Heats of dilution and related thermodynamic properties of aqueous neodymium chloride and erbium chloride solutions

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UMI®
HEATS OF DILUTION AND RELATED THERMODYNAMIC
PROPERTIES OF AQUEOUS NEODYMIUM CHLORIDE AND
ERBIUM CHLORIDE SOLUTIONS

by

Alfred Wayne Neumann

A Dissertation Submitted to the
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INTRODUCTION

Solutions of electrolytes in water play an important role in almost all of man's endeavors. Geologists and uranium prospectors are very much concerned with sedimentary rocks laid down by electrolytic solutions in the distant past. Farmers owe their livelihoods to the action of solutions in converting rocks into fertile soil, and to the solution processes by which plants obtain nutrients for growth. The health of man and other animals is known to be dependent upon the balance of electrolytes in body fluids. Solutions of electrolytes are so common one is hard pressed to name a field that is not concerned with their behavior.

Since water is a common reaction media, solutions of electrolytes in water are of extreme interest to the chemist. Reaction mechanisms and reaction kinetics are dependent upon the conditions within solutions at a molecular level. A knowledge of the forces of interaction between ions, the forces of interaction between ions and solvent molecules, and the microscopic structure of solutions is needed to completely understand solutions and solution phenomena.

Since measurements on individual ions or molecules are not applicable to solutions, the experimental approach to the study of solutions is by necessity restricted to the measurement of properties of the solution as a whole. Theoretical studies then try to infer
microscopic behavior from the results of these macroscopic measurements. This process is complicated by the number of variables responsible for the behavior of solutions. Some of the factors are the concentrations of the electrolytes, the valence type of the electrolytes, the size of the ions, the tendency of the ions to associate, and temperature and pressure effects.

Establishing the effect of ion size is a particularly troublesome problem. In addition to its effect on the energy of interactions between ions and solvent molecules, the ion size also influences the tendency for ions to hydrolyze or associate with other ions in solution. The ideal system for studying the effect of ion size would be ions of a given chemical element that formed strong electrolytes, and whose ion size could be varied. With such a system, all chemical differences exclusive of those dependent on ion size would be eliminated, and those variations in solution behavior due to changes in ion size could be determined directly. This ideal system is approximated in the lanthanide elements.

The electronic configurations of the lanthanide elements in their normal states vary mainly by the number of electrons in the 4f subshells. Likewise, the stable trivalent ions of the lanthanide elements have similar electronic configurations except for the 4f subshells. With increasing nuclear charge, the force exerted by the nucleus on the electron cloud increases, resulting in a decrease in ionic radius. This process, called the lanthanide contraction, leads to a regular decrease in ionic radius through the rare earth series.
The 4f electrons by which the lanthanide elements differ are in well shielded inner orbitals and contribute little to chemical bonding. As a result, the members of the rare earth series are very similar chemically. The lanthanides form soluble salts with the common strong acids. These salts can be considered strong electrolytes. This unique combination of physical and chemical properties results in an almost ideal series for the study of the effect of ion size.

The study of the properties of rare earth solutions is of theoretical interest for reasons other than the determination of the effect of ion size. While modern solution theories for strong electrolytes are able to predict the limiting behavior of electrolytic solutions, no suitable extension to even moderate concentrations has been successful. In general, deviations from theoretical predictions increase with increasing concentration and with increasing complexity of the valence type of the electrolyte. Since the rare earths form strong 3-1 and 3-2 electrolytes, the lanthanide elements afford a more strenuous test for the validity of theoretical treatments than do the more common 1-1 electrolytes.

In addition to theoretical considerations, a study of the properties of rare earth solutions is desirable from a purely practical standpoint. With the availability of pure rare earth elements in large quantities, the appearance of lanthanide elements as fission products in nuclear reactors, and the recent commercial interest in the rare earths (1), a need has arisen for a backlog of fundamental information.
on physical and chemical properties.

The ion exchange separation techniques developed at the Ames Laboratory (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13) made kilogram quantities of nearly all the rare earth elements available in high purity. This made possible an extensive program for the study of rare earth metals and compounds. The study of properties of the soluble rare earth salts was a part of this program.

Activity coefficients have been determined for rare earth chlorides (14, 15, 16, 17) and bromides (15, 17); transference numbers have been determined for rare earth chlorides (15, 16, 17, 18), bromides (15, 17), perchlorates (19), and nitrates (19, 20); and conductances have been measured for rare earth chlorides (15, 16, 17, 21), bromides (15, 17), perchlorates (19), nitrates (19, 20), and sulfates (22). In all cases, the limiting behavior predicted by the interionic attraction theory of Debye and Hückel (23) was approached at extreme dilution, but departures from theoretical predictions were observed at very low concentrations.

These departures from theoretical predictions may be due to hydration effects and association, as well as to failure of mathematical approximations or simplifying physical assumptions. The departures were found not to change regularly with decreasing ionic radius indicating the possibility of discontinuous changes in hydration or association.

Further evidence for discontinuous hydration or association effects was inferred from partial molar volume data for rare earth chlorides and nitrates (24).
If the departures from theoretical predictions observed for the properties above are due to hydration or association phenomena, heat or energy effects should result. The most effective method for observing heat effects in the concentration ranges where departures from theoretical predictions first occur is the measurement of heats of dilution. Heats of dilution data are usually reported in terms of the related thermodynamic property, \( \phi_L \), the relative apparent molal heat content of the solute. The thermodynamic property \( \phi_L \) should be quite sensitive to the heat effects accompanying hydration and association and should yield considerable information concerning the extent to which such phenomena take place. Comparing \( \phi_L \)'s for salts with a common anion should yield information concerning the effect of ion size.

Further, one can hope to obtain information concerning the relative importance of hydration effects and association by comparing \( \phi_L \)'s for a salt suspected of association with data for a salt where little association is expected.

Heats of dilution determinations also contribute to the existing program in other ways. The thermodynamic function \( \phi_L \) is a useful property for testing the validity of new solution theories or extensions of older theories. Theoretical treatments or extensions usually proceed from some physical model to an expression for the activity coefficient of the solute. In many cases, the development of the theory requires a knowledge of some physical property, such as the number of waters of hydration, which cannot be evaluated by an independ-
ment method. A common practice is to choose the value for this property which best represents the existing activity coefficient data. In some cases, this practice leads to little more than an empirical representation of the data. Since the temperature dependence of the activity coefficient is related to the heat of dilution, a theory that represents activity coefficient data well but does not improve the fit for the relative apparent molal heat content is naturally suspect. The relationship between heats of dilution and the temperature dependence of the activity coefficient may also be used to calculate activity coefficients as a function of temperature.

This report gives the heats of dilution and related thermodynamic properties for but two rare earth salts. It is hoped the results of these measurements and the questions they raise will be of sufficient interest to others to stimulate the continuation of this work.
THEORY

For a system of $N$ components, the activity of the $i$th component, $a_i$, is defined in terms of the chemical potential of that component.

$$\mu_i = \mu^0_i + RT \ln a_i$$

where $R = \text{gas constant}$,

$T = \text{absolute temperature}$, and

$\mu^0_i = \text{chemical potential of some arbitrary standard state}.$

By convention, if the $i$th component is an electrolyte, the activity is expressed as

$$a_i = a_\uparrow^\nu$$

where $a_\uparrow = \text{mean ionic activity}$,

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

$\nu_+ = \text{number of positive ions in the electrolyte}$, and

$\nu_- = \text{number of negative ions in the electrolyte}.$

The mean ionic activity can be further subdivided into

$$a_\uparrow = f_\uparrow N_\uparrow$$
where \( f^+ \) = rational activity coefficient,

\[
N^+ = N \left[ \frac{\nu^+}{\nu^-} \right]^{1/\nu}
\]

\( N = \) mol fraction of electrolyte.

For an aqueous solution of lanthanum chloride,

\[
\mu_{\text{LaCl}_3} = \mu_{\text{LaCl}_3}^0 + RT \ln a_{\text{LaCl}_3}
\]

where \( a_{\text{LaCl}_3} = a^4_+ \),

\[
a^+_+ = f^+_+ N^+_+ \), and
\]

\[
N^+_+ = N_{\text{LaCl}_3} \left[ \frac{1}{3} \right]^{1/4}
\]

Combining Equations (1), (2), and (3) yields

\[
\mu_1 = \mu_1^0 + \nu RT \ln f^+_+ + \nu RT \ln N^+_+ .
\]

Since

\[
\frac{3}{3T} \left[ \frac{\mu_2}{T} \right]_P = - \frac{H_2}{T^2} ,
\]

differentiating Equation (5) in respect to \( T \) at constant \( P \) and \( N \)
yields
\[- \nu RT^2 \left[ \frac{\partial \ln f_+}{\partial T} \right]_{P,N} = \overline{H}_2 - \overline{H}_2^0 = \overline{L}_2 \quad (7)\]

where $\overline{H}_2$ = the partial molal heat content of the solute,

$\overline{H}_2^0$ = the partial molal heat content of the solute in the infinitely dilute standard state, and

$\overline{L}_2$ = the relative partial molal heat content of the solute.

The heat content of a two component system can be expressed in two equally acceptable ways:

\[H = n_1 \overline{H}_1 + n_2 \overline{H}_2 \quad (8)\]

or

\[H = n_1 \overline{H}_1^0 + n_2 \overline{\phi}_H \quad (9)\]

where $\overline{H}_1$ = partial molal heat content of the solvent,

$\overline{H}_1^0$ = partial molal heat content of the solvent in the reference state (pure water),

$\overline{\phi}_H$ = apparent molal heat content of the solute, and

$n_1$ and $n_2$ = number of moles of solvent and solute respectively.

Similarly, the infinitely dilute reference state can be expressed,

\[H^0 = n_1 \overline{H}_1^0 + n_2 \overline{H}_2^0 \quad (10)\]
and

\[ H^o = n_1 \overline{H}_1^o + n_2 \phi_H^o. \]  \hspace{2cm} (11)

To be consistent with the existing literature, the following relative heat quantities are defined.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative heat content</td>
<td>( L )</td>
<td>( L = H - H^o )</td>
</tr>
<tr>
<td>Relative partial molal heat content of the solute</td>
<td>( \overline{L}_2 )</td>
<td>( \overline{L}_2 = \overline{H}_2 - \overline{H}_2^o )</td>
</tr>
<tr>
<td>Relative partial molal heat content of the solvent</td>
<td>( \overline{L}_1 )</td>
<td>( \overline{L}_1 = \overline{H}_1 - \overline{H}_1^o )</td>
</tr>
<tr>
<td>Relative apparent molal heat content of the solute</td>
<td>( \phi_L )</td>
<td>( \phi_L = \phi_H - \phi_H^o )</td>
</tr>
</tbody>
</table>

\( \phi_L \) is recognized as the negative of the heat of dilution to infinite dilution.

The following expressions for the relative heat content result from a combination of the above definitions and Equations (8), (9), (10), and (11).

\[ L = n_1 (\overline{H}_1 - \overline{H}_1^o) + n_2 (\overline{H}_2 - \overline{H}_2^o) = n_1 \overline{L}_1 + n_2 \overline{L}_2 \]  \hspace{2cm} (12)

\[ L = n_2 (\phi_H - \phi_H^o) = n_2 \phi_L \]  \hspace{2cm} (13)

\( \overline{L}_2 \) is also defined by

\[ \overline{L}_2 = \left[ \frac{\partial L}{\partial n_2} \right]_{n_1,T,P}. \]  \hspace{2cm} (14)
Hence, from Equations (13) and (14),

\[
\bar{L}_2 = \phi_L + n_2 \frac{\partial \phi_L}{\partial n_2} .
\]  

(15)

Also, from Equations (12) and (13),

\[
\bar{L}_1 = \frac{n_2}{n_1} (\phi_L - \bar{L}_2) .
\]  

(16)

Alternate expressions for Equations (15) and (16) are

\[
\bar{L}_2 = \phi_L + \frac{n_2}{2} \frac{1}{m^{1/2}} \frac{\partial \phi_L}{\partial m^{1/2}} .
\]  

(17)

and

\[
\bar{L}_1 = \frac{m M_1}{1000} (\phi_L - \bar{L}_2) .
\]  

(18)

where \( m \) = molality of solute, and

\( M_1 \) = molecular weight of solvent.

Usually a combination of Equations (7) and (17) constitutes the basis for comparing experimentally determined heats of dilution with theoretical predictions. The Debye-Hückel expression for the rational activity coefficient is
\[ \ln f_+ = \frac{-2.303 \, s(f) \, \Gamma^{1/2}}{1 + A \, \Gamma^{1/2}} \]  

(19)

where \( \Gamma = \sum_{i=1}^{n} c_i z_i^2 \).

\[ s(f) = \frac{1}{\nu} \sum_{i=1}^{n} \nu i \frac{z_i^2}{2.303} \left[ \prod_{i=6}^{H} \frac{1000}{(DkT)^3} \right]^{1/2} \]

\[ A = \frac{0 \, k}{\Gamma^{1/2}}, \text{ and} \]

\[ K = \left[ \frac{4 \, \prod_{i=6}^{E} \frac{H}{2}}{1000 \, DkT} \right]^{1/2} \Gamma^{1/2}. \]

In this expression, \( c_i \) is the concentration of the \( i \)th species in moles per liter; \( z_i \), the charge on the \( i \)th species; \( e_i \), the electronic charge; \( N \), Avogadro's number; \( k \), Boltzmann's constant; \( D \), the dielectric constant of the solvent; and \( A \), the mean distance of closest approach.

Differentiation of Equation (19) with respect to \( \Gamma \) at constant \( P \) and \( \Gamma \) yields

\[ \frac{1}{2} L^2 = \frac{S'(H) \, \Gamma^{1/2}}{1 + A \, \Gamma^{1/2}} + \frac{W(H) \, \Gamma^{1/2}}{[1 + A \, \Gamma^{1/2}]^2} \]  

(20)
where

$$S'_v(H) = -2.303 \cdot \frac{\mu \cdot \eta^2}{S(f)} \cdot \frac{3}{2} \left[ \frac{1}{T} + \frac{3 \ln D}{\partial T} + \frac{\alpha}{3} \right],$$

$$W(H) = 2.303 \cdot \frac{\mu \cdot \eta^2}{S(f)} \cdot A \cdot \frac{1}{2} \left[ \frac{1}{T} + \frac{3 \ln D}{\partial T} + \alpha - \frac{2 \cdot 3 \ln \frac{\alpha}{3}}{\partial T} \right],$$

and

$$\alpha = \text{coefficient of thermal expansion.}$$

For extremely dilute solutions, Equation (20) reduces to

$$\overline{L}_2 = S'_v(H)^{1/2}.$$  \hspace{1cm} (21)

The basic assumptions of the Debye-Hückel treatment were as follows:

(a) Strong electrolytes were assumed to be completely dissociated at all concentrations.

