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Some calorimetric studies of the metals and chlorides of cerium and neodymium

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NOTE TO USERS

SOME CALORIMETRIC STUDIES OF THE

METALS AND CHLORIDES OF CERIUM AND NEODYMIUM

by

Carl Fredrick Miller

A Dissertation Submitted to the

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TABLE OF CONTENTS

INTRODUCTION

The field of thermodynamics has reached its present high state of development mainly through the basic contributions of J. Willard Gibbs (1), who established it on a firm mathematical basis, and of G. N. Lewis and M. Randall (2), who clearly demonstrated the application of the laws of thermodynamics to chemical systems. Since then thermodynamics have been widely applied as a tool to support, extend, or revise the theories which attempt to describe chemical behavior. Further extension of these theories requires additional accurate thermal experimental data.

Among the more notable new theories which arose was the interionic attraction theory for electrolytic solutions as developed by Debye and Hückel; Onsager and Fuoss; A. A. Noyes; and many others. Harned and Owen (3) have recently presented a critical review of the theories of electrolytic solutions and the data on which they are based. They show that, while modern solution theory accounts well for the properties of dilute electrolytes, a great deal of new experimental data will be required to extend its application to more concentrated solutions. Two kinds of assumptions are involved in the analytical expressions of the theory. The first kind is associated with the formulation of the general equations; for example, it is assumed that

complete ionization of the salt occurs and that the dielectric constant is unaffected by the ions at all concentrations. The second includes the mathematical approximations used in solving the equations.

The assumption of complete ionization restricts the theory, since this assumption is not valid for a large number of electrolytes except over a limited concentration range. Association, changes in hydration of the ions, and compound formation could be expected to exert more and more influence on the properties of the electrolyte as the charge density of the medium increases. These factors would not only cause a shift in the ionic distribution but would also alter the forces acting between the ions. It is believed that all of the phenomena mentioned above involve heat effects; therefore the partial molal heat contents and heat capacities of the solutions should be sensitive to such deviations from the ideal ionic solution.

The more simplified form of the theory gives an expression for the mean activity coefficient of the two ions in solution, providing the main assumptions made in deriving the theory hold over the concentration ranges investigated. The first and second derivatives of this expression with respect to temperature give the partial molal heat content and the partial molal heat capacity, respectively, of the electrolyte in solution. The derivatives directly relate

the two thermal properties of the ions to the theoretical
equations. The solving of the equation for concentrated
solutions does not allow the mathematical simplifications
which are premissable for the extremely dilute solutions.
The experimental values of the thermal properties of electro-
lytes are very sensitive to deviations from the simplifying
assumptions made in deriving the theory; therefore, a di-
gression of the experimental values from the predicted ones
should prove very helpful in determining at what concen-
trations the simplifying assumptions are no longer sufficient
to predict these values.

In most of the theoretical equations which give the
thermodynamic properties of the ions in solution, the charge
on the ion enters as a square or higher power of the charge.
Therefore, a deviation from complete ionization would mani-
fest itself a great deal more for an ion of charge three
than for one of lower charge. In addition, the more highly
charged ions tend to associate with negative ions; to hydro-
lyze to a greater extent; and generally to undergo a higher
degree of solvation. The resulting heat effects for a tri-
valent ion would appear at a lower concentration than similar
effects for an ion of smaller charge. The rare earth salts
are known to be strong electrolytes which would be ideally
suited for making studies of the 3-1 valence type. Solutions
of the rare earth chlorides, if properly prepared,are not

hydrolyzed, and measurements of their activity coefficients
(4) indicate that they obey the Debye-Hückel theory at infi-
nite dilution. If this holds true for other properties, the
extension of the measurements of all the properties to higher
concentrations should throw light on the weak or neglected
points in the theory.

While the general chemical properties of the rare earths
have been known for some time it has been very difficult to
obtain pure compounds of most of them because of their very
similar chemical properties. However, the ion-exchange
method of separation as developed at the Ames Laboratory (5)
over the past few years has produced many very pure rare
earth salts in sufficient quantity for extensive experimenta-
tion.

The rare earth elements possess atomic structures with
three electrons in the valence shell; since the valence
electrons determine the chemical properties of an element,
the group furnishes a unique series of salts and ions. As
the nuclear charge increases, from one element to the next,
the additional electron falls into the 4f orbital. The
increased charge on the nucleus exerts, in turn, a greater
force on the electrons in the inner shells thereby pulling
them inwards and shrinking the ionic radius.

The 4f electrons give rise to sharp energy states as
evidenced by their absorption spectra. In the solid state

the neighboring ions set up electric fields which penetrate the inner shells to cause Stark splitting of the energy levels; further splitting is found when magnetic fields are imposed. The observed splitting of these levels aids in determining the symmetry and strength of the electric fields set up in the solid by neighboring atoms. However, the $4f$ electrons have very little or no effect on the chemical properties of the rare earth ions.

All ions of the rare earth elements have a tri-positive charge in their normal state in aqueous solutions; they would, therefore, be expected to act alike except for differences which can be related to their size. Ions with a higher charge are more highly hydrated since their highly intense electric fields tend to tie up the water dipoles more strongly. Smaller ions of the same charge present a relatively larger surface charge density and may orient the surrounding water dipoles to such an extent that the resulting hydrated ion is larger. As a result of the extraordinary increase in size of the small ions, their transport velocities will be decreased due to the fact that they will meet more resistance from other water molecules as they travel through the solution than they would if hydration did not occur. The heats of solution of the salts will be increased because more and stronger ion-dipole bonds are formed with the immediate surrounding solvent water molecules and dipole-dipole bonds

between the solvent molecules further away are formed when the salt is dissolved. Since the charge on the ion is a constant factor for all the rare earth elements and the ionic radius of these elements in crystals is known to decrease with atomic number (6), the properties mentioned above, which depend on the radius of the hydrated ion, can be used to deduce structural details of the hydrated ions. The properties of these ions and salts should show a regular progression related to the gradual change in the radius of the hydrated ion from one rare earth element to another, and other thermal properties of this series of elements, besides the heats of solution of their salts, would be expected to exhibit such a regular change.

Although some measurements of the thermal properties of the rare earth metals and compounds have been made, the information is rather limited in scope and some of the data were obtained from impure compounds. The present thesis, on some of the thermal properties of cerium and neodymium, includes thermal properties of the 3-1 type electrolyte as derived from the appropriate measured heat quantities. The thermal data were obtained in such a manner that the powerful methods of thermodynamics could be applied to these substances.

CALORIMETRY OF SOLUTIONS

Introduction

When a crystalline salt is dissolved in water, the crystal lattice is destroyed; the ions are removed from their positions in the crystal lattice; they are separated to relatively large distances and are hydrated. Since the heats of solution are small compared to the large lattice energies, the heat of hydration of the two ions is also large and nearly the same as the lattice energy of the ions in the crystal. Energy is absorbed in the process of separating the ions and, if the solution process is not offset by solvent reaction with the electrolyte, the heat absorbed will be about the same as that required to melt the crystal; it is exactly equal to the heat of the fusion when the crystal is dissolved to give an ideal solution. The fact that the lattice and hydration energies are nearly equal means that the water dipoles neutralize the electric fields of the ions to about the same extent as the two ions neutralize each other in the crystal lattice. If the negative ion is highly polarized in the crystal and if the cation forms very stable solvates, that is, if it ties up the water dipoles very strongly, the heat of solution will be larger and heat will be absorbed or evolved depending on which process involves the greater energy. It is to be expected

that the water molecules would be more easily polarized
than a halogen ion by a highly charged cation; it follows
that the heat evolved would increase with an increase in
the size of the solvated cation. Born(7) indicates how the
energy of hydration may be calculated if the hydrated ions
are considered spheres. However, since the value of the
dielectric constant of the water in the neighborhood of the
large electrical field of the ion is subject to question,
the usual method of finding the heat of hydration is to
calculate the lattice energy of the crystal (8) and to sub-
tract it from the heat of solution.

According to the Debye-Hückel theory, the energy required
to dilute or separate the ions in solution is equal to the
work required to separate the charges in a solvent of a given
dielectric constant. Mathematically, it is the difference
in energy required to "charge up" the ionic atmosphere from
its value at the initial concentration to its value at the
final concentration.

There is only one report in the literature on the heat
of dilution of a 3-1 electrolyte (9); and there are no re-
ported data on the heat capacities of 3-1 electrolytes.

Theory

The first law of thermodynamics states that if a quantity of heat, DQ, is added to a system it causes a resultant change in the energy content of the system, dE, plus any work, DW, done by the system. In chemical systems of the type under discussion, DW, is restricted to pressure-volume work in which

$$(1) \qquad DW = PdV$$

Hence

$$(2) \qquad DQ = dE + PdV$$

The heat content function is defined as

$$(3) \qquad H = E + PV$$

whose total differential,

$$(4) \qquad dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

is exact, meaning that

$$(5) \qquad \frac{\partial^2 H}{\partial T \, \partial P} = \frac{\partial^2 H}{\partial P \, \partial T}$$

Differentiation of Equation (3) gives

$$(6) \qquad dH = dE + PdV + VdP$$

and combining Equation (6) with Equation (2) gives

$$(7) \qquad DQ = dH - VdP$$

at constant pressure

$$(8) \qquad DQ = dH$$

and for a macroscopic process for a pure substance

$$(9) \qquad Q = \Delta H$$

However, for a system of several components, $\underline{H}$ will be a function also of the quantities of the various materials present, or

(10) $\quad dH = \left(\frac{\partial H}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n_i} dP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_j} dn_i$

in which n_i is the amount, usually expressed in moles, of the ith component present in the system. The partial molal derivative, $\left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_j}$

which is designated as $\overline{H}_i$, is the partial molal heat content of each of the components. The latter quantity is of special interest for the interpretation of the data to be presented. At constant pressure and temperature, Equation (10) becomes

(11) $\qquad dH = \sum_i \overline{H}_i dn_i$

Integration of the above equation gives

(12) $\qquad H = \sum_i \overline{H}_i n_i$

For a two-component system of a salt in water, Equation (12) becomes

(13) $\qquad H = n_1 \overline{H}_1 + n_2 \overline{H}_2$

in which n_1 is the number of moles of water present and n_2 is the number of moles of salt present.

Since heat measurements give differences in the heat content when any system changes from the initial to the final state, it is customary to choose a convenient reference state from which to measure differences in the heat content.

In the case of electrolytic solutions, the reference state for the solvent is pure water and the reference state for the electrolyte is at infinite dilution; these reference states are designated as $\overline{H}_1^o$ for the water and as $\overline{H}_2^o$ for the electrolyte. The heat content of the solution, relative to the chosen reference states, is then given by the equation

$$(14) \qquad L = H - n_1\overline{H}_1^o - n_2\overline{H}_2^o$$

in which H is the heat content of the solution and L is the relative heat content of the solution. If Equation (13) is substituted for H, the relative heat content will be

$$(15) \qquad L = n_1(\overline{H}_1 - \overline{H}_1^o) + n_2(\overline{H}_2 - \overline{H}_2^o) = n_1\overline{L}_1 + n_2\overline{L}_2$$

in which $\overline{L}_1$ and $\overline{L}_2$ are the relative partial molal heat contents of the water and the electrolyte, respectively.

According to Lewis and Randall (2), if M moles of salt are dissolved in 1000 grams (55.506 moles) of water to give a solution of molality, m, the total heat given out or absorbed per mole, is called the total or integral heat of solution; if dm moles of salt are added to a solution of molality m to give a solution of molality $m + dm$, the total change in heat content per mole is the partial or differential heat of solution.

For many of the 1-1 and 1-2 salts which obey the Debye-Hückel laws for dilute solutions (10) it has been found that a quantity defined as the apparent molal heat content, ϕ_h, is a linear function of the square root of the

ionic strength through a greater range of concentrations than is $\bar{L}$. The apparent molal heat content, $\emptyset_h$ is defined by the equation

(16) $$H = n_1\bar{H}_1 + n_2\bar{\bar{H}}_2 = n_1\bar{H}_1^0 + n_2\emptyset_h$$

which requires that

(17) $$\emptyset_h^0 = \bar{H}_2^0 .$$

In the reference state

(18) $$H^0 = n_1\bar{H}_1^0 + n_2\bar{H}_2^0 = n_1\bar{H}_1^0 + n_2\emptyset_h^0$$

so that

(19) $$L = H - H^0 = n_1\bar{H}_1^0 + n_2\emptyset_h - n_1\bar{H}_1^0 - n_2\emptyset_h^0$$
$$= n_2(\emptyset_h - \emptyset_h^0) = n_2\emptyset_L$$

in which $\emptyset_L$ is the relative apparent molal heat content of the electrolyte.

