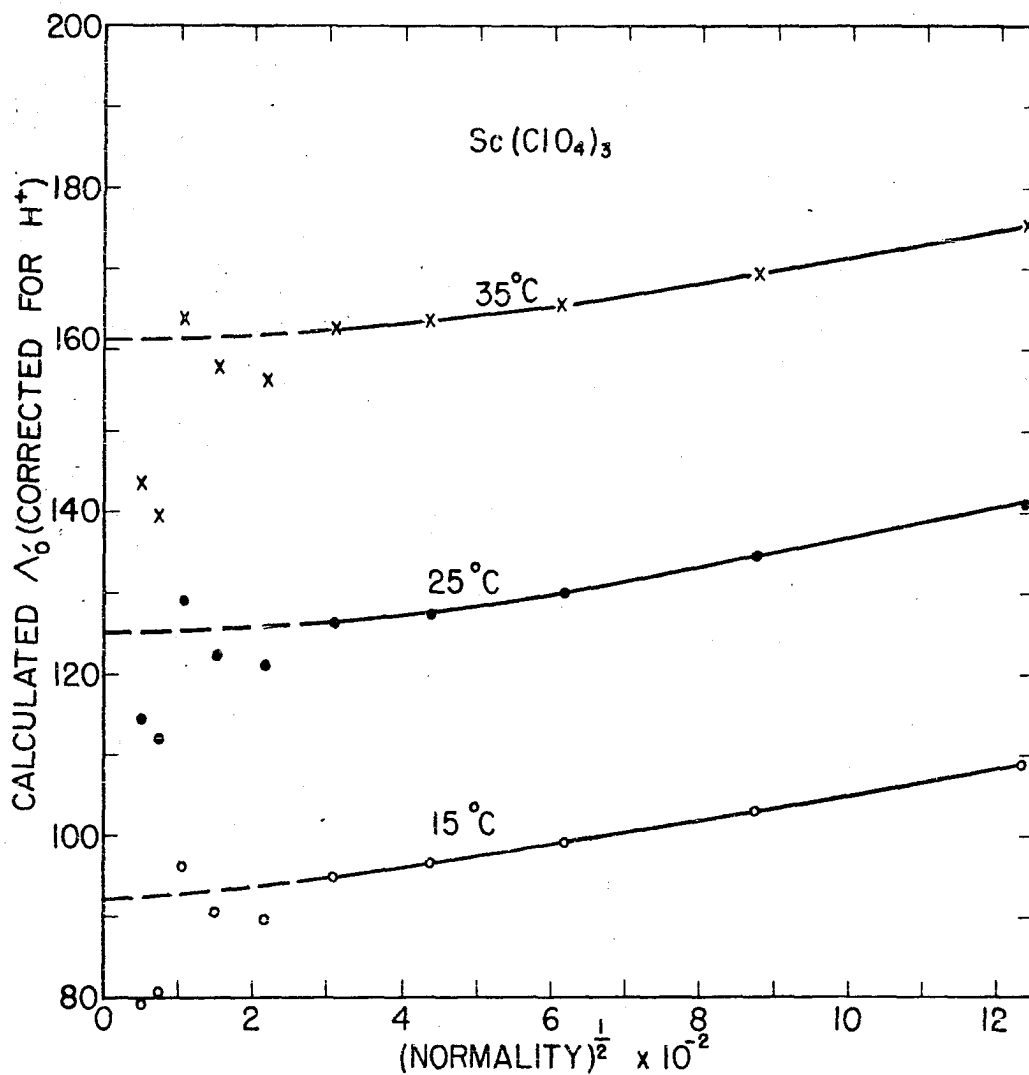
Figure 13. Equivalent conductance at infinite dilution for scandium perchlorate at 15°, 25°, and 35° C., corrected for hydrogen ion conductivity

The formation of the monohydroxy species would not take place to any great extent if it were not for the subsequent formation of the polymeric species since the single acid dissociation constant is on the order of 1.17×10^{-5} followed by a dimerization constant of 7.38×10^5 as found by Kilpatrick and Pokras (82). The dimerization process is strongly temperature dependent, the formation of polynuclear complexes being favored by an increase in temperature and hindered by an increase in ionic strength.

Thus, because species other than Sc^{+3} are present, the use of Onsager's limiting conductance equation for the calculation of Λ_0' is not quite correct since it is derived for the case of a single electrolyte dissociating into two kinds of ions only. Because of this, no value for the conductivity of the Sc^{+3} ion at infinite dilution can be obtained.

If one could work with more concentrated solutions, the polymerization and hydrolysis would be suppressed. However, Onsager's law would not be valid for concentrated solutions. If the transference numbers were known as well as conductivity, then

$$T_+ \, \Lambda = \lambda_+$$

and plots of λ_+ vs. concentration could be extrapolated to zero concentration to obtain $\lambda_+^{\,o}$ values. In such

concentrated solutions, the moving boundary method of determining transference numbers would be useless because a visible boundary probably could not be set up. A Hittorf-type experiment might be possible but the extrapolation of the λ_+ values to zero concentration would require a long, inaccurate extrapolation. Thus, the value of λ_+^o for the scandium ion, Sc^{+3}, will not be known until someone solves the conductance data for the relative contribution of each possible ionic species; a monumental mathematical manipulation.

The entire situation is very much more complex in the presence of anions, other than perchlorate, which may themselves form complexes with the metal ions, since then there is a competition between the anions, water, and OH^- for the available coordination positions. This could be the case with the nitrate since, at low concentrations, it showed a reversal, in the trend of increasing equivalent conductance with decreasing concentration even with the uncorrected data.

The equivalent conductances of the scandium salts are higher than their rare-earth counterparts. Such should be the case since the unhydrated scandium ion has a smaller radius than any of the unhydrated rare earths and, therefore, its mobility should be higher. Even so, the conductance is not as high as it would be if one were measuring the conductivity of the Sc^{+3} ion itself.

The turnover of the corrected equivalent conductance curves at low concentrations can be explained if one considers that the conductivity of the hydrogen ion is a large value as ionic conductivities go and when this contribution is subtracted from the total measured conductivity, the contributions from species such as $Sc(OH)^{+2}$ and $Sc[(OH)_2Sc]_n^{+(3+n)}$ become increasingly important. Since the conductivity of such species would be expected to be much smaller than the Sc^{+3} ion because of size effects and charge effects, the conductivity reverses its original trend and falls. The cusp in the perchlorate curve which had been corrected for hydrogen ion was checked by making fresh dilutions from the stock solutions and it reappeared. The author finds it extremely difficult to reconcile the fact that the equivalent conductivity increases again after falling unless, for some reason, the hydroxy polymers dissociate again upon further dilution.

The uncorrected Λ_o' data for scandium when plotted vs. $\sqrt{N}$ gave curves very reminiscent of those obtained by Jaffe (84) for the rare-earth sulfates. The large minimum in the curves (Figure 10) is a result of inserting the incorrect charge types and incorrect concentrations in the Onsager equation. Only the representative chloride curves are presented as a figure.

The downward trend of the corrected Λ_o' vs. $\sqrt{N}$ curves for the nitrate is probably only another demonstration of the

odd behavior exhibited by the nitrate such as the equivalent conductance curve turning over on itself at low concentrations even before correction for H^+ contribution. This in turn is probably a reflection of the unfortunate circumstance that the nitrate failed to show three nitrates per scandium even though the titration curve looked correct. Apparently, quite stable hydroxy-nitrate species formed which were soluble but not titratable. If one ignores the points at low concentration where scattering starts, the Λ_0' vs. $\sqrt{N}$ curves for the chloride and perchlorate show behavior typical of what was experienced with the rare earths (9, 78, 84) and, for this reason, the curves (corrected for hydrogen ion conductivity) are included in their entirety.

If one ignores the dotted-line portion of the Λ_0' vs. $\sqrt{N}$ curves for chloride (Figure 11) and perchlorate (Figure 13) and observes the actual dip in the curves followed by a definite dropping off, it is evident such behavior starts at about the point the Λ vs. $\sqrt{N}$ curves corrected for hydrogen ion (Figures 5 and 9, respectively) start to fall. The larger, more noticeable deviation in the perchlorate case is a consequence of the dip actually observed in the Λ vs. $\sqrt{N}$ corrected perchlorate curves. Again, it is certain the correct charge types and concentrations were not applied in the Onsager equation so the odd behavior was not wholly unexpected.

It is quite evident why the literature is devoid of electrolytic measurements on hydrolyzable cations.

The errors involved in measuring the resistances of the solutions were negligible compared to uncertainties in the concentrations of about $\pm$ 0.1%. An additional error of about 0.1% due to pH measurement errors may have been introduced into the data which had been corrected for hydrogen ion conductivity.

DENSITIES AND PARTIAL MOLAL VOLUMES

Introduction

Several means of measuring the mass per unit volume, or density have been devised over the years. The methods vary from the most simple type of pycnometer or specific gravity bottle with a precision of about $\pm$ 0.001, to dilatometric and magnetic float methods with an accuracy of about $\pm$ 1 x 10^{-7}. The various methods are reviewed by Bauer (85). The partial molal volumes are derived from the densities and are used to correct the transference numbers. The densities are also used to calculate normalities at 15° and 35° C.

Experimental

Materials

The solutions used in this study were the more concentrated of the solutions prepared for use in conductance measurements.

Apparatus

The densities were determined by use of thermometer-fitted pycnometers. Water baths were set up at 34°, 24°, and

14° C. in which to equilibrate the solutions. All weighings were done on an Ainsworth Chain-o-matic balance.

Procedure and results

The pycnometers were calibrated with conductivity water. All weights were corrected to vacuum weights and a second pycnometer was used as a tare to cancel buoyancy effects. The solutions, previously equilibrated in the thermostated baths were loaded in the pycnometers and the thermometer inserted. Very gradual warming to the desired temperature as indicated by the pycnometer thermometers was accomplished by waving the pycnometer under an infrared lamp. The pycnometer thermometers were checked against the Bureau of Standards-calibrated thermometer. When the desired temperature was reached, the overflow tube was relieved of its bubble of solution, capped, and the entire assembly weighed after the temperatures returned to that of the room (25° C.). The resultant data is included here as Figures 14-16.

Treatment of the data by least squares methods gave the following equations to fit the curves:

For the chloride at 15° C., $\rho = 0.0439$ N + 0.9991,

at 25° C., $\rho = 0.0434$ N + 0.9970,
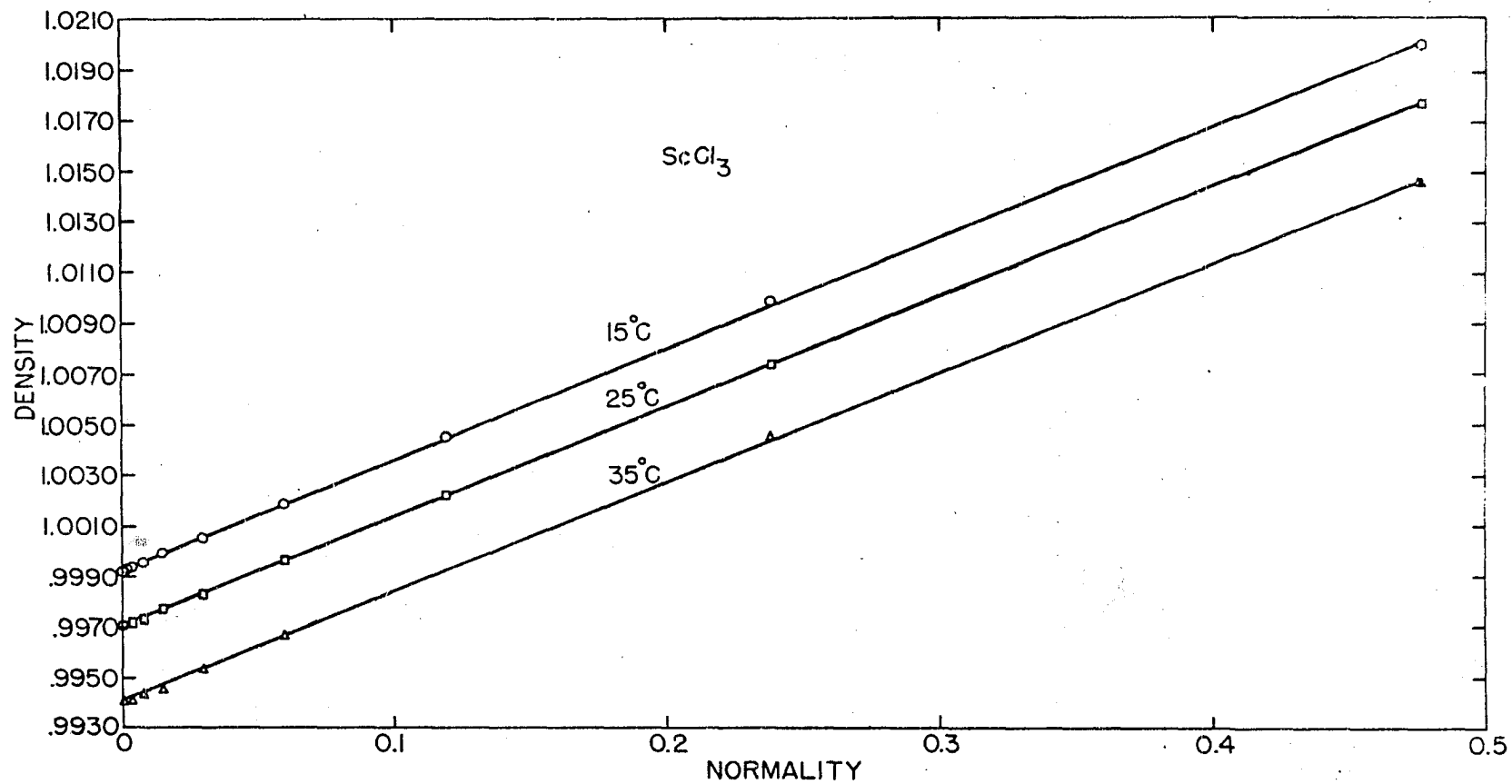
Figure 14. Densities of aqueous scandium chloride solutions as a function of concentration
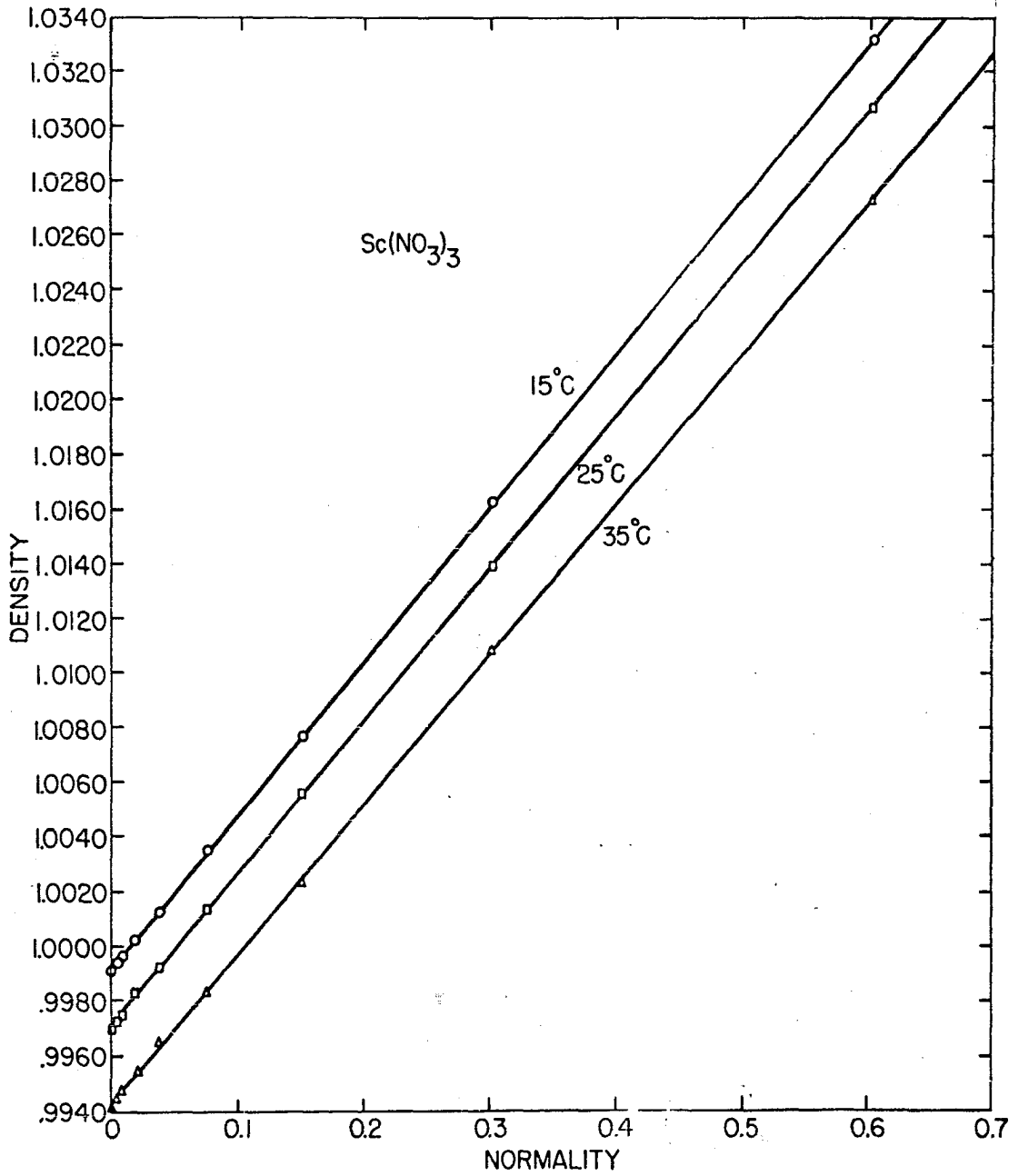
Figure 15. Densities of aqueous scandium nitrate solutions as a function of concentration
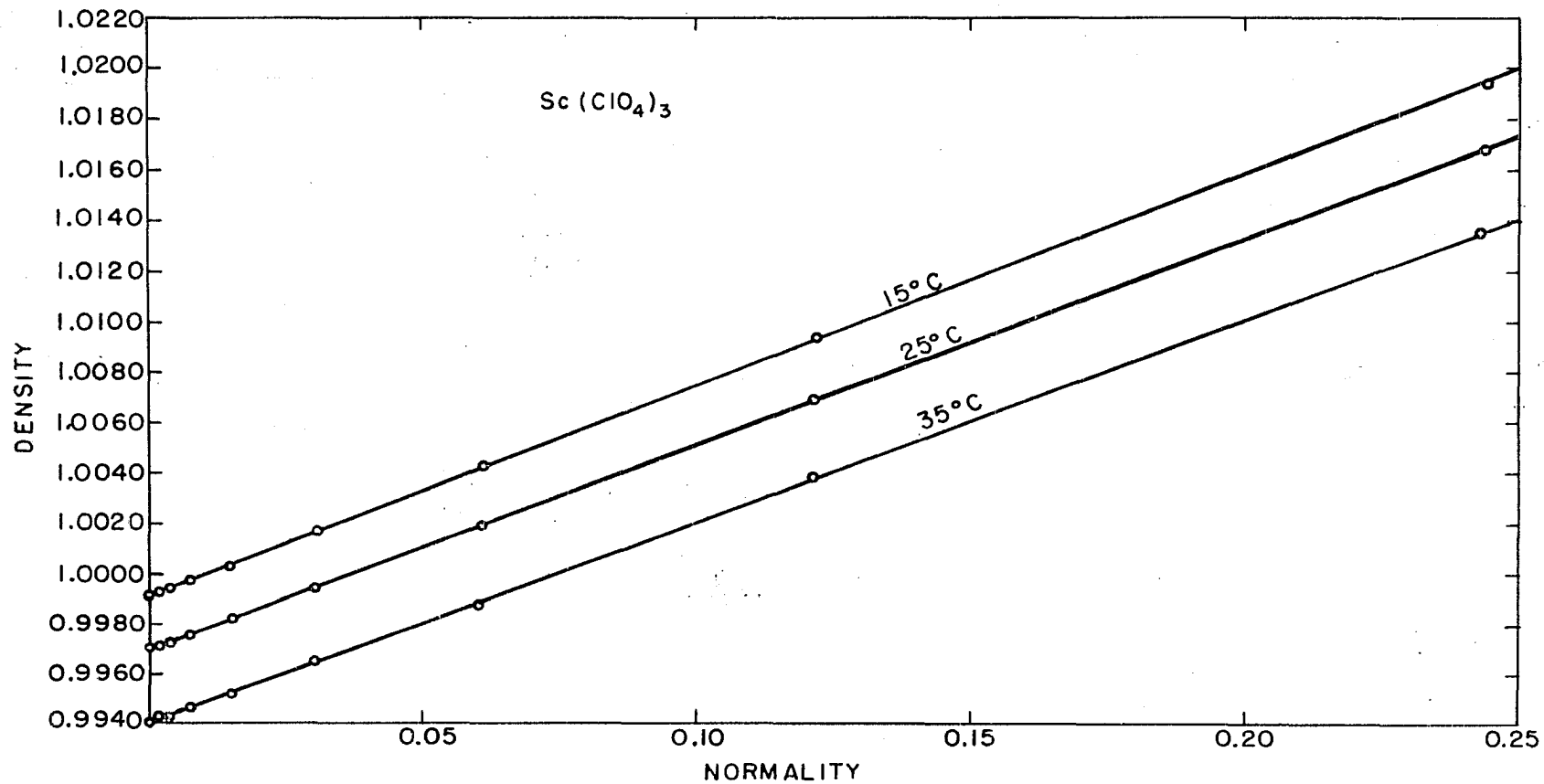
Figure 16. Densities of aqueous scandium perchlorate solutions as a function of concentration

and at 35° C., $\qquad \rho = 0.0429$ N + 0.9941.