(b) It was assumed all departures from ideal behavior are due to Coulombic interactions between ions.

(c) It was assumed the distribution of ions in solution can be described by a combination of Boltzmann's and Poisson's equations.

(d) The linear superposition of fields was assumed; that is, the potential at a distance $x$ from an ion, due to the charge on the ion and its ionic atmosphere, is not influenced by the ionic atmospheres built up by neighboring ions in the solution.
(a) It was assumed the third and higher terms of an expansion of the Boltzmann exponential are negligible.

(f) The ions were considered to be rigid spheres in that a mean distance of closest approach was assumed for the ion centers. No allowance was made for the volume occupied by the ions.

(g) The solvent was considered to be a medium of uniform dielectric constant. The dielectric constant was assumed to be independent of the nature and number of ions present.

A complete development and discussion of the Debye-Hückel theory are given by Harned and Owen (25). Analyses and critiques of the simplifying assumptions are given by Kirkwood (26) and Fowler and Guggenheim (27).

The success of the Debye-Hückel treatment in predicting the behavior of electrolytic solutions at extreme dilution had a great effect on subsequent theoretical studies. Most of the work since 1923 has consisted of modifying the original assumptions to extend the theory to higher concentrations. Unfortunately, very little can be done to make the original assumptions more general without complicating the mathematical development considerably. As a result, extensions to the Debye-Hückel treatment often led to very complex mathematical expressions or to the introduction of simplifying, adjustable parameters. Where the original theory had but one adjustable parameter, 2, the extensions often had two or more. Usually these parameters were identified with some physical property of the system, but were of such a nature they could not be evaluated by an independent method.
The effect of the variation of the dielectric constant with concentration, and the change in dielectric constant for solvent particles in the neighborhood of ions were discussed by Bjerrum (28), Hückel (29), and Debye and Pauling (30). Hückel suggested an empirical term proportional to concentration be added to the activity coefficient expression to correct for these effects. To date, no unambiguous method has been developed to treat variations in dielectric constants adequately, but a group of English workers are now active in the field (31, 32, 33).

Assumption (e) was investigated by Müller (34), and by Gronwall, La Mer, and Sandved (35). Rather than expand the exponential of the Poisson-Boltzmann expression and neglect higher terms to obtain a linear differential equation, Müller employed a graphical integration to obtain an activity coefficient expression. Gronwall, La Mer, and Sandved retained six terms in the expansion of the exponential, and performed a very complicated numerical integration for symmetrical electrolytes. La Mer, Gronwall, and Greiff (36) carried out similar calculations for unsymmetrical electrolytes. These extensions gave better agreement between theoretical predictions and experimental results without resorting to additional parameters, but very serious objections were raised against their method. Fowler and Guggenheim (27) pointed out that the potentials of the system must obey the following relationships to be mathematically consistent.

\[
\frac{\psi_\alpha}{Z_\alpha} = \frac{\psi_\beta}{Z_\beta} = \ldots \ldots \tag{22}
\]
\[
\frac{\partial \psi_\alpha}{\partial Z_\beta} = \frac{\partial \psi_\alpha}{\partial Z_\alpha} = \ldots \tag{23}
\]
where \( \psi_\alpha \) is the potential at the \( \alpha \)th ion and \( Z_\alpha \) is the charge on the \( \alpha \)th ion. The "complete" solutions to the Poisson-Boltzmann equation satisfied Equation (22) but not Equation (23). Fowler and Guggenheim (27) concluded that "complete" solutions can be no more accurate than the simple theory because of this inconsistency.

Assumption (a) also received a great deal of attention. A carefully developed treatment including ionic association was introduced by Bjerrum (37) and extended by Fuoss and Kraus (38). With this treatment, a probability expression based on the Maxwell-Boltzmann distribution law was set up to give the concentration of ions in the neighborhood of a given ion.

\[
P_{ij} = \frac{Nc_i}{1000} \frac{e^{u/kT}}{4\pi r^2} dr \tag{24}
\]

\( P_{ij} \) is the probability of an \( i \) ion at a distance \( r \) from a \( j \) ion; \( c_i \), the concentration of \( i \) ions in moles per 1000 cc; and \( u \), the work required to move the \( i \) ion from distance \( r \) to infinity. When the energy of separation of two ions was \( 2kT \) or greater, the ions were assumed to be associated. The theory was extended to include clusters of two, three, and four ions. All unassociated ions were assumed to obey the Debye-Hückel predictions. This treatment was used primarily to predict the behavior of symmetrical electrolytes in mixed solvents. Little was done to apply the method to aqueous solutions.
of unsymmetrical electrolytes.

A modification of assumption (b) was made by Robinson and Stokes (39). These authors suggested an extension to the Debye-Hückel theory which purports to account for the energy involved in the interaction between ions and neighboring solvent molecules. A similar extension was suggested by Gmuckauf (40). Robinson and Stokes (39) obtained the following expression for the mean molal activity coefficient,

$$\ln \gamma_i^* = \ln f_i^* - \frac{\mu}{\mathcal{U}} \ln a_1 - \ln \left[ 1 + \frac{M_i (\mathcal{U} - m) m}{1000} \right]. \quad (25)$$

In the above, $\ln f_i^*$ is the Debye-Hückel expression for the rational activity coefficient as given by Equation (19); $\mathcal{U}$, the number of ions into which the electrolyte dissociates; $a_1$, the activity of the solvent; $M_i$, the molecular weight of the solvent; $m$, the molality of the solute; and $\mu$, the number of moles of solvent tightly bound to each mole of electrolyte. Differentiation of Equation (25) with respect to $T$ at constant $P$ and $N$ yields

$$\left[ \frac{\partial \ln \gamma_i^*}{\partial T} \right]_{P,N} = \left[ \frac{\partial \ln f_i^*}{\partial T} \right]_{P,N} + \frac{\mu}{\mathcal{U}} \left[ \frac{\partial \ln a_1}{\partial T} \right]_{P,N}. \quad (26)$$

Equation (26) may be placed in a more useful form by the following relationships:

$$\left[ \frac{\partial \ln \gamma_i^*}{\partial T} \right]_{P,N} = \frac{\partial \ln f_i^*}{\partial T} \quad P,N, \text{ and }$$

$$\left[ \frac{\partial \ln \gamma_i^*}{\partial T} \right]_{P,N} = \frac{\partial \ln f_i^*}{\partial T} \quad P,N, \text{ and }$$
\[
\left[ \frac{\partial \ln a}{\partial T} \right]_{P,N} = \frac{N_1 \mu m}{1000} \left[ \frac{\partial \ln f_+}{\partial T} \right]_{P,N} .
\] (28)

Combining Equations (26), (27), and (28) yields

\[
\left[ \frac{\partial \ln f_+}{\partial T} \right]_{P,N} = \frac{1}{1 - \frac{mN_1}{1000}} \left[ \frac{\partial \ln f'_+}{\partial T} \right]_{P,N} = -\frac{L_2}{\nu RT^2} .
\] (29)

Since \( m \) cannot be determined independently, this treatment can be considered little more than an empirical extension.

Recently, two groups of workers have developed variations on the Debye-Hückel treatment involving modifications of assumptions (b) and (c). These treatments attempt to account for the volume occupied by the solute molecules by replacing the Boltzmann distribution function in the Poisson-Boltzmann expression with a distribution function of different form. Dutta and Bagchi (41, 42) derived an expression similar to the Fermi-Dirac function by considering a distribution of solute ions among filled and vacant sites. The statistical development employed was reviewed by Dutta (43). Wicke and Eigen (44, 45, 46, 47) obtained the new distribution function,

\[
\frac{n_j}{n_j} = \frac{N_j - n_j'}{N_j - n_j} = \frac{e^{\frac{-Z_j e^\psi}{kT}}}{1} .
\] (30)
by considering an equilibrium between ions and ion sites in the ionic atmosphere surrounding a central ion. In the above, \( n_j \) is the number of \( j \) ions per cc at a distance \( x \) from a central ion; \( n_j^* \), the number of \( j \) ions per cc at infinite distance from the central ion; and \( N_j \), the number of ion sites per cc corresponding to the reciprocal of the hydrated volume of the ions. The distribution function was used to derive the following expression for the rational activity coefficient.

\[
\frac{\ln f_+}{\ln f_+^{D-H}} = \frac{K}{K'} \left[ 1 - \frac{2n}{N} \right] \left[ 1 - \frac{2\gamma Y}{\gamma} \right] + \frac{2\gamma K'}{K}
\]  

(31)

where \( \ln f_+^{D-H} \) = Debye-Hückel limiting law value,

\( K \) = Debye-Hückel constant,

\( a \) = mean distance of closest approach,

\( n \) = concentration of solute in moles per cc,

\[
\frac{1}{N} = \frac{\sum \nu_i z_i^2}{\sum z_i^2} \cdot \frac{4}{3} \pi a^3,
\]

\( K' = K \left[ 1 - \frac{n}{N} \right]^{1/2} \),

\( \gamma = 1 + a K' \), and

\[
Q = \frac{1}{(a K')^3} \left[ \ln \gamma - a K' + \frac{a^2 K'^2}{2} \right].
\]
A lively discussion concerning the equivalence of these two approaches was carried on in the literature (48, 49, 50, 51, 52, 53).

Lange and Mohring (54) developed an expression for the relative apparent molal heat contents of solutes in solution from the Eigen and Wicke distribution function.

\[
\phi_L = \frac{\phi_L^{D-H}}{\psi} \cdot \left[ \frac{\psi}{\gamma} + \frac{(6Q \gamma - 2)}{\gamma} \frac{d \ln a}{d \ln T} + \frac{N}{N} \frac{(2Q \gamma - 1)}{1 - \frac{N}{N}} \frac{d \ln \bar{N}}{d \ln T} \right]
\]

(32)

where \( \phi_L^{D-H} \) = Debye-Hückel limiting law value, and

\[
\psi = 1 + \frac{d \ln D}{d \ln T}.
\]

In the development of this expression, the variation of concentration with temperature at constant pressure was not included. Scatchard (55) has shown that such an omission introduces considerable error.

The Eigen and Wicke treatment was further extended to include incomplete dissociation. The correction for \( \phi_L \) was of the form,

\[
\phi_L (\text{actual}) = \alpha \phi_L - (1 - \alpha) D_n,
\]

where \( \alpha \) was identified with the degree of dissociation, and \( D_n \) was identified with the heat of dissociation. In reality, both quantities were adjustable parameters.

Wicke and Eigen obtain very good agreement with experimentally determined activity coefficients, heats of dilution, and apparent molal heat capacities, but this is not surprising considering the number of
adjustable parameters they have at their disposal. For $\phi$, for example, the constants $a$, $\frac{d \ln a}{d \ln T}$, $\frac{d \ln E}{d \ln T}$, $\alpha$, and $D_{e,0}$, can all be adjusted. In some cases, the parameters required to fit the experimental data are not realistic. The treatment also suffers from the same mathematical inconsistency encountered earlier in the work of Gronwall, La Mer, and Sandved (35). These objections are discussed by Frank and Tsao (56).

In all treatments discussed thus far, the authors have followed the framework of the Debye-Hückel development in that the electrostatic potentials existing in solution were obtained by the combination of Poisson's equation and some distribution function. Mayer (57) employed a new approach similar to his statistical mechanical evaluation of virial coefficients for real gases. The treatment consisted of considering the potential of average force between ions suspended in a dielectric solvent. Mayer developed an expression for an odd type activity coefficient, and related his calculations to the Debye-Hückel law at infinite dilution. Poirier (58) continued the calculations of Mayer and obtained numerical values for the rational activity coefficients of sodium chloride, calcium chloride, zinc sulfate, and lanthanum chloride. He also worked out simple procedures for calculating partial molal volumes, apparent molal volumes, partial molal heat contents, and relative apparent molal heat contents, and he compiled tables of the quantities needed for these calculations. Poirier was able to fit activity coefficient data for sodium chloride up to 0.4 molar, calcium chloride up to 0.07 molar,
zinc sulfate up to 0.01 molar, and lanthanum chloride up to 0.01 molar. Tsao (56) could not obtain a good fit for the heats of dilution of sodium chloride without the aid of an additional parameter, $d\ln a/dT$.

This survey by no means exhausts the attempts to explain the experimentally determined properties of electrolytic solutions, but instead lists some of the more important or representative developments. The purely empirical extensions were omitted, and many of the extensions giving theoretical significance to empirical parameters were likewise omitted.
EXPERIMENTAL

History of the Method

Thermometric calorimetry, as the name implies, is the process of measuring quantities of heat by determining the temperature change of the system of interest. This study considers a very small segment of this ancient and widely used method: the measurement of extremely small quantities of heat liberated in a short time interval. More comprehensive discussions of calorimetry are given by White (59), Swietoslawski (60), and Sturtevant (61).

Most difficulties encountered in calorimetric measurements occur because the system under study cannot be thermally isolated from its surroundings. Since all materials conduct heat to some extent, there is a constant interchange of heat between a calorimeter and its immediate environment. In addition to conduction, thermal energy can be transferred by convection and radiation. Numerous calorimetric techniques have been developed to reduce or evaluate thermal exchange.