For a reaction of the type

$$mCeCl_3(s) + 55.506H_2O = mCeCl_3 \cdot 55.506H_2O$$
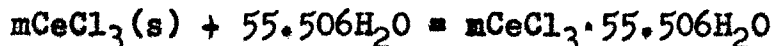
the change in heat content is

(20) $$\Delta H = 55.506\bar{H}_1^0 + m\emptyset_h - 55.506H_1^0 - mH_2(s),$$

in which $H_2(s)$ is the heat content of the solid salt. Since the definition of the reference states requires that $\bar{H}_1^0$ be equal to H_1^0, the above equation can be restated by

adding and subtracting $m\emptyset_h^0$ and by employing equation (17) in the form

(21) $$\Delta H = m(\emptyset_h - \emptyset_h^0) - m(H_2(s) - \bar{H}_2^0)$$

$$= m\emptyset_L - mL_2(s)$$

in which $-L_2(s)$ is the heat of solution of the salt at infinite dilution. Differentiation of Equation (21) with respect to m gives

(22) $d \, \Delta H/dm = \emptyset_L + m \, (d\emptyset_L/dm) - L_2(s)$

However, with the aid of Equation (15) and (20), Equation (21) can be rewritten as

(23) $\Delta H = 55.506\overline{L}_1 + m\overline{L}_2 - mL_2(s)$

Differentiation of Equation (23) with respect to m gives

(24) $d \, \Delta H/dm = \overline{L}_2 - L_2(s)$

subtracting Equation (24) from (23) gives

(25) $\overline{L}_2 = \emptyset_L + m(d\emptyset_L/dm) = \emptyset_L + \tfrac{1}{2}m^{\frac{1}{2}}(d\emptyset_L/dm^{\frac{1}{2}})$

Equations (15) and (19) show that

(26) $m\emptyset_L = m\overline{L}_2 + 55.506\overline{L}_1$

If $\overline{L}_2$ is substituted into Equation (26), $\overline{L}_1$ in terms of $\emptyset_L$ is

(27) $\overline{L}_1 = -\tfrac{1}{2}m^{3/2}/55.506(d\emptyset_L/dm^{\frac{1}{2}})$

The fundamental equations relating the total heat capacity, Cp, of a solution of two components to the partial molal capacities, $\overline{Cp_1}$ and $\overline{Cp_2}$, of each of the components, or to the molal heat capacity Cp_1^O, of the solvent and to the apparent molal heat capacity, $\emptyset cp$, of the solute are given by

(28) $Cp = n_1\overline{Cp_1} + n_2\overline{Cp_2} = n_1Cp_1^O + n_2\emptyset_{cp}$

where $\overline{Cp_2^O}$ is equal to $\emptyset_{cp}^O$. For the heat capacity of a solution relative to its reference states, Harned and Owen (3) employ the symbol J which is defined as

(29) $J = Cp - Cp^o = n_1(\overline{Cp_1} - \overline{Cp_1^o}) + n_2(\overline{Cp_2} - \overline{Cp_2^o})$

$= n_2(\emptyset_{cp} - \emptyset_{cp}^o) = n_2\emptyset_J$

in which $\underline{\emptyset_J}$ is the relative apparent molal heat capacity of the solute. The relative partial molal heat capacities, $\overline{J_1}$, and $\overline{J_2}$, are defined by the equations

(30) $\overline{J_1} = \overline{Cp_1} - \overline{Cp_1^o}$

and

(31) $\overline{J_2} = \overline{Cp_2} - \overline{Cp_2^o}$

from which

(32) $J = n_1\overline{J_1} + n_2\overline{J_2}$

For a reaction of the type,

$mCeCl_3(s) + 55.506H_2O = mCeCl_3 \cdot 55.506H_2O$
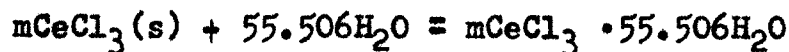
the change in heat capacity is

(33) $\Delta Cp = 55.506\overline{Cp_1^o} + m\emptyset_{cp} - mCp_2(s) - 55.506Cp_1^o$

$= m(\emptyset_{cp} - Cp_2(s)).$

It can be shown, by a mathematical treatment exactly analogous to that used for the partial molal heat contents, that

(34) $\overline{Cp_2} = \emptyset_{cp} + \frac{1}{2}m^{\frac{1}{2}}(d\emptyset_{cp}/dm^{\frac{1}{2}})$

and

(35) $\overline{J_2} = \emptyset_J + \frac{1}{2}m^{\frac{1}{2}}(d\emptyset_J/dm^{\frac{1}{2}})$

and

(36) $\overline{J_1} = \overline{Cp_1} - \overline{Cp_1^o} = -\frac{1}{2}m^{3/2}/55.506(d\emptyset_{cp}/dm^{\frac{1}{2}})$

The relative apparent molal heat capacity $\emptyset_J$, can be determined from a series of values of ΔCp for the given reaction at different molalities by defining ΔCp_M as

(37) $\qquad \Delta Cp_M \equiv \Delta Cp/m = \emptyset_{cp} - Cp_2(s)$

and

(38) $\qquad \Delta Cp_M^O = \emptyset_{cp}^O - Cp_2(s)$

at $\underline{m}$ or $\underline{m^{\frac{1}{2}}} = 0$.

Since from Equation (30)

(39) $\qquad \emptyset_J = \emptyset_{cp} - \emptyset_{cp}^O = \Delta Cp_M - \Delta Cp_M^O$

$\overline{J}_2$ can be directly determined through use of Equation (35) while $\underline{\emptyset_{cp}}$ and $\overline{Cp_2}$ can be determined only if $\underline{Cp_2(s)}$ is known.

For the present work, a development of the complete interionic theory will be unnecessary for the following reasons:

(1) The presentation of the theory by Harned and Owen (3) is entirely adequate and can hardly be improved upon at the present time.

(2) This work is concerned with the question of whether or not 3-1 electrolytes approach the limiting values of the slopes calculated from the theory for these electrolytes. Only after data for many other 3-1 type electrolytes and 3-2 type electrolytes have been obtained and carefully examined, will it be possible to give a better theoretical explanation for the deviations of the observed data from those given by the present theoretical equations.

(3) Many data necessary for calculating the desired coefficients at more than infinite dilution are not yet available. An example is the temperature coefficient of expansion of solutions of the rare earth chlorides.

However, the theory of Debye and Hückel is briefly outlined for the limiting case. The ions are considered to be point charges; they can be assumed to be at any point in the solution, but there is a higher probability that those of opposite charge will be nearer each other with one tending to surround the other. It is assumed that the work required to pull the oppositely charged ions apart in performing a dilution is the cause of deviations from the laws of the perfect solution. The ionic atmospheres are assumed to have spherical symmetry so that the potential due to an ion and its surrounding atmosphere is a function of the distance from the ion only; the potential is represented by $\psi(r)$. For a medium containing electrical charges subject only to forces which vary inversely as the square of the distances, the relation between the charge density, ρ, and the potential is given, in general, by Poisson's equation

(40) $$\nabla^2 \psi(r) = -4\pi\, \rho/D$$

in which D is the dielectric constant of the medium. The probability of a given number of charges being present in a potential region where $\psi(r)$ is the potential, considering

the thermal motion of the ions, is taken as that given by the Maxwell-Boltzmann distribution

(41) $P(n) = n \exp(-\psi(r) Ze/kT)$

in which $\underline{n}$ is the number of ions per cubic centimeter of the solution as a whole. The charge density of the region is

(42) $\rho = \sum_{i=1}^{m} n_i Z_i e \exp(-\psi(r)Z_i e/kT)$

in which $\underline{Z_i e}$ is the charge on an ion. The quantity, $\underline{\psi(r)Z_i e/kT}$, is assumed to be small so that

(43) $\exp(-\psi(r)Z_i e/kT) \simeq 1 - \psi(r)Z_i e/kT$

if higher terms are neglected. Substituting Equation (43) into Equation (42) gives

(44) $\rho = \sum_{i=1}^{m} n_i Z_i e (1 - \psi(r)Z_i e/kT)$

Electroneutrality of the solution as a whole requires that

(45) $\sum_{i=1}^{m} n_i Z_i e = 0$

hence

(46) $\rho = - \sum_{i=1}^{m} (n_i Z_i^2 e^2/kT) \psi(r)$

and

(47) $\nabla^2 \psi(r) = (4\pi e^2/DkT) \sum_{i=1}^{m} n_i Z_i^2 \psi(r) = \kappa^2 \psi(r)$

if

(48) $\kappa^2 = (4\pi e^2/DkT) \sum_{i=1}^{m} n_i Z_i^2$

The general solution of Equation (47) is

(49) $\qquad \psi(r) = (A/r)e^{-Kr} + (B/r)e^{Kr}$

However, $\underline{\psi(r)}$ must be zero for $\underline{r = \infty}$, therefore it follows

that $\underline{B}$ must be zero, and that

(50) $\qquad \psi(r) = (A/r)e^{-Kr}$

is the only acceptable solution. The potential of the ion

without its atmosphere is

(51) $\qquad \psi(o) = Z_1e/Dr$

so that if Equation (50) is written as

(52) $\qquad \psi(r) = A/r - (A/r)(1 - e^{-Kr})$

the constant $\underline{A}$ must be $\underline{Z_1e/D}$, and the second term must be

the potential attributed to the ionic atmosphere. Since

the ion carries its charge with it the only work of di-

lution is the electrical work required to change the ionic

atmosphere. Therefore,

(53) $\qquad \psi(r) = - (Z_1e/Dr)(1 - e^{-Kr}) \simeq Z_1eK/D$

is approximately the potential of the atmosphere, and the

electrical work required to charge an ion in the presence

of the potential $\underline{\psi'(r)}$ is

(54) $\qquad \Delta F_1 = \frac{1}{2} \psi'(r)Z_1e = -\frac{1}{2}Z_1^2e^2K/D$

The electrical work of dilution is associated with the

free energy change of dilution by the thermodynamics

equations which follow. These are:

(55) $\qquad \Delta F = \bar{F} - \bar{F^0} = \nu RT\ln(m_0 x1)/m_{\pm}\gamma_{\pm}$

$\qquad\qquad \simeq \nu RT\ln(C_0/C) - Z_1^2e^2NK/2D$

or

(56) $$\ln \gamma_{\pm} = -\frac{1}{\nu} z_i^2 e^2 K/2DkT$$

in which $\underline{\gamma_{\pm}}$ is the mean activity coefficient of the electrolyte in solution. The above relation can be written more correctly for the very dilute solution as

(57) $$\ln \gamma_{\pm} = -S_f(2d_0\mu)^{\frac{1}{2}}$$

where

(58) $$\mu = \frac{1}{2} \sum_{i=1}^{s} z_i^2 m_i$$

and

(59) $$S_f = \frac{1}{\nu} \sum_{i=1}^{s} \nu_i z_i \left[\pi N e^6/1000(kDT)^3 \right]^{\frac{1}{2}}$$

For a 3-1 type electrolyte, $\underline{\mu = 6m}$, so that

(60) $$\ln \gamma_{\pm} = -S_f(12d_0 m)^{\frac{1}{2}}$$

gives the limiting equation for the mean activity coefficients.

The variation of the above coefficients with temperature is derived in the following manner from thermodynamic relations:

(61) $$\Delta F/T = (\overline{F}-\overline{F}^o)/T = \nu R\ln\gamma_{\pm} + \nu R\ln m_{\pm}$$

and

(62) $$\left[\frac{\partial(\overline{F}-\overline{F}^o)/T}{\partial T} \right]_P = -(\overline{H}-\overline{H}^o)/T^2$$

but

(63) $$\left[\frac{\partial(\overline{F}-\overline{F}^o)/T}{\partial T} \right]_P = \nu R \left[\frac{\partial \ln\gamma_{\pm}}{\partial T} \right]_P$$

hence

(64) $\quad (\bar{H}-\bar{H}^o)/T^2 = \bar{L}/T^2 = -\nu R \left[\dfrac{\partial \ln \gamma_\pm}{\partial T}\right]_P$

and

(65) $\quad \bar{L} = \nu R T^2 \left[\dfrac{\partial}{\partial T} S_f (2d_o\mu)^{\frac{1}{2}}\right]_P = S_H m^{\frac{1}{2}}$

But

(66) $\quad \bar{L} = \bar{H} - \bar{H}^o$

so that

(67) $\quad \left(\dfrac{\partial \bar{L}}{\partial T}\right)_P = \left(\dfrac{\partial \bar{H}}{\partial T}\right)_P - \left(\dfrac{\partial \bar{H}^o}{\partial T}\right)_P = \bar{C}p - \bar{C}_p^o$

$\qquad\qquad = \nu R \dfrac{\partial}{\partial T}\left[T^2 \dfrac{\partial}{\partial T} S_f (2d_o\mu)^{\frac{1}{2}}\right] = S_{cp} m^{\frac{1}{2}}$

The above equations define the limiting slopes in the usual way. An examination of Equation (59) shows that the equations for $\bar{L}$ and for $\overline{Cp} - \overline{Cp^o}$ become increasingly complex when the indicated differentiations are performed. The values for the slopes S_H and S_{cp} have been calculated by Harned and Owen (3) and will be given in appropriate places in this thesis as need for them arises.

General Methods

The measurement of quantities of heat by any method is termed calorimetry. The measurements require no knowledge of the ultimate nature of heat; in fact, the term "quantity of heat" was used when heat was still regarded as a fluid.

The instrument used to measure quantities of heat is called a _calorimeter_; there are two kinds of calorimeter depending on the thermal process utilized to measure the quantity of heat. The first kind is the latent heat calorimeter; its operation depends upon the change of state of some substance placed in the calorimeter. The ice calorimeter is an example of this kind of calorimeter, and is described in detail in a following section on specific heats of solids. The amount of heat added to the calorimeter is determined from a knowledge of the latent heat of fusion of ice and the amount of it that changes state during the course of the reaction taking place.

The second kind is called the thermometric calorimeter; its operation depends on a change in temperature which accompanies the reaction being studied. Estimations of heat quantities are deduced from observation of the temperature changes. In this kind of calorimeter the thermometer is the instrument of prime importance. Regnault built one of the first calorimeters of this kind in 1840; he determined the amount of heat added to a calorimeter, containing water, by measuring the temperature rise of calorimeter and water when a warm body was introduced into the water. The heat capacity of the calorimeter was determined by adding warm water to the water in the calorimeter and noting the initial and final temperatures; this procedure is known as

Regnault's method of mixtures. Dulong and Petit used what
is now called the method of cooling to estimate heat quanti-
ties; they compared the time for different substances of the
same size and shape to cool through the same temperature
range when exposed to the same surroundings. Regnault, how-
ever, pointed out that the method of cooling was not suit-
able for measuring heat capacities of solids while it could
be used for liquids. Detailed descriptions of the early
models of the above mentioned calorimeters are given by
Preston (11) and by Worthing and Holliday (12).