For the nitrate at 15° C., $\qquad \rho = 0.0563$ N + 0.9992,

at 25° C., $\qquad \rho = 0.0556$ N + 0.9972,

and at 35° C., $\qquad \rho = 0.0549$ N + 0.9943.

For the perchlorate at 15°., $\qquad \rho = 0.0836$ N + 0.9991,

at 25° C., $\qquad \rho = 0.0812$ N + 0.9970,

and at 35° C., $\qquad \rho = 0.0805$ N + 0.9940.

where N in all cases is the normality. The density was used to calculate the normalities at 15° C. and 35° C. from data at 25° C.

In addition, partial molal volumes were calculated from the density data to be used in correcting the transference number data in the next section of this thesis. The molalities, needed in calculation of partial molal volumes were arrived at by the following reasoning. Since

m = molality = moles/1000 grams of water,

m/1000 would be moles/gram of water.

If one now multiplies by grams of water/liter or 1000 times the density, the units moles/liter emerge which is the molarity. The molarity, normality, and molality of 3 - 1 electrolytes are all interrelated by

$$N = M/3 = m\ D_{H_2O}/3$$

where N is the normality or equivalents per liter, M is the molarity or moles per liter, while m is the molality or moles per 1000 grams of water.

The partial molal volumes were actually calculated from the apparent molal volumes, which, in turn, came from the densities.

The apparent molal volume, ϕ_V, is related to the molality, m, and density, d, of a solution by

$$\phi_V = \frac{1000\ (d_0 - d)}{mdd_0} + \frac{M_2}{d}$$

where d_0 is the density of the solvent and M_2 is the molecular weight of the solute. The values of ϕ_V were then expressed in terms of a power series in terms of the molality by use of least squares methods. The partial molal volume, $\bar{V}$, is related to the apparent molal volume, ϕ_V, by

$$\bar{V} = \phi_V + m \frac{\partial \phi_V}{\partial m}$$

where m is the molality. Resultant equations for ϕ_V for scandium chloride are

$$\phi_V = 21.70 - 55.53\ m + 416.00\ m^2 - 988.94\ m^3 \text{ at } 15^0 \text{ C.,}$$

$$\phi_V = 25.15 - 58.96\ m + 177.89\ m^2 + 190.58\ m^3 \text{ at } 25^0 \text{ C., and}$$

$$\phi_V = 32.65 - 151.07\ m + 826.80\ m^2 - 1410.9\ m^3 \text{ at } 35^0 \text{ C.}$$

For scandium nitrate

$$\phi_V = 65.60 - 28.78\ m + 124.14\ m^2 + 768.76\ m^3 \text{ at } 15^0 \text{ C.,}$$

$$\phi_V = 66.47 - 9.80\ m - 11.54\ m^2 + 30.35\ m^3 \text{ at } 25^0 \text{ C., and}$$

$$\phi_V = 69.61 - 9.02\ m - 15.39\ m^2 + 2.00\ m^3 \text{ at } 35^0 \text{ C.}$$

For scandium perchlorate

$$\phi_V = 93.94 - 17.59\ m - 35.60\ m^2 - 56.00\ m^3 \text{ at } 15^0 \text{ C.,}$$

$$\phi_V = 100.96 - 17.59\ m - 47.51\ m^2 - 37.82\ m^3 \text{ at } 25^0 \text{ C., and}$$

$$\phi_V = 104.23 - 18.56\ m - 41.18\ m^2 - 24.91\ m^3 \text{ at } 35^0 \text{ C.}$$

The chloride data are valid over the range 0 to 0.15 m; the nitrate, 0 to 0.20 m; the perchlorate, 0 to 0.1 m.

The data with considerable curvature (chloride) was done on the I. B. M. 650 computer while the data having almost straight line character (nitrates and perchlorates) was done by simple progressive curve-fitting.

TRANSFERENCE NUMBERS

Introduction

The transference number of an ion in solution is a measure of that portion of the total current which is carried by that ion.

In an electric field, an ion will migrate through the solution with a velocity dependent upon its mobility. Since each ion has a characteristic mobility the different ions in solution will transport different amounts of current.

The transference number depends on the number of ions or equivalent concentration, C_i, the charge on the ion, Z_i, and its mobility, U_i. The transference number of the ith ion, T_i, is then the ratio of the current, i, carried by the ion to the total current, I, carried by the entire system.

$$T_i = \frac{i}{I} = \frac{C_i Z_i U_i}{\sum_S C_S Z_S U_S} \quad .$$

For the case of the binary electrolyte, $C_+ Z_+ = C_- Z_-$ and the expression reduces to

$$T_+ = \frac{U_+}{U_+ + U_-}$$

for the cation. The mobility, U, is related to the ionic equivalent conductance, λ , by

$$\lambda_+ = U_+ \, F$$

and

$$\lambda_- = U_- \, F$$

where F is the Faraday. Then

$$T_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\lambda} \, .$$

By use of this relationship, one can calculate individual ionic equivalent conductances from total equivalent conductances and transference numbers. Thus, conductances and transference numbers have a close relationship.

If one now uses the Onsager equation for the conductance of a binary electrolyte which was presented in the conductances results section, and substitutes the expression just given for T_+ one obtains

$$T_+ = T_+^o + S_{(T)} \, \Gamma^{1/2}$$

where

$$S_{(T)} = \frac{T_+^o(|z_+| + |z_-|) - |z_+|}{(|z_+| + |z_-|) \Lambda_o} \beta$$

and

$$\beta = \frac{28.98 (|z_+| + |z_-|)^{3/2}}{\eta (DT)^{1/2}} .$$

Actually this equation gives the limiting slope of the transference number as a function of the square root of the equivalent concentration and strictly applies only to the case of 1 - 1 electrolytes in dilute solutions. The extended Onsager equation presented by Dye (78) gives better agreement between theory and experiment but the mathematics are much more involved.

Transference numbers submit the Onsager theory to a more rigorous test than do equivalent conductances since small differences in the individual ionic contributions to the conductivity are masked in the total equivalent conductance of the salt while the transference number is greatly effected.

Measurement of transference numbers can be carried out in three ways.

1. The Hittorf method which depends upon concentration changes in the solutions;

2. The electromotive force method; and

3. The moving boundary method.

The Hittorf method involves electrolyzing a solution of a solute in a three compartment cell. The cell is constructed with an anode compartment, a middle compartment, and a cathode compartment. Samples can be withdrawn from all three compartments and analyzed after the passage of a known amount of current. Before passage of current, the electrolyte concentration is the same in all three compartments.

Washburn (86, p. 276) developed a simple formula for the computation of transference numbers from Hittorf-type data. The number of equivalents of an ion, N_f, left in a given weight of solvent, for example, in the anode compartment, after electrolysis must be equal to the number of equivalents, N_o, present before electrolysis plus the number of equivalents, N_e, introduced by the electrode reaction minus the number of equivalents, $N_e T$, lost by ionic migration

$$N_f = N_o + N_e - N_e T \ .$$

Solving for the transference number then gives

$$T = (N_o - N_f + N_e)/N_e \ .$$

N_e can be obtained from the known number of Faradays passed through the cell during the experiment and N_o and N_f are found

by analysis of the compartment solutions before and after electrolysis. N_e is positive if the ion is added to the solvent by dissolution of the electrode and negative if the ion plates out on the electrode. The concentration of the middle compartment must remain unchanged during electrolysis.

The e.m.f. method involves the use of concentration cells. The potentials of a cell with liquid junction and a cell without liquid junction (both having the same concentrations of solutes) are measured and compared. For a cell with liquid junction

$$-FdE_t = Td\mu ,$$

where F is the Faraday, E_t is the potential of the cell with transference, and μ is the chemical potential. For a cell without liquid junction,

$$-FdE = d\mu .$$

Therefore, solving for T one obtains

$$\frac{dE_t}{dE} = T .$$

This method is the least accurate of the three and is, therefore, not often used.

The moving boundary method, which was used in this research, is the simplest to execute and affords the greatest accuracy. The solution to be measured is placed in a calibrated tube of uniform cross-section with a narrow bore. An indicator solution is placed above the solution to be measured and is mechanically separated from it. The cell is fitted with an anode in the indicator solution and a cathode in the solution to be measured. When a potential is applied across the cell leads and the solutions are allowed to come into intimate contact, the cations of the solution to be measured migrate towards the cathode with a characteristic velocity. The indicator cations follow the leading cations but will not pass them because the indicator cations have a slower mobility. An interface or boundary is formed between the leading and following solutions which moves with the velocity of the leading ions. If the solutions have different colors of sufficient intensity or sufficiently different indices of refraction, the boundary becomes visible.

The boundary remains sharp because of the potential gradients developed in the cell. These potentials are a function of the distance along the calibrated tube as shown in Figure 17. When the slower-moving following ions get ahead of the boundary at b in Figure 17, they are then in an environment having too small a potential gradient and are slowed down. Likewise, the leading ions find too great a
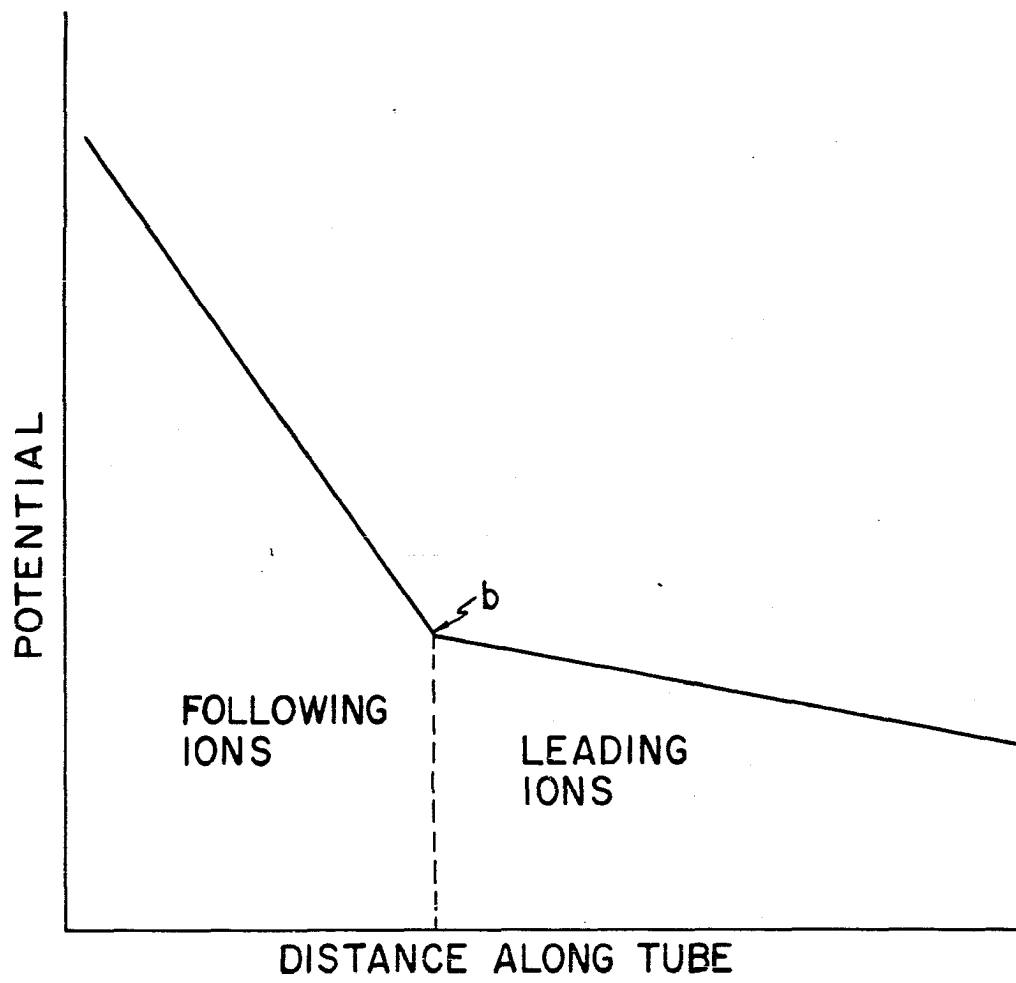
Figure 17. Potential gradients along the measuring tube during electrolysis

potential gradient and are speeded up should they wander into the region behind the boundary.

The equation for calculation of the transference number from moving boundary data was derived by Miller (87).

Consider the cell initially loaded with two solutes, MA and NB, with a boundary between the two at a - b as in Figure 18 (a). A potential difference is then applied across the cell by the electrodes E^+ and E^- and the movement of the interface or boundary is followed. The anions, A^-, of the compound M^+A^- cross y - y to form the anion boundary a - a between solutions N^+B^- and N^+A^-. Likewise, the cations will move toward the negative electrode, E^-, crossing y - y, to form the boundary c - c between the solutions N^+A^- and M^+A^-. For a solution of C equivalents of a binary salt per liter, the volume swept out per Faraday of current passed is 1000/C milliliters. T_+ 1000/C milliliters of the total milliliters is due to the motion of the cations while T_- 1000/C is due to anion movement. If now X Faradays of current are passed through the solution, a different volume, V_+ will be swept out by the cation boundary and V_- by the anion boundary. The following then holds:

$$\frac{F}{T_+\ 1000/C} = \frac{X}{V_+} \quad \text{and} \quad \frac{F}{T_-\ 1000/C} = \frac{X}{V_-}$$
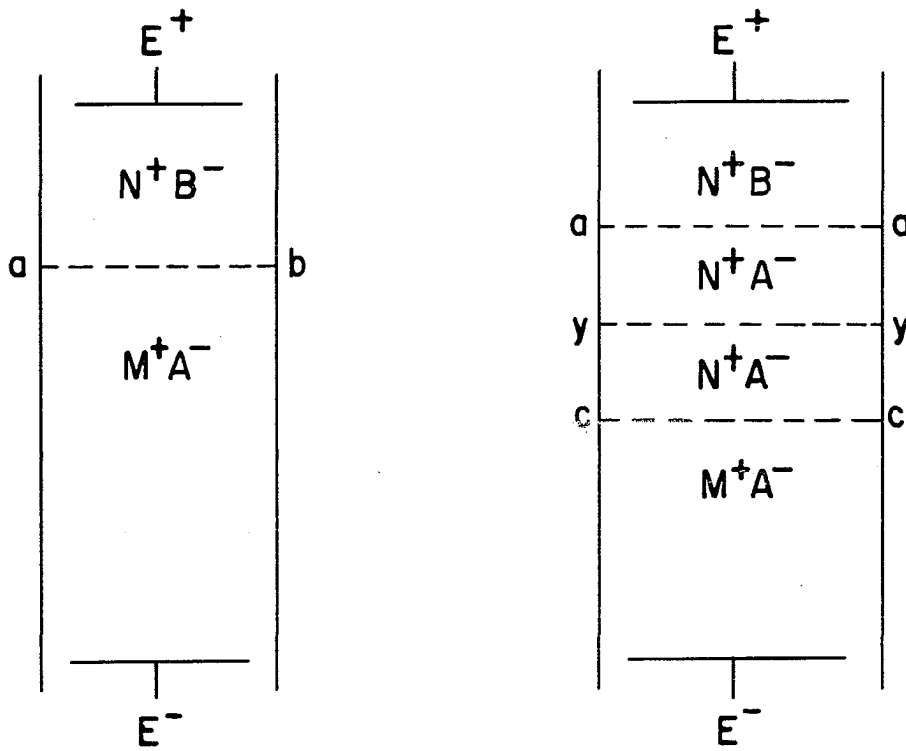
where F is the Faraday.

Figure 18. Motion of the solutes in the cell during electrolysis

Solving for T_+ and T_- gives

$$T_+ = \frac{F\ V_+\ C}{1000\ X} \quad \text{and} \quad T_- = \frac{F\ V_-\ C}{1000\ X} \ .$$

For a constant current of I amperes flowing for t seconds X = It and when this is substituted the expressions for T_+ and T_- become

$$T_+ = \frac{F\ V_+\ C}{1000\ It} \quad \text{and} \quad T_- = \frac{F\ V_-\ C}{1000\ It} \ .$$

In this expression, V_+ and V_- are in milliliters, C is in equivalents per liter, t is in seconds, and I is in amperes.

History of Transference Number Measurements

Two of the earliest investigators to discover that the positive and negative ions in solution do not transport the same amount of current were Daniell (88) and Hittorf (89). Daniell used a cell having three compartments separated by bladder-diaphragms. He observed unequal concentration changes in the cathode and anode compartments.

Hittorf's investigations in 1853-1903 confirmed Daniell's results and helped lead to Kohlrausch's independent migration theory in 1876 and Arrhenius' dissociation theory in 1884.

Early measurements using the Hittorf method have been summarized by Noyes and Falk (90). More recent work by Jones and Dole (91), Jones and Bradshaw (92), and MacInnes and Dole (93) used improved methods. Nowadays, the Hittorf method is not often used because it is time-consuming.

The use of cells with and without transference was studied by MacInnes and Parker (94), MacInnes and Beattie (95), Hammer (96), and Jones and Dole (97).

The moving boundary method was originated by Lodge (98) who used a gelatin medium through which the ions migrated. He incorporated an indicator ion in the gel which formed either a precipitate or a colored complex with the ion being studied and measured the boundary velocity but erroneously assumed the potential gradient was constant throughout the gel.

Whetham (99) pointed out this error in 1893 and stated that the potential gradient depended on the conductivity of the ionic species and was not the same on both sides of the boundary.

Other advances in the field of transference number measurements by observation of moving boundaries were made by Steele (100) in 1901, and Denison and Steele (101) in 1906. Steele formed his boundaries by use of gelatin plugs. The boundaries were then allowed to move into a gelatin-free tube where they were observed. He conceived the idea of

making use of the difference in refractive indices of un-
colored solutions to follow the boundary movement. Denison
and Steele then used a parchment cone to take the place of
the gelatin plugs.

Methods for improving the boundary by other boundary-
forming devices include those of MacInnes and Smith (102),
MacInnes and Brighton (103), and Spedding, Porter, and Wright
(2, 3). MacInnes and Brighton used a "shearing disk" and
Spedding, Porter, and Wright introduced the use of a hollow-
bore stopcock to produce the boundary initially.

In 1904 Franklin and Cady (104) used a boundary forming
method which has come to be called the "autogenic boundary
method". This consisted of a metal electrode such as mer-
cury, copper or cadmium acting as an anode in contact with
the solution. The electrode reaction produced cations of the
electrode metal which acted as the indicator ions and the
concentration was automatically adjusted to the Kohlrausch
ratio by the electric field action. In 1929-32 Longsworth
(105) and Cady and Longsworth (106) again used this method.

In 1897, Kohlrausch (107) derived an important relation
between the concentration changes and the movement of the
concentration gradient at the boundary. For the passage of
one Faraday of current,

$$T_+ = \frac{F\ V_+\ C}{1000\ It}$$

reduces to

$$T_{+1} = C_1 V_1$$

where T_{+1} is the cation transference number of the leading solution, V_1 is the volume in liters swept out by the cations of the leading solutions, and C is the concentration in equivalents per liter. If the cations of the indicator solution are to keep up to the boundary they must sweep out the same volume as the leading ions so that

$$T_{+f} = C_f V_f$$

where T_{+f} is the cation transference number of the indicator solution, C_f is the concentration of the following solution in equivalents per liter, and V_f is the volume swept out by the cations of the following solution. Then since $V_1 = V_f$, the two equations can be combined to give

$$T_{+1}/C_1 = T_{+f}/C_f .$$

This has come to be known as the "Kohlrausch ratio". Recent work has shown that the range of concentrations over which this relation operates is about 3-5%, contrary to Kohlrausch's belief that the concentration adjustment of the indicator

electrolyte just behind the boundary of any system will take place automatically. There is no such effect on the leading solution by the boundary, however. Thus, the transference number of the leading solution can be quite accurately determined even if the indicator solution does not quite meet the "Kohlrausch ratio" requirements.

A study of this effect was made by MacInnes and Smith (102). The observed transference number gave a cubic equation-type curve when $T_{obs.}$ was plotted vs. C_f. The plateau corresponded to the correct value of the transference number so the following solution concentrations were adjusted to operate within this plateau region. A representative curve for the scandium chloride system can be seen in Figure 23. The plateau region was found to be greater for small-bore tubes, dilute solutions, and rising boundaries. Thermal mixing is larger for wide-bore tubes and concentrated solutions, and may cause the solutions to fail to adjust to the concentration given by the "Kohlrausch ratio" if the initial concentration is off by more than 3-8%.

Since the Hittorf method measures the transference number of an ion with reference to the water of the solution and the moving boundary method measures the motion relative to a fixed mark on the tube, correction must be made for the motion of the water relative to the tube. The partial molal volumes are used to make this correction. The idea of correcting

the moving boundary data so that it would then coincide with the Hittorf data obtained with the same solution was proposed by Miller (87) and later calculated quantitatively by Lewis (108). If one side of the cell is left open to the atmosphere and the other is closed, the volume correction calculation is simplified since then one needs to consider only the volume changes between the boundary and the closed side.