The oldest and simplest method consists of surrounding the calorimeter with an insulated jacket. Such a jacket reduces but does not eliminate heat transfer. This method is now seldom used except for rather crude measurements, because the residual heat leak cannot be evaluated accurately. With a similar but more refined method, the
Small quantities of heat or for processes of long duration.

method, like the adiabatic method, is often used for the determination of
comparisons with a known thermal process in the other. The differentials

magnitude of a thermal process in one calomelimeter is determined by

each calomelimeter and the surroundings will be nearly identical. The
under identical conditions. In this system, the thermal exchange between
that method. The method consists of two identical calomelimeters placed
another technique requiring no heat corrections is the different-
duration.

of heat are involved or whether the thermal process or interest is of long
approximations. The adiabatic method is widely used where small quanti-
ties need to be handled. In practice, the condition cannot be
and radiation is a function of the thermal heat. no heat transfer will occur
true as the calomelimeter. Since heat transfer by condensation, convection,
the calomelimeter is surrounded by a jacket maintained at the same temper-
thermal exchange to a low level. at can be neglected. With this method,
surroundings, another technique, the adiabatic method, strives to reduce
attitude to correct for the thermal exchange between a calomelimeter and the
where the thermal junction temperature occurs the existence of, and
a short period of time.

for thermal processes where large quantities of heat are liberated in
for such a system. Initially jacketed calomelimeters are best suited
62, 63, 64, 65] have treated the evaluation of the heat loss corrections
4

calomelimeter is surrounded by an inothermal jacket. Several authors (62, 63, 64, 65)
All of the above techniques and combinations of these have been applied to the measurement of heats of dilution of strong electrolytes. Bjerrum (66) aroused great interest in these measurements in 1926 when he pointed out that an expression for heats of dilution could be derived from the interionic attraction theory of Debye and Hückel (23). The theory predicted the relative apparent molal heat contents, $\phi_L$, will be positive for all salts following the Debye-Hückel assumptions. The theory further predicted the concentration dependence of $\phi_L$ will be the same for all "ideal" salts of a given valence type. Bjerrum found no agreement with theory when he compared the theoretical prediction with the then available measurements of Richards and Rowe (67, 68).

Richards and Rowe used an adiabatic calorimeter to measure the heats of dilution of several 1-1 salts. The lowest concentration studied was 0.139 molal. Temperature measurements were made with a Beckman thermometer, and adiabatic control was maintained manually to within a few hundredths of a degree. At the lowest concentration studied, the apparent molal heat contents were positive for some salts and negative for others.

In 1926, Hernst and Ortmann (69) extended heats of dilution measurements to a more dilute range, but again the solutions were too concentrated to obtain agreement with theory. They employed a differential calorimeter to measure the heats of dilution of several salts at concentrations of 0.1 and 0.03 molar. Temperature measurements were made with a 20 junction iron-constantan thermopile and a sensitive
Seltzer and Gurney measured the metalloidy of a number of metals and found that the metalloidy of the metals was proportional to the square root of the metalloidy of the metal. This proportionality was used to determine the metalloidy of the metals.

The metalloidy of the metals was determined by measuring the magnetic moment of the metal. The magnetic moment of the metal was measured using a sensitive galvanometer. The galvanometer was calibrated with a known magnetic moment and the magnetic moment of the metal was determined by comparing the signal from the metal to the signal from the calibration.

The metalloidy of the metals was found to be proportional to the square root of the metalloidy of the metal. This proportionality was used to determine the metalloidy of the metals.

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A complete description of the Lange type calorimeter was given by Lange and Robinson (72). Improved methods for data treatment, rather than further calorimetric refinements, were responsible for obtaining quantitative agreement with theory.

Gucker, Pickard, and Planck (73) described an adiabatic differential calorimeter of somewhat different design. Their apparatus consisted of two separate containers of one liter capacity housed in a closed container and submerged in an adiabatic water jacket. The temperature difference between the calorimeter containers was determined by a 60 junction copper-constantan thermopile. An extremely sensitive galvanometer made possible the use of a 60 junction thermopile in place of a 1000 to 1500 junction thermopile. The sensitivity of the system was about $6 \times 10^{-4}$ calories per mm galvanometer deflection. Adiabatic control was maintained automatically by two 10 junction copper-constantan thermopiles. In the apparatus of Gucker, et al., the individual containers were separated from each other and from the adiabatic jacket by a three cm air gap. This resulted in less heat exchange between containers and less heat exchange between the containers and the adiabatic jacket than for a Lange type calorimeter. In addition, there was less heat conductivity through Gucker's long 60 junction thermopile than through Lange's short 1000 junction thermopile. For these reasons, Gucker's apparatus can be considered an improvement over calorimeters of the Lange type.
Apparatus

The apparatus used for these measurements was patterned after the one developed by Gucker, Pickard, and Planck (73). A schematic diagram of this apparatus is given in Figure 1, and a schematic diagram of the calorimeter circuits is given in Figure 2. References to Figure 1 will be designated (1-A), (1-B), etc.; references to Figure 2 will similarly be designated (2-A), (2-B), etc. The nomenclature used by Gucker was retained where possible.

The calorimeter containers (1-C) were fabricated from 15 mil tantalum. Tantalum was chosen for its ease of fabrication, its structural strength, and its chemical inertness. These containers were four inches in diameter and six inches deep. Four inch butt welded tantalum tubing was used for the sides of the containers. Long narrow holes with edges flanged outwards were formed in the sides of the containers to accommodate the wells for the main thermal. The thermal wells were formed from two pieces of butt welded tantalum tubing and were welded into the sides of the container. This tubing was flattened over a brass form to give a well 2 1/4 inches deep and with an opening of 3 3/8 inches by 5/16 inches. Dish shaped bottoms were welded into the ends of the thermal wells. The lids for the containers were made from 15 mil annealed tantalum sheet. A 1/4 inch 45 degree flange was turned on the lids to match a similar flange on the containers. The lids were fitted with
Figure 1. Differential Calorimeter for Measuring Heats of Dilution.
Figure 2. Schematic Circuits for Differential Calorimeter.
flanged 5/8 inch holes for the heater wells (1-H), and plain 1/4 inch holes for the stirrers (1-F), sample holders (1-G), and control thermels (1-E). The container bottoms were fabricated from the same material used for the lids. A 90 degree flange was turned on the bottoms to give a snug fit and to form a weldable joint. The heater wells were formed by flattening the ends of 5/8 inch annealed seamless tubing. All joints were arc welded in a helium atmosphere.

The tops of the calorimeter containers were mounted permanently to the under surface of the submarine jacket lid by four lucite spacers (1-S) one inch in diameter and three cm long. The lids were fastened to the spacers by small screws, and the spacers in turn were fastened to the lid of the submarine jacket by small brass screws. When assembling the apparatus for a determination, the flanges of the calorimeter containers were held snug against the flanges of the lids, and strips of Scotch electrical tape were applied to seal the lids to the containers. Brass snap rings were fitted over the Scotch tape as an added precaution. The containers were held in place during a determination by lucite rings (1-R) suspended from the lid of the submarine jacket by three strands of 30 pound test nylon fish line.

The calorimeter containers were stirred by vane type stainless steel stirrers. The stirrer shafts were suspended by stainless steel ball bearings as shown in Figure 1, and were rotated by a 150 rpm synchronous motor. A sprocket and chain drive gave a stirring speed of 282 rpm.
The water bath consisted of a copper inner tank and an outer casing with sides of 20 B and S gauge galvanized iron and a bottom of 3/4 inch plywood. The outside casing was 26 inches in diameter and 23 inches high; the inner tank was 19 inches in diameter and 18 7/8 inches deep. Fourteen B and S gauge copper was used for the wall of the inner tank and for the collar covering the space between the walls. One-eighth inch copper was used for the bottom of the inner tank. The inner tank was supported above the plywood base by two 3 1/4 inch boards, and the remaining space between the walls was filled with exploded mica insulation. The lid for the water bath consisted of a 1/4 inch aluminum plate and a 1/2 inch plywood top separated by 1 3/4 inches of hair felt insulation.

The water bath was fitted with a cooling coil (1-A) of 1/4 inch annealed copper tubing. The cooling coil was fastened by means of brass fittings to two outlets located three inches from the top and on opposite sides of the water bath. The cooling coil consisted of 1 1/2 turns at the bottom of the tank and the two lengths of tubing from the above outlets to the bottom of the tank.

The water bath was stirred by means of a centrifical pump rated at 2100 gallons per hour at zero head. This pump was powered by a 1/4 horsepower, 1725 rpm motor. Water was removed from the bath at a 5/8 inch I.D. opening three inches from the top of the tank, and was returned to the bath through a 1/2 inch I.D. tube at the bottom of the tank.

The submarine jacket (1-J) was suspended from the lid of the water
bath by eight brass tubes. These tubes were soldered to the top of the submarine jacket and to brass collars which were threaded into the under surface of the aluminum water bath lid. Two 1/2 inch O.D. tubes accommodated the calorimeter stirrer shafts, and two 1/2 inch O.D. tubes carried six conductor shielded cables for the calorimeter heaters. Two 7/16 inch O.D. tubes carried four conductor shielded cables for the main thermal and the control circuit, and two 5/16 inch O.D. tubes held the stems of the sample holders. All tubes except those for the stirrer shafts extended 1/8 inch above a brass plate on the top of the water bath lid. The stirrer shaft tubes extended 2 1/2 inches above the lid and were capped with brass holders for the top stirrer shaft bearings.

The submarine jacket was 8 3/4 inches deep. Its horizontal cross section had straight, parallel sides terminating in semicircular ends. The straight segments of the jacket were 6 1/2 inches long and were 6 5/8 inches apart. The rounded ends gave the jacket an over-all length of 12 3/8 inches. One-eighth inch copper was used for the top and bottom, and 16 B and S gauge monel was used for the side wall. Brass flanges were soldered to the top and the bottom of the side wall. The bottom of the jacket was fastened permanently to the bottom flange with brass machine screws. Studs were placed in the top flange for fastening the jacket to the lid. The top and bottom of the jacket were chromium plated before assembling, and the inner surface of the monel side wall was polished.

The holders for the control thermels (1-B) were constructed from
two sections of 1/4 inch hard copper tubing. The semicircular sections soldered to the lid of the jacket were joined to straight sections by means of brass couplings as shown in Figure 1.

The water bath lid was suspended 54 inches above the floor by an angle iron frame. The water bath, circulating pump, and motor were mounted on a movable platform which could be rolled under the water bath top. A permanently mounted hydraulic bumper jack was used to raise and lower the platform.

The temperature difference between the two calorimeter containers was measured by a 60 junction copper-constantan thermopile (1-T, 2-U, 2-U'). This thermopile was constructed of 24 B and S gauge enameled constantan wire and 32 B and S gauge double silk covered copper wire with 30 B and S gauge single Vitrotex covered copper wire for external leads. The enamel coating was scraped off both ends of 60 sections of constantan wire 11 cm long, and copper wires of slightly longer length were wrapped tightly around one end of 58 of these sections. The resulting junctions were soldered by dipping them into a molten pool of a special solder with thermoelectric properties approaching those of copper. This solder was furnished by the Liston-Becker Instrument Company for use in input circuits of their breaker type D.C. amplifier. A solution of rosin in ethyl alcohol was used as a flux. After trimming the resulting soldered junctions, the constantan and copper wires were arranged on two thin 7 cm by 11 cm mica sheets to form two thermopiles of 30 junctions each. The mica sheets were notched along their seven cm sides.
to hold the thermopile wires in place. The second series of soldered
junctions were formed by dipping the mica sheet and the 30 exposed
junctions into a pool of molten solder. After a careful visual inspec-
tion for shorts, the two 30 junction thermopiles were rinsed with water
and acetone, coated with Krylon acrylic spray, and mounted in a copper
and lucite protective case. This case consisted of two 0.022 inch
copper shields to fit over the ends of the thermopiles and a three cm
wide lucite collar made of 1/8 inch lucite which was grooved to hold
the two copper shields in place. When mounting the thermopiles in
the protective case, the two sections were separated by a sheet of thin
mica, and sheets of mica were bent around the ends of the thermopile to
insulate them from the copper shield. Two leads from each thermopile
were brought out through the lucite collar. After mounting the thermo-
pile in the case, the case was filled with naphthalene for stability and
for improvement of the thermal conduction between the thermopile and the
copper shields.

The thermopile leads were joined to the wires of a four conductor
shielded cable at a junction block (l-D) under the lid of the submarine
jacket. The junction block consisted of pure copper screws mounted in
a lucite strip. The screws, nuts, and wires involved at these junc-
tions were cleaned with a diluted mixture of hydrochloric and nitric
acids and with a cleaning solution consisting of nitric, phosphoric,
and acetic acids.

The four conductor shielded cable was passed through a brass
tube in the lid of the submarine jacket and was connected to a Leeds
and Northrup, number 31-3-0-3, 12 position, silver contact selector switch (2-A). This switch was chosen for its low, stable contact resistance and low thermal emf of switching. The selector switch was mounted in a steel casing to which the braided shielding of the incoming four conductor cable and an outgoing two conductor cable were fastened. The switch and casing were buried under three inches of exploded mica insulation in a large, covered Dewar flask.

A two conductor shielded cable connected the selector switch with a model 14 Liston-Becker breaker type D.C. amplifier (2-B). An amplifier of this type is described by Liston, Quinn, Sargent and Scott (74). The selector switch was wired so that the two 30 junction sections of the main thermel could be connected with the amplifier separately, in series, or in opposition with either direct or reversed polarities. In addition, the selector switch was equipped to place shunts of 0, 10, and 30 ohms into the input circuit. These shunts were used as base lines for adjusting the gain of the amplifier. The output of the amplifier was fed into a filter circuit (2-C) which attenuated the signal slightly and removed much of the extraneous noise. The signal was recorded on a Brown recording potentiometer (2-D) with a 0 to 60 millivolt range. A type I E 5101 Stabiline voltage regulator (2-E) was used as a power source for both the amplifier and the potentiometer.

The sensing elements for the control of the water bath temperature were two 10 junction copper-constantan thermopiles (2-V, 2-V'). Thirty B and S gauge constantan wire and 36 B and S gauge copper wire were used. These thermopiles (1-B) were mounted in the water bath and the
calorimeter containers as shown in Figure 1.

The over-all length of the thermopiles was 42 cm. The portions of the thermopiles that were immersed in the calorimeter containers had five junctions at the ends and the remaining five junctions two cm from the ends. The portions of the thermopiles that were surrounded by the water bath had single junctions spaced at two cm intervals from the ends to the semicircular sections of the thermopile holders. The thermopiles were constructed in the same fashion as the main thermal. The wires of each thermopile were tied together in a long bundle with thread and painted with clear Corex insulating varnish. The bath ends of the thermopiles were mounted in naphthalene filled copper tubes; the calorimeter ends were placed in naphthalene filled glass tubes which were fastened into the lids of the container with Apiezon W wax.

Two leads from each thermopile were joined to the wires of a four conductor shielded cable in the same manner as the leads from the main thermal. The four conductor cable connected the thermopiles with a Leeds and Northrup number 31-3-C-3 selector switch (2-A'). This switch was wired so that each section could be placed in the circuit of a Leeds and Northrup type K-2 potentiometer (2-B) either individually or in series with direct or with reversed polarities. Another section of the switch connected one thermopile or the two thermopiles in series to a Leeds and Northrup Cat. number 2285A galvanometer (2-0) through an Aryton shunt (2-Y).