The science of calorimetry centers about the invention
of temperature-measuring devices and methods of operation
that will lead to a more accurate measurement of the temper-
ature and to a better estimate of corrections involving
the exchange of heat between substances. The detailed at-
tention given to these problems by many scientists is evi-
denced by the improvement of calorimetric data in the
literature over a period of time.

The requirements of modern calorimeters, including
their design and operation, are so fully covered by White
(13) and by Swietoslawski (14) that only a brief survey of
the general types of the thermometric calorimeters will be
necessary in this thesis. Among the best of the calo-
rimeters designed for studies of electrolytes are the
models developed by Lang and his coworkers (15, 16, 17),

and by Gucker and his associates (18).

The present-day calorimeters which employ the use of temperature measurement to obtain the estimation of heat quantities are of three types: (1) the thermally insulated-jacker model, (2) the adiabatic type, and (3) the iso-thermally-jacketed calorimeter. A great deal of the work with oxygen-bomb combustion calorimeters is done with the insulated-jacket calorimeter. The quantity of heat produced is usually large; when calibrations are done by the use of standard materials the heat measurements are fairly accurate, especially if the heat leakage is properly taken into account. The adiabatic calorimeter is best adapted for measuring small quantities of heat. Its main advantage is that the heat exchanges with the surroundings are negligible and so that it can be used to measure quantities of heat which develop over a long period of time. However, it is difficult to maintain strictly adiabatic conditions between the calorimeter and its surroundings when large quantities of heat are evolved or absorbed by rapid processes. Of the three types mentioned above, the adiabatic calorimeters are necessarily more complicated in design and construction because additional mechanical means have to be employed to heat or cool a bath in order to maintain temperature equality between the bath and the calorimeter. The isothermally-jacketed calorimeter is well

suited for the measurements of large amounts of heat pro-
duced in a rapid process as well as those of longer duration.
It is not, when properly constructed and operated, inferior
to the adiabatic calorimeter (19). However, the heat
leakage must be accurately accounted for and the calculation
of the corrections is a tedious task. The advantages of the
isothermally-jacketed calorimeter in the present work are:
(1) it is more simple in design and construction than an
adiabatic calorimeter of equal precision; (2) it can be
operated by a minimum amount of labor and personnel; (3) it
is best suited to the given laboratory environment; and
(4) it is to be used for measuring fairly large quantities
of heat developed by rapid chemical reactions.

Experimental

Preparation of materials

The source materials for the anhydrous cerous chloride
were c.p. hydrated cerous chloride and standard ceric
ammonium nitrate procured from the G. Frederick Smith Company.
The analyses of the above chemicals as well as those of all
other source materials are given in Table 1. The hydrated
cerous chloride gave a slightly turbid solution when it was
dissolved in dilute hydrochloric acid and a small amount of
gelatinous precipitate formed when the solution was boiled

with concentrated acid. The solution was diluted and the
precipitate filtered out. A second boiling produced no
further precipitate; the process of boiling the solution
to a syrup in concentrated acid, diluting, and filtering
was repeated two more times before the solution was boiled
in concentrated acid until the temperature reached 130°C
and the cerous chloride allowed to crystallize. The hy-
drated crystals were then placed in a long pyrex drying-
tube which was put into a resistance furnace. One end of
the drying-tube was connected to an aspirator, by means of
pieces of rubber vacuum tubing, through a series of flasks
used as gas traps. The other end of the drying tube was
connected to a source of purified dry hydrogen chloride
gas. The gas was passed through a tube containing calcium
chloride at 400°C to decompose any hydrocarbons present in
the gas; the calcium chloride was replaced before each
drying run. After the gas was started through the system
under reduced pressure from action of the aspirator, the
temperature of the furnace containing the hydrated chloride
was increased slowly to 80 or 90°C, again to 130°C, and
then more rapidly until it reached 400°C. The slow pro-
cedure of raising the temperature of the furnace was used
in order to minimize the possibility of forming the oxy-
chloride and to keep the dried chloride from matting to-
gether in hard lumps. The bulk of excess water was removed

Table 1

Purity of Source Materials

Source Material	Purity*
Hydrated cerous chloride	No other rare earths or thorium detected by emission spectrography; iron 0.0023%; calcium oxide 0.03%; magnesium oxide 0.03%; traces of silicon prior to boiling in concentrated hydrochloric acid solution.
Ceric ammonium nitrate	No other rare earths, thorium, or common elements detected by emission spectrography.
Neodymium oxide	No other rare earths, thorium, or common elements detected by emission spectrography.
Cerium metal	No other rare earths or thorium detected by emission spectrography; iron 0.05%; calcium oxide 0.05-0.1%; magnesium and tantalum not detected.
Neodymium metal	Other rare earths, mainly praseodymium 0.1%; faint traces of calcium and magnesium; iron 0.02%.

*The limit of detection of the rare earths was about 0.02 to 0.03 per cent; that f common elements was about 0.01 per cent.

at 75-100°C. The rare earth chlorides melt in their own
water of crystallization at a temperature slightly above
100°C. In order to obtain a pure anhydrous chloride which
is also small grained, it is necessary that the crystals
do not melt before they are dried. All but one of the
waters of crystallization are removed at about 130°C, and
therefore it is again advisable to approach this temper-
ature slowly so the gas stream can sweep out the vaporized
water as rapidly as it is expelled from the crystalline
mass.

When the temperature of the dried chloride reached
400°C, the hydrogen chloride was shut off and dry helium
was introduced into the system by means of a three-way
stopcock in the gas line. The furnace was then disconnected
from its power source and the crystals allowed to cool in
a stream of helium gas. The anhydrous chloride, when
cooled to room temperature, was quickly transferred to a
dry bottle which then was capped, sealed, and placed in a
dry-box. Samples were taken from this supply of chloride
for test runs and experiments as needed. After about two
months this source of chloride gave indications that it was
picking up moisture. Therefore, another portion of salt,
made from the ceric ammonium nitrate, was dissolved and
boiled in strong hydrochloric acid until the solution no
longer gave a positive test for nitrate. The chloride was

then crystallized and dried as previously described.

The anhydrous neodymium chloride was prepared from neodymium oxide supplied by the ion-exchange separations section of this laboratory under the direction of Dr. F. H. Spedding. The oxide was dissolved in hydrochloric acid, boiled to $132^{\circ}C$, crystallized, and dried.

The hydrated crystals of cerium and neodymium chlorides were prepared from the source materials as follows. A 400 ml. portion of a solution of each chloride, which had been boiled to about $110^{\circ}C$ in approximately 2N hydrochloric acid, was placed in a beaker in a vacuum desiccator. The desiccator was evacuated daily by use of an aspirator for a short period of time. After about a week, when crystals began to appear, the supernate was transferred to another 400 ml. beaker; one or two of the larger crystals were selected for seeding the saturated solution. The beakers were placed in large desiccators containing fresh anhydrone and the crystals allowed to grow for about fourteen months.

The oxalic acid was reagent grade hydrated oxalic acid; it was twice recrystallized from warmed conductance water.

The metals of cerium and neodymium were furnished by the metallurgy section of this laboratory. They were prepared by methods developed by Dr. A. H. Daane (20), and Mr. W. J. McGinnis (21) under the direction of Dr. F. H. Spedding.

Conductance water was used for the preparation of all solutions; some of it was prepared by the use of a conductivity-water distilling apparatus and some of it by passing distilled water through an ion-exchange resin bed. All of the water gave a measured conductance of 10^{-6} mhos or less.

The rare earth ions were analyzed either by burning weighed portions of the chloride crystals covered with oxalic acid or by precipitating them from weighed amounts of solution with oxalic acid, filtering, and igniting the oxalate to about $900^{\circ}C$ for about twelve hours. A second ignition rarely changed the weight of the oxide by more than a few tenths of a milligram. The precision on three or four samples usually averaged about 0.1 per cent.

The chloride content of the solid salts, in the rare earth chloride solutions, and in the hydrochloric acid solutions was determined gravimetrically by following the procedure given by Willard and Furman (22). Either weighed amounts of the salt were dissolved in water or weighed portions of solutions were used. The analyses were carried out at night in subdued artificial light as recommended. In addition, it was found that a precision of better than 0.1 per cent could be easily attained if very clean polished glassware was used and if the silver chloride precipitates were cooled in an ice-water bath after their digestion in a hot water bath. Results of the analyses of the rare

earth anhydrous chlorides are given in Table 2.

The oxalate solutions were analyzed by adding an excess of standard ceric sulfate solution and titrating the excess ceric ion with freshly standardized ferric sulfate solution. The oxalate solutions were generally too dilute to obtain an accurate end-point by direct titration with ceric sulfate.

All the solutions were weighed by the use of weight burettes. The weight of each substance used was corrected to weight in vacuum at standard conditions.

After 14 months in the desiccators the hydrated chlorides had grown massive crystals completely filling the bottom of the 400 ml. beakers to a height of one to one and a half inches. The small amount of liquid which remained was poured off and the crystals were washed with a small amount of water and then with alcohol. They were cracked loose and broken into a number of large massive crystals. Typical crystals of neodymium chloride and of cerium chloride are shown in Figure 1. The crystals were rinsed thoroughly in absolute alcohol, air dried, and placed in stoppered bottles. Before use, the large crystals were crushed in an agate mortar and allowed to set in a dry nitrogen atmosphere in the dry-box. From analysis of the crushed crystals and the final solutions formed in the heat of solution experiments, Cl/Ce was found to be 3.001 ± 0.001;

by assuming the excess weight to be water, H_2O/Ce was
found to be 7.008 ± 0.012. For the hydrated neodymium
chloride it was found that Cl/Nd was 2.998 ± 0.003, and
H_2O/Nd was 6.011 ± 0.016.

Table 2

Composition of Anhydrous Chlorides

Compound	R/RCl$_3$ x100	Cl/RCl$_3$ x100	Cl/R
CeCl$_3$(I)	56.83	43.14	3.000
CeCl$_3$(I)*	56.72	42.96	2.995
CeCl$_3$(II)	56.84	43.15	3.001
NdCl$_3$	57.55	42.45	2.997

*Analysis two months later
Theoretical: Ce/CeCl$_3$= 56.85 per cent by weight
                Nd/NdCl$_3$= 57.56 per cent by weight
Average Errors: R/RCl$_3$= ± 0.05 per cent
                Cl/RCl$_3$= ± 0.02 per cent

The oxalic acid was analyzed only from the prepared
solutions and was found to contain, within limits of
experimental error, the calculated amount of oxalate added
by weight as the hydrate.

Approximately half of the final solutions from the
heat of solution experiments were analyzed to check the

Figure 1.   Massive Crystals of Hydrates of Neodymium
            Chloride (left) and Cerium Chloride.

initial weights of the chloride added. Typical analyses
are given in Table 3.

Table 3

Typical Analysis of Final Solutions

	$CeCl_3$	$NdCl_3$
Number of samples	7	7
Total weight of chloride	108.7690	79.3211
Weight of water used	1268.273	1310.952
Total weight of solution	1377.042	1390.273
Grams chloride/grams solution, calculated	0.078987	0.057054
Grams chloride/gram solution found by analysis	0.078946 ± .000017	0.057015 ± .000043
Cl/R found by analysis	2.995 ± 0.007	3.003 ± 0.005

Samples for the heat of solution experiments were pre-
pared by loading various sizes of thin-walled pyrex bulbs
with the solid material. The pyrex bulbs were blown from
six millimeter pyrex tubing. The tube was cut off about
two inches from the bulb and the end of the remaining stem
was made funnel-shaped to facilitate loading. The bulbs
were rinsed with acetone and dried at $110^\circ C$ for at least 24
hours before they were weighed. After weighing, the bulbs

were closed with numbered cork stoppers and filled with the salt in a dry-box. Preliminary experiments indicated that it made no difference whether or not the chlorides were in powdered form; since the powdered chloride was more difficult to load, the chlorides were used as dried, with the exception of particles larger than six millimeter which were crushed and mixed with the bulk material. The bulbs were again stoppered after loading, and the ends of tubing were pulled off by heating them in a very small flame of an oxygen torch. The weight of the chloride was determined by difference and corrected to weight in vacuum. All samples, excepting those of the metals, were prepared in the same way. The metals were prepared by taking off thin turnings of metal from a large cast metal cylinder on a lathe. The cylinder and turnings were kept coated with mineral oil; benzene was used to dissolve the oil from the turnings. The thin strips of metal were transferred to the glass bulbs under benzene. After the excess benzene was drained off, the bulbs were evacuated and flushed with helium. Before the bulbs were sealed, helium was let in to a pressure slightly less than atmospheric. Prepared samples of a metal and a salt are shown in Figure 2.
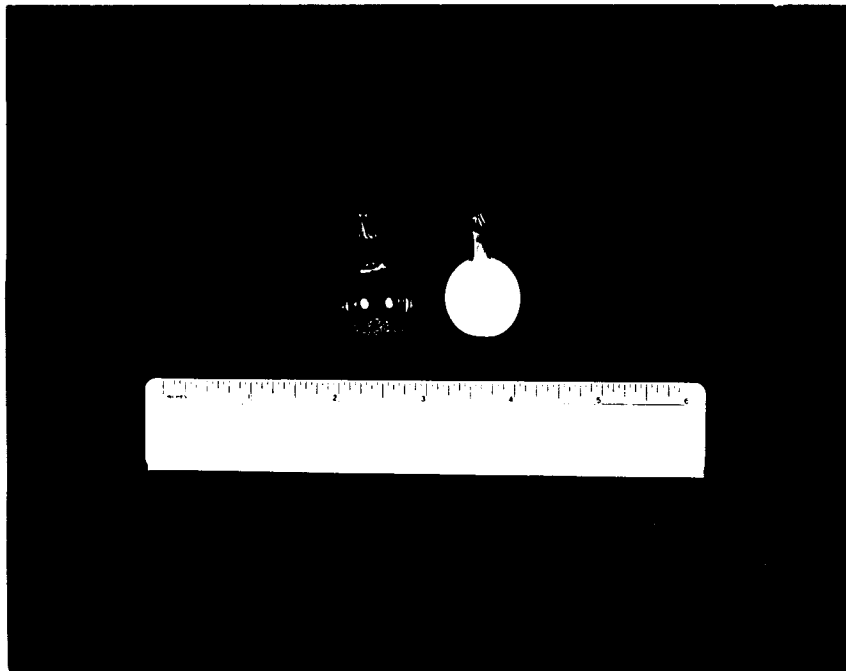
Figure 2. Samples used for Heat of Solution Experiments;
left, neodymium metal; right, anhydrous neodymium
chloride.