Longsworth (105) proposed an additional correction. He observed that in dilute solutions the sum of the cation and anion transference numbers was not exactly one. He reasoned that this was due to that small fraction of the total current which was carried by impurities in the solvent. Therefore, he derived the following to correct for these impurities:

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

where L is the respective specific conductances.

The complete equation used in calculating the corrected transference number is then

$$T_+ = \frac{F\,C\,V}{1000\,It} - \frac{C\,\Delta V}{1000} + T_+ (L_{solvent}/L_{solution}) \cdot$$

The first correction term for the volume change during electrolysis is the more important of the two in concentrated solutions while the second specific conductance correction

term becomes most important in dilute solutions. This is
because the specific conductivity of the solution becomes
smaller with decreased concentration while the specific con-
ductivity of the solvent remains constant. More will be said
of the volume correction for the scandium case in the
following Experimental Procedure section. The validity of the
volume correction was tested and confirmed by Smith (109)
and MacInnes and Longsworth (110).

Some of the necessary properties of the indicator solu-
tion are:

1. The indicator solute must not react with the ion
    undergoing measurement.

2. The transference number of the indicator ion must
    be less than that of the leading ion.

3. The density of the following solution must be less
    than that of the leading solution for falling bound-
    aries and greater than that of the leading solution
    for rising boundaries to prevent mixing.

4. There must be a sufficient difference in some
    property of the leading and following ions which
    will permit observation of the boundary. Examples
    of such properties are color and refractive index.

In 1923, MacInnes undertook a very extensive study of the
moving boundary method; his work being summarized in a review
article by MacInnes and Longsworth (110). Quite a few

improvements were made in technique and equipment and they are discussed in the review article.

LeRoy and Gordon (111) and Hartley and Donaldson (112) used an electronic current controller. Until this time the current often was kept constant manually.

A novel method of transference number measurement was employed by MacInnes (113) who measured the effect of gradients of centrifugal force on the e.m.f. of simple galvanic cells.

Transference numbers of the rare earths which share group III of the periodic table with scandium and yttrium have been measured by personnel of the Ames Laboratory (3, 5, 6, 8).

Experimental

Materials

The solutions of the chloride and perchlorate used in the conductance measurements were also used in the transference number measurements. Their preparation and the analysis of the oxide used is fully covered in the Experimental section under Conductances. The samples having concentrations between those samples which were used in conductance measurements were prepared by dilution of the conductance samples. Lithium chloride was used as the indicator solution. A stock solution

was prepared from reagent grade lithium carbonate by the
method of Scatchard and Prentiss (114). The lithium carbonate
was treated with reagent grade hydrochloric acid and flushed
with nitrogen until the pH was 6.6. The solution was analyzed
by taking aliquots, evaporating to dryness in the presence of
sulfuric acid, igniting at 800° C., and weighing as the sul-
fate. Solutions to be used in measurements were then made
from this stock solution by dilution with conductivity water.

Apparatus

The complete apparatus consisted of an electrolytic cell,
two stop watches, a telescope for viewing the boundary, a
constant current source with accompanying voltage measuring
circuit, a light box on an elevator for illumination of the
cell to make observation of the boundary possible, and a
constant temperature bath. A block diagram of the apparatus
is given in Figure 19. A pictorial representation of the
entire set up is included as Figure 20.

The transference cell was patterned after MacInnes and
Longsworth's cell (110) except that the boundary was sheared
by a hollow bore stopcock (2, 3). Figure 21 is a drawing of
the component parts of the cell. It was constructed entirely
of pyrex, the calibrated tube being a 2 milliliter pyrex
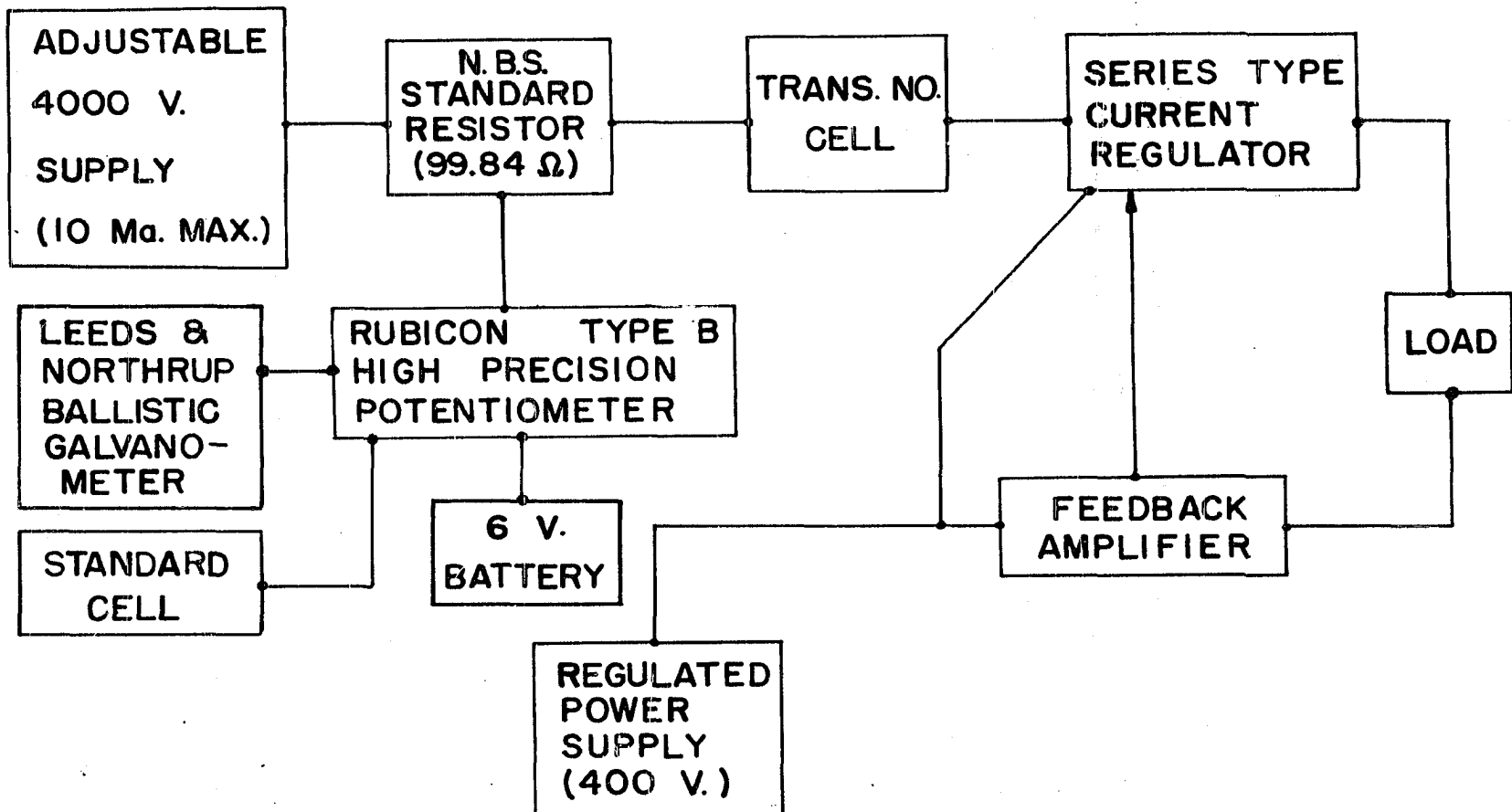measuring pipette, graduated in 0.1 milliliter intervals,

Figure 19. Block diagram of the apparatus used in transference number determinations

HOLLOW BORE STOP COCK
ELECTRODE CHAMBER
ELECTRODE
MOTOR AND CABLE DRUM
GROUND GLASS JOINT
BRASS CLAMP
LIGHT SOURCE ELEVATOR
TELESCOPE
LIGHT SOURCE
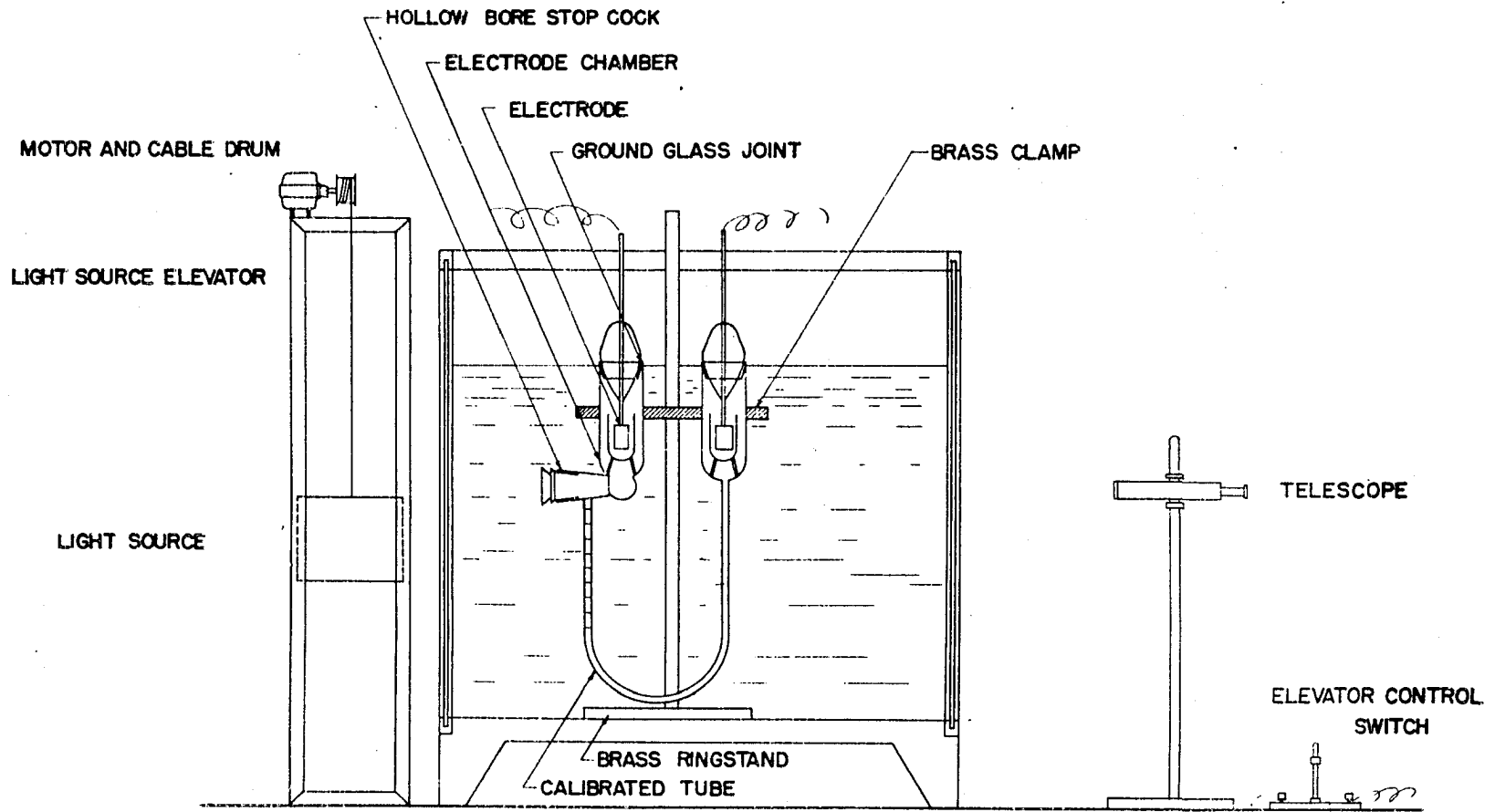ELEVATOR CONTROL SWITCH
BRASS RINGSTAND
CALIBRATED TUBE

Figure 20. Pictorial representation of the components of the transference number apparatus
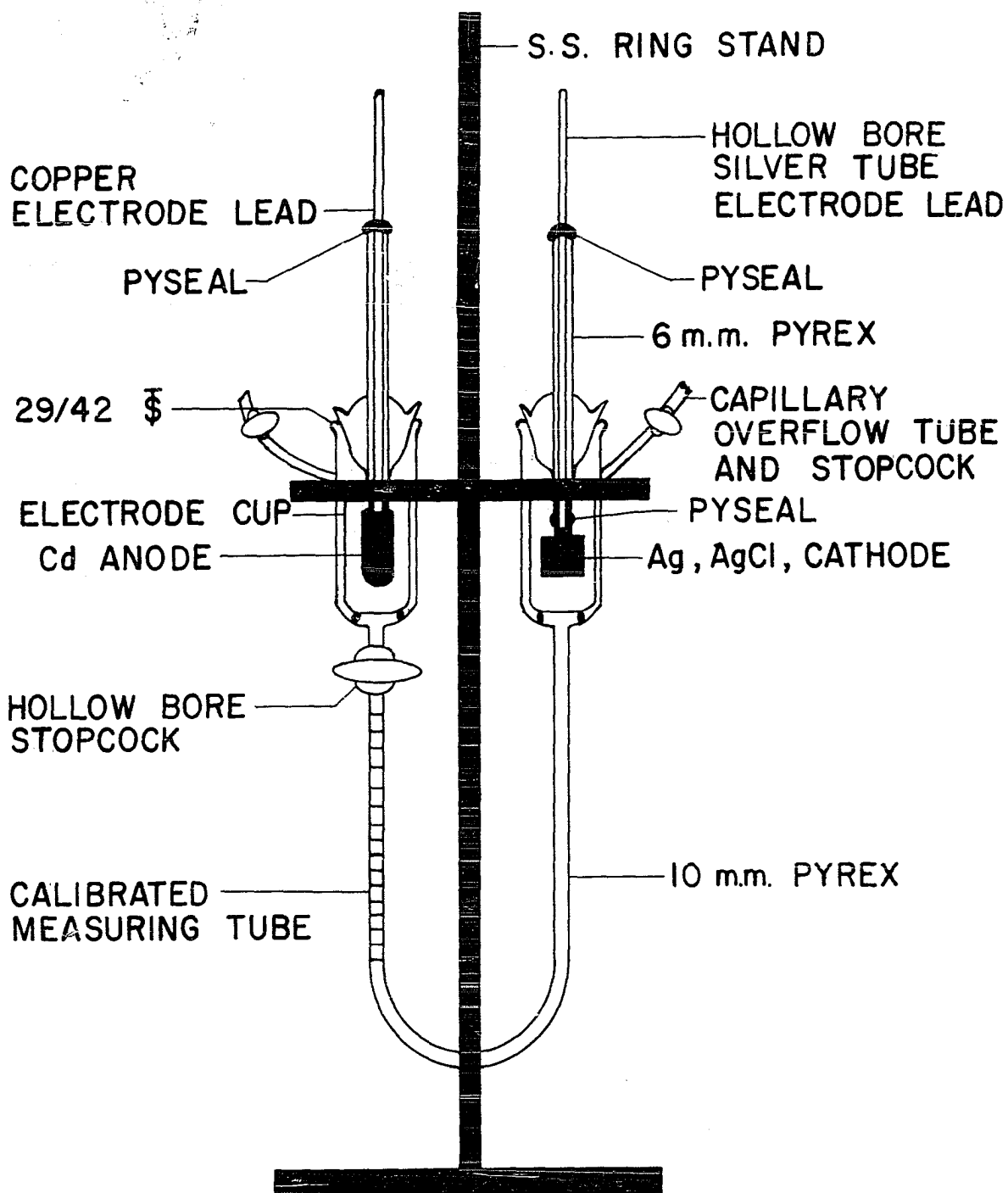
Figure 21. Component parts of the transference number cell

which was sealed into the apparatus. The silver electrodes were purchased from the Klett Manufacturing Co., New York, New York, and consisted of a hollow silver tube threaded into a silver cylinder. The cylinder was composed of alternate layers of flat and corrugated plates of silver. The silver chloride was plated on by electrolysis in a 1 N hydrochloric acid solution at 0.45 amps for about 1 hour. The measuring tube was calibrated by previous workers of the Ames Laboratory by weighing the mercury delivered between the marks. This was done prior to incorporation of the measuring pipette into the cell. The anode was made by melting pure cadmium metal in a test tube under vacuum. When cool, a hole was drilled into the center, threaded, and the threaded copper lead screwed into it. The copper was shielded from the solution by a glass tube which extended into a well drilled in the cadmium for it and which was sealed in with Pyseal. The two glass electrode cups prevent any electrode reaction products from getting into the measuring tube. The entire cell was 50 cm. high and 10 cm. wide.

The time the boundary took to pass between the graduations on the measuring tube was measured by two stop watches. They had previously been checked on a Western Electric Time Rate Recorder and shown to be accurate to within 4-5 seconds for a twenty-four hour period. The watches were mounted in a wooden frame which had a hinged lid resting on the crowns of

the watches. When the hinged lid was depressed, the one watch was stopped and the other started. By resetting the watches after taking a reading, the cycle could be repeated. This then gave a method of taking continuous, consecutive, individual time readings between marks on the measuring tube.

The boundary was observed by making use of the differences in refractive indices of the leading and following solutions. A light was mounted in a box, connected to a reversible elevator so it could be raised and lowered, and having a frosted glass plate across a narrow slit in the box. When the light was placed on the side of the cell opposite the viewer and adjusted so that it passed through the tube at a critical angle for total reflection, the boundary appeared as a sharp line in the tube. A telescope cathetometer was used for viewing this boundary.

The electronic circuit of the constant current controller which was designed and constructed by the Electronics Shop of the Ames Laboratory is shown in Figure 22. This unit consisted of a high voltage rectifier and filter section which was adjustable to provide up to 4000 volts output at 10 milliamperes, a regulated 400 volt power supply which provided power for the current regulator amplifier, and a series type current regulator. The controller provided current which was constant within 0.1% during a 45 minute period. A 100 ohm standard resistor, calibrated by the National Bureau of

Figure 22. Electronic circuit of the constant current controller and voltage source used in the transference number measurements

Standards, was connected in series with the transference cell and the current regulator. The potential drop across this resistor was measured by a Rubicon Type B High Precision Potentiometer manufactured by the Rubicon Division of The Minneapolis Honeywell Co., Philadelphia, Pennsylvania. The current through the cell was then calculated by use of Ohm's law. Essentially, the cell was also in series with an electronic rheostat whose resistance was controlled by feedback. In turn, the feedback was controlled in such a manner as to tend to keep the current constant. The electronic rheostat was essentially a modification of a conventional voltage regulator. Because of the extremes of cell voltage needed, the equipment was designed with the load in the plate circuit of the rheostat tube instead of the cathode circuit which is the usual arrangement for such current sources.

A large, glass-walled, aquarium-type, water bath filled with distilled water was used to control the temperature of the cell. The temperature was controlled at $25 \pm 0.05^{\circ}$ C. About 45 minutes were required for the cell to reach thermal equilibrium.

Procedure

The cathode compartment and the lower loop of the cell, up to the hollow-bore stopcock, was filled with the scandium

solution to be measured and the cell assembled as in Figure 21. The anode compartment was filled with lithium chloride solution which was made up to a concentration as dictated by the "Kohlrausch ratio". After rinsing the outside, the cell was placed in the bath and checked for current leaks with a vacuum-tube voltmeter. After allowing the cell to come to thermal equilibrium, the hollow-bore stopcock was opened, the anode compartment overflow stopcock closed, and the current impressed across the cell. The positive lead was connected to the cadmium anode and the negative lead to the silver-silver chloride cathode.