Temperature control of the water bath was obtained through the
latter part of the selector switch. Light from a Warner model 62L light source (2-L) was reflected from the galvanometer onto a Warner model 62R photoelectric receiver and relay (2-I) located three meters from the galvanometer. When the temperature of the water bath was midway between the temperature of the two containers, the emf's produced by the two thermopiles exactly cancelled, and no current flowed through the galvanometer. When the light fell on the photocell, a relay switch closed in the input line of a type 116 Powerstat (2-N) set at 35 volts. Two 600 watt knife heaters were connected in parallel to this transformer.

The rate of flow of cooling water through the coils at the bottom of the water bath was adjusted to give approximately equal 30 second intervals of heating and cooling. The temperature of the water bath was measured with a recently calibrated (1953) Leeds and Northrup Cat. number 8163 platinum resistance thermometer and a Leeds and Northrup Cat. number 8069 Mueller temperature bridge. Bath control was maintained to better than ± 0.003 degrees.

Each calorimeter heater (1-H, 2-W, 2-W') consisted of a 50 ohm winding of 38 B and S gauge enamelled, double silk covered manganin wire and a 1.5 ohm winding of 30 B and S gauge, double silk covered constantan wire. The manganin circuit was used to supply the heat necessary for calorimetric measurements, while the constantan circuit was used to adjust and regulate temperature drifts in the calorimeter containers. The heaters were constructed by wrapping the resistance
wire around 0.5 inch by 4.5 inch sheets of thin mica. The windings covered about 1/3 the length of these sheets. One lead wire was attached to each end of the constantan winding, and two lead wires were attached to each end of the manganin windings. Thirty B and S gauge single Vitrolox covered copper wires were used for these leads. The heaters were mounted in the lid of the tantalum containers by holding the mica strips away from the sides of the heater wells and filling the wells with naphthelene.

The leads from the calorimeter heaters, six from each heater, were joined to the wires of a shielded six conductor shielded cable in the same fashion as discussed earlier for the main thermal.

The leads from the trickle heaters were connected directly to the current source shown in Figure 3. One lead from each end of both manganin heaters terminated at a three gang selector switch (2-M); the remaining leads at a second three gang selector switch (2-M'). Switch (2-M) was wired to permit the measurement of the potential drop across either manganin heater independently, across the two manganin heaters in series, across the dummy heater (2-S), or across the standard resistor. Switch (2-M') was wired to pass current from the current source (2-C) through either of the manganin heaters independently, through the two manganin heaters in series, or through the dummy heater. When current was passed through the manganin heaters, switch (2-M') turned on an electronic timer (2-T). The circuit for the current source is given in Figure 3. The electronic timer was calibrated
CURRENT SOURCE FOR MANGANIN CALORIMETER HEATERS

CURRENT SOURCE FOR TRICKLE HEATERS

Figure 3. Current Sources for Calorimeter Heaters.
frequently with the National Bureau of Standards station W.W.V., and measured time intervals to better than 0.02 seconds. The standard resistor and the standard cell used for potential measurements were calibrated by the National Bureau of Standards, and were compared periodically with other instruments calibrated by the National Bureau of Standards.

An exploded view of one of the calorimeter sample holders is given in Figure 4. The barrels of the sample holders had inside diameters of two cm and were four cm long. The screw-on tops held platinum disks 0.0005 inch thick firmly against the ends of the tubes. Tight seals were obtained by lubricating the ends of the tubes lightly with silicon grease and placing Teflon gaskets behind the platinum disks.
Figure 4. Sample Holder for Differential Calorimeter
Preparation of Solutions

The rare earths employed in this research were obtained as the oxides from the rare earth separation group of the Ames Laboratory of the Atomic Energy Commission. The methods of rare earth separation and purification have been described elsewhere (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13).

Spectrographic analysis of the neodymium oxide indicated trace impurities of samarium oxide. The presence of samarium oxide in neodymium oxide can be detected when less than 0.06 per cent samarium oxide is present. Spectrographic analysis of the erbium oxide indicated the presence of less than 0.01 per cent thulium oxide. No other rare earths were detected.

The experimental measurements were carried out on solutions that were prepared by diluting stock solutions. Two neodymium chloride and two erbium chloride stock solutions were used. For one neodymium chloride stock solution and one erbium chloride stock solution, the rare earth oxides were converted to the chlorides by adding a slight excess of the oxides to redistilled C.P. Baker and Adamson hydrochloric acid. The resulting solutions were held near the boiling point for several hours, and the excess oxides removed by filtration. The filtrates were diluted to approximately 0.25 molar, and 25 ml aliquots were titrated with 0.05 normal hydrochloric acid. Typical strong acid-weak base titration curves resulted. The bulk solutions were
brought to the pH of the inflection points of the titration curves and again held near boiling for several hours. After cooling, aliquots of the bulk solutions were made basic with a few drops of sodium hydroxide and the titrations were repeated. This procedure was repeated until reproducible equivalence pH's were obtained and the bulk solutions showed no Tyndall cones. The neodymium chloride solution was brought to a pH of 5.34, and the erbium chloride solution to a pH of 4.20.

The second neodymium chloride stock solution was prepared by Gordon Atkinson of the Ames Laboratory. Mr. Atkinson treated neodymium oxide with a slight excess of redistilled hydrochloric acid, and held the resulting solution near boiling until crystals formed. Conductivity water was added, and the solution was evaporated until crystals had formed three times. After the third heating, the solution was diluted to about one molal and titrated as described above. The solution was adjusted to a pH of 4.83.

The second erbium chloride stock solution was prepared from hydrated erbium chloride crystals. The hydrated erbium chloride crystals were grown by dissolving erbium oxide in a slight excess of redistilled hydrochloric acid, heating the resulting solution until viscous, and drying over calcium chloride in an evacuated dessicator. A 0.2602 molal solution was found to have a pH of 5.46.

The stock solutions were analyzed for both rare earth content and chloride ion content. Gravimetric chlorides were carried out
following the method described by Kolthoff and Sandell (75). Neodymium and erbium contents were determined by precipitating the rare earths as the oxalates in weighed porcelain crucibles, evaporating to dryness, and firing to the oxides by heating to 1000°C in a muffle furnace. The rare earth and chloride analyses agreed to better than two parts per thousand, except for the second erbium chloride solution where agreement was only four parts per thousand.

A copper sulfate stock solution was prepared from recrystallised Mallinkrodt analytical reagent cupric sulfate pentahydrate. The copper concentration of this stock solution was determined electrolytically.

Dilutions of the stock solutions were made by weight. The following relationship was used for calculating the concentrations of the final solutions.

\[ p = \frac{w p_o}{w + w} \]  

(34)

where \( p \) = moles of solute per 1000 grams of final solution,

\( p_o \) = moles of solute per 1000 grams of stock solution,

\( w \) = weight of stock solution added, and

\( W \) = weight of water added.

The molality of each solution was calculated by means of the relationship
\[
m = \frac{P \times 10^3}{1000 - K_2 P}
\]  \hspace{1cm} (35)

where \( K_2 \) = molecular weight of solute.

The density data of B. O. Ayers (24) was used to calculate vacuum corrections. Conductivity water with a specific conductivity of \( 1.5 \times 10^{-6} \) mhos or less was used for all dilutions.

**Procedure**

Before each run, all parts of the apparatus in contact with the solution under study were rinsed thoroughly with conductivity water. The sample holders were soaked in conductivity water until no unusual rise in conductance occurred.

The solutions under study were brought to 25°C in a constant temperature water bath. Ten ml samples were measured into the sample holders with a volumetric pipet, and the samples were weighed. It was found this filling procedure gave samples reproducible to within ± 0.003 gram. The holders were soaked in conductivity water for several hours and again reweighed. If no unusual rise in the conductance of the water and no change in weight occurred, the sample holders were assumed to be free of leaks. After completing this test for leakage, the holders were mounted on their supporting stems.

The tantalum calorimeter containers were filled with water to
give a total liquid content, water plus samples, of 900 grams for
each container. These weighings were made to the nearest drop with
a two kg capacity analytical balance.

The main thermal was installed in the thermal wells of the
tantalum calorimeter containers, and the containers were raised into
place with a scissors jack. The containers were sealed to their lids
with strips of Scotch electrical tape and held in place by lucite rings
supported by three strands of 30 pound test nylon fish line. The sub-
marine jacket was fastened into place, and the water bath raised
around the submarine jacket to complete the assembly.

Stirring was started in the calorimeter containers and the water
bath, and water bath temperature control was established. The tempera-
ture difference between the calorimeter containers was reduced to a
few microdegrees. This condition was realized when the temperature
difference between containers could be followed on gain 17 of the
Liston-Becker amplifier. The system was brought to within 0.02° of
25°C by manipulating the water bath temperature. The temperatures
of the calorimeter containers were slowly raised or lowered by main-
taining a thermal head of a few degrees between the containers and
the water bath. When the calorimeter containers reached the desired
temperature range, bath control was quickly re-established, and the
system was allowed to come to equilibrium. The temperature difference
between the calorimeter containers was again reduced to a few micro-
degrees, and the current through the calorimeter trickle heaters was
adjusted to compensate for drifts in this temperature difference. The
current required seldom exceeded ten milliamperes.

The procedure varied somewhat depending upon the nature of the
determination to be made. For electrical calibrations, the temperature
difference between the calorimeter containers was recorded for from 15
to 30 minutes before each heating period. A current of 15 milliamperes
was passed for from 8 to 40 seconds through one of the calorimeter
heaters after the fore drift was obtained. During the heating period,
the potential was measured across either the standard resistor in the
heating circuit or across the calorimeter heater. After the system
returned to equilibrium, the temperature difference between containers
was again recorded for from 15 to 30 minutes. Straight lines were drawn
through the fore and after drifts, and the displacement resulting from
the electrical heating was measured. One line was drawn perpendicular
to the fore drift at a point near the beginning of the heating period,
and a second line was drawn perpendicular to the after drift at a point
after the system returned to equilibrium. A measurement of the displace-
ment was made along both of these lines. This procedure was followed
because the fore and after drifts frequently had different slopes. The
significance of these changes in slope will be discussed in a later
section. The amount of heat liberated during the heating period was
calculated from the heater resistance, the standard resistance, the emf
measurement, and the duration of the heating period. The sensitivity
of the system was obtained by dividing the heat input by the observed
displacement.

Several experiments were carried out with current passing through both calorimeter heaters in series. The procedure was the same as for normal calibrations except the heating periods were much longer, 200 to 500 seconds, permitting several potential measurements across both the heater and the standard resistor.

The procedure for determining the heat evolved by a dilution experiment varied depending upon the concentration of the sample. For pure water samples, for all solutions below 0.01 molal, and for some solutions in the range 0.01 molal to 0.02 molal, the procedure was similar to that used for the electrical calibrations. That is, a fore drift was recorded, a sample holder was opened, and an after drift was recorded when the system had returned to equilibrium. The deflections resulting from the heat inputs were determined in the same manner as for electrical calibrations. The temperature of the system was assumed to be the mean temperature of the water bath.

For all other heats of dilution determinations, a fore drift was recorded as for the calibrations, and the temperature of the water bath was measured. A sample was opened in one calorimeter container, and the calorimeter heater was turned on in the other container. The heat liberated by the dilution process was balanced as nearly as possible with electrical heating. A heating current of fifteen milliamperes was used for samples with concentrations less than 0.1 molal. The heating current was increased to 23 to 24 milliamperes for concentrations
above 0.1 molal in order to shorten the heating period. An after drift was recorded when the system returned to equilibrium, and the residual deflection was measured as for the electrical calibrations.

The heat liberated by a dilution process was derived from a knowledge of the heating current, the heater resistance, the duration of the heating period, the residual displacement, and the sensitivity of the system. That is,

\[ q = q_{\text{electrical}} + q_{\text{displacement}} \quad (36) \]

where \( q_{\text{electrical}} = \frac{E_I E_K t}{4.184 R_S} \),

\[ q_{\text{displacement}} = \text{residual displacement \times sensitivity}, \]

\( E_I = \text{potential across the standard resistor}, \)

\( E_K = \text{potential across the heater}, \)

\( t = \text{time in seconds, and} \)

\( R_S = \text{resistance of the standard resistor}. \)

For these calculations, the residual deflection was taken to be the average of the deflection measured perpendicular to the fore slope and the deflection measured perpendicular to the after slope. The use of the average deflection will be discussed in more detail in a later section.
RESULTS

Treatment of Data

The experimental determinations were of two types. In the first type, samples containing \( \frac{n_2}{n_1} \) moles of salt in \( \frac{n_1}{n_1} \) moles of water were diluted with \( x \) grams of water. In determinations of the second type, samples containing \( \frac{n_2''}{n_1''} \) moles of salt in \( \frac{n_1''}{n_1''} \) moles of water were diluted by solutions resulting from determinations of the first type.

The heat evolved by a determination of the first type was

\[
q_1 = - n_2' \left[ \delta_L(m_2) - \delta_L(m_1) \right] + q_B .
\]

Similarly, the heat evolved by a determination of the second type was

\[
q_2 = - (n_2'' + n_2') \delta_L(m_3) + n_2'' \delta_L(m_1) + n_2' \delta_L(m_2) + q_B .
\]

In the expressions above, \( m_1 \) is the molality of the samples; \( m_2' \), the molality following a dilution of the first type; \( m_3 \), the molality following a dilution of the second type; \( \delta_L \), the relative apparent molal heat content of the solute; and \( q_B \), the heat of opening of the sample holders.

The following definitions were made to be consistent with the existing literature.
\[ \Delta H_{1,2} = \phi_L(m_2) - \phi_L(m_1) \]  
(39)

\[ \Delta H_{1,3} = \phi_L(m_3) - \phi_L(m_1) \]  
(40)

\[ \Delta H_{3,2} = \phi_L(m_2) - \phi_L(m_3) \]  
(41)

\( \Delta H_{1,2} \) is the heat absorbed when a solution of concentration 1 containing one mole of solute is diluted with enough water to form a solution of concentration 2.

The following expressions were obtained by combining Equations (39), (40), and (41) with Equations (37) and (38).

\[ \Delta H_{1,2} = - \frac{q_1 - q_2}{n_2} \]  
(42)

\[ \Delta H_{1,3} = - \frac{q_1 + q_2 - 2q_B}{n_2 + n_2'} \]  
(43)

\[ \Delta H_{3,2} = - \frac{(q_1 - q_2) - \frac{n_2'}{n_2} (q_2 - q_B)}{n_2' + n_2''} \]  
(44)

When \( \frac{n_2''}{n_2} \approx \frac{n_2'}{n_2} \), Equation (44) reduces to

\[ \Delta H_{3,2} = - \frac{q_1 - q_2}{n_2' + n_2''} \]  
(45)
This approximation was valid for the measurements reported here, since a volumetric pipet was used to fill the sample holders.