Apparatus

The design of the calorimeter was somewhat similar to
that of the "tantalum" calorimeters built by Maier (23)
and by Southard (24). Figure 3 is a picture of the appa-
ratus; however, the schematic diagram shown in Figure 4
will be more useful in describing its construction and
operation. The calorimeter vessel was a two-quart Dewar
flask sealed onto a brass cylinderical flange with Apiezon-
W wax. The wax seal was protected on the outside by a
double layer of Scotch electrical tape. The Dewar vessel
was held in place by six hexagonal brass bolts which passed
through holes in the top brass plate and bakelite plate.
The bakelite plate held the calorimeter in place in a steel
frame. Each brass plate was separated from the bakelite by
a one-eighth inch thick soft rubber gasket. The whole
calorimeter vessel was immersed, during operation, in a
water bath thermostatically controlled at 25.00 $\pm$ .01°C.
The thermometer, $\underline{T}$, was a fixed bridge arrangement very
similar to Maier's transposed bridge thermometer (25). It
consisted of four resistances, alternately manganin and
copper. Such a bridge arrangement is in balance at one
temperature only; the amount of unbalance of the bridge at
other temperatures was measured potentiometrically with a
White double potentiometer as an indicator of the tempera-
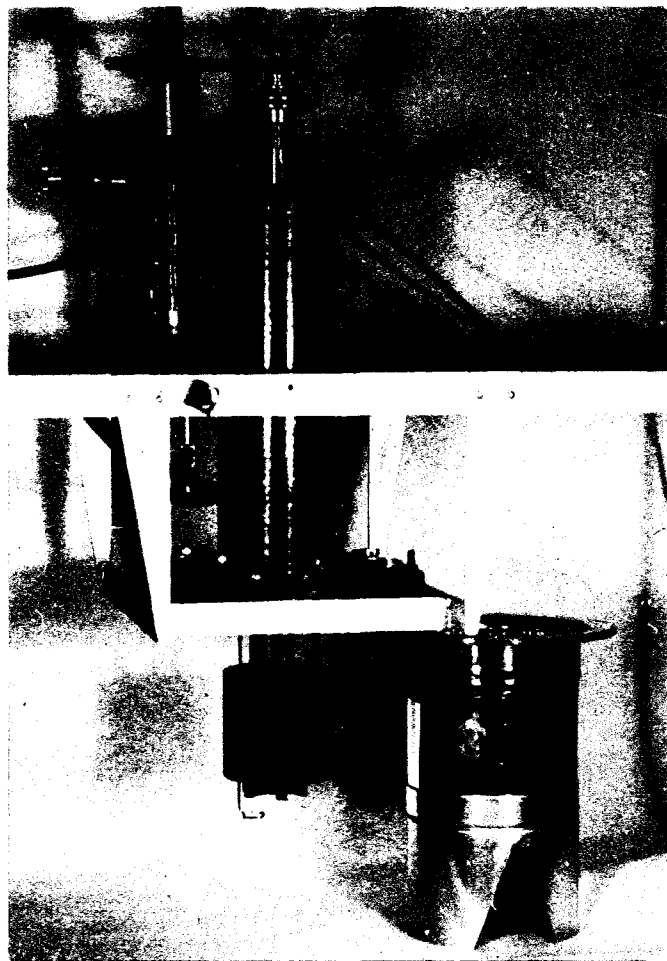ture rise of the calorimeter. The second circuit of the

Figure 3. Heat of Solution Calorimeter and
Dewar Vessel.

(WATER LEVEL LINE)
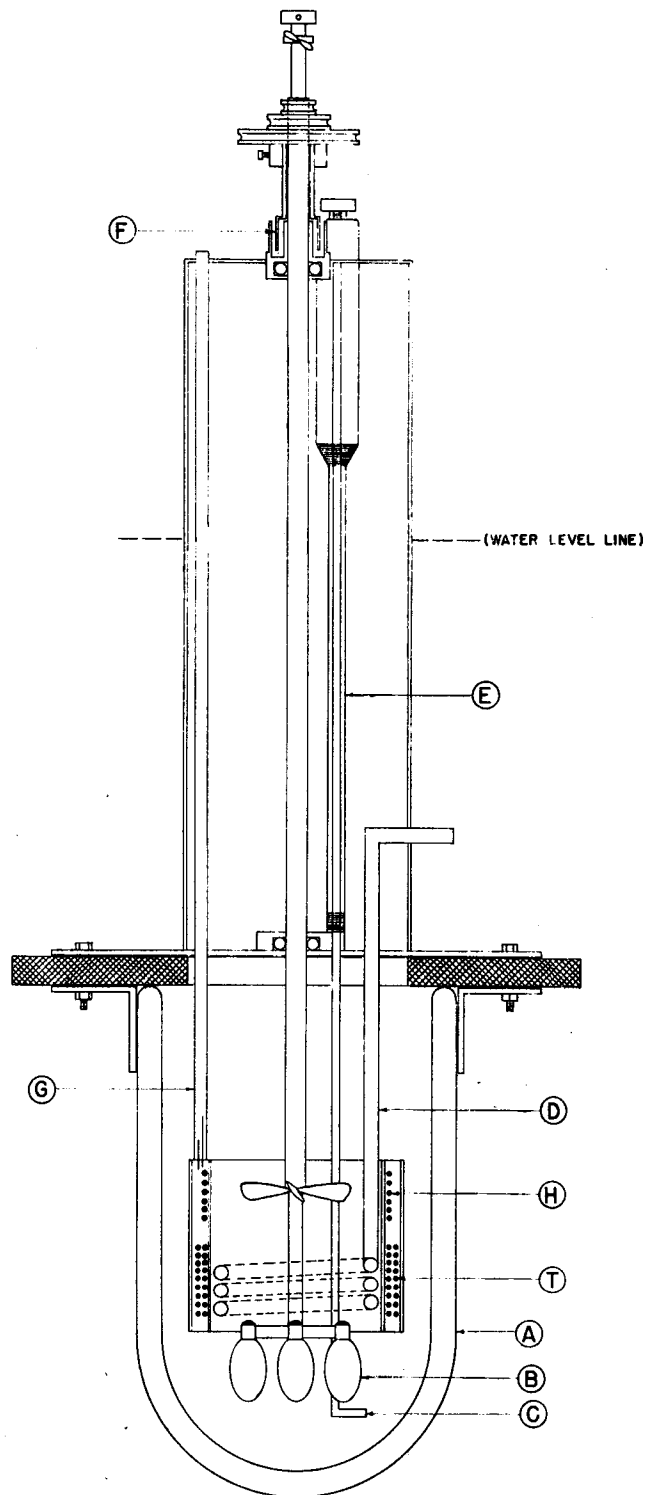
Figure 4. Heat of Solution Calorimeter

potentiometer was used to maintain a constant current through the bridge by balancing the drop across a standard resistor against a fixed dial setting on the potentiometer. Each arm of the temperature bridge had a resistance of about 370 ohms and a set current of approxiamtely 0.005 amps was maintained. The thermometer, under these conditions, dissipated about 0.1 calorie per minute to the calorimeter; the sensitivity of the bridge, under the above conditions was about 3×10^{-4} degrees per micro-volt. The emf was read to 0.1 micro-volt. The thermometer circuit is shown in Figure 5. The copper thermometer coils were wound with No. 42 AWG enameled wire in a single layer on a thin-walled copper cylindrical tube which had been previously insulated with a thin layer of bakelite varnish and baked at 110° C. Two heavy copper rings had been silver-soldered to the ends of the copper cylinder; two one-fourth inch monel tubes, G, were silver-soldered into holes in the upper copper ring. The monel tubes held the thermometer in place and served as conduits for the electrical leads. The two manganin coils of No. 38 AWG enameled wire were wound on the outside of the copper coils. A 120 ohm manganin coil of No. 26 AWG wire was non-magnetically wound on the upper portion of the copper cylinder. It was used to add known amounts of heat to the system. Four leads of No. 30 AWG enameled and glass-covered copper wire were threaded through one monel tube

and soldered to the appropriate pairs of copper and manganin thermometer coils. Four similar lead wires were brought down the second monel tube and soldered to the heater coil wires; the potential leads were fixed so as to be midway between the top of the copper cylinder and the top brass plate. When all the lead wires were installed, the assembly of coils was coated with bakelite varnish and baked. The coils were tested for potential leaks, and then another copper cylinder was slipped over the terminal rings and soldered to them. The two monel tubes were next put in place in the calorimeter head. The tubes were held in place at the top with brass lugs by set screws, and the lead wires fixed to solid copper lugs mounted in bakelite. The annular space between the wires and outer copper cylinder and in the monel tubes was filled with paraffin.

In order to calibrate the thermometer in an absolute sense, a brass case, E, was made and placed in the brass chamber so that it could hold a platinum resistance thermometer so that the tip of the thermometer passed between the stirrer propeller and the thermometer assembly. When the heats of solution were to be measured, the sample-breaker, L, was placed in the brass case, E. The breaker was a one-eighth inch stainless steel rod which was held at the top of the calorimeter by a notched brass head with set screws and was bent at the bottom. The shaft portion was centered

THERMOMETER DIAGRAM
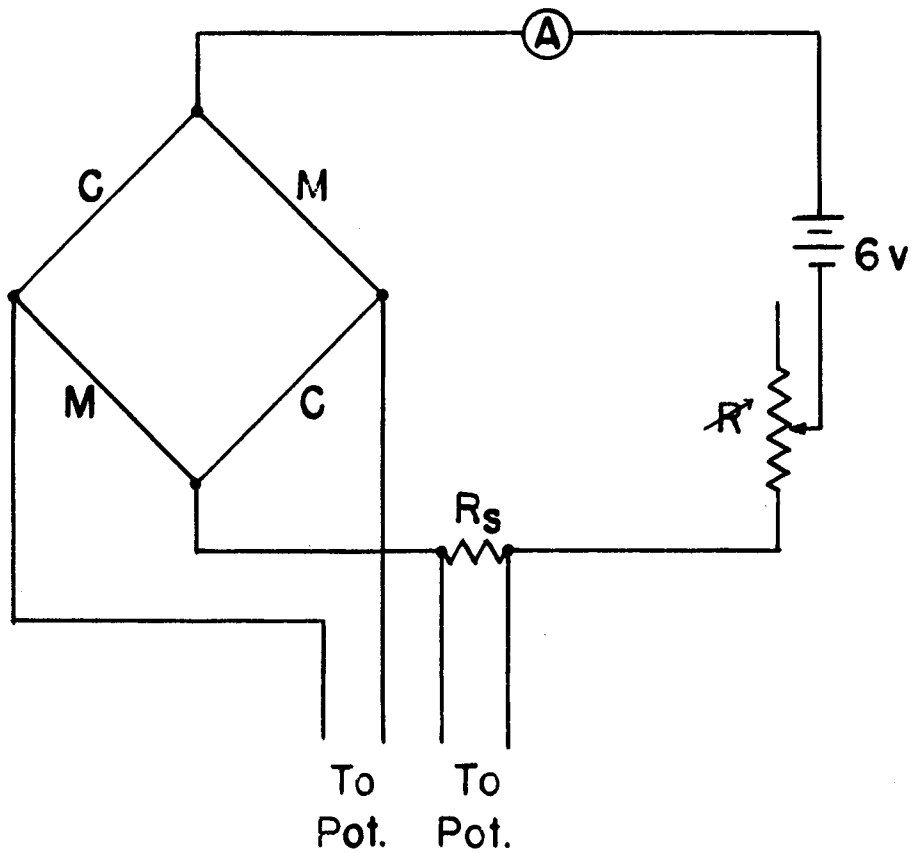
C = Copper

M = Manganin

R' = 10,000 decade box plus 1 ohm slide wire

R_s = 10 ohms

Figure 5. Thermometer Circuit Diagram.

with rubber stoppers cut to size. The stoppers were fitted tightly to prevent evaporation and the center holes were greased with vaseline to aid smooth movement of the breaker. A cooling coil of thin-walled, one-fourth inch copper tubing was held in place by thin-walled monel tubes, $\underline{D}$. A thin strip of stainless steel was fitted across the bottom of the coil anchoring the bottom of the breaker and centering the sample holder. The sample holder was a six-pronged spider with holes for sealing in six sample bulbs, $\underline{B}$, with Apiezon-W wax. The spider was held up by a three-sixteenth inch stainless steel rod which passed up through the center of the stirring shaft and was attached to the frame by means of a rod and clamps. A notched knob at the top indicated which sample was above the breaker. An oil seal, $\underline{F}$, prevented evaporation to the outside.