The first runs were made at constant scandium concentration with varying lithium concentration so the "Kohlrausch ratio" could be determined. This was done with both the chloride and perchlorate. Once the position of the plateau region was found, all following runs were made with lithium solutions of a concentration which would operate in the center of the plateau region. A representative curve for the chloride is included here as Figure 23. The "Kohlrausch k" is defined as

$$k = \frac{\text{concentration of lithium chloride}}{\text{concentration of scandium salt solution}} \cdot$$

The value of k was found to be 0.6 for scandium while the people working with rare earths used 0.8. The boundary
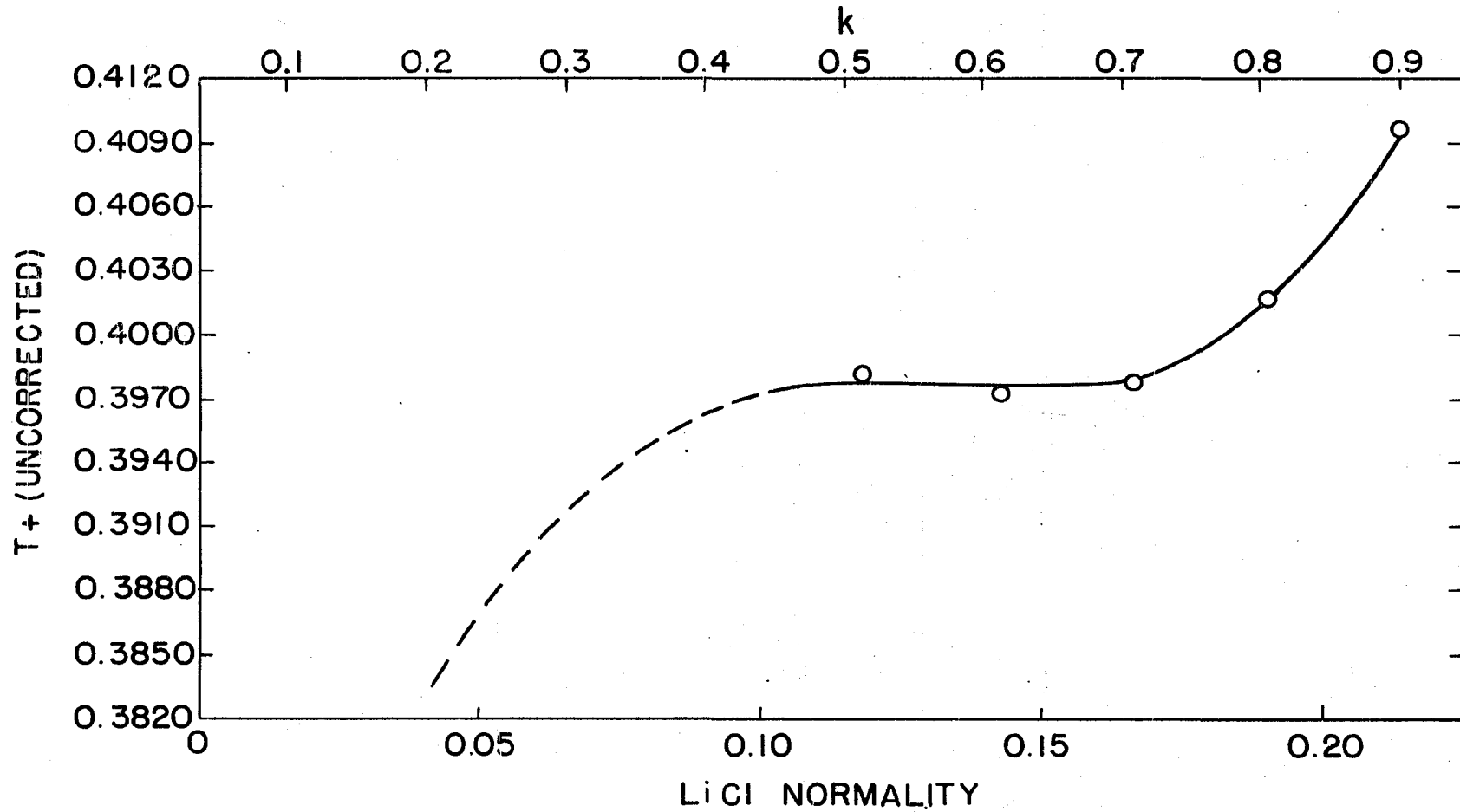
Figure 23. Representative curve for the determination of the "Kohlrausch ratio" in the case of scandium chloride

became too diffuse to observe at the lower end. However, the curve for KCl was found to follow the pattern portrayed by the dotted line (40, p. 119).

The progress of the boundary as it moved down the tube was followed by keeping the light source slightly below the boundary and observing it with the cathetometer. The hairline was lined up with the marks on the tube. As the boundary crossed the hairline, the stopwatch was started. The voltage was read each time the boundary passed a mark also.

Results

A typical set of data is shown in Table 14. The average current was computed from the series of voltage readings. The calibrated volumes of the measuring tube and the corresponding times were grouped into sets to minimize errors. A transference number was then calculated for each set and the observed transference number taken as the average over all the sets.

If the measured voltage is reasonably constant, the average value can be used in calculating the observed transference number. As has been shown before, since

$$T_+ = \left[\frac{(\text{Conc. of soln.}) \ F \ R}{1000 \ V_{\text{measured}}} \right] \left[\frac{\text{volume}}{\text{time}} \right] ,$$

Table 14. A representative set of transference number data

Date: 1/14/59   Salt: $ScCl_3$ Concentration: 0.1537 N

Concentration Indicator Electrolyte: 0.0922 N

R = 99.84   k = 0.6

Average voltage: 1.02930   Average T_+(Observed): 0.4102

Marks	Time	Voltage	Marks	Volume	Time	T_+ (obs)
0		1.02882	0-8	0.8077	2,832.6	0.4102
0.1	5' 57.8"	1.02894	0-9	0.9081	3,184.4	0.4102
0.2	5' 56.9"	1.02910	0-10	1.0071	3,530.8	0.4103
0.3	6' 2.8"	1.02917	0-11	1.1095	3,898.2	0.4094
0.4	5' 49.3"	1.02923	0-12	1.2114	4,249.0	0.4101
0.5	5' 58.1"	1.02932	1-9	0.8066	2,826.6	0.4105
0.6	---	1.02932	1-10	0.9055	3,173.0	0.4105
0.7	11' 44.7"	1.02938	1-11	1.0079	3,540.4	0.4095
0.8	5' 43.0"	1.02934	1-12	1.1099	3,891.2	0.4103
0.9	5' 51.8"	1.02938	2-10	0.8046	2,816.1	0.4110
1.0	5' 46.4"	1.02957	2-11	0.9069	3,183.5	0.4098
1.1	6' 7.4"	1.02962	2-12	1.0088	3,534.3	0.4106
1.2	5' 50.8"	1.02966	3-11	0.8031	2,820.7	0.4096
			3-12	0.9050	3,171.5	0.4105
			4-12	0.8054	2,822.2	0.4105

K = 1,438,589.17

then by grouping sets and using the average voltage

$$T = \left[\frac{(\text{Conc. of soln.}) \, F \, R}{1000 \, V_{average}} \right] \left[\frac{\sum \text{volume}}{\sum \text{time}} \right] ,$$

where K, as given in Table 14, is the first term in the above expression. The solution concentration is in equivalents per liter, the volume in milliliters, and the time in seconds. R has the value of 99.84 ohms as measured by the National Bureau of Standards.

The volume change correction which was referred to in the transference number introduction section was determined using the following values:

$$\overline{V}_{Cd} = 13.0 \text{ ml. } (115);$$

$$\overline{V}_{CdCl_2} = 24.339 + 19.982 \, m - 26.196 \, m^2 \, (9, \text{ p. } 97).$$

The scandium solution partial molal volumes are to be found in the section of this thesis on Densities and Partial Molal Volumes. The molalities of the scandium solutions were calculated from their normalities by using the densities in the following manner:

$$m = \frac{1000 \, N/3}{1000 \, D_{25^\circ} - N \, (\text{G. E. W.})}$$

where N is the normality (equivalents per liter), D_{25^o} is the density of the solution at 25° C., and (G. E. W.) is the gram equivalent weight. The molality of the $CdCl_2$ was calculated on the basis of the total charge passed through the cell during an experiment and was

$$m = \frac{(It/F)\ 1000}{total\ volume\ change\ swept\ out\ by\ the\ boundary} .$$

The conditions in the cell both before and after electrolysis are pictured in Figure 24. A descending boundary was used. Before the passage of current the boundary is at B. During the passage of one Faraday of current, the observed rare-earth boundary moves from B to C-C while if there had been no accompanying volume change, it would have been at C'-C'. Of interest then are the volume changes which occur between A-A and C-C during the passage of one Faraday of current. The losses and gains behind C-C are:

For the passage of one Faraday through the cell,

1. There is a loss of 1/2 mole of cadmium metal from the anode so $\Delta \bar{V}_1 = - \bar{V}_{Cd}/2$;

2. There is a gain of 1/2 mole of cadmium ions, Cd^{+2}, in the form of $CdCl_2$ so $\Delta \bar{V}_2 = + \bar{V}_{Cd^{+2}}/2$;

3. There is a gain of 1 mole of chloride ions from LiCl to $CdCl_2$ so $\Delta \bar{V}_3 = + \bar{V}_{Cl^-}$;
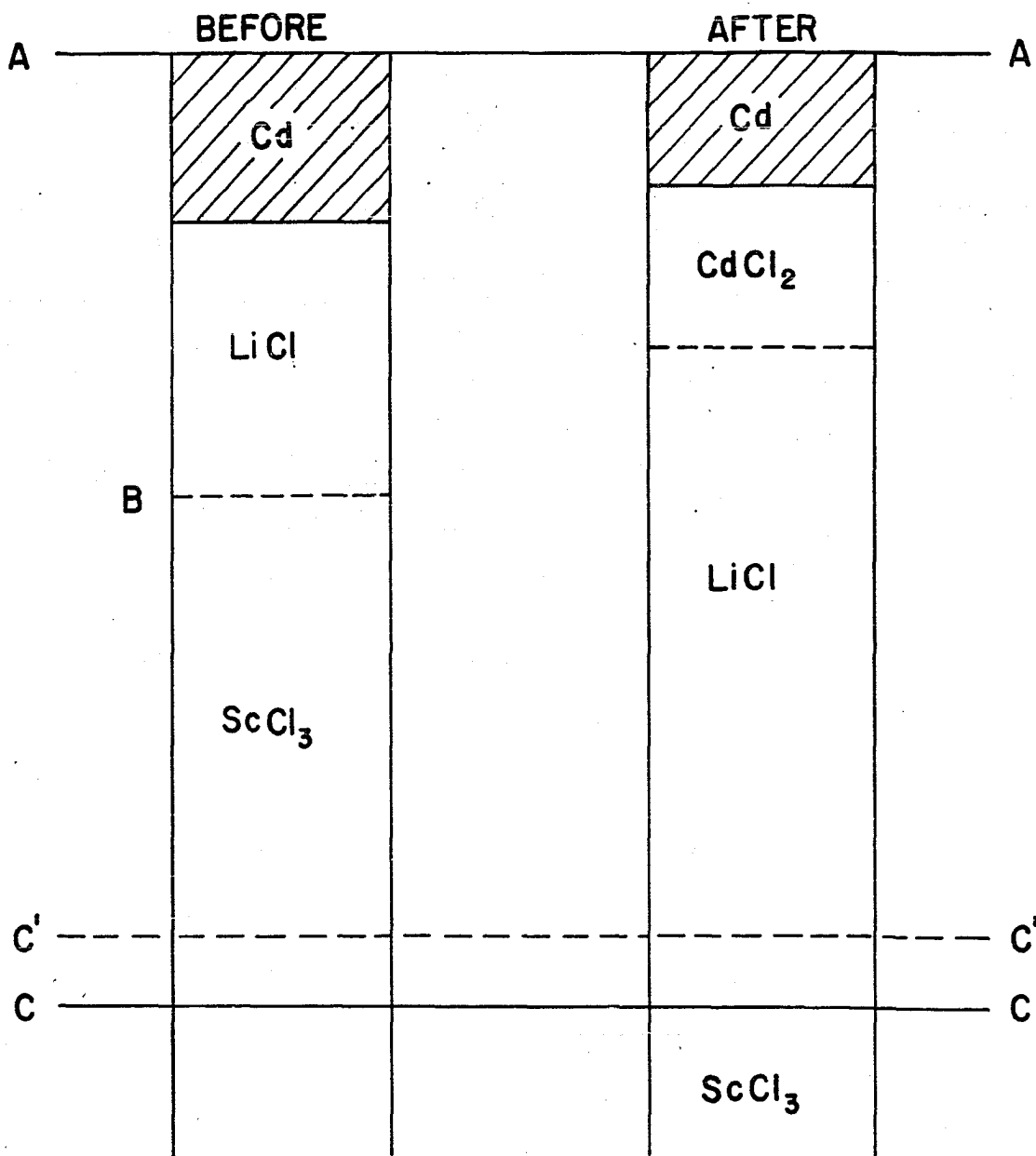
Figure 24. Conditions in the cell both before and after electrolysis for the case of the chloride. In the case of the perchlorate, an additional region of $LiClO_4$ is built up between the LiCl and the $Sc(ClO_4)_3$

4. There is a loss of one mole of chloride ions to $CdCl_2$ from LiCl so $\Delta \bar{V}_4 = - \bar{V}_{Cl-}$;

5. There is a gain of T_- mole of chloride ions into the lithium region due to migration of chloride ions toward the anode so $\Delta \bar{V}_5 = + (T_-)\bar{V}_{Cl-}$;

6. There is a gain of T_+ moles of chloride ions in the lithium region due to downward motion of the boundary so $\Delta \bar{V}_6 = + (T_+)\bar{V}_{Cl-}$;

7. There is a loss of $T_+/3$ moles of scandium ions from the scandium chloride region due to migration toward the cathode so $\Delta \bar{V}_7 = - (T_+/3)\bar{V}_{Sc^+3}$;

8. There is a loss of T_+ moles of chloride ions from the scandium chloride region so $\Delta \bar{V}_8 = -(T_+)\bar{V}_{Cl-}$.

The net change in volume as calculated from the closed side of the cell is then

$$\Delta \bar{V}_{net} = \sum_{1}^{n} \Delta \bar{V}_n = -\bar{V}_{Cd}/2 + \bar{V}_{Cd^+2}/2 + \bar{V}_{Cl-} - \bar{V}_{Cl-} + (T_-)\bar{V}_{Cl-}$$

$$+ (T_+)\bar{V}_{Cl-} - (T_+/3)\bar{V}_{Sc^+3} - (T_+)\bar{V}_{Cl-}.$$

Since $T_+ + T_- = 1$ by definition then

$$(T_+ + T_-)\bar{V}_{Cl-} = \bar{V}_{Cl-}$$

and the expression for $\Delta \bar{V}_{net}$ can then be simplified to

$$\Delta \overline{V}_{net} = -\overline{V}_{Cd}/2 + \overline{V}_{CdCl_2}/2 - (T_+/3)\overline{V}_{ScCl_3} .$$

This was then used in

$$T_+ = T_+' - \frac{c \ \Delta \overline{V}_{net}}{1000}$$

where T_+ is the volume-change corrected transference number and T_+' is the uncorrected or observed transference number.

For the perchlorate case, the situation is a little more complex since a $LiClO_4$ region must also be considered. The expression is then

$$\Delta \overline{V}_{net} = \sum_1^n \Delta \overline{V}_n = -\overline{V}_{Cd}/2 + \overline{V}_{CdCl_2}/2 - \overline{V}_{Cl^-} + \overline{V}_{ClO_4^-}$$

$$- (T_+/3)\overline{V}_{Sc(ClO_4)_3} .$$

Since individual ionic partial molal volumes cannot be measured, an approximation

$$\overline{V}_{ClO_4^-} - \overline{V}_{Cl^-} \approx \overline{V}_{LiClO_4} - \overline{V}_{LiCl} = 26.48 \ (84, \ p. \ 115)$$

was used.

In addition, the conductance correction was applied to the transference number data. The resultant corrected and

uncorrected data are given in Tables 15 and 16 with their accompanying Figures 25 and 26.

The concentration range could not be extended beyond the range shown here since at one extreme the boundary became too diffuse to follow (concentrated end) and at the other extreme, the boundary moved too fast to conveniently measure it (dilute end).

Table 15.   Cation transference numbers for scandium chloride

Normality	Normality$^{\frac{1}{2}}$	T_+ (obs.)	Volume correction	Solvent correction	T_+ (corr.)
0.2382	0.4880	0.3973	-0.0010	+ 0.0000	0.3963
0.1936[a]	0.4400	0.4033	-0.0009	+0.0001	0.4025
0.1537[a]	0.3920	0.4102	-0.0007	+0.0001	0.4096
0.1191	0.3451	0.4168	-0.0005	+0.0001	0.4164
0.0864[a]	0.2940	0.4260	-0.0003	+0.0001	0.4258
0.0596	0.2440	0.4368	-0.0002	+0.0002	0.4368

[a]These samples were diluted from the original scandium chloride stock solution using the same conductivity water that was originally used in making up the series. The respective conductances were then read from Figure 4.
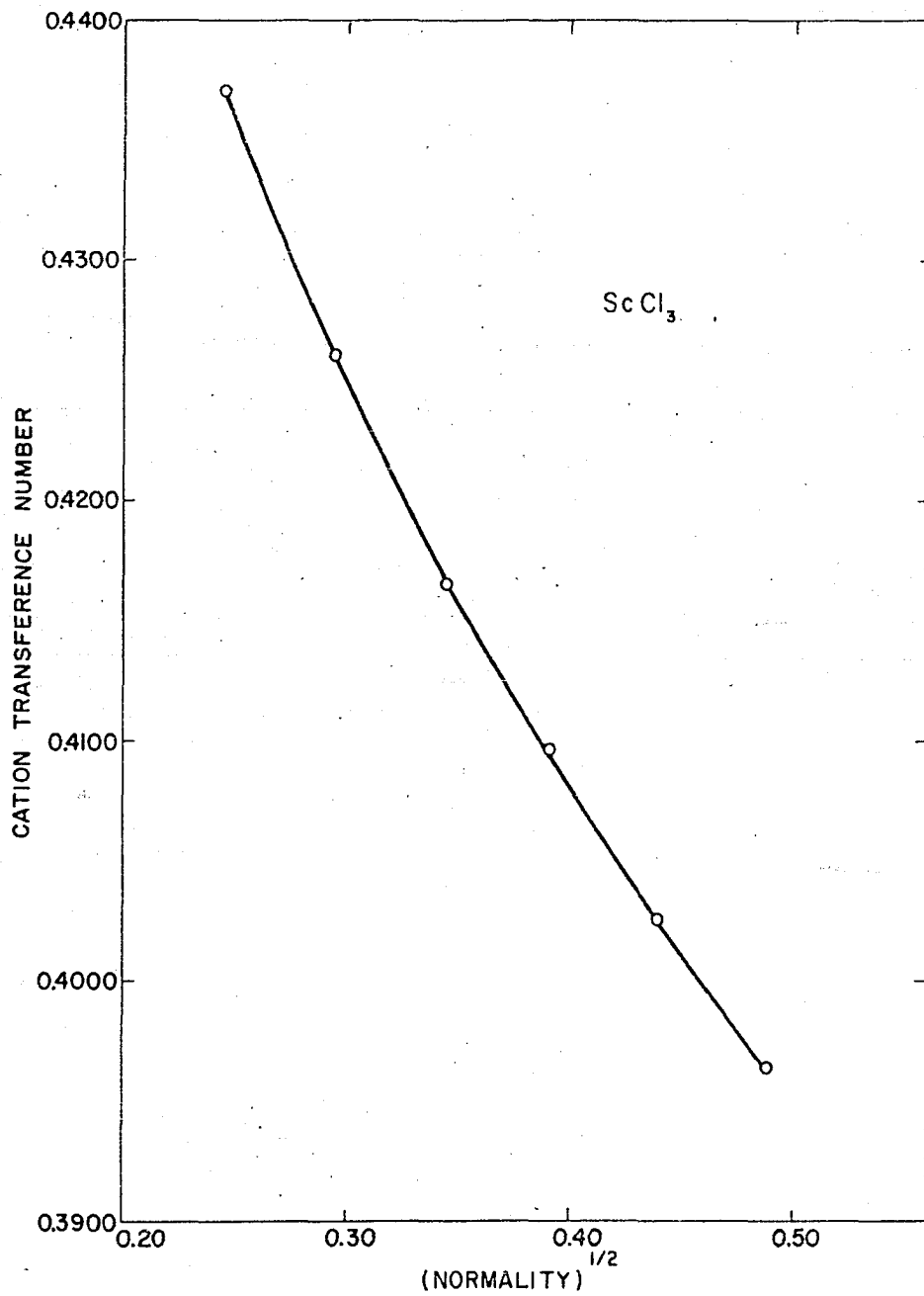
Figure 25. Cation transference numbers for varying
scandium chloride concentrations

Table 16. Cation transference numbers for scandium perchlorate

Normality	Normality$^{\frac{1}{2}}$	T_+ (obs.)	Volume correction	Solvent correction	T_+ (corr.)
0.2436	0.4936	0.4390	-0.0038	+0.0000	0.4352
0.1989[a]	0.4460	0.4447	-0.0038	+0.0000	0.4409
0.1576[a]	0.3970	0.4506	-0.0029	+0.0000	0.4478
0.1218	0.3490	0.4594	-0.0023	+0.0001	0.4572
0.0901[a]	0.3001	0.4695	-0.0016	+0.0001	0.4680
0.0609	0.2468	0.4778	-0.0010	+0.0001	0.4769

[a]These samples were diluted from the original scandium perchlorate stock solution using the same conductivity water that was originally used in making up the series. The respective conductances were then read from Figure 8.