The quantities $\Delta H_{1,2}$ and $\Delta H_{1,3}$ are sometimes referred to as "long chord dilutions" because their heat effects appear as chords of extreme length on a plot of heat of dilution versus concentration. The quantity $\Delta H_{3,2}$ is termed a "short chord dilution" for the same reason.

The quantities $\Delta H_{1,2}$, $\Delta H_{1,3}$, and $\Delta H_{3,2}$ were used to facilitate the utilization of the experimentally determined quantities $q_1$, $q_2$, and $q_3$ in establishing the concentration dependence of the thermodynamic property, $\phi_L$. Values for $q_1$ and $q_2$ were determined for each of several concentrations, and average values for $q_1$, $q_2$, and $q_1 - q_2$ were obtained for each concentration. These values were used to calculate the quantities $\Delta H_{1,2}$, $\Delta H_{1,3}$, and $\Delta H_{3,2}$ for each concentration.

Unfortunately, the determination of absolute values for $\phi_L$ from a knowledge of differences in $\phi_L$ is not a straightforward process. The method of data treatment described here was developed by Young and co-workers (76, 77), and was later extended by Wallace and Robinson (78). In this method, the quantity $\Delta H_{3,2}$ was used to establish the concentration dependence of $\phi_L$ in the extremely dilute range. To apply the method, the quantity $\bar{p}_1$ was calculated for each concentration range, where
\[
\bar{P}_1 = -\frac{\Delta H_{3,2}(1)}{m_3^{1/2} - m_2^{1/2}}.
\] (46)

The quantity \( \bar{P}_1 \) represented the average slope of a \( \phi_L \) versus \( m^{1/2} \) plot in the concentration range \( \frac{m_1^{1/2}}{m_3^{1/2}} \) to \( \frac{m_2^{1/2}}{m_2^{1/2}} \).

It was assumed the slope, \( S \), of \( \phi_L \) versus \( m^{1/2} \) was expressible as a power series in \( m^{1/2} \), and that only three terms were needed in the very dilute range; that is,

\[
S = S^0 + B m^{1/2} + C m.
\] (47)

To make use of the dilution data, Equation (47) was altered to

\[
\bar{P}_1 = S^0 + B x_1 + C x_1^2
\] (48)

where \( x_1 = \frac{1}{2} \left[ \frac{m_3^{1/2}}{m_3^{1/2}} + \frac{m_2^{1/2}}{m_2^{1/2}} \right] \), and

\[
P_1 = \text{the true value of the slope of the } \phi_L \text{ versus } m^{1/2} \text{ plot at the midpoint of the concentration range } \frac{m_3^{1/2}}{m_3^{1/2}} \text{ to } \frac{m_2^{1/2}}{m_2^{1/2}}.
\]

\( \bar{P}_1 \) represented the average slope in the concentration range \( \frac{m_3^{1/2}}{m_3^{1/2}} \) to \( \frac{m_2^{1/2}}{m_2^{1/2}} \); therefore, from the definition of an average quantity,

\[
\bar{P}_1 = \frac{\int_{m_3^{1/2}}^{m_2^{1/2}} S \, dm^{1/2}}{m_2^{1/2} - m_3^{1/2}}
\] (49)
\[ \bar{F}_i = S^0 + B x_i + \frac{c}{3} \left( 4 x_i^2 - m_3^{1/2} - m_2^{1/2} \right). \]  

(50)

From Equations (48) and (50),

\[ P_i - \bar{P}_i = -c \frac{s_i^2}{12} \]  

(51)

where \( s_i = m_3^{1/2} - m_2^{1/2} \).

Hence, from Equations (48) and (51),

\[ \bar{F}_i = S^0 + B x_i + c \left( x_i^2 + \frac{s_i^2}{12} \right). \]  

(52)

Equations (49) and (50) were considerably simplified when \( S \) was assumed to be of the form

\[ S = S^0 + B m^{1/2}. \]  

(53)

In this case,

\[ \bar{F}_i = P_i, \]  

(54)

and

\[ P_i = S^0 + B x_i. \]  

(55)

The constants \( S^0, B, \) and \( C \) were obtained from Equations (52) and (55) by the method of least squares. The least squares determinations were weighted by the inverse square of the probable errors of \( \bar{F}_i \). The assignment of the probable errors will be discussed in a later section.
The constants obtained by the least squares method were substituted into Equation (56); an expression equivalent to Equation (47).

\[ S = \frac{d \phi_L}{d n^{1/2}} = s^0 + B n^{1/2} + C n \]  \hspace{1cm} (56)

Integration of Equation (56) yielded an expression for \( \phi_L \) for the extremely dilute range.

\[ \phi_L = s^0 n^{1/2} + \frac{B}{2} n + \frac{C}{3} n^{3/2} \] \hspace{1cm} (57)

The relative apparent molal heat contents, \( \phi_L \), for higher concentrations were obtained by combining Equations (39), (40), and (57).

**Electrical Calibrations**

The results of the electrical calibrations from which the sensitivity of the differential calorimeter was evaluated are summarized in Table 1. The sensitivity of the system was defined as the amount of heat necessary to displace the pen of the recording potentiometer a distance of one mm. Hence, the electrical calibrations were not used to determine the absolute heat capacities of the calorimeter containers, but rather were used as a means of obtaining the amount of heat corresponding to a given pen displacement.
### Table 1. Electrical Calibration of Differential Calorimeter

<table>
<thead>
<tr>
<th>Container</th>
<th>Amplifier Gain</th>
<th>Number of Dets.</th>
<th>Deflections Measured Perpendicular to the</th>
<th>Average Calibration in cal/mm</th>
<th>10^4 x Standard Deviation in cal/mm</th>
<th>10^4 x 99% Confidence Limits in cal/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>17</td>
<td>20</td>
<td>fore slope</td>
<td>6.83 x 10^{-4}</td>
<td>0.50</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after slope</td>
<td>6.85 x 10^{-4}</td>
<td>0.46</td>
<td>0.29</td>
</tr>
<tr>
<td>B</td>
<td>17</td>
<td>23</td>
<td>fore slope</td>
<td>6.31 x 10^{-4}</td>
<td>0.36</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after slope</td>
<td>6.35 x 10^{-4}</td>
<td>0.35</td>
<td>0.20</td>
</tr>
<tr>
<td>A</td>
<td>18</td>
<td>14</td>
<td>fore slope</td>
<td>4.96 x 10^{-4}</td>
<td>0.29</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after slope</td>
<td>5.10 x 10^{-4}</td>
<td>0.35</td>
<td>0.28</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>13</td>
<td>fore slope</td>
<td>4.75 x 10^{-4}</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after slope</td>
<td>4.82 x 10^{-4}</td>
<td>0.23</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Electrical heating was used to balance out as nearly as possible the heats of dilution for all determinations where more than 0.07 calorie was evolved. Any residual pen displacement was accounted for by means of the calibrated sensitivity. In this way, the determined heat quantities were relatively insensitive to the uncertainties in the calibration. On the other hand, no compensating electrical heating was necessary for determinations involving very dilute samples or for determinations of the heat of opening of the sample holders. In these cases, the deflections did not exceed the chart width of the recorder, and the heat quantities were determined solely from the total deflection and the calibrated sensitivity. Accordingly, determinations where very small quantities of heat were evolved were the most sensitive to uncertainties in the electrical calibrations, and the effect of these uncertainties became less important as the magnitude of the heat quantities increased.

As stated earlier in the procedure section of this report, two deflections were measured for each heating process. This practice was necessary because the potentiometer tracings of the main thermal output before and after a heating process were often not parallel. In these cases, the distance between the extensions of the tracings was dependent upon where the measurements were taken. The measurement made perpendicular to the fore drift at the beginning of the heating process and the measurement made perpendicular to the after drift at some point after the system had returned to equilibrium represented
the extreme values.

The output of the main thermal was dependent upon the temperature difference between the calorimeter containers. Changes in the drift of the potentiometer tracings of the thermal output were ascribed to such factors as slight fluctuations in the water bath temperature, changes in the energy generated by stirring, differing evaporation losses, and drifts in the electronic circuits. These changes in drift are not to be confused with the fore and after slopes encountered in isothermal calorimetry where the system under study is in thermal exchange with a constant environment. To point up this difference, the potentiometer tracings were called fore and after drifts instead of fore and after slopes.

In Table 1, calibrations based on both the deflections measured perpendicular to the fore slope and the deflections measured perpendicular to the after slope are reported. The standard deviations of the electrical calibrations as defined by the expression

$$q = \left[ \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1} \right]^{1/2}$$

where $X_i$ = value obtained for calibration $i$, 
$\bar{X}$ = average value, and
$n$ = number of determinations

are given in column six. The significances of the 99 per cent confidence
limits reported in column seven are that, if the uncertainties in the calibrations result from random errors, there is but one chance in 100 that the true value of the calibration falls outside the reported uncertainties. The reader is referred to Youden (79) for a discussion of confidence limits.

Excellent agreement was obtained between calibrations based on deflections measured perpendicular to the fore slope and those measured perpendicular to the after slope for calibrations obtained at gain setting 17. Somewhat poorer agreement was obtained for calibrations carried out at gain setting 18. A statistical $t$ test was carried out to determine the significance of the observed differences between these fore and after calibrations.

The basis of the $t$ test is as follows. If two series of measurements are carried out on a single property, the resulting averages of the two series will probably differ somewhat because of random errors in the individual measurements. The quantity $t$ serves as a measure of how much the averages can be expected to vary. The quantity $t$ is defined

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s} \left[ \frac{n_1 n_2}{n_1 + n_2} \right]^{1/2}$$

(59)

where

$$s^2 = \frac{\sum_{i=1}^{n_1} (x_{1i} - \bar{x}_1)^2 + \sum_{i=1}^{n_2} (x_{2i} - \bar{x}_2)^2}{n_1 + n_2 - 2}$$
\[ n_1 = \text{number of determinations in series 1,} \]
\[ n_2 = \text{number of determinations in series 2,} \]
\[ \bar{X}_1 = \text{average value for series 1, and} \]
\[ \bar{X}_2 = \text{average value for series 2.} \]

Critical values of \( t \) have been tabulated. For a system where \( n_1 + n_2 = 2 \) equals 22, the critical value for \( t \) at a 50 per cent probability level is 0.686, while the critical value for a one per cent probability level is 2.819. That is, if two series of 12 determinations subject only to random errors are carried out on a single property, the probability the quantity \( t \), as calculated from Equation (59), will exceed 0.686 is \( P = 0.50 \), while the probability the quantity will exceed 2.819 is only \( P = 0.01 \). A discussion of the \( t \) test is given by Youden (79).

The \( t \) test can be used to compare the averages of two series of measurements to determine whether a significant difference between the averages exists. A calculated value for \( t \) considerably larger than the tabulated critical values is interpreted as evidence for the non-equivalence of the two series of measurements. The comparison of results of analytical procedures is an application of this method.

When the \( t \) test was applied to the fore and after calibrations at gain 18, a probability level of 20 to 30 per cent was obtained for container A, and a probability level of greater than 50 per cent was obtained for container B. These low \( t \) values did not indicate a
For comparison at a given setting, the average error per cent larger than the average of the sensitivity determination was more so the result of the sensitivity determination for comparison. For comparison, it was concluded that the sensitivity determination based on a few

determination would lead to correct average values.

based on either the fore or the after slope.

temperature drifts occurred in a nearly random

from perfect randomness.

calibrations were interpreted as evidence for a slight departure
random fashion. The slightly larger values for the after slope
responsible for the difference determinations occurred in a nearly
the after slope, it was concluded that the temperature drifts
of the calibrations based on determinations measured perpendicular to
measured perpendicular to the fore slope agreed with the average

1. Since the averages of the calibrations based on determinations

for the following conclusions:

the good agreement between the fore and after calibrations led

relatively large confidence limits.

consistent with the small differences between calibrations and the

significant difference between the calibrations. This result was
sensitivities varied by five per cent. The t test was applied to the differences between the calibrations of containers A and B at both gain settings. As might be expected, the results were inconclusive. The t values were relatively large, but not large enough to establish conclusively that a real difference existed.

On the basis of other information, the difference in heat capacity for the two containers was known to be negligible. Each container had a heat capacity of approximately 1100 calories per degree. Of this, 900 calories per degree are due to water or solutions, and the remainder due to the containers themselves, their mountings, their nonaqueous contents, and the main thermal. If a difference in sensitivity of five to eight per cent existed, container A would have had a heat capacity of 50 to 90 calories per degree larger than container B. This was inconsistent with what was known of the construction and mounting of the two containers. For example, the tantalum containers differed in weight by only 1.5 grams, the lucite supporting rings by 0.3 gram, the sample holders by 0.1 gram, and the brass snap rings by 2.7 grams.

Direct evidence that the two containers had nearly equal heat capacities was obtained by heating both containers simultaneously for heating periods considerably longer than was possible for the calibration experiments. Table 2 summarizes the results of ten determinations of this type.