The stirrer was a multivaned propeller mounted at the end of a very thin-walled three-eighth inch monel tube. The monel shaft was supported by two ball-bearings and had practically a "bearing" fit in the lower brass plate to restrict evaporation to the upper chamber; it was rotated in such a direction as to force the stream of water downward. A constant stirring rate of 580 r.p.m. was provided by an adjustable synchronous electric motor. This vigorous rate of stirring, which contributed about 0.3 calorie

per minute, was used to facilitate as rapidly as possible
the dispersion of the extremely hygroscopic anhydrous
chlorides. When the rare earth chlorides are dissolved
in water a large amount of heat is produced at the point
where the salt contacts the water; hydrogen chloride gas
is dispelled from the surface of the water if the salt is
added to water in an open beaker. If very much acid is
lost to the air, the pH of the solution is increased by
the subsequent hydrolysis and the solution becomes turbid.
In spite of such vigorous stirring as was used, some of the
resulting solutions from the preliminary experiments were
found to be turbid. When this occurred, the heat effects
continued to manifest themselves for a long time after the
solution experiment was initiated; the temperature con-
tinued to rise in an erratic fashion for some time before
the calorimeter came to equilibrium. Such experimental
curves are very difficult, if not impossible, to interpret
properly. Therefore, samples were kept quite small; and,
for experiments which were carried out starting with an
initial known concentration of the salt in the calorimeter
vessel, the initial solutions were prepared by using a
system of flasks in which a weighed amount of the salt was
kept separate from the water until the system was closed.
By tipping and shaking, the salt could be added slowly to
the water and when the salt was completely dissolved, the

solution was run back and forth between the two compartments
to redissolve any gaseous hydrogen chloride gas. The so-
lution and rinsings were then transferred to a large weight-
burette and diluted to the proper concentration.

All of the metal parts of the calorimeter were covered
with quick-drying, acid-resistant Ajax varnish which had
been diluted with Skelly-B to an appropriate thickness.
This could be removed easily with trichloroethylene, and a
new coat of paint was easily put on by dipping the assembly
into a beaker of varnish. Heavier coats were applied when
acid solutions were used.

For single heat of solution experiments, the sample-
holder and breaker were removed. The samples were held in
a tantalum-foil basket attached to the end of a long hollow
glass rod. The glass rod was inserted into the stirrer
shaft from the bottom before the calorimeter was assembled
and was held at the top by a hollowed rubber stopper. The
bulbs were broken with a blunt stainless steel rod which
was held about an inch above the level of the solution by
a compression spring above the top end of the glass rod; a
quick push on the steel rod broke the bulb.

The energy input during calibration experiments was
determined by following the emf drop across a 0.1 ohm
Reichsanstalt type standard resistor, calibrated by the
National Bureau of Standards, which was kept at 25° C. in

an oil bath. The total time of heating was measured with
a calibrated stopwatch. Intermittent times were read on a
0.1-second timer at given settings of the potentiometer.
The circuit used is shown in Figure 6. A White single
and a K-2 type potentiometer were used interchangeably to
measure the drop across this resistor. If circuit $\underline{C}$ was
used, the drop across R_F was measured on one of the circuits
of the White double potentiometer; when this was done the
temperature-time curve of the calorimeter was neglected
until the heating was terminated.

All resistances were measured by comparing them with
Bureau of Standards type resistors calibrated by the
National Bureau of Standards, by measuring the emf drop
across each of them on the White double potentiometer as
the current passed through them in a series arrangement.
The measured resistance was made at the temperature it was
used.

A Mueller G-2 type temperature bridge was used in con-
junction with the platinum resistance thermometer for cali-
bration of the thermometer. The bridge was previously cali-
brated on the absolute scale according to the recommended
procedure given by the manufacturer.

Before performing an experiment, the samples were
waxed into the spider in the desired order and were tested
for leaks by immersing them in water. When dry, the spider

CIRCUIT FOR HEAT MEASUREMENTS
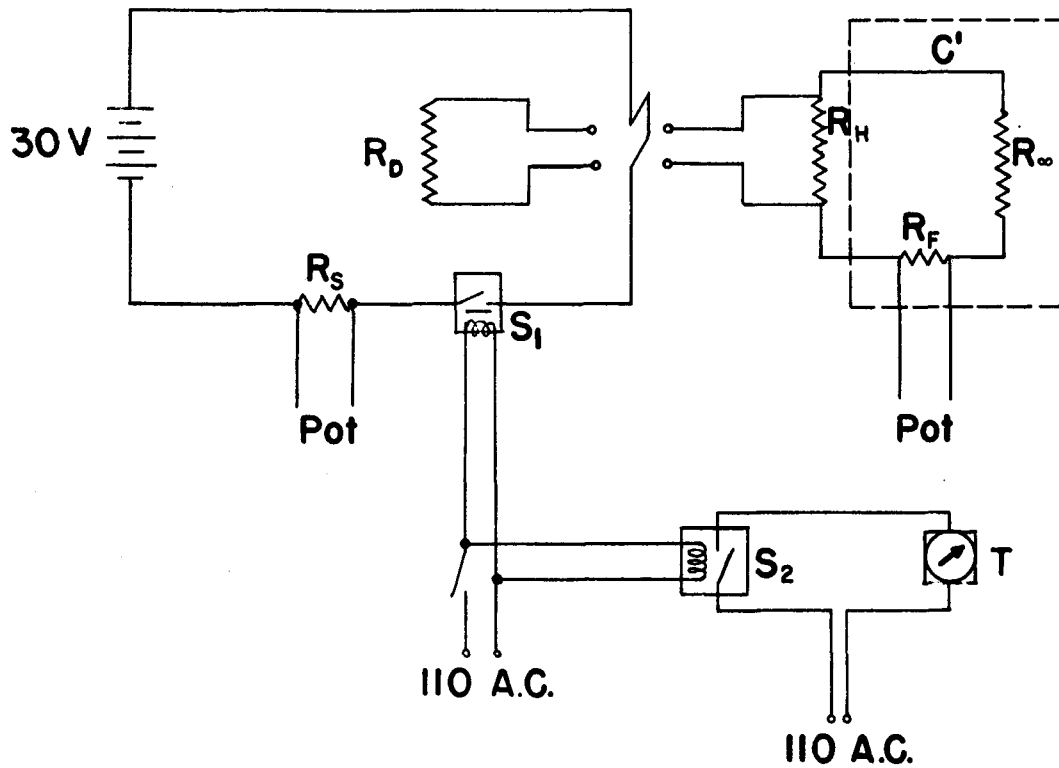
R_S = Standard 0.1 ohm resistance

R_D = Dummy Heater

R_H = Calorimeter Heater

S_1 & S_2 = Power Relays

T = 0.1 second timer

R_F = Standard 10 ohm resistance

R_∞ = Standard 10,000 ohm resistance

C' = Circuit used only for checking and calibrating

Figure 6. Diagram of Electrical Circuit used to Calibrate the Calorimeter.

was inserted from the bottom of the calorimeter and was clamped into position at the top with the dial on the knob set at first position. Either conductance water or the solution was weighed in a 1400 ml. weight burette and run into the calorimeter vessel. The vessel was quickly bolted in position and the calorimeter and frame was placed into the thermostat. Stirring was initiated immediately and all the electrical leads connected. By using either warm or cold water the calorimeter was brought to a temperature slightly below the desired operating temperature and after about 20 or 30 minutes the first temperature readings were taken. The readings were made every half minute for ten minutes. During this time the batteries were allowed to discharge through a dummy heater of the same resistance as that of the heater in the calorimeter. If, at the end of ten minutes the increment of temperature rise or fall per half minute was constant, the current was immediately switched into the calorimeter heater circuit. Heating was usually continued long enough to approximately match the temperature rise of the preceding heat of solution experiment. A few heating periods were as long as 15 minutes, but most of them were of 300 to 500 seconds in duration. After the heating was stopped, the temperature was read until a steady state was assured for at least ten minutes. The calorimeter was then brought to approximately the same

temperature it was before the heat was added. When the calorimeter and contents came to thermal equilibrium the temperature was again read at half-minute intervals for at least ten minutes. The sample bulb was then broken and the temperature changes observed as in the heating experiment. This process of alternately heating and dissolving samples was continued until all six samples were dissolved. A total of seven heat capacity calibration experiments was made during the procedure of dissolving a set of six samples. The theoretical equations necessary for the interpretation of the data obtained from the described isothermally-jacketed calorimeter are given according to the accepted methods of King and Grover (26); Jessup (27); and Coops, Van Nes, Kentie, and Dienske (28).

Assume that, for a given process under consideration, a development of a quantity of heat Q_o, occurs in the calorimeter only between times t_B and t_F, and causes a temperature rise of $\theta_F - \theta_B$ of the calorimeter; then, during this period, if corrections of the second order are neglected, the basic heat balance for the calorimeter is

$$(68) \qquad Q_T + Q_S + Q_O = W(\theta_F - \theta_B) + Q_U$$

in which Q_T is the heat furnished by the thermometer current

$\qquad$ Q_S is the heat added due to stirring

$\qquad$ Q_O is the heat added electrically or by chemical

$\qquad\qquad$ reaction

$\underline{W}$ is the heat capacity or "water equivalent" of

the calorimeter

$\underline{\theta_F}$ is the final temperature

$\underline{\theta_B}$ is the initial temperature

$\underline{Q_U}$ is the heat exchange to surroundings (water

bath kept at a temperature $\underline{\theta_W}$)

$\underline{Q_U}$ is determined from the Fourier expression

(69) $$dQ_U = - A(\theta - \theta_W)dt$$

and if $\underline{A}$ is constant, that is, if the system satisfies

Newton's law of cooling

(70) $$Q_U = - A \int_{t_B}^{t_F} (\theta - \theta_W)dt$$

If the rate of stirring is constant

(71) $$dQ_S/dt = B$$

and

(72) $$Q_S = B(t_F - t_B)$$

is the heat added during the main course of the heat de-

velopment. For small changes of temperature, the re-

sistance of the thermometer element can be given by

(73) $$R = R_0(1 + \alpha\theta)$$

in which R_0 is the thermometer resistance at 0° C and $\underline{\alpha}$

is the temperature coefficient of resistance of the copper

wire. If the current through the thermometer is kept

constant, the rate of heat input of the thermometer is

(74) $$dQ_T/dt = R_0(1 + \alpha\Theta) I^2/J$$

and

(75) $$Q_T = (R_0 I^2/J)(t_F - t_B) + (R_0 I^2 \alpha/J) \int_{t_B}^{t_F} \Theta dt$$

in which J is equal to 4.1855 absolute joules/calorie (29).

The calorimeter constants, A and B, are related in a given experimental situation by the convergence temperature, Θ_K, in the following manner. If the rate of stirring and the current in the thermometer are maintained constant and no other heat is generated in the calorimeter, it will, after a long time, reach a constant temperature $\Theta_K > \Theta_W$. Under this condition the rate at which heat is generated within the calorimeter is equal to the rate at which it is lost to the surroundings, hence

(76) $$dQ_U/dt = dQ_T/dt + dQ_S/dt$$

Substituting Equations (70), (72) and (75) into Equation (76) evaluated at Θ_K gives

(77) $$-A(\Theta_K - \Theta_W) = B + (R_0 I^2/J)(1 + \alpha\Theta_K)$$

During any period outside t_B to t_F when the calorimeter is not precisely at the temperature Θ_K it will experience, under the above operating conditions, a temperature rise or fall in drifting toward Θ_K; the rate of heat exchange with surroundings will be

(78) $$dQ/dt = W\,d\Theta/dt = d(Q_U - Q_S - Q_T)/dt$$

Using Equation (78) to eliminate the constant B from Equations (70), (72), and (75) gives

(79) $\quad d(Q_U - Q_S - Q_T)/dt = -(A + R_o I^2 \alpha /J)(\Theta - \Theta_K)$

in which $\underline{(A + R_o I^2 \alpha /J)}$ is the observed cooling constant

for a given thermometer current and rate of stirring.

If, for convenience, the symbols $\underline{g}$ and $\underline{G}$ are defined as

(80) $\quad\quad\quad\quad\quad g = d\Theta/dt$

and

(81) $\quad\quad\quad\quad G = (1/W)(A + R_o I^2 \alpha /J)$

then

(82) $\quad\quad\quad\quad\quad g = -G(\Theta - \Theta_K)$

For a given set of experimental conditions the constants

$\underline{G}$ and $\underline{\Theta_K}$ can be evaluated by observed values of $\underline{g}$ and $\underline{\Theta}$

before $\underline{t_B}$ and after $\underline{t_F}$ so that

(83) $\quad\quad\quad\quad g_1 = -G(\Theta_1 - \Theta_K)$

and

(84) $\quad\quad\quad\quad g_2 = -G(\Theta_2 - \Theta_K)$

in which $\underline{g_1}$ is the rate of temperature change observed at

the temperature $\underline{\Theta_1}$, before $\underline{t_B}$; $\underline{g_2}$ and $\underline{\Theta_2}$ are the corres-

ponding quantities observed after $\underline{t_F}$. Equations (83) and

(84) are solved simultaneously to give

(85) $\quad\quad\quad\quad G = (g_1 - g_2)/(\Theta_2 - \Theta_1)$

and

(86) $\quad\quad\quad \Theta_K = (g_1 \Theta_2 - \Theta_1 g_2)/(g_1 - g_2)$

The integration of Equation (79), between the times $\underline{t_B}$ and

$\underline{t_F}$, to obtain the total amount of heat lost or gained by

the calorimeter during that period gives

$$(87) \qquad Q_U - Q_S - Q_T = -WG \int_{t_B}^{t_F} (\Theta - \Theta_K) dt$$

Combining Equations (68) and (87) gives

$$(88) \qquad Q_O = W \left[(\Theta_F - \Theta_B) - G \int_{t_B}^{t_F} (\Theta - \Theta_K) dt \right]$$

It is necessary to know $\underline{\Theta}$ as a function of $\underline{t}$ to evaluate the integral. Equations (78), (79) and (81) can be combined and written in the form

$$(89) \qquad d \ln(\Theta - \Theta_K)/dt = -G$$

which has a general solution of the form

$$(90) \qquad \Theta = \Theta_K + (\Theta_B - \Theta_K)e^{-G(t - t_B)}$$

when the constants of the integration are determined from the condition that $\underline{\Theta = \Theta_B}$ at $\underline{t = t_B}$.