Discussion of Results

The concentration of the solutions were known to $\pm$ 0.1%. Since the accuracy of the measurements also depends on the measurement of the time it takes the boundary to travel between marks, the measurement of the current passing through the solution, and the volume of the tube between each set of marks, the total error could be as great as 0.3% for the un- corrected data and 0.2% for the corrected data.
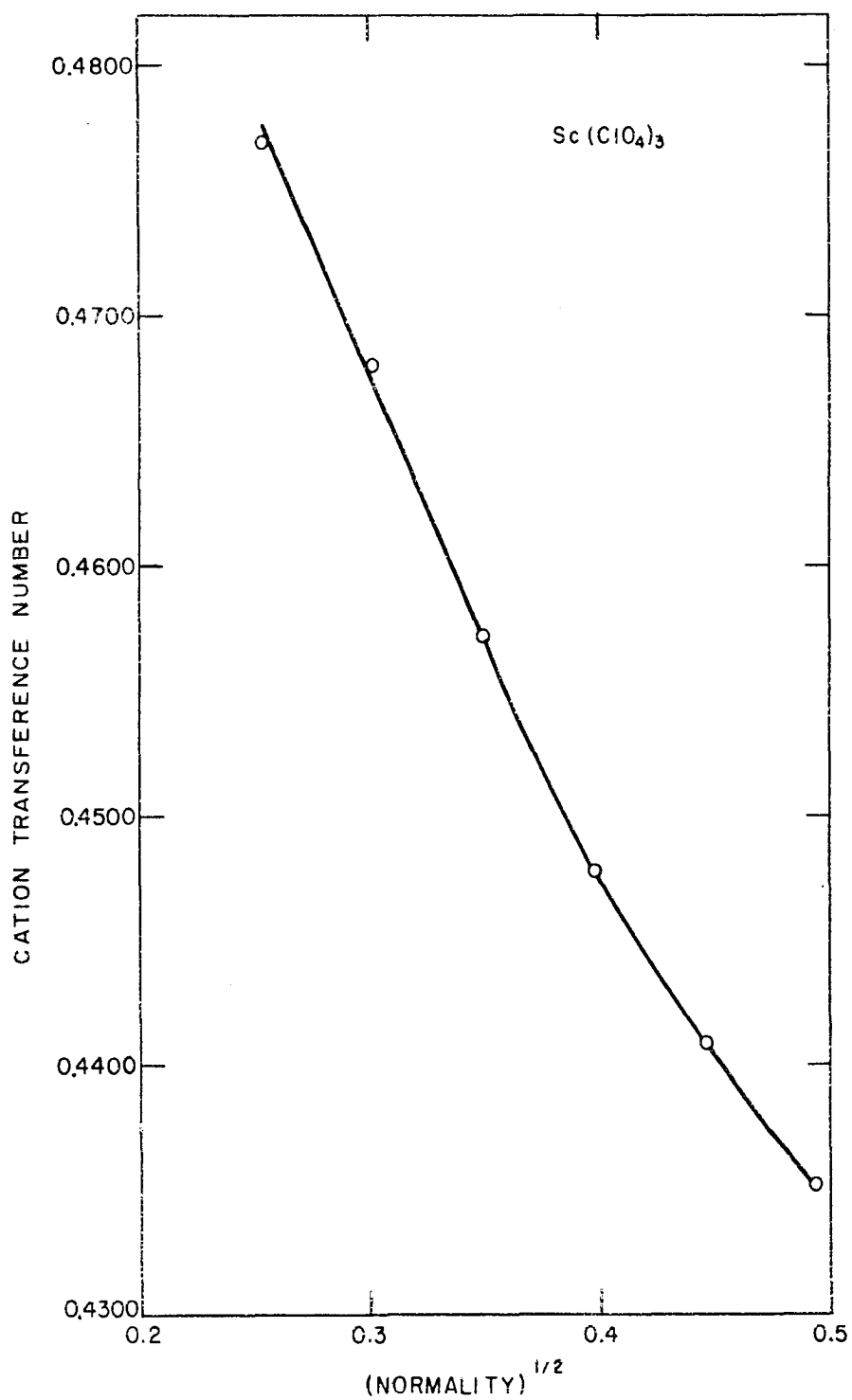
Figure 26.   Cation transference numbers for varying
             scandium perchlorate concentrations

The time required for the boundary to travel between marks was at least 120 seconds and the stopwatch could be read to 0.2 second or 0.17%. The average voltage across the standard resistor in series with the cell was usually within 0.03% of any experimental readings. The volume calibrations were probably good to 0.05%.

The transference numbers for the scandium salts compared with the corresponding rare-earth salts were in all cases considerably larger than those for the rare earths.

As in the case of the conductance measurements, hydrolysis again plays a significant part but to a much lesser degree since the transference number runs made use of samples on the concentrated end of the series where the degree of hydrolysis is relatively small.

SOLUBILITIES

Introduction

Since baths were already available at 25° and 60° C. due to other solubility determinations being carried out and since data on solubilities for scandium salts is lacking in the handbooks, it was decided to do some solubilities as a side issue.

Experimental

Apparatus

An oil bath at 60° C. and a water bath at 25° C. both $\pm\ 0.1^\circ$ C. and regulated by micro-set thermoregulators was used. A motorized shaker was used in conjunction with the baths.

Materials

The chloride and perchlorate were prepared by dissolving the oxide in the appropriate acid and recrystallizing from solution. The N'-(hydroxyethyl)ethylenediamine-N,N,N'-triacetate was obtained from the eluate from a separation

run. The solution was reduced in volume and the solid

separated from the liquid. The solid was then dried at 80°

C. with no apparent decomposition. Spectrographic analysis

showed the compound to contain no metal ions other than scan-

dium. An attempt was made to prepare the hydrogen scandium

ethylenediamine N,N,N',N'-tetraacetate but the empirical

formula of the compound which resulted was found to be

$Sc[Sc(EDTA)]_3 \cdot 6\ H_2O$. Moss (116) found the same type of

compounds for the rare earths.

Procedure

The solubilities were approached from both the saturated

and unsaturated sides. After an equilibration time of 2

weeks for the chloride and perchlorate and 2 months for the

chelate compound, samples of the solutions were removed and

weighed. The solutions were then transferred to crucibles,

taken to dryness with heat lamps, treated with nitric acid to

avoid oxychloride formation, covered with recrystallized

oxalic acid to prevent spattering, and gently ignited to the

oxides at 800° C. The chelate was likewise destroyed with

nitric acid to prevent the compound from swelling out of the

crucible during ignition.

An analysis of the crystals in equilibrium with the

solutions was made on the samples which were saturated at

the start. In this way, the crystals which were analyzed

were all grown at the temperature of the respective baths.

The crystals were blotted as much as possible, between filter

paper, transferred to a weighing vial, weighed, and then

transferred to the crucibles for ignition.

Results

The results of the solubility tests are given in Table

17. The analysis of the perchlorate crystals was difficult

because of the extremely hygroscopic nature of the crystals.

To completely resolve this difficulty, it would be necessary

to do complete vapor pressure determinations over the crys-

tals as well as perhaps crystal structures at different

temperatures. Again, these would have to be done in a

carefully controlled atmosphere.

Discussion

In his thesis, Pokras (117) states that the solubility

of the perchlorate should be at least 310 grams per 100 grams

of water at 25° C. but that the solution upon which he based

this estimate could not be made to recrystallize even when

the container was set on dry ice. Indeed, if one calculates

the data given in this thesis on the basis of $Sc(ClO_4)_3 \cdot 6 H_2O$,

Table 17.   Solubilities of scandium salts

Salt	Temp., °C.	Grams/100 grams of water on basis of empirical formula shown	Grams/100 grams of water on anhydrous basis
$ScCl_3$	25	$155.1-ScCl_3 \cdot 6\ H_2O$	54.96
	60	$202.6-ScCl_3 \cdot 5\ H_2O$	138.3
$Sc(ClO_4)_3$	25	----	184.4
	60	----	192.5
$Sc(HEDTA)$	25	$0.51-Sc(HEDTA) \cdot 6\ H_2O$[a]	0.37
	60	$3.32-Sc(HEDTA) \cdot 10\ H_2O$[a]	2.10

[a]The abbreviation, HEDTA, stands for N'-(hydroxyethyl)-N,N,N'-triacetic acid.

one obtains a value of 578.0 grams of $Sc(ClO_4)_3 \cdot 6\ H_2O$ per 100 grams of water at 25° C.

Pokras also measured the vapor pressure over his salt at 25° C. by isopiestic methods. He assumed he had the hexahydrate. The salt was found to gain weight in the presence of a solution of sulfuric acid and water having the composition of 2.8 moles of water per mole of sulfuric acid and the salt lost weight in a 2.40:1 mixture. Since the vapor pressure of a 2.80:1 mixture is 1.75 mm. at 24° C.

and 1.90 mm. at 26° C. while a 2.40:1 mixture is 2.48 at 24° C. and 2.70 at 26° C., the scandium perchlorate had a vapor pressure of 2-3 mm. at 25° C. Calcium chloride in a saturated solution has a vapor pressure of 4-5 mm. so the perchlorate is a much better desiccant than calcium chloride. This is the cause of the difficulty in trying to determine accurately the empirical formula of the crystals in equilibrium with the saturated solutions. Formulas having from 5 to 7 waters were obtained with the perchlorate at from 25° C. to 60° C. For this reason, no data are given for the perchlorate in Table 17 for other than the anhydrous salt.

STABILITY CONSTANTS

Introduction

Until recently, the rare earths and yttrium have been in short supply because of the lack of a good purification method. The work performed at the Ames Laboratory (118, 119, 120) on the separation of macroscopic quantities of rare earths paved the way to an abundant supply of pure rare earths for research and industrial applications. The method involved the use of ion-exchange resins in conjunction with chelating agents. Stability constants are of interest to workers in the field of ion-exchange separations since they allow an estimation of the separation possible as well as the distance of elution required. Powell (121) has reviewed the possible application of several chelating agents to the ion-exchange separation of the rare-earth elements.

Wheelwright (122) measured the stability constants for the rare-earth series with ethylenediamine-N,N,N',N'-tetraacetic acid (hereafter referred to as EDTA) and N'-(hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (hereafter referred to as HEDTA).

It has been found that EDTA separates all the members of the rare-earth series but requires a retaining ion while

HEDTA gives a very good separation with all but Sm, Eu, Gd, Tb, Dy, Ho, and Er. On the other hand HEDTA requires no retaining ion other than H^+ and does a remarkable job of separating several of the common ions from the rare earths (121). Thus, it appears that each chelating agent has its advantages and drawbacks. Ion-exchange workers are continually searching for new chelating agents to use in separation processes.

This research was intended to measure the stability constants of two new chelating agents; 1,2-bis-[2-di(carboxymethyl)-aminoethoxy] ethane (hereafter referred to as DE since it has a diether linkage in the central carbon chain, and 2,2'-bis-[di(carboxymethyl)-amino] diethyl ether (hereafter referred to as ME because it has a monoether linkage) as well as to extend the measurements with EDTA, HEDTA, 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (hereafter referred to as DCTA), and carboxymethyl-bis-[2-di(carboxymethyl)-aminoethyl] amine (hereafter referred to as DETPA) to include scandium.

The structural formulae for the chelating agents just mentioned are given in Figure 27.

The stability constants of half of the rare-earth series have been measured for DCTA (123) and all of the rare-earth series for DETPA (124).
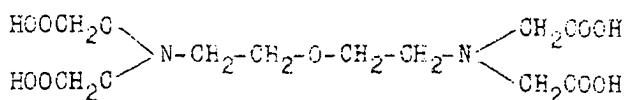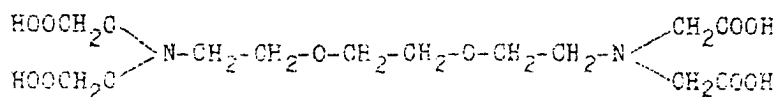
$$HOOCH_2C \diagdown N-CH_2-CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad\qquad \diagdown CH_2COOH$$

<p align="center">EDTA</p>

$$HOOCH_2C \diagdown N-CH_2-CH_2-N \diagup CH_2CH_2OH$$
$$HOOCH_2C \diagup \qquad\qquad\qquad \diagdown CH_2COOH$$

<p align="center">HEDTA</p>

$$N \diagup CH_2COOH$$
$$\diagdown CH_2COOH$$
$$N \diagup CH_2COOH$$
$$\diagdown CH_2COOH$$

<p align="center">DCTA</p>

$$HOOCH_2C \diagdown N-CH_2-CH_2-N-CH_2-CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad | \qquad\qquad \diagdown CH_2COOH$$
$$CH_2$$
$$COOH$$

<p align="center">DETPA</p>

$$HOOCH_2C \diagdown N-CH_2-CH_2-O-CH_2-CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad\qquad\qquad \diagdown CH_2COOH$$

<p align="center">ME</p>

$$HOOCH_2C \diagdown N-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad\qquad\qquad\qquad\qquad \diagdown CH_2COOH$$
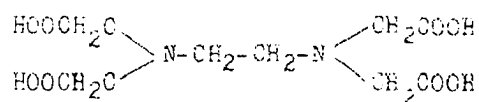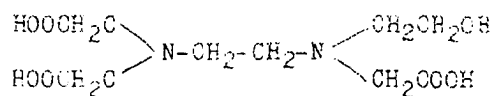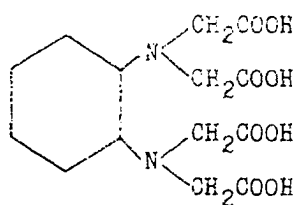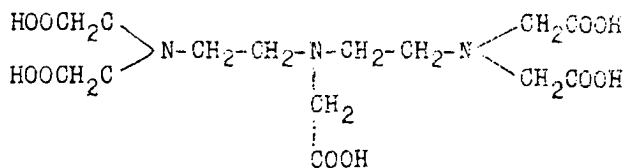
<p align="center">DE</p>

Figure 27. Structural formulas of the chelating
agents used in this research

An electron donor, combined with a metal ion, constitutes what is commonly known as a complex or coordination compound. When the substance which combines with the metal ion contains two or more donor groups, structural rings are formed and the resulting complex is more properly known as a chelate. Both ionic and covalent types of complexes and chelates have been realized, depending upon the particular metal used and the nature of the complexing or chelating agent.

Chelates can be detected by several means among which are:

1. Preparation, isolation, purification, and analysis of prepared compounds;

2. Alteration of normal chemical behavior of a metal ion such as failure of a rare-earth chelate solution to precipitate rare-earth hydroxide when treated with base;

3. Intensification of color, an example of which is the deepening of the blue copper solution color;

4. Conductometric titrations;

5. Measurement of peak shifts in the absorption spectra; and

6. Polarographic analysis in which the half-wave voltage is shifted to more negative values by chelation.

It is an established fact that EDTA can act as a tetra-, penta-, or hexadentate chelating agent depending on the metal ion involved and the conditions of the solution such as pH. The hexadentate structure may be visualized as utilizing all four groups as well as the two nitrogen atoms. In the case of DETPA and DE an octadentate chelate structure is possible, utilizing the carboxyls, nitrogens, and oxygens and, in the case of ME, a heptadentate structure is possible. As will be seen later, this complicates the measurement of the stability constants by allowing the formation of bimetallic chelate species with copper.

Several methods of measuring the stability constants of metal chelates have been developed. Schwarzenbach, Willi, and Bach (125) and Schwarzenbach and Ackerman (126) determined the stability constants of the alkaline earth-EDTA complexes by titration of EDTA with standard potassium hydroxide in the presence of a fifteen-fold excess of the metal ion. The titrations were done with silver-silver chloride and hydrogen electrodes in 0.1 M potassium chloride. The results were explained by postulating

$$M^{+2} + H_2Ch^{-2} \rightleftharpoons MHCh^- + H^+$$

and

$$M^{+2} + HCh^{-3} \rightleftharpoons MCh^{-2} + H^{+} .$$
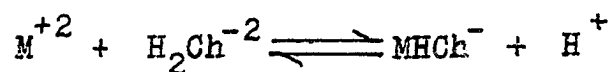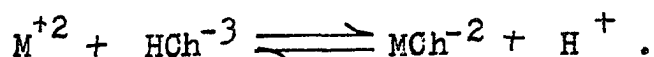
Schwarzenbach used a graphical procedure to calculate the constants for the above chelates and Martell and Calvin (127) proposed an algebraic method for accomplishing the same task. For complexes of low or intermediate stability, this method was applicable but, with the rare earths, the equilibria were too far to the right to permit accurate calculations.

In order to render it applicable to measurements of stability constants of very stable complexes, the original pH method was modified by Ackerman and Schwarzenbach (128), and Schwarzenbach and Freitag (129). Two chelating agents were used which competed with each other for bonding with a heavy metal ion. A second metal was introduced which formed a very stable complex with one of the chelating agents and no complex with the other chelating agent. To measure the rare-earth constants, Wheelwright (122) used copper and β, β', β''-triaminotriethylamine (tren) in the reaction

$$CuCH^{-2} + H_3 tren^{+3} + M^{+3} \rightleftharpoons MCh^{-} + Cu\, tren^{+2} + 3\,H^{+} .$$
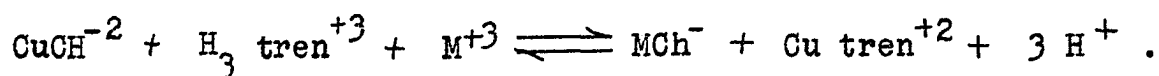
Partial neutralization of the released hydrogen ion with standard sodium hydroxide and subsequent measurement of the pH enabled him to calculate the rare-earth stability constants.

Two non-pH potentiometric methods have also been applied
to stability constant determinations. Schwarzenbach and
Heller (130) used a gold electrode to follow the titration of
iron (II) sulfate with iodine in the presence of an excess
of EDTA. Measurements were done in 0.1 M potassium chloride
at 20° C. By use of a complicated graphic and algebraic
treatment of the data, they were able to calculate stability
constants for the iron (II) and iron (III) complexes, $FeCh^{-2}$
and $FeCh^-$, as well as constants for the various hydroxy-
complexes formed from the above species. Carini and Martell
(131) devised a method for measurement of the true thermo-
dynamic equilibrium constants for the alkaline earth-EDTA
reactions. Experimentally, the e.m.f. of the cell

$$Pt-H_2, \quad K^+ (m_1), \quad M^{+2} (m_2), \quad Cl^- (m_3), \quad H_nCh^{n-4} (m_4), \quad AgCl-Ag$$
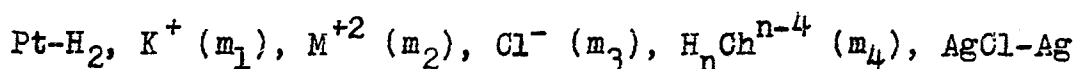
was measured at various temperatures and concentrations $(m_1,$
$m_2, m_3, m_4)$ for n's of 0 to 2. The standard free energy
change was calculated at each temperature for the reaction

$$M^{+2} (aq) + Ch^{-4} (aq) \rightleftharpoons MCh^{-2} (aq) .$$
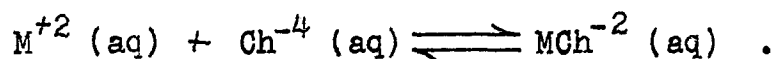
The iron (III) complex with EDTA has been measured by
Kolthoff and Auerbach (132) using spectrophotometric means.
The measurements were done in 0.6 to 1 molar perchloric acid

to suppress the ionization of the acid-EDTA species and to prevent 100% formation of iron chelate. This was necessary since iron has such a large stability constant. The concentration of uncomplexed iron was determined by difference from the known total iron content and the spectrophotometric value of the FeCh⁻ content. The Ch^{-4} concentration was gotten from the four acid dissociation constants and the pH. The iron (III) constant was then determined from

$$K_{FeCh^-} = \frac{[FeCh^-]}{[Fe^{+3}][Ch^{-4}]} .$$

Martell and Plumb (133) and Plumb, Martell, and Bersworth (134) employed a competition reaction utilizing two metal cations reacting with half the theoretical amount of chelating agent required to completely chelate both cations. Adjustment of the pH caused the uncomplexed material to precipitate. Because of the solid phase present, several weeks of equilibration, with shaking, was necessary. The individual phases were analyzed spectrophotometrically. Rather large errors were experienced since no correction for possible complexes between free cations and buffer components was made and because the solid phase introduced complications. Only stability constant ratios could be obtained by this

method so an independent determination was necessary to obtain absolute values.

Radioactive exchange offers another means of measurement leading to stability constant values. Cook and Long (136) used the method to determine the nickel-EDTA constant. Nickel (II) ions were added to a radioactive nickel-EDTA chelate solution which was prepared from Ni^{63}. The exchange

$$\overset{*}{Ni}Ch^{-2} + Ni^{+2} \rightleftharpoons NiCh^{-2} + \overset{*}{Ni}^{+2}$$

took place where the asterisks stand for the radioactive ion. Timed aliquots were treated with hydroxide to precipitate the uncomplexed ions from the mixture, measurement of the activity and pH then gave stability constants.

The use of ion-exchange techniques for determining stability constants is based on the fact that, in a system consisting of the metal cation to be measured, the chelating agent, and the ion-exchange resin, the amount of cations picked up by a definite amount of resin is proportional to the amount of free cations over a wide concentration range. It is necessary to determine the exchange constant in the presence of the chelating agent, α, as well as the exchange constant in the absence of the chelating agent, α_0. Ionic strengths of both solutions must match. The stability constant is then

$$K = \frac{\frac{\alpha_o}{\alpha} - 1}{Ch^{-n}} .$$

The theory of the method is developed fully in publications by Fronaeus (136) dealing with the copper acetate, nickel acetate, and nickel thiocyanate complexes. The method is best applied to complexes of low stability.

Conductivity methods (137) can be used to obtain stability constants but are applicable only when the complex is uncharged as with oxalates and malonates of bivalent metals.

Distribution of a metal ion between two immiscible solvents (138, 139, 140, 141) amounts to determining the concentration of the uncharged complex, and consequently this method is limited to systems where an uncharged complex is formed.

The last method which will be discussed here is the polarographic measurement of the concentration of free cations released from the chelated form upon exchange for a second metal ion. Two general approaches have been used. The first depends on the determination of the shift in half-wave potential for the metal ion upon chelation. The shift of the potential as a function of concentration of the chelating ion gives information as to the composition and stability of the complex. Koryta and Kössler (142) measured the nitrilotriacetate complexes of cadmium, lead, and zinc and Matyska and

Kössler (143) measured the formation constants for the mercury-EDTA complexes, $HgCh^{-2}$, $HgHCh^{-}$, and $HgOHCh^{-3}$ using this basic procedure.

The second general polarographic method is the one used in the research for this thesis. It depends on the fact that each ionic species is reduced at the dropping mercury electrode at a characteristic potential. Individual waves are thus produced provided their half-wave potentials differ by at least 0.2 of a volt. Ackerman and Schwarzenbach (144) studied the reaction between copper (II) and the cadmium-EDTA complex using this method. Titanium-EDTA complexes were studied by Blumer and Kolthoff (145) and Pecsok and Maverick (146).