The following definitions were necessary to interpret the data of Table 2.
Table 2. The Ratio $Q_A/Q_B$ for the Calorimeter Containers

<table>
<thead>
<tr>
<th>$Q_A \times 10^{-3}$ calories</th>
<th>$Q_B \times 10^{-3}$ calories</th>
<th>$\delta_d$ mm</th>
<th>$1 + \frac{\delta_d}{Q_B}$</th>
<th>$\frac{Q_A}{Q_B}$</th>
<th>$\frac{C_A}{C_B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.93</td>
<td>286.90</td>
<td>1</td>
<td>1.0017</td>
<td>1.0071</td>
<td>1.0054</td>
</tr>
<tr>
<td>578.86</td>
<td>574.78</td>
<td>12</td>
<td>1.0102</td>
<td>1.0071</td>
<td>.9959</td>
</tr>
<tr>
<td>117.11</td>
<td>116.28</td>
<td>0</td>
<td>1.0000</td>
<td>1.0071</td>
<td>1.0071</td>
</tr>
<tr>
<td>866.94</td>
<td>860.81</td>
<td>31</td>
<td>1.0177</td>
<td>1.0071</td>
<td>.9896</td>
</tr>
<tr>
<td>1156.87</td>
<td>1148.69</td>
<td>20</td>
<td>1.0086</td>
<td>1.0071</td>
<td>.9985</td>
</tr>
<tr>
<td>1318.90</td>
<td>1321.59</td>
<td>0</td>
<td>1.0000</td>
<td>.9980</td>
<td>.9980</td>
</tr>
<tr>
<td>1318.41</td>
<td>1321.11</td>
<td>28</td>
<td>1.0140</td>
<td>.9980</td>
<td>.9842</td>
</tr>
<tr>
<td>1056.12</td>
<td>1058.34</td>
<td>15</td>
<td>.9907</td>
<td>.9979</td>
<td>1.0073</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>0</td>
<td>1.0000</td>
<td>.9980$^1$</td>
<td>.9980</td>
</tr>
<tr>
<td>530.98</td>
<td>531.85</td>
<td>32</td>
<td>.9603</td>
<td>.9984</td>
<td>1.0397</td>
</tr>
</tbody>
</table>

(Excluding last entry) average 0.9983
Standard deviation .0078
99 % Confidence limit .0087

$^1$ The heat inputs were not measured for this experiment. The ratio $Q_A$ to $Q_B$ was determined from the resistances of the calorimeter heaters.
\[ Q_A = \text{heat input in container } A \]
\[ Q_B = \text{heat input in container } B \]
\[ d_A = \text{deflection resulting from heat input } Q_A \text{ in container } A \]
\[ d_B = \text{deflection resulting from heat input } Q_B \text{ in container } B \]
\[ C_A = \text{sensitivity or calibration of container } A \]
\[ C_A = \frac{Q_A}{d_A} \quad (60) \]
\[ C_B = \text{sensitivity or calibration of container } B \]
\[ C_B = \frac{Q_B}{d_B} \quad (61) \]
\[ \delta_d = \text{resultant deflection} = d_A - d_B \]

The definitions for \( C_A \) and \( C_B \) were rearranged to obtain
\[ Q_A = C_A d_A \quad (62) \]
and
\[ Q_B = C_B d_B \quad (63) \]

Equation (64) was obtained by dividing Equation (62) by Equation (63), and substituting the definition of \( \delta_d \).
\[ \frac{Q_A}{Q_B} = \frac{C_A d_A}{C_B d_B} = \frac{C_A}{C_B} \left[ 1 + \frac{\delta_d}{d_B} \right] \quad (64) \]

Since \( \delta_d/d_B \) was small compared to one, the expression in brackets was relatively insensitive to errors in \( d_B \). The quantity \( d_B \) was approx-
imated from Equation (61), and Equation (64) became

\[
\frac{Q_A}{Q_B} = \frac{C_A}{C_B} \left[ 1 + \frac{\delta_d}{Q_B} \right].
\]  

(65)

Equation (65) was rearranged to obtain

\[
\frac{C_A}{C_B} = \frac{\frac{Q_A}{Q_B}}{1 + \frac{\delta_d}{Q_B}}.
\]  

(66)

The ratios of \( C_A \) to \( C_B \) given in Table 2 did not indicate a significant difference in heat capacity for the two containers. Accordingly, a sensitivity of \( 6.57 \times 10^{-4} \) calories per mm was assigned for determinations carried out at gain 17, and a sensitivity of \( 4.91 \times 10^{-4} \) calories per mm was assigned for determinations carried out at gain 18.

Blank Experiments

Nineteen measurements were made with water samples to determine the "heat of opening" of the sample holders. The results of these measurements were as follows.

- Average heat of opening: \( 12.3 \times 10^{-3} \) calories
- Standard deviation: \( 2.6 \times 10^{-3} \) calories
- 99% confidence limit: \( 1.7 \times 10^{-3} \) calories
Copper Sulfate

The heats of dilution of two copper sulfate solutions were determined to serve as checks on the performance of the differential solution calorimeter and on the procedures employed. Copper sulfate was chosen because the thermodynamic properties of copper sulfate solutions approach those of rare earth chloride solutions, because copper sulfate was available in pure form, and because copper sulfate solutions could be analyzed easily and precisely. The heat of dilution determinations were in good agreement with the data of Lange, Monheim, and Robinson (80). Table 3 compares the values for $\phi_L$ calculated from the observed heat of dilution with the values reported by Lange, Monheim, and Robinson (80).

Table 3. $\phi_L$'s for Copper Sulfate Solution at 25°C.

<table>
<thead>
<tr>
<th>Molality of Samples</th>
<th>$\phi_L$ (Ames Laboratory)</th>
<th>$\phi_L$ (Lange, Monheim, Robinson)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04981</td>
<td>1107 ± 9</td>
<td>1100</td>
</tr>
<tr>
<td>0.09836</td>
<td>1221 ± 9</td>
<td>1235</td>
</tr>
</tbody>
</table>

1 Heat quantities are given in defined calories.
2 The reported uncertainties are mean deviations.

Neodymium Chloride

The experimentally determined heats of dilution and related thermochemical properties for neodymium chloride solutions at 25°C are
listed in Tables 4 through 7. Graphical representations of some of these quantities are given in Figures 5 and 6. The solution numbers in column one of Table 4 were assigned as a matter of convenience and refer to the order in which the solutions were prepared rather than to the order in which the determinations were carried out. Solutions one through six were dilutions of the stock solution prepared by the excess oxide method; solutions seven and eight were dilutions of the stock solution prepared by the excess acid method. In Figures 5 and 6, solutions one through six were represented as open triangles, and solutions seven and eight were shown as filled triangles.

Even though salts of the rare earth elements are considered strong electrolytes, they are known to associate and hydrolyze to some extent. In some cases, these phenomena can lead to metastable species or aggregates in solution. Heat of dilution measurements were carried out on solutions prepared by different procedures to determine whether the results were influenced by the method of preparation. As seen in Figures 5 and 6, no difference was detected.

The short chord data from which the concentration dependence of \( \phi_1 \) at extreme dilution was obtained are summarized in Table 5. The short chords are shown graphically in Figure 5. In Table 5, \( m_1 \) refers to the sample concentration; \( m_2 \), the concentration following a break into water; \( m_3 \), the concentration following a break into solution; \( q_1 - q_2 \), the difference in heat evolved for a break into water and a break into solution; and \( n_2' + n_2'' \), the total number of moles of salt involved in
<table>
<thead>
<tr>
<th>Sample</th>
<th>( q_1 )</th>
<th>( q_2 )</th>
<th>( q_1 - q_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside B Water</td>
<td>31.9</td>
<td>31.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Outside A Water</td>
<td>40.2</td>
<td>40.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Inside A Solution</td>
<td>27.9</td>
<td>27.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Outside B Solution</td>
<td>42.3</td>
<td>42.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Inside B Water</td>
<td>33.5</td>
<td>33.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Outside A Solution</td>
<td>48.9</td>
<td>48.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Inside A Solution</td>
<td>35.7</td>
<td>35.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Outside B Solution</td>
<td>33.7</td>
<td>33.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4. Heats of Dilution of Nuclein Chloride Solutions at 25°c.
<table>
<thead>
<tr>
<th>Solution</th>
<th>m</th>
<th>Sample</th>
<th>In</th>
<th>q₂</th>
<th>q₃</th>
<th>q₁</th>
<th>q₂</th>
<th>q₁ - q₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.02777</td>
<td>Inside B Water</td>
<td>304.1</td>
<td>-18.3</td>
<td>265.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outside B Solution</td>
<td>239.2</td>
<td>3.8</td>
<td>243.0</td>
<td>42.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outside A Water</td>
<td>347.3</td>
<td>-60.9</td>
<td>286.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inside A Solution</td>
<td>239.1</td>
<td>3.3</td>
<td>242.4</td>
<td>44.0</td>
<td></td>
<td></td>
</tr>
<tr>
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1 All heat quantities are given in defined calories x 1000.

2 Values not included in the averages.
Table B. Short chord data for medium chlorine solutions at 35°C.

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All heat quantities are given in definite calories.
Table 6. Relative Apparent Molal Heat Contents of Neodymium Chloride Solution at 25°C.

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<th>$q_1 - q_2 \times 10^3$</th>
<th>$q_1 + q_2 - 2q_B \times 10^3$</th>
<th>$-\Delta H_{1,K}$</th>
<th>$\phi_L(m_1^{1/2})$</th>
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1 All heat quantities are given in defined calories.
Table 7. Thermodynamic Properties of Neodymium Chloride Solution at 25°C.

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<th>$\bar{V}_L^1$ Eq. (74)</th>
<th>$\bar{V}_L^2$ Eq. (77)</th>
<th>$\bar{V}_L^2$ Eq. (79)</th>
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1 Heat quantities are given in defined calories.
2 Values obtained from Equation (71).
Figure 5. Short Chords for Neodymium Chloride Solutions at 25°C.
Figure 6. Relative Apparent Molal Heat Contents of Neodymium Chloride Solution at 25°C.
the processes. The quantity $\bar{F}_1$ was defined by Equation (46), and was expressed in terms of $q_1 - q_2$ by a combination of Equations (45) and (46).

$$\Delta H_{3,2} = -\frac{q_1 - q_2}{n_2^' + n_2^\''}$$ (45)

$$\bar{F}_1 = \frac{-\Delta H_{3,2}}{m_3^{1/2} - m_2^{1/2}}$$ (46)

$$\bar{F}_1 = \frac{q_1 - q_2}{[m_3^{1/2} - m_2^{1/2}][n_2^' + n_2^\'']}$$ (67)

The probable errors in $q_1 - q_2$, listed as $F_q$ observed, were obtained from the defining relationship

$$p = \frac{0.6745\sigma}{n^{1/2}}$$ (68)

where $p$ = probable error of the mean of a series of determinations,

$\sigma$ = standard deviation of the mean, and

$n$ = number of determinations.

Figure 5 illustrates how the uncertainty in $\bar{F}_1$ decreased rapidly with increasing concentration. The observed values for the probable errors in $q_1 - q_2$ as listed in Table 5 did not exhibit a marked trend. The absence of a regular trend in the most dilute concentration range
suggested the possibility that the errors in \( q_1 - q_2 \) for that range were of equal magnitude. This possibility was investigated by applying Bartlett's test for homogeneity of variance to the uncertainties in the short chord data. Bartlett's test is discussed by Youden (79) and Snedecor (61). The test indicated that, if variances were perfectly homogeneous, the observed variations in probable errors for sample concentrations below 0.09 molal could be expected seven out of ten times. It was concluded that variances were homogeneous for values of \( q_1 - q_2 \) up to 0.1 calorie, and an adjusted estimate of \( 5.3 \times 10^{-3} \) calories was assigned for the standard deviation of the system. Smoothed values for \( p_q \) calculated by means of Equation (68) are tabulated in Table 5. The probable errors for \( \bar{F}_1 \) in Table 5 were calculated from the smoothed values for \( p_q \).

The concentration dependence of \( \bar{F}_1 \) was determined by the method of least squares using the inverse square of the probable error in \( \bar{F}_1 \) as a weighting factor. A least squares treatment with two free parameters yielded the expression

\[
\bar{F}_1 = 6627 - 22325 x_1.
\]  

(69)

The limiting value for \( \bar{F}_1 \) agreed within experimental error with the Debye-Hückel limiting law value of 6925. The good agreement with theory suggested the use of a modified least squares treatment with one free parameter and the theoretical limiting slope. The following expression resulted from this treatment.
\[ \bar{F}_{1} = 6925 - 28496 x_{1} \quad (70) \]

The straight lines defined by Equations (69) and (70) are shown in Figure 5 as a solid line and a broken line respectively. This plot shows that Equation (69) represented the data as well as Equation (70).

An expression for \( \phi_{L} \) for the short chord dilution range was obtained by integrating Equation (70).

\[ \phi_{L} = 6925 \, m^{1/2} - 14248 \, m \quad (71) \]

One should note that the listings of \( \bar{F}_{1} \) and \( x_{1} \) in Table 5 are given to more places than are significant. The author was in the habit of carrying forward several extra digits when applying the least squares method. The nonsignificant digits were tabulated to enable any reader interested in the arithmetic of the calculations to reproduce Equations (69) and (70) exactly.

The long chord dilution data for neodymium chloride are tabulated in Table 6. The values for the relative apparent metal heat contents of the solute were obtained by rearranging Equations (39) and (40) to obtain

\[ \phi_{L}(m_{1}) = \phi_{L}(m_{K}) - \Delta H_{1,K} \quad (72) \]

where \( \Delta H_{1,K} \) = an intermediate integral heat of dilution corresponding to some \( \Delta H_{1,2} \) or \( \Delta H_{1,3} \).
Values for $\phi_L(m)$ were obtained from Equation (71). The derived values for $\phi_L$ are shown graphically in Figure 6.

According to Equation (17) and (18),

$$\bar{L}_2 = \phi_L + \frac{m^{1/2}}{2} \frac{\partial \phi_L}{\partial m^{1/2}},$$

and

$$\bar{L}_1 = \frac{m N_1}{1000} (\phi_L - \bar{L}_2).$$

(17)

An analytic function giving a faithful representation of the concentration dependence of $\phi_L$ was needed to derive the thermodynamic properties $\bar{L}_1$ and $\bar{L}_2$. Nine least squares determinations were carried out to obtain such an expression. The $\phi_L$'s for the six more concentrated solutions and the $\phi_L$ value predicted for 0.0049 m by Equation (71) were used for these calculations. Of the nine expressions obtained in this way, the data was best represented by Equations (73) and (74).

$$\phi_L = 6925 m^{1/2} - 16056 m + 17523 m^{3/2}$$

(73)

$$\phi_L = 6925 m^{1/2} - 16725 m + 22278 m^{3/2} - 7596 m^{2}$$

(74)

These expressions were derived from Equations (75) and (76) respectively.

$$\frac{\phi_L - 6925 m^{1/2}}{m^{1/2}} = b m^{1/2} + c m$$

(75)

$$\frac{\phi_L - 6925 m^{1/2}}{m^{1/2}} = b m^{1/2} + c m + d m^{3/2}$$

(76)
Attempts to extend the range of Equation (71) by adding higher terms were not successful.