Dickinson (30) gave a method of evaluating the integral in Equation (88) which he found to be good to about one part in 10,000. The method essentially involves finding a mean time for the heat development process which occurs between $\underline{t_B}$ and $\underline{t_F}$. The mean time, $\underline{t_X}$, is defined in such a way that the "radiation" correction, $\underline{\Delta\Theta_R}$, is given by

$$(91) \qquad \Delta\Theta_R = g_1 (t_X - t_B) + g_2(t_F - t_X) = G \int_{t_B}^{t_F} (\Theta - \Theta_K) dt$$

if $\underline{g_1}$ and $\underline{g_2}$ are slopes of the temperature-time curve at

t_B and t_F, respectively. The conditions required by Equation (91) can be shown in a simple way by the geometry of the rating-curve shown in Figure 7 in which

$$(92) \qquad \Theta_2 = \Theta_F - g_2(t_F - t_X)$$

and

$$(93) \qquad \Theta_1 = \Theta_B + g_1 (t_X - t_B)$$

The corrected temperature rise at t_X is

$$(94) \qquad \Theta_2 - \Theta_1 = (\Theta_F - \Theta_B) - g_1 (t_X - t_B) - g_2(t_F - t_X)$$

Comparing Equation (94) with the portion of Equation (88) inside the brackets shows that the last two terms of Equation (94) are those defined in Equation (91).

In order to find t_X, let $\Theta_B = 0$ at $t_B = 0$ so that Equation (90) becomes

$$(95) \qquad \Theta = \Theta_K(1 - e^{-Gt})$$

The condition that t_X be a "mean" time is that the shaded areas of Figure 7 be equal; for a one degree temperature rise, if $\Theta_B = 0$, and $\Theta_K = \Theta_F = 1$, the condition is applied as follows (disregarding the ordinate scale and slopes shown by Figure 7):

$$(96) \qquad \int_0^{t_X} (1 - e^{-Gt})dt = \int_{t_X}^{\infty} \left[1 - (1 - e^{-Gt}) \right] dt$$

or

$$t + \frac{e^{-Gt}}{G} \Big|_0^{t_X} = -e^{-Gt}/G \Big|_{t_X}^{\infty}$$
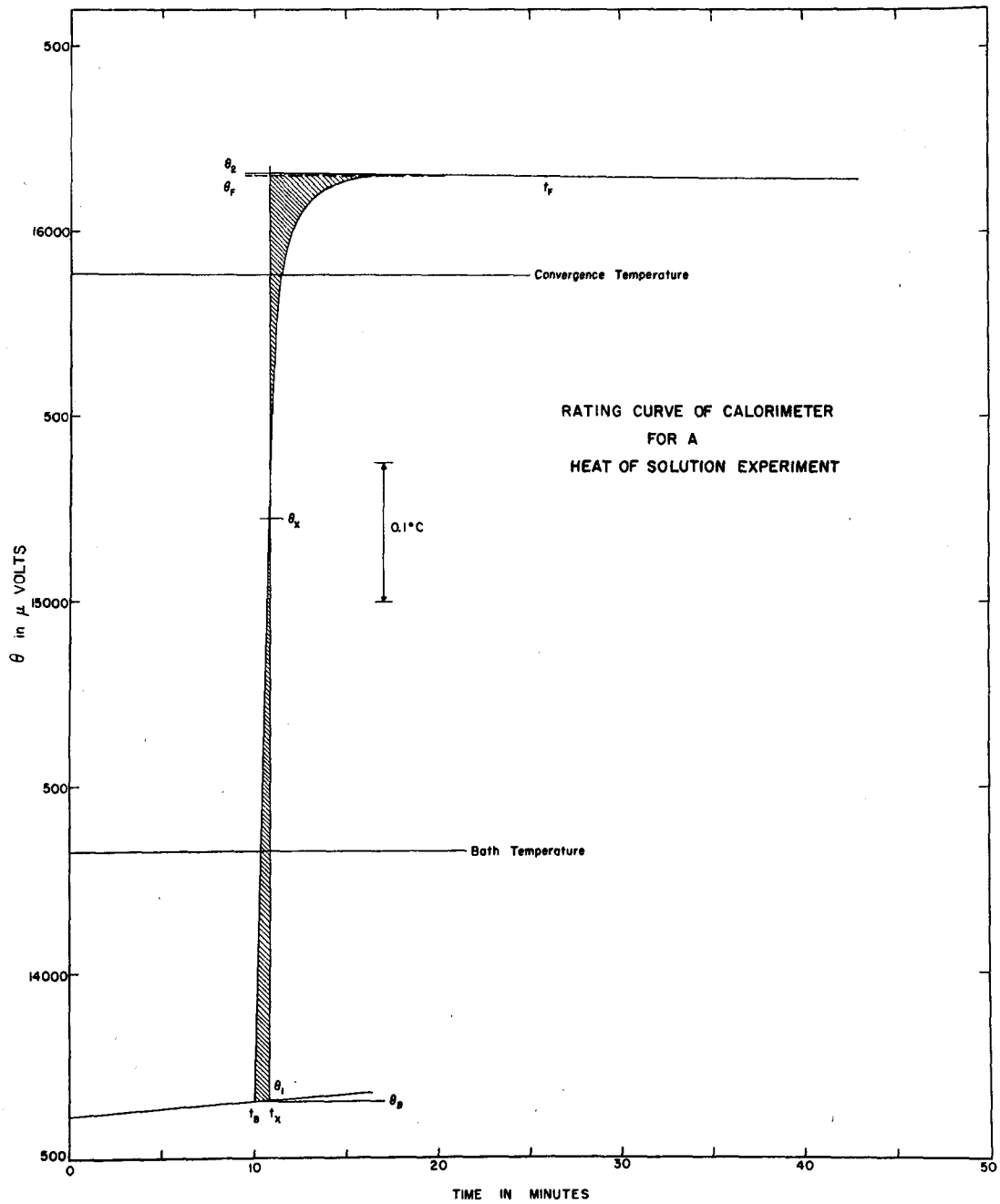
Figure 7. A Rating-Curve for a Heat of
Solution Experiment.

and

(97)
$$t_X = 1/G$$

Hence

(98)
$$\Theta_X = 1 - e^{-G/G} = 0.63$$

and the time at which the temperature is 63% of its final

value is t_X. Therefore, when the value of

(99)
$$\Theta_X = 0.37\Theta_B + 0.63\Theta_F$$

is found, t_X can be taken from the rating curves; and

$\Delta\Theta_R$ is easily computed.

During the calibration experiments, Θ was found to be

a linear function of t from t_B to t_F. Therefore, Θ, can be

represented by

(100)
$$\Theta = at + b$$

or

$$\Theta = \left[(\Theta_F - \Theta_B)/(t_F - t_B)\right] t$$

$$+ \left[\Theta_F(t_F - t_B) - (\Theta_F - \Theta_B)t_F\right]/(t_F - t_B)$$

when the conditions $\Theta = \Theta_B$ at t_B and $\Theta = \Theta_F$ at t_F are imposed.
With these restrictions

(101)
$$\Delta\Theta_R = G \int_{t_B}^{t_F} (\Theta - \Theta_K)dt$$

$$= G(t_F - t_B)\left[(\Theta_B + \Theta_F)/2 - \Theta_K\right]$$

Therefore, for a calibration experiment, if $q(H)$ is the

heat added electrically, Equation (88) is

(102) $\quad q(H) = W \left\{ (\Theta_F - \Theta_B) - G(t_F - t_B) \left[(\Theta_B + \Theta_F)/2 - \Theta_K \right] \right\}$

The heat given out or absorbed by a thermal reaction, $\underline{q_O}$, is

(103) $\quad\quad\quad q_O = W \left[(\Theta_F - \Theta_B) - \Delta\Theta_R \right]$

in which $\underline{\Delta\Theta_R}$ is given by Equation (91) and $\underline{W}$ is determined from Equation (102).

Treatment of data

The heat input during a calibration experiment was determined from a graphical plot of the emf drop across the standard 0.1 ohm resistor against the time in seconds. The emf-time curve was divided into a number of short chords for graphical integration of the integral,

$$(104) \qquad H = (R_H/R_S^2) \int_0^t E^2 dt$$

in which R_H is the resistance of the calorimeter heater coil; R_S is 0.1 ohm; E is the emf drop across R_S at the time, t; and H is the heat in absolute joules. The midpoints of the chords were taken as the mean emf E_i, for the time length of the chord t_i. The above integral is transformed to

$$(105) \qquad H = (R_H/R_S^2) \sum_i E_i^2 t_i$$

A heat input calculation is given in Figure 8. The power input, H/t, was used for detecting errors in calculations because it remained very nearly constant for all calibration experiments.

The temperature change, $\Theta_F - \Theta_B$, (hereafter designated as ε_F and ε_B, respectively), and the heat leakage were determined from plots of the emf of the thermometer in

in microvolts against the time in minutes. The slopes, g_1 and g_2, and the initial and final temperatures, ε_B and ε_F, were taken from plots of the initial and final portions of the rating-curves on a scale of 0.1 microvolt per division. The times, t_B, t_F, and t_X were determined from plots expanded along the time axis to a scale of 0.05 minutes per division and contracted in the temperature ordinate to five microvolts per division. The above quantities were used in Equation (102) to calculate $\underline{W}$, the heat capacity of the calorimeter and its contents. Due to the calorimeter thermometer construction and lag effects, the times, t_B and t_F, differed somewhat from the time the current was started through the heater and the time when it was stopped. Since the heater coil was wound on the same copper cylinder as the thermometer, the observed temperature was higher than the true temperature of the main body of the solution as long as the current passed through the heater. The calorimeter lag was the time required for the stirring to distribute the heat to the body of the solution so that the temperature of the calorimeter and contents was increased at the same rate as that of the thermometer. For the above case the calorimeter lag is defined by

(106)
$$(t - \varepsilon_c) = L \frac{d\varepsilon}{dt}$$

Plot of Emf Drop Across
0.1 Ohm Standard Resistance
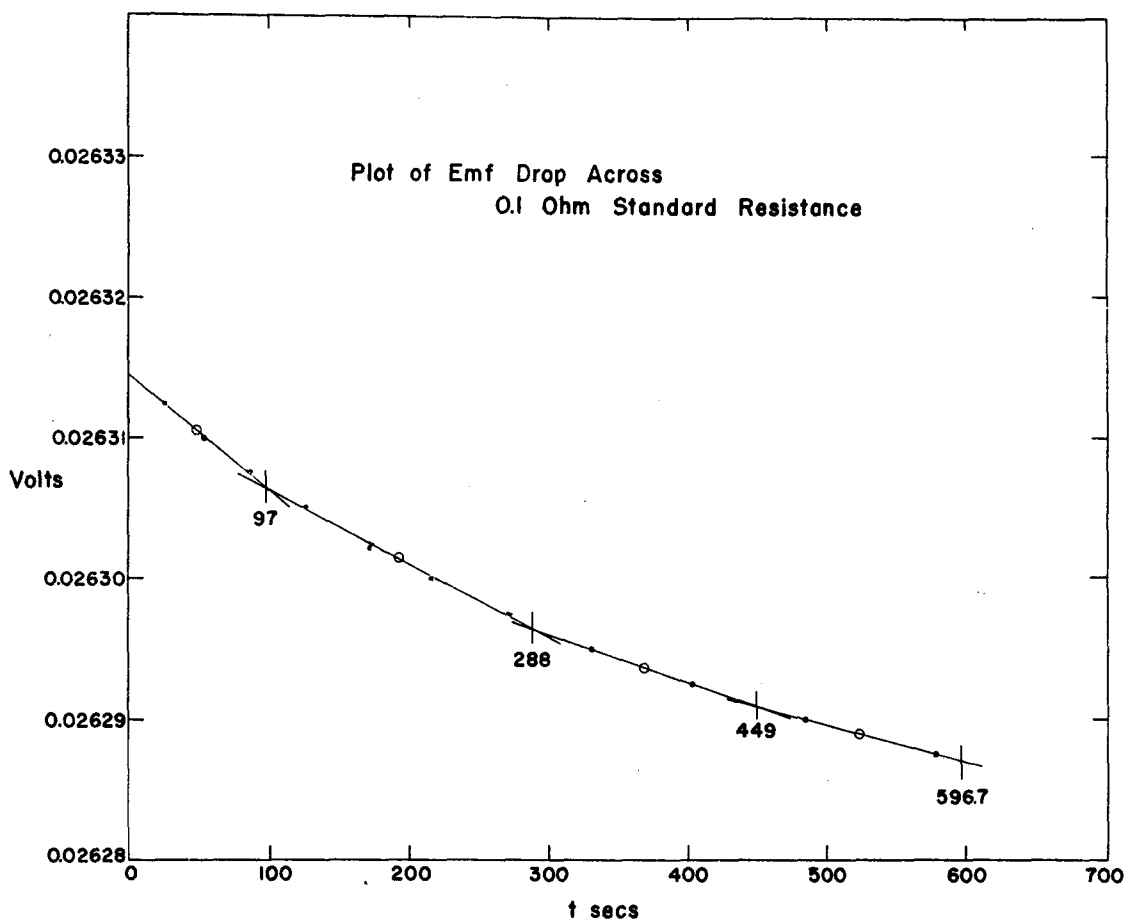
E_i	t_i	$E_i^2 t_i$
0.0263105	$97._0$	0.067148
0.0263014	$191._0$	0.132127
0.0262937	$161._0$	0.111309
0.0262889	147.7	0.102076
Σ	596.7	0.412660

$R_H/R_s^2 = 11,865.8_7$
$H = 4896.6$ abs. joules
$H = 1169.8_8$ cals.
$H/_t = 1.9606$

Figure 8. A Typical Heat Input Calculation.