Bril and Krumholz (147) evaluated a series of stability constant ratios for copper-EDTA with nickel, cadmium, and zinc; cadmium-EDTA with zinc; and lead-EDTA with zinc. The reaction was essentially

$$M^{+2} + NCh^{-2} \rightleftharpoons MCh^{-2} + N^{+2}$$

and the equilibrium constant is the ratio of the two metal-chelate stability constants.

Schwarzenbach, Gut, and Anderegg (149) have measured a large number of various metal chelate stability constants by use of this method.

Experimental

Materials

The rare-earth oxides used in this research were produced
by ion-exchange techniques utilizing the methods perfected in
the Ames Laboratory (118, 119, 120, 121). All were equal to
or greater than 99.9% pure. Nitrate stock solutions were
prepared by dissolving an excess of oxide in reagent-grade
nitric acid and filtering off the excess oxide. The solutions
were analyzed gravimetrically for rare-earth content. Hun-
dredth-molar solutions were prepared from these stock solu-
tions.

The chelating agents (EDTA, HEDTA, DCTA, DETPA, ME, and
DE) were obtained from Geigy Industrial Chemicals, a division
of Geigy Chemical Corporation, Ardsley, New York.

Standard, carbonate-free potassium hydroxide was prepared
by the method of Powell and Hiller (73) for use in standardiz-
ing and preparing the 0.0100 molar potassium chelates.

Hundredth-molar scandium nitrate was prepared by dilution
of the stock solution prepared for use in conductance measure-
ments.

All other chemicals used in this research were reagent-
grade chemicals. One molar potassium nitrate was used to
adjust the ionic strength; 0.1000 molar sodium acetate-acetic

acid buffer to hold the pH at 4.65; and 0.0100 molar cadmium
and copper nitrate for standards.

Apparatus

A Sargent model XXI polarograph sold by Sargent and
Company, Chicago, Illinois was used in this research. The
cell was fashioned from a 100 milliliter beaker. The satu-
rated calomel electrode was connected to the cell by a
potassium nitrate-agar bridge. The cell was immersed in a
constant temperature bath.

Procedure

The samples were prepared by combining:

1. Ten milliliters of 0.0100 molar cadmium or copper
   nitrate,

2. Ten milliliters of 0.1000 molar buffer,

3. Ten milliliters of rare-earth or scandium nitrate,

4. Ten milliliters of 0.0100 molar tri-, tetra-, or
   penta-potassium chelate depending on which chelating
   agent was being used,

5. Enough potassium nitrate to adjust the ionic strength
   to 0.1 (taking into account the potassium nitrate

formed in the reaction of the potassium chelates

with the rare-earth and scandium nitrates).

The mixtures were then diluted to a total volume of 100

milliliters.

The completely complexed reference solutions contained

the same concentrations of copper or cadmium, chelate, and

buffer with an ionic strength of 0.1 while the free-metal

reference solutions contained the same concentrations of

copper or cadmium and buffer with an ionic strength of 0.1.

The europium runs were done by replacing cadmium with

europium.

Two drops of 0.2% basic fuchsin were added to the ali-

quots introduced to the cell in the case of copper. This

effectively suppressed the maxima. No suppressant was neces-

sary with the cadmium or europium.

Helium or argon was bubbled through the cell prior to

making a measurement to remove oxygen.

The diffusion currents of the samples and attendant

standards were used to calculate the percentage of released

cation.

Derivation of the necessary equations proceeds as

follows:

When equal molar amounts of the potassium metal chelate

and rare-earth nitrate equilibrate, the rare earth competes

with the metal ion for the chelate,

$$\text{MCh}^{-2} + \text{R}^{+3} \rightleftharpoons \text{RCh}^- + \text{M}^{+2} \quad ,$$
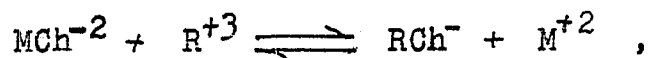
where M is copper or cadmium, R is the rare earth or scandium, and Ch stands for a tetrabasic chelate. The reduction waves which were measured for this research were
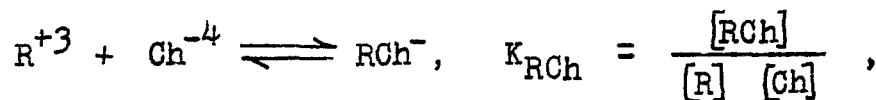
$$2\text{e}^- + \text{Cu}^{+2} \rightleftharpoons \text{Cu}, \quad E_{\frac{1}{2}} \approx -0.05 \quad ,$$

$$2\text{e}^- + \text{Cd}^{+2} \rightleftharpoons \text{Cd}, \quad E_{\frac{1}{2}} \approx -0.60 \quad , \text{ and}$$

$$\text{e}^- + \text{Eu}^{+3} \rightleftharpoons \text{Eu}^{+2}, \quad E_{\frac{1}{2}} \approx -0.68 \quad .$$
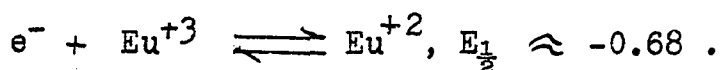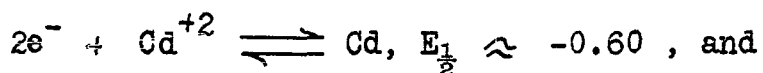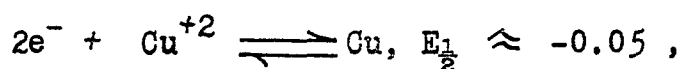
The diffusion current is proportional to the concentration of the species producing the polarographic wave. The percentage of uncomplexed copper was calculated from the ratio of the diffusion currents of each of the rare-earth runs to those of the two reference solutions. Since the metal-chelate waves were far enough removed from the free-metal waves in all cases, no correction for contribution by the completely complexed reference solution was necessary.

Since the reactants were originally present in equimolar quantities, the following expressions hold at equilibrium: $[\text{RCh}] = [\text{M}]$ and $[\text{MCh}] = [\text{R}] = \text{C} - [\text{M}]$ where C is the initial concentration of both reactants. The equilibrium constant for the exchange reaction is

$$K_{eq.} = \frac{[M] \; [RCh]}{[MCh] \; [R]} \; .$$

If one writes the equations for the complexing of the rare earth and cadmium and their accompanying constants,

$$R^{+3} + Ch^{-4} \rightleftharpoons RCh^{-}, \qquad K_{RCh} = \frac{[RCh]}{[R] \; [Ch]} \; ,$$

and

$$M^{+2} + Ch^{-4} \rightleftharpoons MCh^{-2}, \qquad K_{MCh} = \frac{[MCh]}{[M] \; [Ch]} \; ,$$
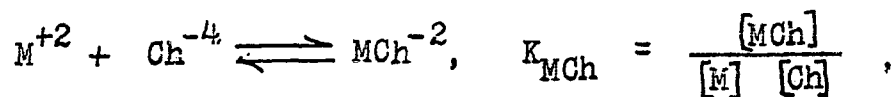
it is evident that

$$K_{eq.} = \frac{K_{RCh}}{K_{MCh}} = \frac{[M] \; [RCh]}{[MCh] \; [R]} = \frac{[M]^2}{(C - [M])^2} \; .$$

Therefore,

$$K_{RCh} = K_{MCh} \frac{(\% \; M)^2}{(100 - \% \; M)^2}$$

or

$$2 \log \frac{\% \; M}{100 - \% \; M} = \log K_{RCh} - \log K_{MCh} \; .$$

The values of log K_{MCh} for copper and cadmium which were used to compute the rare-earth and scandium constants are given in Table 18.

When stability constants for EDTA, HEDTA and DCTA with scandium were measured against copper no extraneous waves were noted in the polarograms. Data for these measurements are presented in Table 24. Figure 28 is the HEDTA-Sc-Cu

Table 18. Copper-chelate and cadmium-chelate stability constants used in calculating the rare-earth and scandium-chelate constants

Chelating agent	Copper constant	Cadmium constant	Temperature °C.
EDTA	18.80[a]	16.62[b]	20
HEDTA	17.4[c]	13.0[c]	29.6
DCTA	21.30[d]	19.23[d]	20
DETPA	---	18.93[e]	20
DE	---	16.73[b]	20
ME	---	16.27[b]	20

[a]Reference 123, p. 76.

[b]Reference 150.

[c]Reference 123, p. 78.

[d]Reference 123, p. 89.

[e]Reference 151.

Figure 28. Polarographic curves obtained for the HEDTA-scandium-
copper case

HEDTA
29.6° C
sens = 0.06
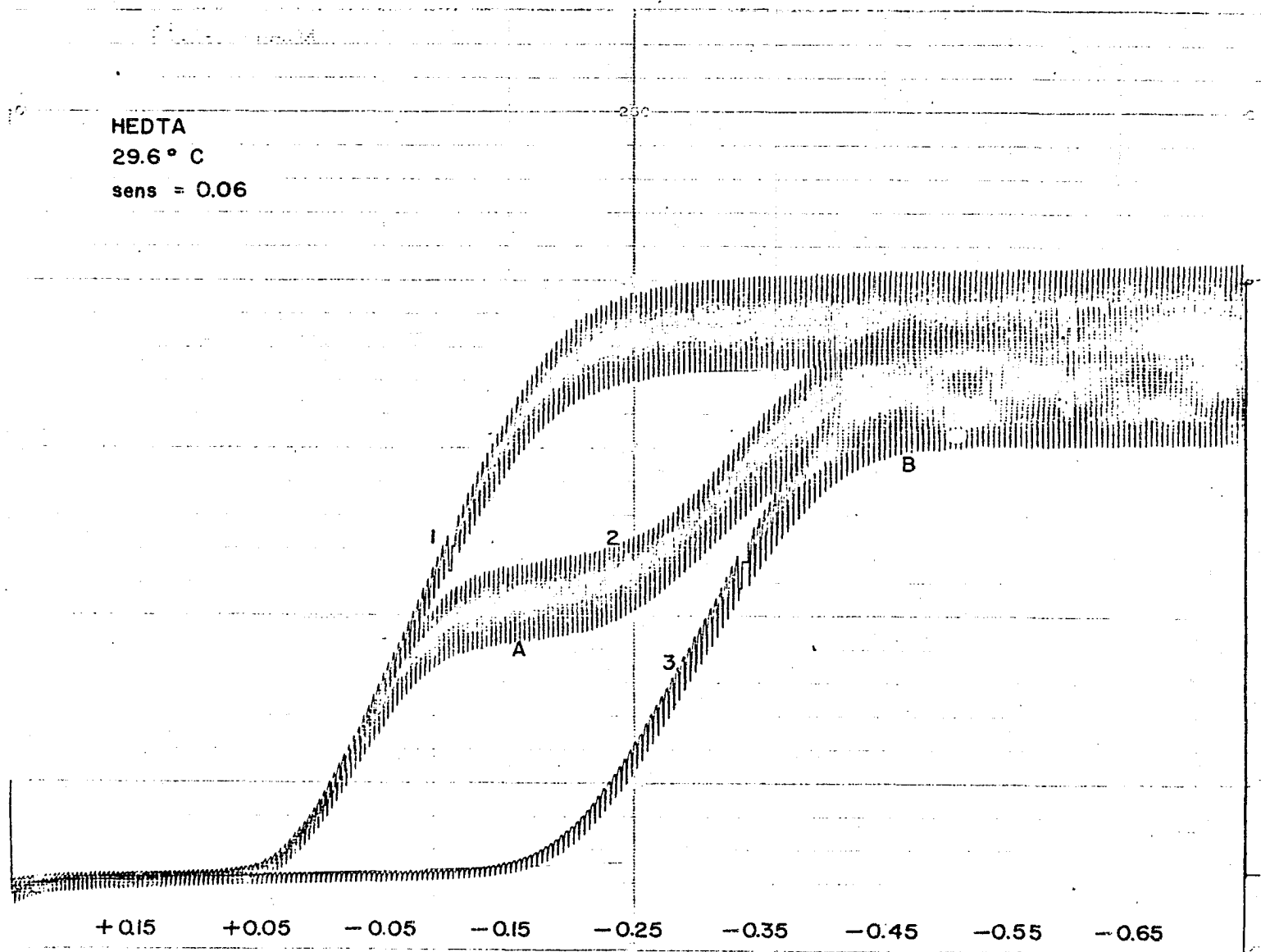
curve which illustrates the general appearance of the measurable polarographic curves. In the case of DETPA, ME, and DE, however, it was impossible to use copper as the standard because curves such as shown in Figure 29 resulted. The waves labeled A, B, and C on curve number 2 were due to copper ion, di-copper chelate, and copper chelate species, respectively. Since it was known that cadmium-DETPA gave a single break when titrated with base, indicating complete dissociation of the hydrogen-cadmium chelate, and also exhibited no tendency to form a di-cadmium species, as indicated by titration curves and polarographic studies, it was decided to use cadmium as a standard for the scandium and rare-earth chelate measurements. However, it was soon discovered that the cadmium-chelate stability constants were so much smaller than the scandium-chelate constants that almost 100% of the cadmium was released in every case. As a consequence large errors resulted.

The method used in measuring the diffusion currents for all of the polarographic determinations is shown in Figure 30. The lines are drawn in order from A-A' to H-H'. J-J' is then drawn through the intersection of C-C' and H-H'. The diffusion current is measured as the length from the intersection of B-B' with J-J' to the intersection of A-A' with J-J'. The half-wave potential is the ratio of the length R-L to the voltage per unit length.

Figure 29. Polarographic curves obtained for the DETPA-scandium-copper
            case. Curve 1 is due to the free copper ion; curve 2 is
            the equilibrium mixture; and curve 3 is the completely
            chelated copper. The letters on each curve mark the
            individual waves observed in that curve

DETPA
20° C
sens = 0.04
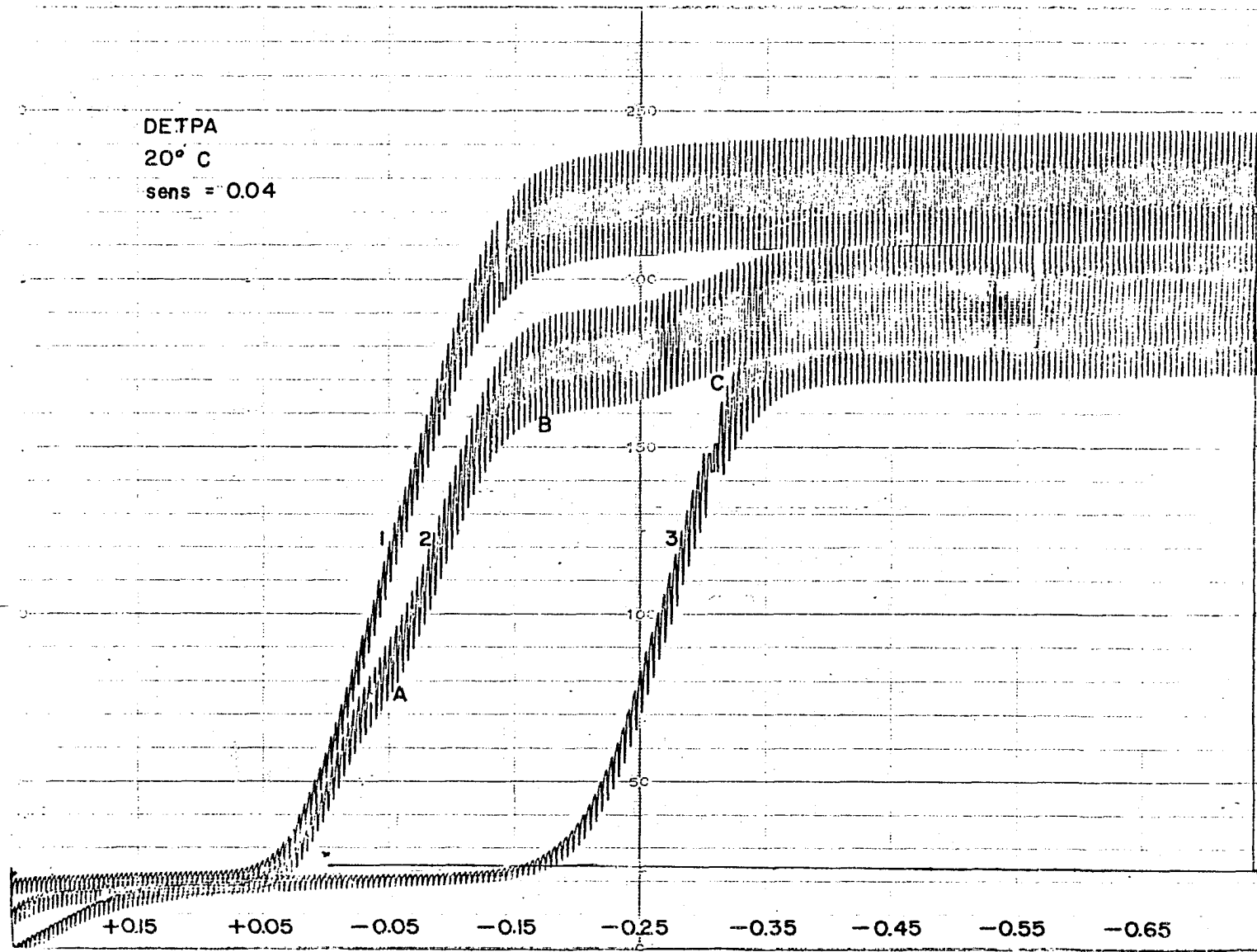
142b

Figure 30. Construction of lines for determining the diffusion
current from the polarographic curves

—VOLTS—

—AMPERES—
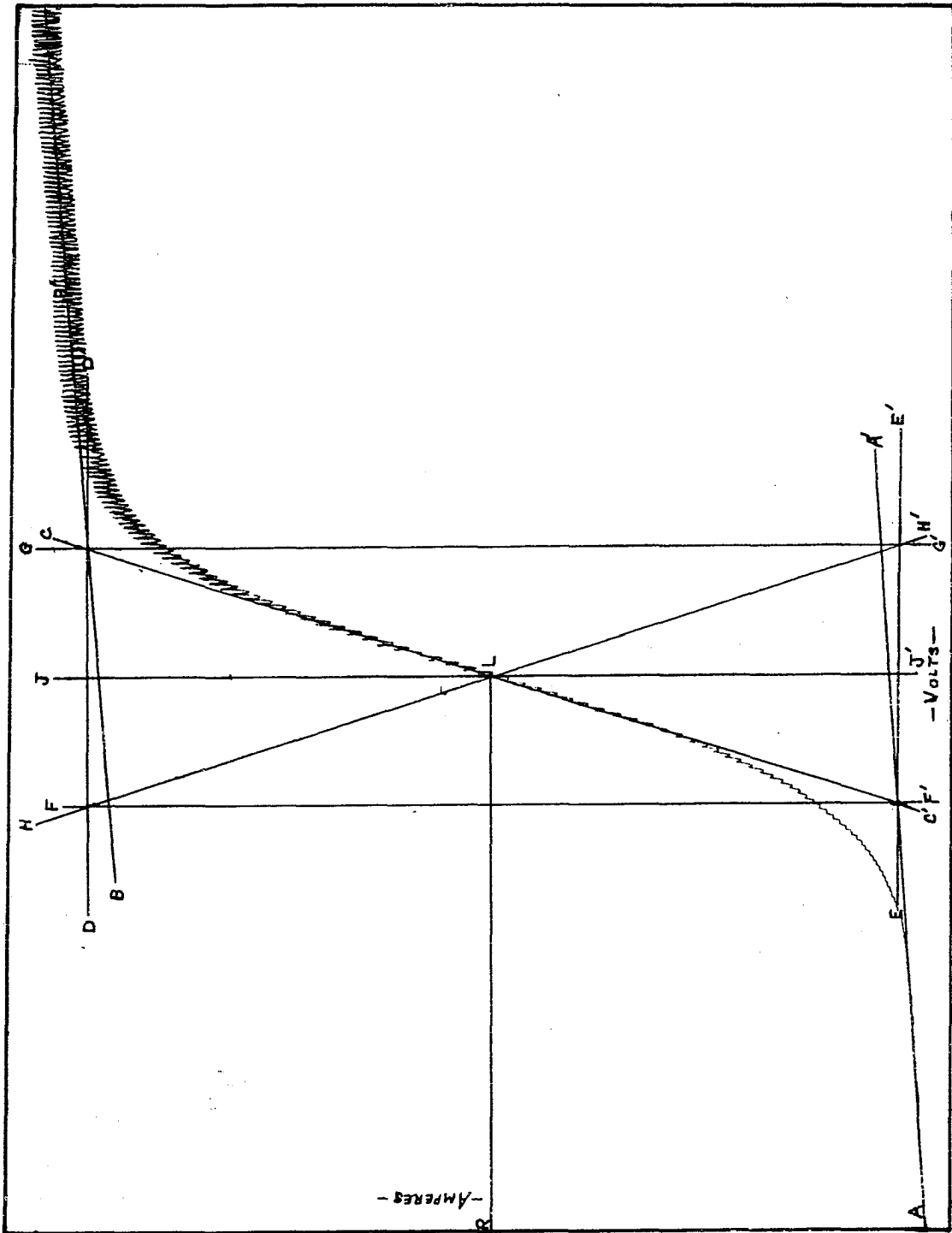
Because of the failure of the cadmium to give measurable
answers with scandium, a standard was needed which had a much
larger stability constant. Europium met this requirement and
subsequently, all the scandium chelates were done against
europium and the ME-rare earth and DE-rare earth constants
were measured against both cadmium and europium. The
europium constants are given in Table 19.