Equations (77) and (78) were derived from Equation (73) by means of Equations (17) and (18); correspondingly, Equations (79) and (80) were derived from Equation (74).

\[
\begin{align*}
\overline{L}_2 &= 10387 m^{1/2} - 32112 m + 43808 m^{3/2} \\
\overline{L}_1 &= -62.37 m^{3/2} + 289.26 m^2 - 473.55 m^{5/2} \\
\overline{L}_2 &= 10387 m^{1/2} - 33450 m + 55695 m^{3/2} - 22788 m^2 \\
\overline{L}_1 &= -62.37 m^{3/2} + 301.32 m^2 - 602.04 m^{5/2} + 273.70 m^3
\end{align*}
\]

Table 7 lists the derived values for \( \overline{L}_2 \) and the values for \( \overline{L}_1 \) as calculated from Equations (73), (74), and (77) through (80). Equations (73) and (74) represented the data well from 0 to 0.18 m, with Equation (74) giving the slightly better fit. The solid curve of Figure 6 is defined by Equation (74), and also illustrates the ability of this expression to reproduce the experimental points. The values for \( \overline{L}_2 \) from Equations (77) and (79) and the values for \( \overline{L}_1 \) from Equations (78) and (80) agreed well except for the most concentrated solution.

As shown in Figure 6, the curve defined by Equation (74) had an inflection point between \( m^{1/2} = 0.3 \) and \( m^{1/2} = 0.4 \). The curve defined by Equation (73) had a more pronounced inflection point in this
concentration range. Since the thermodynamic properties $\bar{L}_2$ and $\bar{L}_1$ are functions of the derivative of $\Phi_L$, the differing curvature of the two expressions gave rise to a spread in values for $\bar{L}_2$ and $\bar{L}_1$ at $x^{1/2} = 0.43$. The experimentally determined points did not indicate the presence of an inflection point. The less pronounced inflection point of Equation (74) probably makes this expression and those derived from it more reliable than the series of expressions based on Equation (75). The use of any of the expressions for $\Phi_L$, $\bar{L}_2$, or $\bar{L}_1$ for extrapolations to higher concentrations would be risky.

Erbium Chloride

The experimentally determined heats of dilution and related thermochemical properties of erbium chloride are listed in Tables 8 through 11. Some of these quantities are represented graphically in Figures 7 and 8.

Solutions two through seven were dilutions of the stock solution prepared by the excess oxide method. Solutions 8 through 12 were dilutions of the stock solution prepared from hydrated crystals. Solutions 8 and 12 were acidified to $p\bar{H} 4$ with hydrochloric acid to form solutions 8A and 12A. In Figure 7 and 8 solutions two through seven were represented as open circles; solutions 8 through 12 as half filled circles; and solutions 8A and 12A as filled circles.

The short chord data for erbium chloride are summarized in Table 5 and are plotted in Figure 7. The uncertainties in $\bar{P}_A$ for erbium
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|          |       | Outside A | Solution | 82.2 | 27.0 | 109.2 | 0.3 |           |
|          |       | Inside B  | Water   | 141.2 | -16.8 | 124.4 |     |           |
|          |       | Outside B | Solution | 149.1 | -28.7 | 120.4 | 4.0 |           |
|          |       |           |         | 117.0 | 114.8 | 2.2 |     |           |

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|          |       | Inside A  | Solution | 138.0 | -17.2 | 120.8 | 12.5 |           |
|          |       | Outside B | Water   | 121.8 | 18.9 | 140.7 |     |           |
|          |       | Inside B  | Solution | 120.0 | 10.3 | 130.3 | 10.4 |           |
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<td>255.7</td>
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</tr>
<tr>
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<td>0.1843</td>
<td>Outside A</td>
<td>Water</td>
<td>2113.0</td>
<td>23.6</td>
<td>2136.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inside A</td>
<td>Solution</td>
<td>1769.7</td>
<td>47.0</td>
<td>1816.7</td>
<td>319.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inside B</td>
<td>Water</td>
<td>2205.2</td>
<td>-41.5</td>
<td>2161.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outside B</td>
<td>Solution</td>
<td>1779.6</td>
<td>36.2</td>
<td>1815.8</td>
<td>345.9</td>
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Table 8. (Cont'd)

<table>
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<tr>
<th>Solution</th>
<th>m</th>
<th>Sample</th>
<th>In</th>
<th>q_H</th>
<th>q_D</th>
<th>q_L</th>
<th>q_2</th>
<th>q_L - q_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.1843</td>
<td>Outside A</td>
<td>Water</td>
<td>2140.0</td>
<td>23.2</td>
<td>2163.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>Inside A</td>
<td>Solution</td>
<td>1737.5</td>
<td>56.4</td>
<td>1793.9</td>
<td>369.3</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>Outside B</td>
<td>Water</td>
<td>2159.1</td>
<td>- 6.4</td>
<td>2151.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>Inside B</td>
<td>Solution</td>
<td>1891.8</td>
<td>-80.6</td>
<td>1811.2</td>
<td>340.5</td>
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</tr>
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</table>

1 All heat quantities are given in defined calories x 1000.
<table>
<thead>
<tr>
<th>$m_1^{1/2}$</th>
<th>$n_2 + n_2^\prime$</th>
<th>$m_2^{1/2}$</th>
<th>$m_3^{1/2}$</th>
<th>$q_1 - q_2$</th>
<th>Observed</th>
<th>Smoothed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1050</td>
<td>0.2194</td>
<td>1.110</td>
<td>1.561</td>
<td>0.28</td>
<td>1.0</td>
<td>1.21</td>
</tr>
<tr>
<td>0.1214</td>
<td>0.2933</td>
<td>1.283</td>
<td>1.804</td>
<td>4.3</td>
<td>1.2</td>
<td>1.71</td>
</tr>
<tr>
<td>0.1389</td>
<td>0.3838</td>
<td>1.468</td>
<td>2.064</td>
<td>2.2</td>
<td>1.3</td>
<td>2.42</td>
</tr>
<tr>
<td>0.1432</td>
<td>0.4084</td>
<td>1.514</td>
<td>2.129</td>
<td>11.5</td>
<td>0.7</td>
<td>2.42</td>
</tr>
<tr>
<td>0.1436</td>
<td>0.4107</td>
<td>1.518</td>
<td>2.135</td>
<td>10.6</td>
<td>4.7</td>
<td>2.42</td>
</tr>
<tr>
<td>0.1489</td>
<td>0.4415</td>
<td>1.574</td>
<td>2.214</td>
<td>8.9</td>
<td>1.4</td>
<td>1.71</td>
</tr>
<tr>
<td>0.2005</td>
<td>0.7997</td>
<td>2.119</td>
<td>2.980</td>
<td>37.0</td>
<td>1.5</td>
<td>2.42</td>
</tr>
<tr>
<td>0.2013</td>
<td>0.8059</td>
<td>2.127</td>
<td>2.991</td>
<td>45.8</td>
<td>3.5</td>
<td>2.42</td>
</tr>
<tr>
<td>0.2134</td>
<td>0.9061</td>
<td>2.255</td>
<td>3.172</td>
<td>35.6</td>
<td>2.1</td>
<td>1.71</td>
</tr>
<tr>
<td>0.2726</td>
<td>1.477</td>
<td>2.880</td>
<td>4.050</td>
<td>99.8</td>
<td>4.8</td>
<td>2.42</td>
</tr>
<tr>
<td>0.3024</td>
<td>1.819</td>
<td>3.196</td>
<td>4.494</td>
<td>122.1</td>
<td>2.7</td>
<td>2.70</td>
</tr>
<tr>
<td>0.3818</td>
<td>2.897</td>
<td>4.034</td>
<td>5.673</td>
<td>255.7</td>
<td>5.1</td>
<td>5.09</td>
</tr>
<tr>
<td>0.4293</td>
<td>3.657</td>
<td>4.533</td>
<td>6.375</td>
<td>343.9</td>
<td>6.9</td>
<td>6.85</td>
</tr>
</tbody>
</table>

1 Heat quantities are given in defined calories.
Table 10. Relative Apparent Molar Heat Contents of Erbium Chloride Solutions at 25°C.

<table>
<thead>
<tr>
<th>$n_1^{1/2}$</th>
<th>$n_X^{1/2} \times 10^2$</th>
<th>$q_1 - q_2 \times 10^3$</th>
<th>$q_1 + q_2 - 2q_B \times 10^3$</th>
<th>$\Delta H_{1,X}$</th>
<th>$\phi_L(n_X)$</th>
<th>$\phi_L(n_1)$</th>
<th>$\bar{\phi}_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1050</td>
<td>1.110</td>
<td>47.8</td>
<td>436</td>
<td>55</td>
<td>491</td>
<td>501</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.561</td>
<td>95.3</td>
<td>434</td>
<td>78</td>
<td>512</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1214</td>
<td>1.283</td>
<td>69.7</td>
<td>475</td>
<td>64</td>
<td>539</td>
<td>545</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.804</td>
<td>135.1</td>
<td>461</td>
<td>90</td>
<td>551</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1389</td>
<td>1.468</td>
<td>104.7</td>
<td>546</td>
<td>73</td>
<td>619</td>
<td>631</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.064</td>
<td>207.2</td>
<td>540</td>
<td>103</td>
<td>643</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1432</td>
<td>1.514</td>
<td>124.7</td>
<td>611</td>
<td>76</td>
<td>687</td>
<td>689</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.129</td>
<td>238.0</td>
<td>583</td>
<td>107</td>
<td>690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1436</td>
<td>1.518</td>
<td>122.9</td>
<td>599</td>
<td>73</td>
<td>675</td>
<td>678</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.135</td>
<td>235.2</td>
<td>573</td>
<td>107</td>
<td>680</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1489</td>
<td>1.574</td>
<td>132.3</td>
<td>599</td>
<td>79</td>
<td>678</td>
<td>684</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.214</td>
<td>255.7</td>
<td>579</td>
<td>111</td>
<td>690</td>
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<td>0.2005</td>
<td>2.119</td>
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<td>769</td>
<td>106</td>
<td>875</td>
<td>874</td>
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</tr>
<tr>
<td></td>
<td>2.980</td>
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<td>150</td>
<td>872</td>
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<td></td>
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<td>0.2013</td>
<td>2.127</td>
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<td>107</td>
<td>888</td>
<td>882</td>
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<tr>
<td></td>
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<td>583.4</td>
<td>724</td>
<td>151</td>
<td>875</td>
<td></td>
<td></td>
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<td>2.255</td>
<td>350.0</td>
<td>773</td>
<td>113</td>
<td>886</td>
<td>889</td>
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<tr>
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<td>732</td>
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<td>892</td>
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</table>
Table 10. (Cont'd)

<table>
<thead>
<tr>
<th>m_1/2</th>
<th>m_K/2</th>
<th>q_1 - q_B</th>
<th>q_1 + q_2 - 2q_B</th>
<th>- ΔH_{1,K}</th>
<th>\phi_{L}(m_K)</th>
<th>\phi_{L}(m_1)</th>
<th>\bar{\phi}_{L}</th>
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<tr>
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<td>2.880</td>
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<td>1252.1</td>
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<td></td>
<td>848</td>
<td>206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3024</td>
<td>3.196</td>
<td>869.4</td>
<td>1616.8</td>
<td>956</td>
<td>161</td>
<td>1117</td>
<td>1118</td>
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<tr>
<td></td>
<td>4.494</td>
<td></td>
<td></td>
<td>889</td>
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<td></td>
<td></td>
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<tr>
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<td>1304</td>
<td>1303</td>
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<td>1404</td>
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</table>

1 Heat quantities are given in defined calories.
Table 11. Thermodynamic Properties of Erbium Chloride Solutions at 25°C.

<table>
<thead>
<tr>
<th>1/2 m</th>
<th>$\phi_L^{-1}$</th>
<th>$\bar{L}_2$</th>
<th>$-\bar{L}_1 \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Derived</td>
<td>Eq. (87)</td>
<td>Eq. (89)</td>
</tr>
<tr>
<td>.0100</td>
<td>50²</td>
<td>56</td>
<td>84</td>
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<tr>
<td>.0300</td>
<td>151²</td>
<td>163</td>
<td>241</td>
</tr>
<tr>
<td>.0500</td>
<td>255²</td>
<td>254</td>
<td>236</td>
</tr>
<tr>
<td>.0700</td>
<td>362²</td>
<td>358</td>
<td>519</td>
</tr>
<tr>
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<td>501</td>
<td>510</td>
<td>726</td>
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<tr>
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<td>545</td>
<td>576</td>
<td>813</td>
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<td>631</td>
<td>642</td>
<td>899</td>
</tr>
<tr>
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<td>688</td>
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<td>660</td>
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<td>1400</td>
</tr>
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<td>1118</td>
<td>1126</td>
<td>1489</td>
</tr>
<tr>
<td>.3818</td>
<td>1303</td>
<td>1306</td>
<td>1723</td>
</tr>
<tr>
<td>.4293</td>
<td>1404</td>
<td>1409</td>
<td>1877</td>
</tr>
</tbody>
</table>

1 Heat quantities are given in defined calories.
2 Values calculated from Equation (84).
Figure 7. Short Chords for Erbium Chloride Solutions at 25°C.
Figure 8. Relative Apparent Molal Heat Contents of Erbium Chloride Solution at 25°C.
chloride, like the uncertainties in $P_4$ for neodymium chloride decreased rapidly with increasing concentration. Bartlett's test for homogeneity of variance was applied to the uncertainties in $q_1 - q_2$ for erbium chloride. The test indicated that the variations in probable error observed for values of $q_1 - q_2$ less than 0.1 calorie would be expected 7.5 times in 10 if the variances were homogeneous. Accordingly, the variances were assumed to be homogeneous, and an adjusted estimate of $5.1 \times 10^{-3}$ calories was assigned for the standard deviation of values of $q_1 - q_2$ less than 0.1 calorie. Smoothed values for $P_4$ and $P_{P_4}$ were calculated from the adjusted standard deviation. These values are tabulated in Table 9.

As seen in Figure 7, the short chords for erbium chloride did not approach the theoretical value of 6925 as did the short chords for neodymium chloride. The short chords for concentrations greater than $4 \times 10^{-4}$ molal were not inconsistent with an extrapolation to 6925, but the values for concentrations less than $4 \times 10^{-4}$ molal were consistently low. The uncertainties in the short chords for concentrations less than $4 \times 10^{-4}$ molal were quite large. As a result, the trend shown by the short chords could not be interpreted with certainty as being real, but rather were interpreted as strong evidence that some departure from ideal behavior had occurred.

The possibility that the anomaly was due to associated species or to some other phenomena dependent upon the history of the solutions was investigated somewhat by making measurements on solutions prepared by
different methods and on solutions that were made slightly acid. All results agreed within experimental error.