in which $\underline{L}$ is the lag in minutes; ε_c is the temperature
of the calorimeter; and $\underline{\varepsilon}$ is the temperature of the ther-
mometer. In the experiment shown in Figure 9, the heating
was started at exactly 10.00 minutes; an extrapolation of
the linear observed temperature rise of the thermometer
intercepts the initial rating line at about $\underline{t_B}$ = 9.70
minutes, or $\underline{\delta t_B}$ = 0.30 minute. The slope, from the graph,
is

$$(107) \qquad (dE/dt)_{t \ = \ 10} \quad \frac{-(\varepsilon_c - \varepsilon)_{t \ = \ 10}}{\delta t_B}$$

in which ε_c is the calorimeter temperature as observed at
the tenth minute if the thermometer lag is neglected, and
$\underline{\varepsilon}$ is the extrapolated value of the thermometer temperature
at the ten minute period. Therefore, the lag is about
equal to $\underline{\delta t_B}$ which is the time required to equilibrate
the calorimeter in the sense that the heat is distributed
at a rate equal to its dissipation by the heater. Hence,
for the above case in which the heating was started ex-
actly at the tenth minute, the linear rise of the calo-
rimeter temperature would intersect the initial rating-
curve very nearly at 10.00 + $\underline{\delta t_B}$ minutes; this time is
taken as $\underline{t_B}$. If the intercept of the final rating-curve
and the linear thermometer temperature rise is designated
as t_F', as it is in Figure 10, then

$$(108) \qquad\qquad \Delta t = t_F' - t_B'$$

is the total time of the main period, and
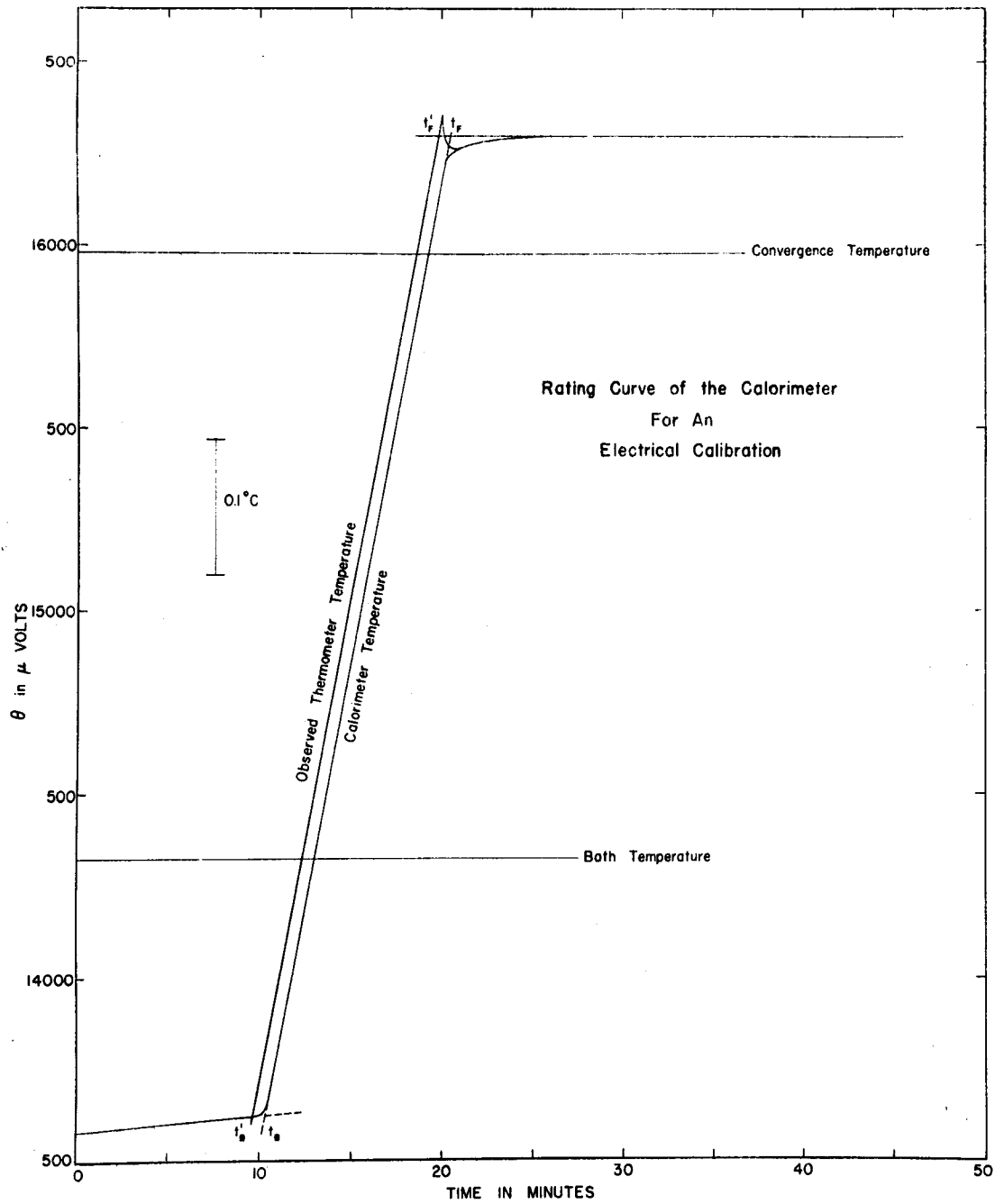
Figure 9. A Rating Curve for an Electrical Calibration.

(109) $$t_F = \Delta t + t_B$$

is the end of the main period with respect to the calorimeter and its contents. When t_B and t_F are determined, the corresponding values of ε, ε_B and ε_F, are read from extensions of the initial and final rating-curves.

The lag of the thermometer and heater is represented by the quantity, $\frac{1}{2}(\Delta t - t_H)$, in which Δt is defined by Equation (108) and t_H is the exact time of heat input. But since the heater lag was very small, the time lag of $\frac{1}{2}(\Delta t - t_H)$ was attributed to the thermometer. It was not taken into account in calculating W because the same lag was present for the heat of solution experiment and its effect on the value of heat of solution was therefore considered negligible (13). In the heat of solution experiments, t_B, was taken at the moment the bulb was broken, and t_F was read from the plot as the time at which the observed temperature, ε_F, first reached the final steady-state rating-curve. Table 4 gives the tabulated analysis of the heat of solution and calibration curves for three samples of neodymium chloride.

In performing a set of experiments to determine the heats of solution, the calorimeter is loaded with m moles of salt in a number of bulbs and $X \times 10^3$ grams of water. A quantity of heat, $q(H)$, is added electrically and W_1 is determined. The salt is then dissolved and the temperature

change followed as previously described; the second quantity

of heat, $\underline{q(H)}$, is added and $\underline{W_2}$ is determined. Since $\underline{W_2}$

corresponds to the heat capacity of the final solution, it

is used to compute $\underline{q_o}$ of the heat of solution experiment

which preceded the determination of $\underline{W_2}$. Since

(110) $W_1 = W(salt) + W(H_2O) + W \text{ (Calorimeter)}$

and

(111) $W_2 = W(Soln) + W(Calorimeter)$

in which $\underline{W}$ is the heat capacity in calories per microvolt,

then

(112) $\Delta W = W_1 - W_2 = W(Soln) - W(Salt) - W(H_2O)$

in which $\underline{\Delta W}$ is the change in heat capacity of the reaction.

Taking the mean temperature of the reaction to be

$(\varepsilon_B + \varepsilon_F)/2$, the heat of the reaction at 25° C; that is,

at $\underline{\varepsilon_{25}}$, is

(113) $q_o^{25} = q_o + \delta q_o^{25}$

in which

(114) $-\delta q_o^{25} = \int_{\bar{\varepsilon}}^{\varepsilon_{25}} W d\varepsilon = W \left[\varepsilon_{25} - (\varepsilon_B + \varepsilon_F)/2 \right]$

The minus sign is used because $\underline{q_o}$, as defined by Equation

(103) is the heat evolved, so that

(115) $q_o = -\Delta H$

and

Table 4

Analysis of Calorimeter Rating-Curves

No.	g_i	e_B, e_F	t_B, t_F	$e_F - e_B$	$G \times 10^3$	e_K	t_x, e_x	t_H	$\Delta t - t_H$
I	+2.971 -1.522	14084.0 16706.2	10.37 20.50	2622.2	1.714	15818		10.13	0.16
II	+4.075 +0.180	13649.6 15761.2	10.27 35.50	2111.6	1.845	15859	10.38 14980		
III	+3.670 -1.097	13994.5 16594.6	10.83 20.80	2600.1	1.833	15996		9.97	0.16
IV	+3.690 -0.172	13613.7 15918.8	10.37 37.00	2305.1	1.675	15816	10.44 15066		
V	+3.760 -1.200	13811.2 16550.2	10.33 20.79	2739.0	1.811	15887		10.74	0.16
VI	+3.990 -0.471	13675.4 16146.8	10.47 34.00	2489.4	1.792	15884	10.74 15226		
VII	+4.426 -0.609	13627.1 16302.0	10.34 20.51	2674.9	1.882	15978		10.17	0.17

64

$$(116) \qquad \left(\frac{\partial q_o}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P = -\Delta C_P = -f(t/\varepsilon)\,\Delta W$$

in which f(t/ε) in a function given by the calibration of the thermometer is degrees per microvolt.

Certain quantities which will be used to interpret the calorimetric data are given as follows:

$$(117) \qquad q_o^{25} = W\left[(\varepsilon_F - \varepsilon_B) - \Delta\varepsilon_R\right] + \delta q_o^{25}$$

is the heat given off at 25° C. by $\underline{n_1}$ moles of salt dissolving in $\underline{X \times 10^3}$ grams of water.

$$(118) \qquad q_M = q_o^{25}/n_1$$

is the heat given off per mole of salt.

$$(119) \qquad q_m = \Delta m q_M = q_o^{25}/X$$

in which $\underline{\Delta m_1}$ is the change in molality of the solution when $\underline{n_1}$ moles of salt are dissolved, and

$$(120) \qquad \Delta m_1 = n_1/X$$

and

$$(121) \qquad Q_m = \sum_1 q_m$$

gives the molal heat of solution.

$$(122) \qquad Q_M = Q_m/m$$

is the total or integral heat of solution. A similar set of notations will be used for an analysis of the heat capacity data.

For a series of experiments which increase the concentration of the electrolyte such as

(a) $n_1 CeCl_3(s) + X \, x10^3$ grams $H_2O = CeCl_3(soln, m_1)$

(b) $n_2 CeCl_3(s) + CeCl_3(soln, m_1) = CeCl_3(soln, m_2)$
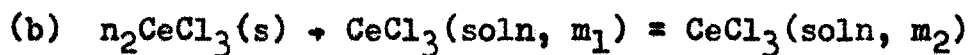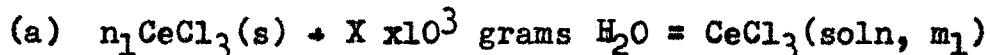
and so forth, the values $\underline{W_0}$, $\underline{W_1}$, $\underline{W_2}$, were determined. The various $\underline{W}$ values were then converted to $\underline{C_p}$ in cals/deg. $^\circ C$ by application of the calibration formula of the thermometer as follows:

(123) $t^\circ C = a + b\varepsilon + c\varepsilon^2$

so that

(124) $\Delta t = t_F - t_B = b(\varepsilon_F - \varepsilon_B) + c(\varepsilon_F^2 - \varepsilon_B^2)$

or

(125 $\Delta t / \Delta \varepsilon = b + 2c\bar{\varepsilon}$

in which $\bar{\varepsilon} = (\varepsilon_B + \varepsilon_F)/2$. The constants $\underline{a}$, $\underline{b}$, and $\underline{c}$ are given in Figure 10.

The changes in the heat capacities for the above reactions are

(a) $\Delta C_{p1} = C_{p1} - C_{po}$

$= C_p(soln, m_1) - C_p\left[n_1 CeCl_3(s)\right] - C_p(H_2O)$

(b) $\Delta C_{p1-2} = C_{p2} - C_{p1}$

$= C_p(soln, m_2) + C_p\left[(n_2 + \cdots)CeCl_3(s)\right]$

$- C_p(soln, m_1)$

Calibration of Thermometer
for
$\xi/10\,\Omega = 50,000\,\mu V$

$\xi(25^\circ C) = 14,326.6$

$t^\circ C = 21,081_2 + 2.7661_2 \times 10^{-4}\xi - 0.02149_1 \times 10^{-8}\xi^2$

20,000
18,000
16,000
14,000
12,000
10,000
8,000
6,000
μV 4,000
2,000
0
−2,000
−4,000
−6,000
−8,000
−10,000
−12,000
−14,000
−16,000