Table 19. Europium-chelate stability constants used in
calculating the scandium-chelate constants

Chelating agent	Europium constant	Temperature $^{\circ}$C.
EDTA	17.35[a]	20
HEDTA	15.21[b]	25
DCTA	18.62[c]	20
DETPA	22.91[d]	25
DE	17.80[e]	20
ME	17.72[e]	20

[a]Reference 123, p 76.

[b]Reference 122.

[c]Reference 123, p. 89.

[d]Unpublished data of Harder and Chaberek.

[e]This research.

The trend in the polarographic waves for the DE-rare earth case is shown in Figure 31 and the data obtained from all the polarographic runs on DE and ME are presented in Tables 20-23 with accompanying Figures 32-35 while the scandium results are to be found in Table 24.

All runs were done at an ionic strength of 0.1 with potassium nitrate as the supporting electrolyte. The voltage limits used in measurements on copper were + 0.25 to -0.75, those for cadmium were -0.30 to -1.30, and those for europium were -0.40 to -1.1

Discussion

The error made in the determination of the per cent uncomplexed metal ion amounts to about $\pm$ 2% and should be constant for all the determinations. The errors range from $\pm$ 0.08 to $\pm$ 0.17 for the rare-earth DE and ME cases.

The determinations made with europium as a standard give an independent means of determining the absolute stability constants for the rare-earth ME and DE series if the europium constant is determined independently in the future.

Two values for the scandium-EDTA constant can be found in the literature. Schwarzenbach, Gut and Anderegg (149) give 23.1 and Schwarzenbach in another publication (152) gives 21.3. The discrepancy was not clarified by Schwarzenbach
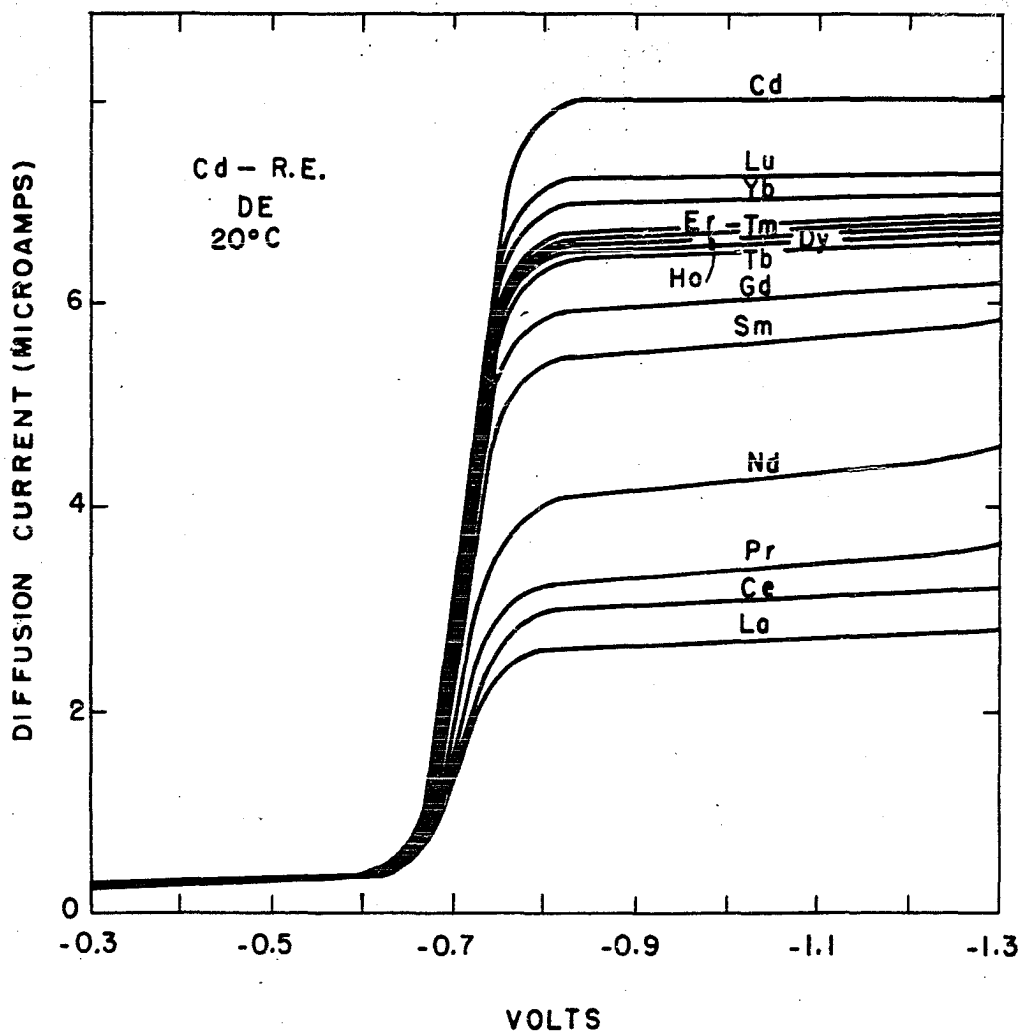
Figure 31. Progressive trends in the polarographic curves for the DE-rare earth system using cadmium as the standard. The general character of the ME curves was identical

Table 20.   Rare earth-DE stability constants at 20.00
$\pm$ 0.02° C. vs. cadmium

Rare earth	% Uncomplexed cadmium	Log K_{MCh}
La	27.1	15.87
Ce	32.5	16.09
Pr	35.2	16.20
Nd	46.8	16.62
Sm	65.4	17.28
Eu[a]		17.80
Gd	71.6	17.53
Tb	77.9	17.83
Dy	78.9	17.87
Ho	80.0	17.93
Er	81.8	18.03
Tm	80.9	17.99
Yb	85.2	18.25
Lu	88.6	18.51
Y	63.2	17.19

[a]The europium could not be measured against cadmium
since the half-wave potentials for europium and cadmium are
too close.   The value given here was obtained by comparing
europium to neodymium, gadolinium, and dysprosium.
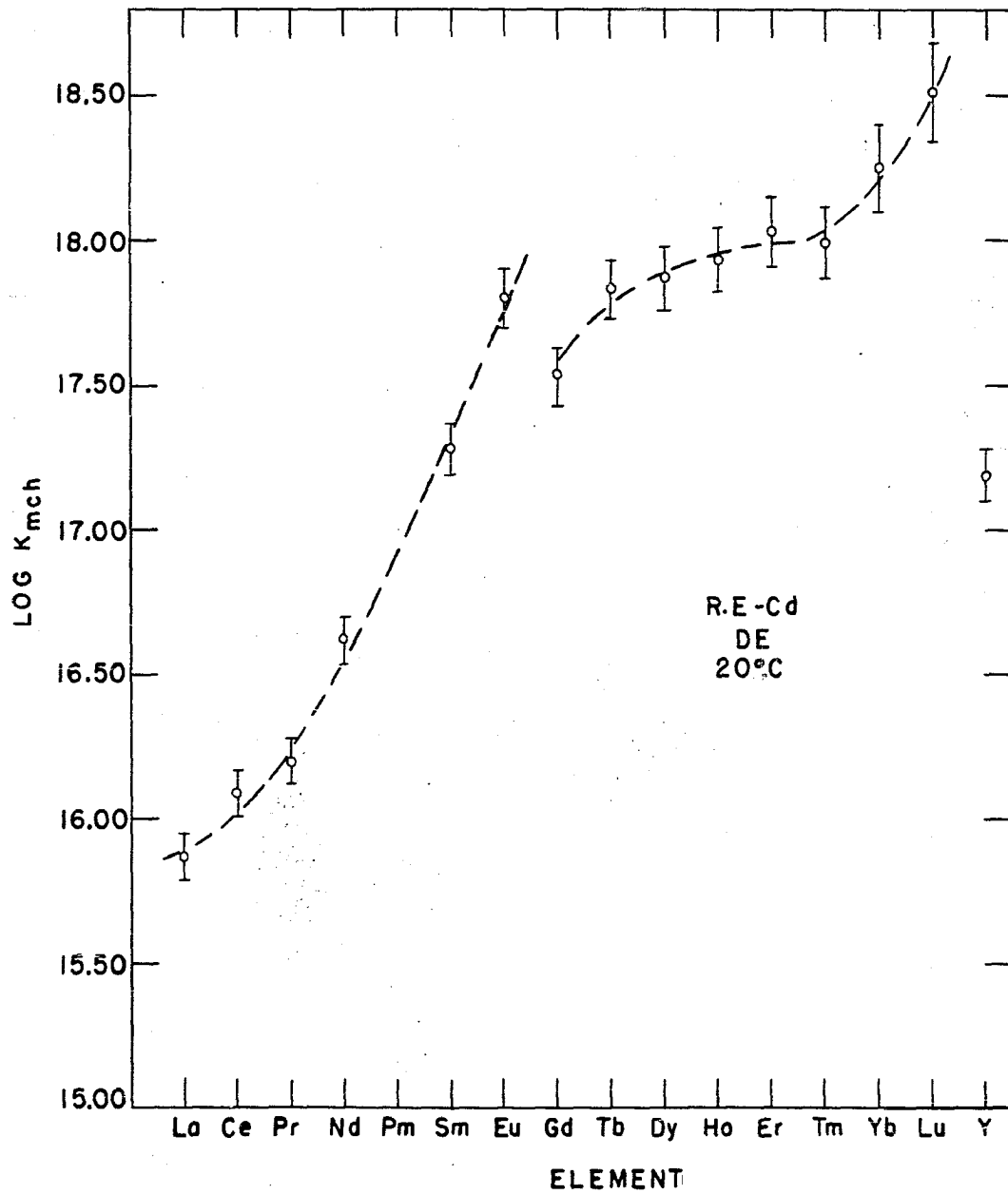
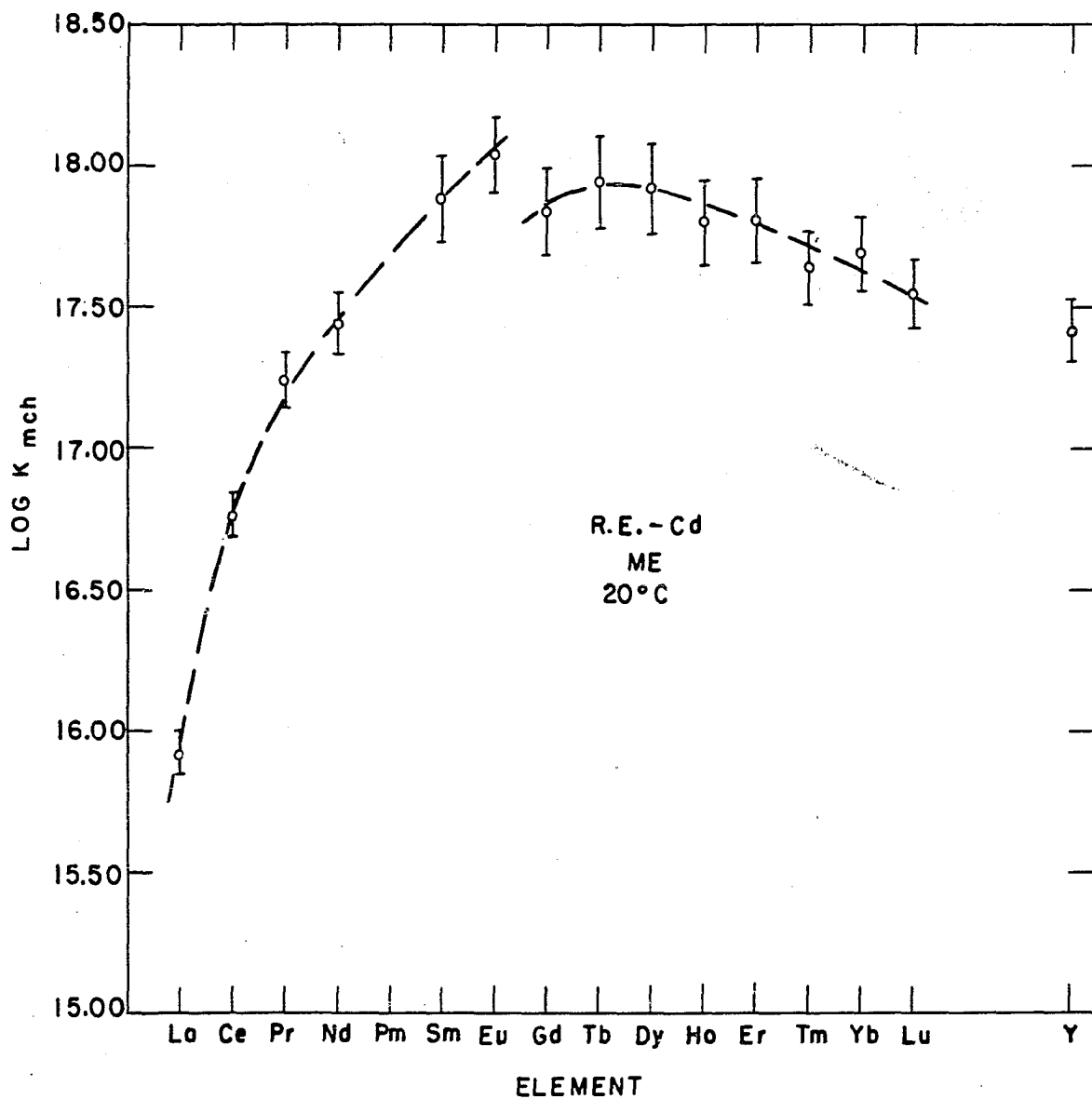Figure 32. Rare earth-DE-stability constants at 20.00 ± 0.02° C., based on cadmium, and showing the uncertainty range

Table 21. Rare earth-DE stability constants at 20.00
± 0.02° C. vs. europium

Rare earth	% Uncomplexed europium	Log K_{MCh}
La	9.81	-1.93
Ce	13.0	-1.65
Pr	15.6	-1.47
Nd	20.3	-1.19
Sm	35.2	-0.52
Eu		Standard
Gd	42.3	-0.27
Tb	52.2	+0.08
Dy	52.8	+0.10
Ho	54.4	+0.15
Er	55.4	+0.19
Tm	57.0	+0.25
Yb	61.9	+0.42
Lu	67.2	+0.60
Y	35.1	-0.53
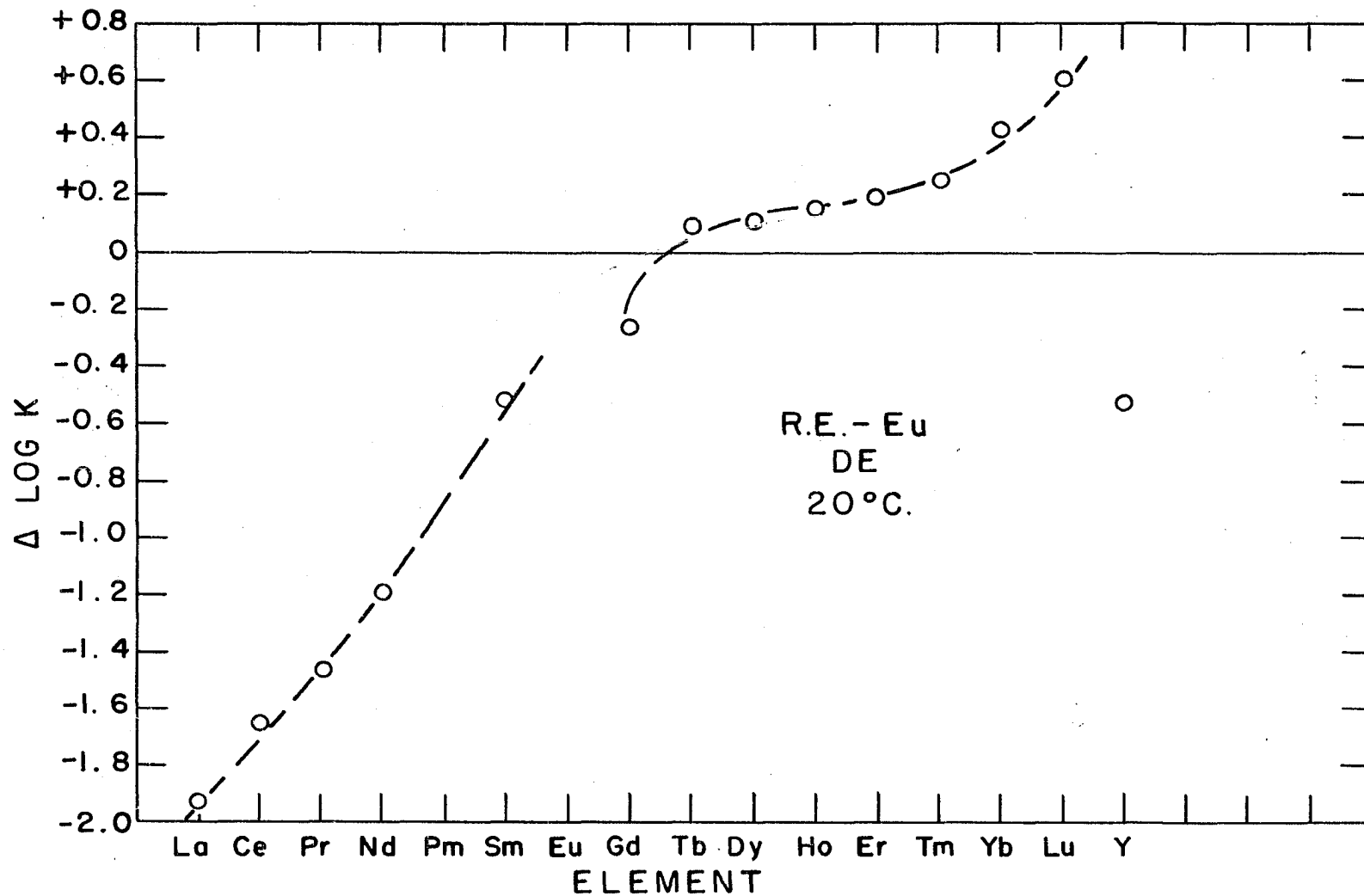
Figure 33. Rare earth-DE-stability constants at 20.00_0.02° C., based on europium

Table 22.   Rare earth-ME stability constants at 20.00
± 0.02° C. vs. cadmium

Rare earth	% Uncomplexed cadmium	Log K_{MCh}
La	40.2	15.92
Ce	63.8	16.76
Pr	75.3	17.24
Nd	79.3	17.44
Sm	86.4	17.88
Eu[a]		18.04
Gd	85.9	17.84
Tb	87.2	17.94
Dy	87.0	17.92
Ho	85.4	17.80
Er	85.5	17.81
Tm	82.9	17.64
Yb	83.7	17.69
Lu	81.4	17.55
Y	79.0	17.42

[a]The europium could not be measured against cadmium
since the half-wave potentials for europium and cadmium are
too close. The value given here was obtained by comparing
europium against neodymium, gadolinium, and dysprosium.