The anomalous behavior of the short chords complicated the determination of the concentration dependence of \( F_1 \). A three parameter least squares treatment resulted in Equation (81).

\[
\bar{F}_1 = 465 + 242.114 \, x_1 - 2.867 \times 10^6 \left( x_1^2 + \frac{\sigma^2}{12} \right)
\]  (81)

The curve defined by Equation (81) appears as a broken line in Figure 7. Equation (81) gave an excellent representation of the short chord data in the concentration range studied, but the pronounced curvature for the regions above and below the range covered made the expression unsuitable for extrapolation.

A two parameter least squares treatment yielded Equation (82) which appears as a solid line in Figure 7.

\[
\bar{F}_1 = 4933 + 6965 \, x_1
\]  (82)

Equation (82) gave some, but not much, weight to chords with concentrations below \( 4 \times 10^{-4} \) molal, and gave a good representation of the data. A modified two parameter treatment with \( g^0 \) chosen as the theoretical limiting slope and the second parameter free resulted in Equation (83).

\[
\bar{F}_1 = 6925 - 39433 \, x_1
\]  (83)

The straight line defined by Equation (83) appears as alternate dots and dashes in Figure 7. Equation (82) was chosen as the most reliable
representation of the short chords, and was integrated to obtain an expression for \( \psi_L \) for concentrations below \( 5 \times 10^{-3} \) molal.

\[
\psi_L = 4933 \, m^{1/2} + 3483 \, m
\]  

(84)

The intermediate heats of dilution and relative apparent molal heat contents of erbium chloride solutions at 25°C are tabulated in Table 10. The derived values for \( \bar{\psi}_L \) are represented graphically in Figure 8.

The method of least squares was used to develop an empirical expression for the concentration dependence of \( \bar{\psi}_L \). For this purpose, equations of the type

\[
\psi_L = s_0 \, m^{1/2} + b \, m + c \, m^{3/2} + d \, m^2
\]  

(85)

and

\[
\frac{\psi_L}{m^{1/2}} = s_0 + b \, m^{1/2} + c \, m + d \, m^{3/2}
\]  

(86)

were employed. The \( \bar{\psi}_L \) values for solutions 8 through 12, 8A, and 12A were weighted by unity; the values for solutions 3 through 7 were weighted by 2; and the value for solution 2 and the value predicted by Equation (84) for 0.0049 molal were weighted by 4. These weighting factors were assigned in proportion to the number of determinations carried out at each concentration. Equation (86) with \( d = 0 \) gave rise to

\[
\psi_L = 5687 \, m^{1/2} - 8637 \, m + 7066 \, m^{3/2}.
\]  

(87)

The solid curve of Figure 8 is defined by Equation (87). Values for \( \bar{\psi}_L \)
calculated from Equation (87) along with the $\bar{\rho}_m$ values of Table 10 are listed in Table 11.

A modified treatment of Equation (86) with $S^0$ chosen as 5687 and with $b$, $c$, and $d$ adjustable did not give an appreciably better fit than Equation (87). A four free parameter expression based on Equation (86) gave a poor representation of data above 0.09 molal. Attempts to obtain an adequate representation of the $\bar{\rho}_m$ values with $S^0$ chosen as 6925, the theoretical limiting slope, and 4933, the limiting slope of Equation (84), were not successful.

Expressions for $\bar{L}_1$ and $\bar{L}_2$ were derived from Equation (87) by means of Equations (17) and (18).

$$\bar{L}_1 = -51.23 m^{3/2} + 155.60 m^2 - 190.95 m^{5/2} \quad (88)$$

$$\bar{L}_2 = 8531 m^{1/2} - 17274 m + 17665 m^{3/2} \quad (89)$$

Values for $\bar{L}_1$ and $\bar{L}_2$ as calculated from Equations (88) and (89) are tabulated in Table 11.

Error Analysis

Estimates of the uncertainties in the electrical calibrations of the differential calorimeter, the heat of opening of the sample holders, and the short chords were given as these data were presented in the preceding sections. No mention was made of the more significant quantities, the uncertainties in the relative apparent molal heat contents.
Estimates of the uncertainties in \( \Phi_L \) were obtained by the method of propagation of precision indexes as described by Worthing and Geffner (82). With this method, the probable error of a calculated quantity is derived from the probable errors of the independent, measurable quantities from which the quantity was calculated. A generalized form of the method of propagation of precision indexes is as follows:

If \( \hat{U} = f(\bar{X}_1, \bar{X}_2, \ldots, \bar{X}_n) \),

then

\[
\frac{P_{\hat{U}}}{\hat{U}} = \sum_{i=1}^{i=n} \left( \frac{\partial \hat{U}}{\partial \bar{X}_i} \right)^2 \frac{P_{\bar{X}_i}}{\bar{X}_i^2}.
\] (91)

That is, if \( \hat{U} \) is some function of the mean values of the independent and measurable quantities \( \bar{X}_1, \bar{X}_2, \ldots, \bar{X}_n \), the probable error, \( \frac{P_{\hat{U}}}{\hat{U}} \), of \( \hat{U} \) can be calculated from the probable errors \( P_{\bar{X}_1}, P_{\bar{X}_2}, \ldots, P_{\bar{X}_n} \) by means of Equation (91).

The values for \( \Phi_L \) were derived from the following equations:

\[
\Phi_L(m_1) = \Phi_L(m_K) - \Delta H_{1,K} \]
(72)

\[
\Phi_L(m_K) = s^o x_k^{1/2} + B m_K \]
(57)

\[
\Delta H_{1,K} = \Delta H_{1,2} = -\frac{q_1 - q_2}{n_2} \]
(42)

or

\[
\Delta H_{1,K} = \Delta H_{1,3} = -\frac{q_1 + q_2 - 2q_3}{n_2 + n_2} \]
(43)
\[ q_x = q_{\text{deflection}} + q_{\text{electrical}} \quad x = 1, 2 \quad (36) \]

The results of an error analysis based on the equations above and Equation (91) are summarized in Table 12.

Table 12. Summary of Error Analysis

<table>
<thead>
<tr>
<th>m</th>
<th>( n_2 )</th>
<th>( q_{\text{def}} \times 10^3 )</th>
<th>( \Delta H_{1,2} )</th>
<th>( \phi_{L(m_k)} )</th>
<th>( \phi_{L(m_1)} )</th>
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</thead>
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1 All heat quantities are given in defined calories.
2 \( n_2 \) given in moles \( \times 10^6 \).

The probable error in the heat of opening of the sample holders was taken to be \( 1 \times 10^{-3} \) calories. The uncertainty in \( q_{\text{electrical}} \) was found to contribute less than one per cent to the uncertainty in \( q_x \), and for this reason was not considered further in determining the probable error in \( \phi_L \). The method of propagation of precision indexes estimated a probable error of 600 in \( s^2 \) and 5000 in \( R \) for the constants in Equation (57).
DISCUSSION

The relative apparent molal heat contents, \( \bar{\phi}_u \), of lanthanum chloride, neodymium chloride, and erbium chloride solutions along with several theoretical curves appear in Figure 9. The data for lanthanum chloride is that of Nathan, Wallace, and Robinson (83), the only previously reported values for a salt of the 3-1 valence type. Of the theoretical curves, the Debye-Hückel limiting law is represented as a dashed line, the Debye-Hückel law with 5.49 Å for \( \bar{\theta} \) and zero for \( \frac{d\bar{\theta}}{dT} \) appears as a solid line, Eigen and Wicke's (47) treatment with 5.49 Å for \( \bar{\theta} \) and zero for \( \frac{d\bar{\theta}}{dT} \) and \( \frac{d\bar{H}}{dT} \) appears as a dotted line, and Mayer and Poirier's (58) treatment appears as alternate dots and dashes. The experimentally determined \( \bar{\phi}_u \)'s followed none of these curves.

The modification of Robinson and Stokes (39) was not represented graphically. It was found that the derived values for \( L_2 \) could be represented in a crude fashion assuming 100 waters of hydration for each rare earth chloride molecule. Such a high value seemed unrealistic.

The thermodynamic properties of lanthanum chloride, neodymium chloride, and erbium chloride solutions were the same, within experimental error, for concentrations above 0.02 molar. For concentrations below \( 4 \times 10^{-4} \) molar, the thermodynamic properties of neodymium chloride solutions followed the Debye-Hückel law predictions, but the thermodynamic properties of lanthanum and erbium chloride solutions appeared
Figure 9. Theoretical and Observed Relative Apparent Molal Heat Contents for 3-1 Electrolytes.
to depart from theoretical predictions.

The short chord data for neodymium chloride was found to be represented by the equation

$$\phi_L = 6925 \ m^{1/2} - 14.248 \ m \ .$$

(71)

The corresponding expression for erbium chloride was

$$\phi_L = 4933 \ m^{1/2} + 3483 \ m \ .$$

(84)

Nathan, Wallace, and Robinson (83) reported Equation (92) for the short chord data of lanthanum chloride.

$$\phi_L = 3129 \ m^{1/2} + 41.121 \ m \ .$$

(92)

The Debye-Hückel theoretical limiting slope is 6925 as compared to 4933 and 3129 found for erbium and lanthanum chlorides respectively.

The estimated uncertainty in the limiting slope was ± 600 for this work; Nathan, Wallace, and Robinson (83) estimated the probable error in the limiting slope of lanthanum chloride to be ± 930. The limiting slopes for lanthanum chloride and erbium chloride differed from the theoretical slope by considerably more than the estimated probable errors.

The anomalous behavior of $\phi_L$ for lanthanum chloride and erbium chloride solutions for concentrations below $4 \times 10^{-4}$ molal is unique. There is evidence that the bivalent sulfates (84) also have maxima in $\bar{F}_4$ in the range $10^{-3}$ to $10^{-4}$ molal, but in these cases the $\bar{F}_4$'s for the most dilute concentrations approach, rather than depart from,
the theoretical values.

The anomalous behavior of lanthanum chloride and erbium chloride solutions may be due to changes in the species present in solution. The solutions resulting from dilutions of very dilute samples had pH values approaching that of the water used for the dilutions, i.e., greater than six. At these high pH's, hydrolysis can occur. Hydrolysis to form polymeric aggregates containing two or more cations is a possibility. Changes in the manner or degree to which ions in solution are hydrated and resulting changes in the energy of hydration is another possibility. Unfortunately, the direct determination of the nature of the species present in rare earth solutions with concentrations of $4 \times 10^{-4}$ molal or less is extremely difficult, if not impossible, at the present time. The concentration range is much too dilute for determining species with any certainty by spectrophotometric, conductometric, titration, or ultracentrifuge methods. As a result, evidence for the confirmation or explanation of the trend indicated by the heats of dilution of lanthanum chloride and erbium chloride solutions is not readily obtainable.

As seen in Figure 9, the $\phi_p$ values for lanthanum chloride, neodymium chloride, and erbium chloride were essentially indistinguishable for concentrations above 0.02 molal. This behavior was in contrast to other solution properties where the rare earths exhibit independent behavior for all but the most dilute concentration range. Aside from experimental or computational errors, the lack of individuality in the
concentration dependence of $\varphi_L$ has two possible explanations: either the rare earth solutions studied were so similar their differences could not be detected through heats of dilution, or the solutions differed in such a fashion as to balance out heat effects.

The first possibility would require that the rare earth ions associate and interact with the solvent to the same extent, or that heats of dilution be relatively insensitive to association or hydration. An assumption that neodymium and erbium ions associate to the same extent and have nearly identical hydration spheres is in conflict with the observed individuality in such properties as conductances, activity coefficients, and partial molal volumes, and with the well established variation in basicity due to the lanthanide contraction (85). Information concerning the magnitude of the heat effects due to association or to hydration effects of rare earth ions is scarce. Little is known of the importance of associated species in solution, or of the energetics of their formation. As a result, the sensitivity of heats of dilution for such phenomena cannot be established with certainty. In general, solutions of electrolytes which have similar activity coefficients also have similar values for $\varphi_L$. In all other cases other than the rare earths, however, there has been individuality in the concentration dependence of $\varphi_L$ where there has been individuality in activity coefficients.

Compensating heat effects leading to indistinguishable values for $\varphi_L$ could have come about in two or more ways. The solutions may have differed in such a fashion that the heat effects accompanying differences
in the degree of association of rare earth ions with negative species were cancelled by heat effects resulting from differences in hydration. Balanced heat effects may also have resulted from differences in hydration alone. The total energy of hydration can be considered as the sum of the energies of interaction for the interactions of inner hydration spheres bound tightly to the charged ions plus weaker long interactions. The solutions may have differed such that heat effects resulting from differences in inner sphere hydration were balanced by heat effects resulting from differences in long range interactions.
A differential calorimeter has been constructed to measure the heats of dilution of electrolytic solutions. The differential method made possible the determination of heats of dilution to within a few thousands of a calorie. Precision of this order was necessary to obtain meaningful values for the thermodynamic properties of very dilute solutions.

The heats of dilution of neodymium chloride and erbium chloride solutions have been measured at 25°C for concentrations up to 0.2 molal. Empirical expressions for the relative apparent molal heat content of the solute, $\bar{\phi}_L$; the relative partial molal heat content of the solvent, $\bar{L}_1$; and the relative partial molal heat content of the solute, $\bar{L}_2$, have been derived from the heats of dilution. The following equations have been derived for neodymium chloride solutions:

$$\phi_L = 6925 \, m^{1/2} - 16725 \, m + 22378 \, m^{3/2} - 7596 \, m^2,$$  (74)

$$\bar{L}_1 = -62.37 \, m^{3/2} + 301.32 \, m^2 - 602.04 \, m^{5/2} + 273.70 \, m^3,$$  (80)

$$\bar{L}_2 = 10387 \, m^{1/2} - 33450 \, m + 55695 \, m^{3/2} - 22788 \, m^2.$$  (79)

The corresponding equations for erbium chloride solutions were as follows:

$$\phi_L = 5687 \, m^{1/2} - 8637 \, m + 7066 \, m^{3/2},$$  (87)

$$\bar{L}_1 = -51.23 \, m^{3/2} + 155.60 \, m^2 - 190.95 \, m^{5/2},$$  (88)
\[ L_2 = 8531 \ m^{1/2} - 17274 \ m + 17665 \ m^{3/2} \]  

The thermodynamic properties of neodymium chloride and erbium chloride solutions were the same, within experimental error, for concentrations above 0.02 molal. For concentrations below \( 4 \times 10^{-4} \) molal, the thermodynamic properties of neodymium chloride solutions followed the Debye-Hückel law predictions, but the thermodynamic properties of erbium chloride solutions appeared to depart from theoretical predictions.
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