Figure 34. Rare earth-ME stability constants at 20.00
± 0.02° C., based on cadmium, and showing the
uncertainty range

Table 23. Rare earth-ME stability constants at 20.00 ± 0.02° C. vs. europium

Rare earth	% Uncomplexed europium	Log K_{MCh}
La	3.05	-3.00
Ce	11.3	-1.79
Pr	21.4	-1.13
Nd	26.4	-0.89
Sm	41.7	-0.29
Gd	45.4	-0.16
Eu		Standard
Tb	46.9	-0.11
Dy	45.5	-0.16
Ho	43.8	-0.22
Er	39.8	-0.36
Tm	34.5	-0.56
Yb	31.0	-0.70
Lu	25.7	-0.92
Y	25.4	-0.94
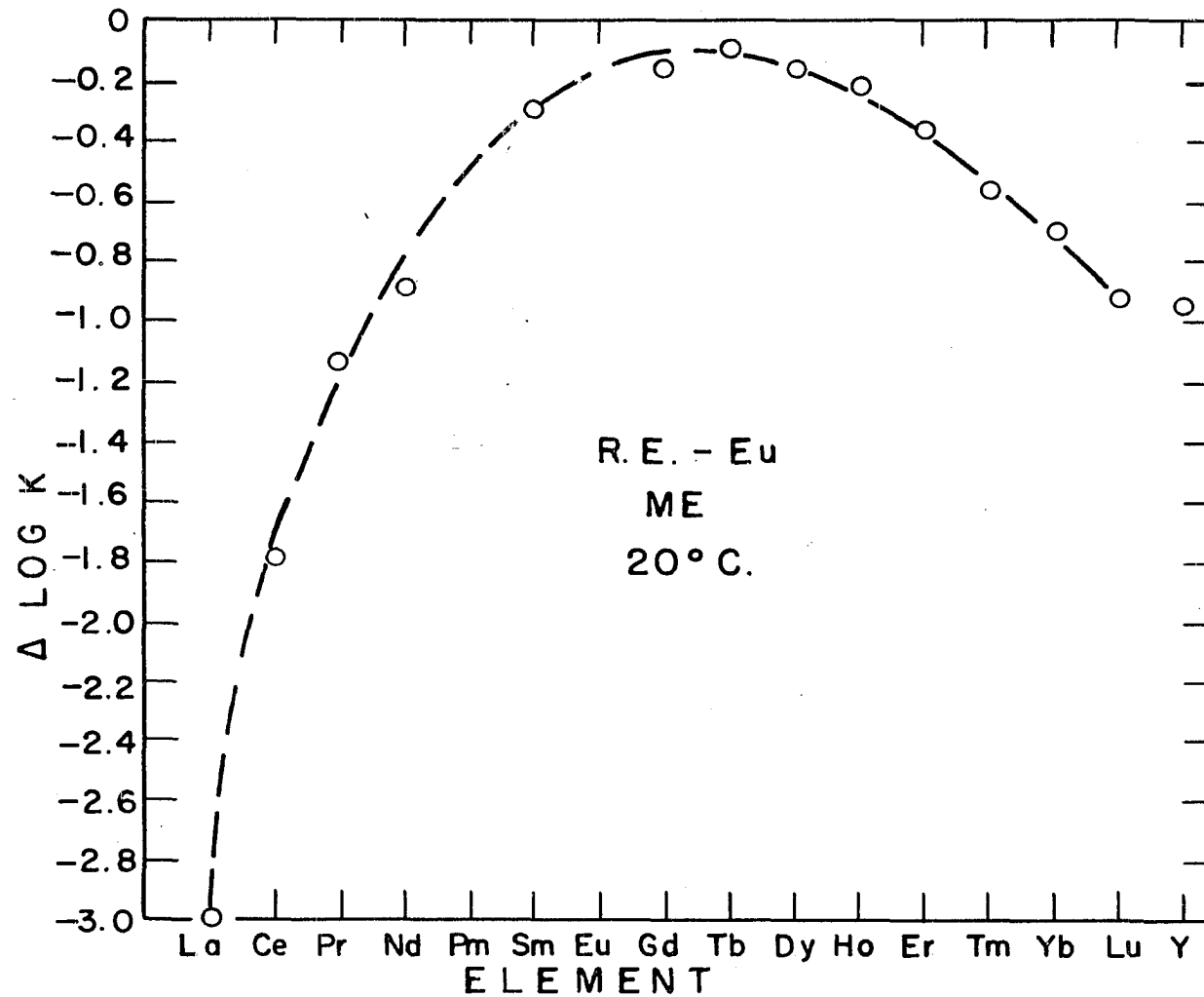
Figure 35. Rare earth-ME stability constants at 20.00 _ 0.02° C., based on europium

Table 24. Scandium-chelate stability constants as measured
against europium and copper

Chelating agent	% Uncomplexed metal ion		Temperature ± 0.02° C.	Log K_{ScCh}	
	Eu	Cu		From Eu	From Cu
EDTA	----[a]	92.5	20	----[a]	20.98±0.90
HEDTA	85.9	47.2	25	16.78±0.15	17.30±0.07
DCTA	----[a]	90.0	20	----[a]	23.21±0.23
DETPA	84.5		25	24.38±0.14	
DE	90.6		20	19.80±0.23	
ME	49.6		20	18.13±0.07	

[a]The europium-chelate stability constants in these cases
were so much smaller than the scandium-chelate constants that
it was impossible to obtain accurate values of the scandium
chelate stability constants by this route.

in reply to a letter from the author. The value obtained in
this research supports the value of 21.3. In view of the re-
sults obtained by the author in separating lutetium and
scandium (153), it would seem the value of 21.3 is more nearly
correct since better separations should have resulted if the
value were 23.1.

In considering the mixtures used in determining the
stability constants polarographically, it was seen that
perhaps hydrogen metal chelate species and metal acetate
complexes should be considered.

To facilitate the discussion and derivations, from here on, the equations will be numbered, a practice not deemed necessary until now.

If we consider the reaction

$$CdCh^{-2} + R^{+3} \rightleftharpoons RCh^- + Cd^{+2} \qquad (Eq. 1)$$
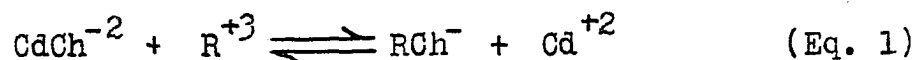
which is the basic process being measured, an "exchange constant", K_{ex}, can be written,

$$K_{ex} = \frac{[RCh^-] [Cd^{+2}]}{[CdCh^{-2}] [R^{+3}]} \qquad (Eq. 2)$$

where R stands for rare earth.

Material balance equations which can be written are:

$$\text{total chelate} = Ch_T = RCh^- + HRCh + CdCh^{-2} +$$

$$HCdCh^- + H_4Ch + H_3Ch^- + H_2Ch^{-2} +$$

$$HCh^{-3} + Ch^{-4} ; \qquad (Eq. 3)$$

$$\text{total rare earth} = R_T = R^{+3} + RCh^- + HRCh +$$

$$RAc^{+2} + RAc_2^+ + RAc_3 ; \qquad (Eq. 4)$$

total cadmium = Cd_T = Cd^{+2} + $CdCh^{-2}$ +
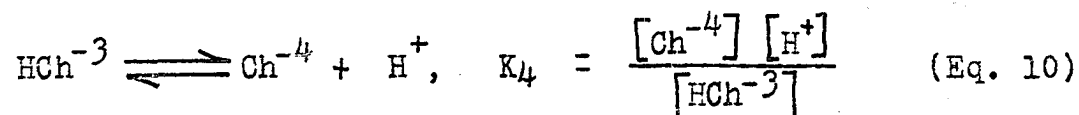
$HCdCh^-$ + $CdAc^+$ + $CdAc_2$ + $CdAc_3^-$;   (Eq. 5)
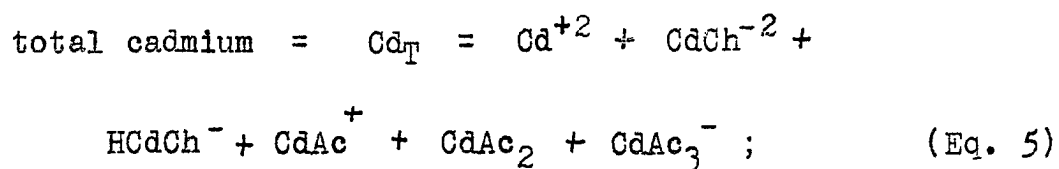
and, since in the case of the research reported here, the cadmium, rare-earth, and chelate concentrations are equal;

$$Cd_T = R_T = Ch_T .$$ (Eq. 6)

The equations and their accompanying ionization constants for the free-acid chelate species are:

$$H_4Ch \rightleftharpoons H_3Ch^- + H^+ , \quad K_1 = \frac{[H_3Ch^-][H^+]}{[H_4Ch]} ;$$ (Eq. 7)

$$H_3Ch^- \rightleftharpoons H_2Ch^{-2} + H^+, \quad K_2 = \frac{[H_2Ch^{-2}][H^+]}{[H_3Ch^-]} ;$$ (Eq. 8)

$$H_2Ch^{-2} \rightleftharpoons HCh^{-3} + H^+, \quad K_3 = \frac{[HCh^{-3}][H^+]}{[H_2Ch^{-2}]} ,$$ (Eq. 9)

and

$$HCh^{-3} \rightleftharpoons Ch^{-4} + H^+, \quad K_4 = \frac{[Ch^{-4}][H^+]}{[HCh^{-3}]}$$ (Eq. 10)
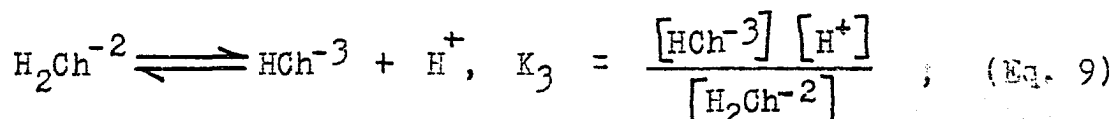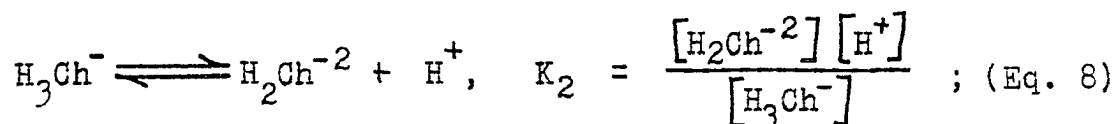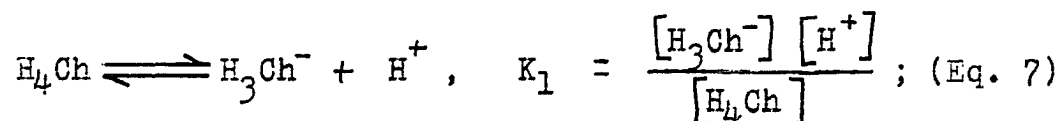
where, for the EDTA case, $K_1 = 10^{-1.99}$, $K_2 = 10^{-2.67}$, $K_3 = 10^{-6.16}$, and $K_4 = 10^{-10.26}$ at 20° C. (118, p. 76).

By combination of Eqs. 7-10, one obtains

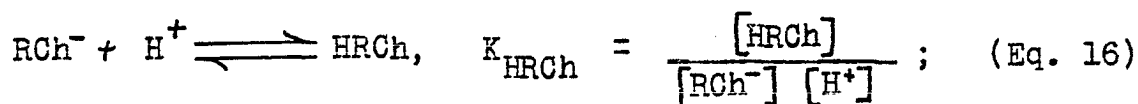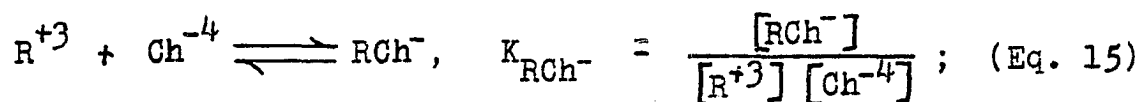$$[H_4Ch] = \frac{[H^+]^4 [Ch^{-4}]}{K_1 K_2 K_3 K_4} \quad , \qquad \text{(Eq. 11)}$$

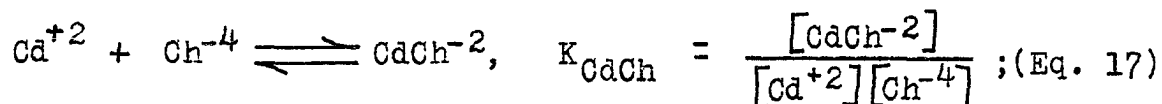$$[H_3Ch^-] = \frac{[H^+]^3 [Ch^{-4}]}{K_2 K_3 K_4} \quad , \qquad \text{(Eq. 12)}$$

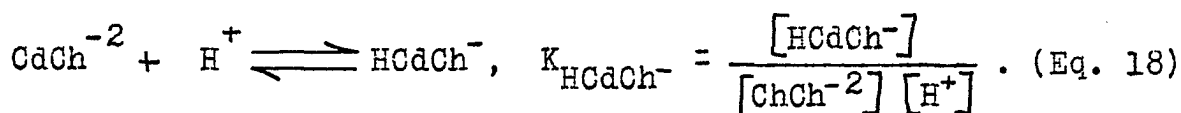$$[H_2Ch^{-2}] = \frac{[H^+]^2 Ch^{-4}}{K_3 K_4} \quad , \qquad \text{(Eq. 13)}$$

and

$$[HCh^{-3}] = \frac{[H^+] [Ch^{-4}]}{K_4} \quad . \qquad \text{(Eq. 14)}$$

In addition, several other formation constants are needed; these are

$$R^{+3} + Ch^{-4} \rightleftharpoons RCh^-, \quad K_{RCh^-} = \frac{[RCh^-]}{[R^{+3}] [Ch^{-4}]} \; ; \quad \text{(Eq. 15)}$$

$$RCh^- + H^+ \rightleftharpoons HRCh, \quad K_{HRCh} = \frac{[HRCh]}{[RCh^-] [H^+]} \; ; \quad \text{(Eq. 16)}$$

$$Ca^{+2} + Ch^{-4} \rightleftharpoons CdCh^{-2}, \quad K_{CdCh} = \frac{[CdCh^{-2}]}{[Ca^{+2}][Ch^{-4}]} \; ; (Eq. \; 17)$$

and

$$CdCh^{-2} + H^+ \rightleftharpoons HCdCh^-, \quad K_{HCdCh^-} = \frac{[HCdCh^-]}{[ChCh^{-2}][H^+]} \cdot (Eq. \; 18)$$

By solving Eq. 15 for $[RCh^-]$, Eq. 16 for $[HRCh]$, Eq. 17 for $[CdCh^{-2}]$, Eq. 18 for $[HCdCh^-]$, and substituting these in Eq. 3 along with the values of $[H_4Ch]$, $[H_3Ch^-]$, $[H_2Ch^{-2}]$, and $[HCh^{-3}]$ from Eqs. 11-14, respectively, one obtains

$$Ch_T = \left[K_{RCh^-}[R^{+3}] + K_{HRCh}K_{RCh^-}[H^+][R^{+3}] + K_{CdCh^{-2}}[Ca^{+2}] + \right.$$
$$K_{HCdCh^-}K_{CdCh^{-2}}[H^+][Ca^{+2}] + [H^+]^4/K_1K_2K_3K_4 +$$
$$\left. [H^+]^3/K_2K_3K_4 + [H^+]^2/K_3K_4 + [H^+]/K_4 + 1 \right][Ch^{-4}] \quad (Eq. \; 19)$$

The H_2CdCh species was neglected since at the pH of the buffer (4.65) the $HCdCh^-$ or $CdCh^{-2}$ would be expected to be predominant.
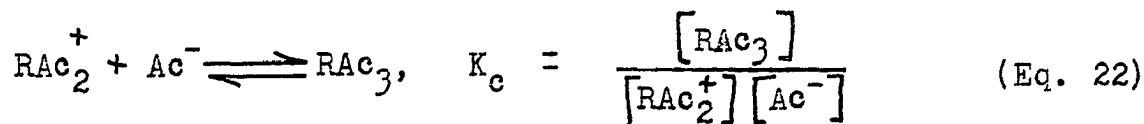
We can make some substitutions in Eq. 19 for the EDTA case which will show the hydrogen-metal-chelate species to be unimportant compared to the RCh^- and $CdCh^{-2}$ species.

If we use the average value of 10^{16} for K_{RCh^-} and $10^{16.5}$ for $CdCh^{-2}$ as given by Bjerrum, Schwarzenbach, and Sillén (123, p. 76), 10^2 for K_{HRCh} according to Hagiwara (154), and $10^{2.5}$ for K_{HCdCh^-} as given by Powell, Fritz, and James (155), then at a pH of 4.5 the $[H^+]$ is $10^{-4.5}$ and at 50% complexing $[Cd^{+2}]$ is $10^{-3.3}$ and $[R^{+3}]$ is $10^{-3.3}$. Substituting these values into Eq. 19 shows that all terms except those relating to the RCh^- and $CdCh^{-2}$ species are negligible in the case of EDTA at a pH of 4.5.
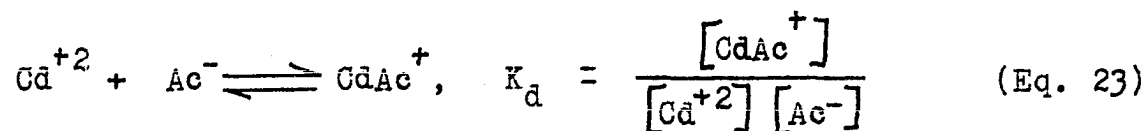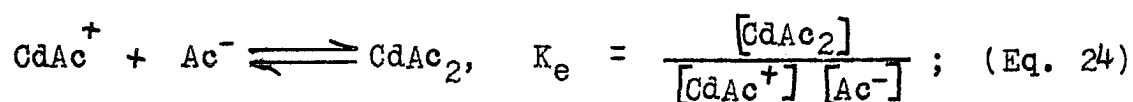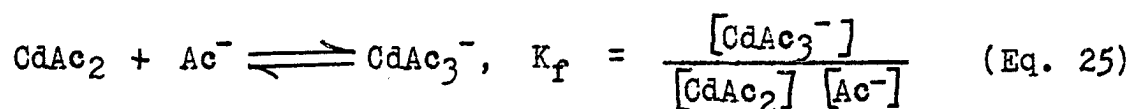
Likewise, one can write

$$R^{+3} + Ac^- \rightleftharpoons RAc^{+2}, \quad K_a = \frac{[RAc^{+2}]}{[R^{+3}][Ac^-]} ; \qquad \text{(Eq. 20)}$$

$$RAc^{+2} + Ac^- \rightleftharpoons RAc_2^+, \quad K_b = \frac{[RAc_2^+]}{[RAc^{+2}][Ac^-]} ; \qquad \text{(Eq. 21)}$$

and

$$RAc_2^+ + Ac^- \rightleftharpoons RAc_3, \quad K_c = \frac{[RAc_3]}{[RAc_2^+][Ac^-]} \qquad \text{(Eq. 22)}$$
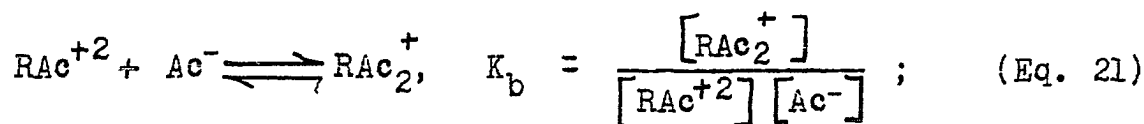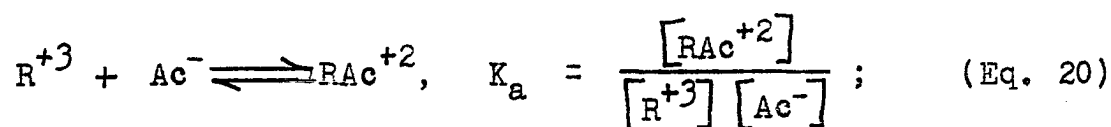
for the rare-earth species and

$$Cd^{+2} + Ac^- \rightleftharpoons CdAc^+, \quad K_d = \frac{[CdAc^+]}{[Cd^{+2}][Ac^-]} \qquad \text{(Eq. 23)}$$

$$CdAc^+ + Ac^- \rightleftharpoons CdAc_2, \quad K_e = \frac{[CdAc_2]}{[CdAc^+][Ac^-]} \; ; \quad (Eq.\ 24)$$

and

$$CdAc_2 + Ac^- \rightleftharpoons CdAc_3^-, \quad K_f = \frac{[CdAc_3^-]}{[CdAc_2][Ac^-]} \quad (Eq.\ 25)$$

for the cadmium species.

Combination of Eqs. 20-25 with Eqs. 4 and 5 give

$$R_T = [RCh^-] + \left\{ 1 + K_a[Ac] + K_aK_b[Ac]^2 + K_aK_bK_c[Ac]^3 \right\}[R^{+3}] \quad (Eq.\ 26)$$

and

$$Cd_T = [CdCh^{-2}] + \left\{ 1 + K_d[Ac] + K_dK_e[Ac]^2 + K_dK_eK_f[Ac]^3 \right\}[R^{+3}]. \quad (Eq.\ 27)$$

Now from Eqs. 26 and 27,

$$[R^{+3}] = \frac{R_T - [RCh^-]}{F(Ac)} \quad (Eq.\ 28)$$

and

$$[Ca^{+2}] = \frac{Cd_T - [CdCh^{-2}]}{f(Ac)} \quad (Eq.\ 29)$$

where $F(Ac)$ and $f(Ac)$ are functions of the acetate concentration as expressed by the bracketed terms in Eqs. 26 and 27.

Substitution of Eqs. 28 and 29 in Eq. 2 then gives

$$K_{ex} = \frac{K_{RCh^-}}{K_{CdCh^{-2}}} = \frac{[RCh^-]\,[Cd_T - CdCh^{-2}]\,F(Ac)}{[CdCh^{-2}]\,[R_T - RCh^-]\,f(Ac)} \ . \qquad (Eq. \ 30)$$

In the mixtures which were used in this research, Eq. 19 was shown to reduce to

$$Ch_T = [RCh^-] + [CdCh^{-2}] \ . \qquad (Eq. \ 31)$$

Then, by virtue of Eq. 6,

$$[RCh^-] = Ch_T - [CdCh^{-2}] = R_T - [CdCh^{-2}] = Cd_T - [CdCh^{-2}]. \qquad (Eq. \ 32)$$

Thus Eq. 30 can be further revised to give

$$K_{ex} = \frac{[Ch_T - CdCh^{-2}]^2\,F(Ac)}{[CdCh^{-2}]^2\,f(Ac)} \ . \qquad (Eq. \ 33)$$

The $F(Ac)$ and $f(Ac)$ effectively cancel for the case of rare earth vs. europium, copper or cadmium since $K_a \approx K_d$, $K_b \approx K_e$, and $K_c \approx K_f$ (123, p. 3). This leaves an expression

for K_{ex} which is identical with the original constant that was to be measured polarographically (Eq. 2).

The acetate and hydrogen-chelate stability constants should be determined in the future at an ionic strength of 0.1 to make sure that the above assumptions are valid for chelating agents other than EDTA. The polarograms obtained with the lighter rare earths in the case of both ME and DE showed a small wave which was attributed to the presence of a small concentration of hydrogen metal chelate species (HCdCh or HEuCh). No correction was made for this since the values of K_{HCdCh} and K_{HEuCh} were not known for the case of ME and DE.

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ACKNOWLEDGMENTS