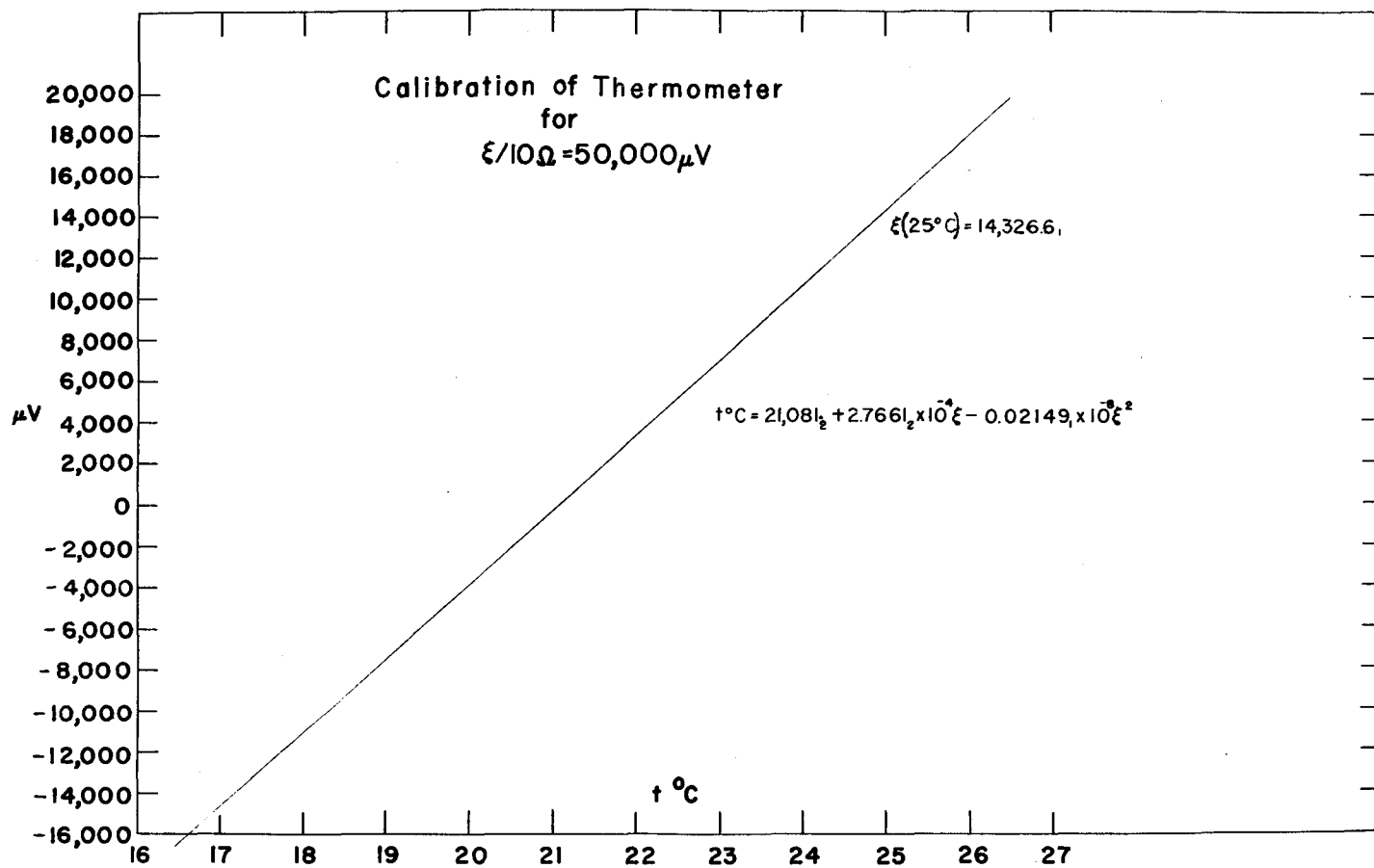16 17 18 19 20 21 22 23 24 25 26 27

$t\ ^\circ C$

Figure 10. Calibration of Transposed Bridge Thermometer.

(c) $\Delta Cp_2 = Cp_2 - Cp_0$

$= Cp \text{ (soln, } m_2) - Cp \left[(n_1 + n_2)CeCl_3(s) \right] - Cp(H_2O)$

and so forth. The ΔCp_i are the changes in the heat capacities which occur when a given amount of salt is added to the initial solution; the initial solution in the above equations is pure water. In this case, when Cp_i is divided by the sum of the moles of the salt dissolved, the quantity Cp_M, is obtained.

The corresponding molal quantity is

(126) $\Delta C_{pm} = m \Delta C_{pM}$

For a given series of experiments starting with a solution of concentration, m_0, instead of water, the values of

(127) $\Delta Cp(m_0 \longrightarrow m_1) = \Delta Cpi/X$

in which $X \times 10^3$ is the weight of water used, are found. If these values, for each series, are plotted against m and the resulting curves fitted so that ΔC_{pm} is a continuous function, ΔC_{pM} can be calculated by Equation (126) and plotted against $m^{\frac{1}{2}}$ for continuity tests. When the curves for each series of experiments are properly fitted, the ΔC_{pM} plot can be extrapolated to $m^{\frac{1}{2}} = 0$ to determine

(128) $\Delta C_{pM}^0 = \emptyset_{cp}^0 - C_{p2}(s) = \overline{C}_{p2}^0 - C_{p2}(s)$

In addition, the smoothed values of either ΔC_{pm} or $\Delta C_p(m_0 \longrightarrow m_1)$ were taken from the graphs and converted

back to smoothed values of $\Delta C_{p1} = C_{p1} - C_{p_0}$ by Equation (127); by using the measured values of C_{p1}, $i + 1$ values of C_{p_0} were obtained and averaged. The average value of C_{p_0} was used, along with the smoothed values of ΔC_{p1}, to recalculate values of C_{p1}; the latter were then converted to W_i at the mean temperature, $\overline{t}$, of the preceding the heat of solution experiment. The use of the C_{p1} in this manner assumes that C_{p1} but not W_i is constant over the observed temperature rise, and the W used will differ slightly from the value found in the calibration experiment unless the mean temperature is the same in both experiments.

The heat of solution, q_M, for a single experiment was calculated by the use of Equations (117) and (118). In order to join the curves of two series of experiments in which the concentration range of the second series overlapped that of the first, an adaptation of the chord method (3) of plotting was used. When all of the values were computed for each series, they were plotted against $\overline{m^{\frac{1}{2}}} = (m_i^{\frac{1}{2}} - m_j^{\frac{1}{2}})/2$ in which i and j were the neighboring points. The best curve was drawn through the points, and smoothed values of the q_M were taken from it; then, by the use of Equations (119) and (121), Q_m was calculated through all the points to determine the best value of Q_{m_0} of the second of the two sets. This was done because, for

any series of experiments not starting with water in the
calorimeter, Equation (121) was changed to

(129) $\qquad Q_m = \sum_i q_m + Q_{m0}$

The total or integral heat of solution,

(130) $\qquad Q_M = - \Delta H$

was then calculated by Equation (122) and plotted against
$m^{\frac{1}{2}}$.

Results

The calorimeter and experimental procedure were
tested by measuring the heat of solution of pure potassi-
um chloride since the heat of solution of this compound
had been determined previously by a large number of in-
vestigators and was considered to be one of the best
known of all heats of solution. The potassium chloride
was twice crystallized from conductance water and then
was fused under an argon atmosphere; the crystals were
crushed and loaded into sample bulbs in a dry-box con-
taining dry nitrogen.

The data on the heat of solution of potassium chloride
obtained by other investigators was corrected to $25^{\circ}C$ and
to infinite dilution by the use of the heat capacity
equations and smoothed-values of the apparent molal heat
content of solutions of potassium chloride at $25^{\circ}C$ given
by Harned and Owen (3). The equation

(131) $$L_2(s) = \phi_L - \Delta H$$

was used to calculate the heat of solution at infinite
dilution; these data are given in Table 5. The data on
the heat of solution of potassium chloride at $25^{\circ}C$
obtained in the present work are summarized in Table 6.
The values for the quantity $\underline{L_2(s)}$, in Table 6, were also
calculated by the use of Equation (131); the average

value, -4144 cals/mole, compares favorably with those obtained adiabatically by Miscenko (34), and by Lange and Monheim (35).

Table 5

Heats of Solution at Infinite Dilution of Potassium
Chloride by Previous Authors

Authors	Literature Reference	t°C	$L_2(s)$
Cohen, Heldermann, and Moesveld	31	18	-4071
Wüst and Lange	32	25	-4175 ± 10
Cohen and Kooy	33	18	-4121 ± 5
		20	-4119 ± 5
		20	$-4162*$
		25	-4113 ± 5
Roth and Eymann	19	12.5	-4148
		18	-4122
		20	-4118 ± 5
		21	$-4115 \pm 5*$
		21	-4145
Miscenko	34	25	-4140 ± 3
Lange and Monheim	35	12.5	-4147 ± 7

* Obtained by the use of an isothermal calorimeter
 t°C is temperature at which the cited work was done
 $L_2(s)$ is in cal/mole at 25°C

Table 6

Heats of Solution of Potassium Chloride at 25°C

m	$m^{\frac{1}{2}}$	ΔCp_M	$\emptyset_J$	Q_M	$L_2(s)$
0.02641	0.1625	-37.5	3.7	-4200	-4142
0.08931	0.2988	-34.9	6.3	-4225	-4148
0.1676	0.4092	-38.4	2.8	-4224	-4143
				Average:	-4144 ± 3

m is the final molality; ΔCp_M is the change in heat capacity in cal/mole°C; $\emptyset_J$ is the relative molal heat capacity in cal/mole°C; Q_M is the heat of solution in cal/mole; and $L_2(s)$ is in cal/mole.

The data obtained for the heat capacities of solutions of cerium chloride and of neodymium chloride are given in Tables 7 and 8, and are plotted in Figures 11, 12, and 13. The limiting values of ΔCp_M^0, which are given as $\Delta Cp_M(\infty)$ in Figure 13, were obtained by extrapolating a plot of ΔCp_M against $m^{\frac{1}{2}}$ to infinite dilution. They could also have been obtained by determining the limiting slopes of the curves in Figure 11 and Figure 12.

The data obtained for the heats of solution of cerium chloride and of neodymium chloride are summarized in Tables 9 and 10 and are plotted in Figures 14 and 15. The chord method of analysis of thermal data as described by

Harned and Owen (3) was applied to the data in order to determine the values of $\underline{L_2(s)}$; the results of this analysis of the data for both electrolytes are plotted in Figure 16 and show that, within the limits of experimental error, the limiting slope of 6925 as given by the Debye-Hückel equation is approached. Therefore, an equation of the form

(132) $\qquad Q_M = a + bm^{1/2} + cm + dm^{3/2}$

in which $\underline{b} = 6925$ was fitted to the data. The derived constant, $\underline{a}$, is $\underline{L_2(s)}$; the constants of Equation (132), with the exception of $\underline{b}$, were determined by the method of successive approximations as given by Worthing and Goeffner (36). The equation which represents the data for the heat of solution of cerium chloride at $25^{\circ}C$ was found to be

(133) $\qquad Q_M = 34,010 - 6,925m^{1/2} + 8,485m - 5,201m^{3/2}$

The equation which represents the data for the heat of solution of neodymium chloride at $25^{\circ}C$ was found to be

(134) $\qquad Q_M = 37,100 - 6,925\ m^{1/2} + 8,953m - 5,460m^{3/2}$

The first four values for the heat of solution of cerium chloride were not considered in the calculation of Equation (133) since the first value of that series of four experiments, although being within the calculated limits of error for such a small sample, was low; the amount it falls below the calculated value is equivalent

Table 7

Heat Capacity of Solutions of Cerium Chloride

at 25°C

m	$m^{\frac{1}{2}}$	$- \Delta Cp_m$	$- \Delta Cp_M^*$	ϕ_J
0.001611	0.04014	1.08	-----	----
0.005688	0.07542	3.17	-----	----
0.008689	0.09322	1.45	-----	----
0.01482	0.1217	6.76	346.8	15.5
0.03284	0.1812	11.10	338.0	24.3
0.03562	0.1887	11.81	331.5	30.8
0.05371	0.2318	17.89	333.1	29.2
0.06243	0.2498	21.05	337.2	25.1
0.08662	0.2943	27.63	319.0	43.3
0.1071	0.3273	34.32	320.3	42.0
0.1276	0.3573	40.42	316.7	45.6
0.1461	0.3823	45.79	313.3	49.0
0.1565	0.3956	49.94	319.2	43.1
0.1789	0.4230	53.86	301.0	61.3
0.1957	0.4424	58.27	297.8	64.5
0.2159	0.4646	67.26	311.6	50.7
0.2318	0.4814	72.94	314.7	---
0.2543	0.5043	75.61	297.4	64.9
0.2769	0.5262	82.08	296.4	65.9
0.2997	0.5474	87.26	291.2	71.1
0.3238	0.5691	92.97	287.1	75.2
0.3477	0.5897	91.91	276.1	86.2

$*-\Delta Cp_M^O = - \Delta Cp_M(\infty) = 362.3$ cal/mole°C
(m is the final molality; ΔCp_m is in cal/°C;
ΔCp_M is in cal/mole°C; and ϕ_J is in cal/mole° C)

Table 8

Heat Capacity of Solutions of Neodymium Chloride

at 25°C

m	$m^{\frac{1}{2}}$	$- \Delta Cp_m$	$- \Delta Cp_M^*$	ϕ_J
0.002744	0.05238	1.00	-----	----
0.005745	0.07580	-0.35	-----	----
0.009230	0.09608	4.22	-----	----
0.01084	0.1041	3.12	287.9	13.9
0.01331	0.1154	4.81	-----	----
0.02818	0.1679	8.41	298.4	21.9
0.03202	0.1739	9.06	299.7	20.6
0.04583	0.2141	18.87	-----	----
0.04653	0.2157	13.52	290.7	29.7
0.06703	0.2589	19.97	297.9	27.4
0.09123	0.3020	25.84	283.2	37.1
0.09245	0.3040	25.94	290.6	39.7
0.1064	0.3262	30.04	282.4	37.9
0.1159	0.3404	24.57	-----	----
0.1213	0.3483	33.33	274.7	45.6
0.1350	0.3674	43.88	-----	----
0.1414	0.3760	37.77	267.2	53.1
0.1541	0.3926	37.90	-----	----
0.1743	0.4175	44.10	255.3	65.0
0.1952	0.4419	51.28	262.6	57.7
0.2174	0.4662	56.38	259.4	60.9
0.2413	0.4912	63.42	262.8	57.5
0.2580	0.5079	65.07	252.2	68.1
0.3155	0.5617	75.12	238.1	82.2
0.3640	0.6033	88.57	243.4	76.9
0.4129	0.6426	93.96	227.6	92.3

$*- \Delta Cp_M^0 = - \Delta Cp_M(\infty) = 320.3$ cal/mole°C ($\underline{m}$ is the final molality; ΔCp_m is in cal/°C; ΔCp_M is in cal/mole°C; and ϕ_J is in cal/mole°C)
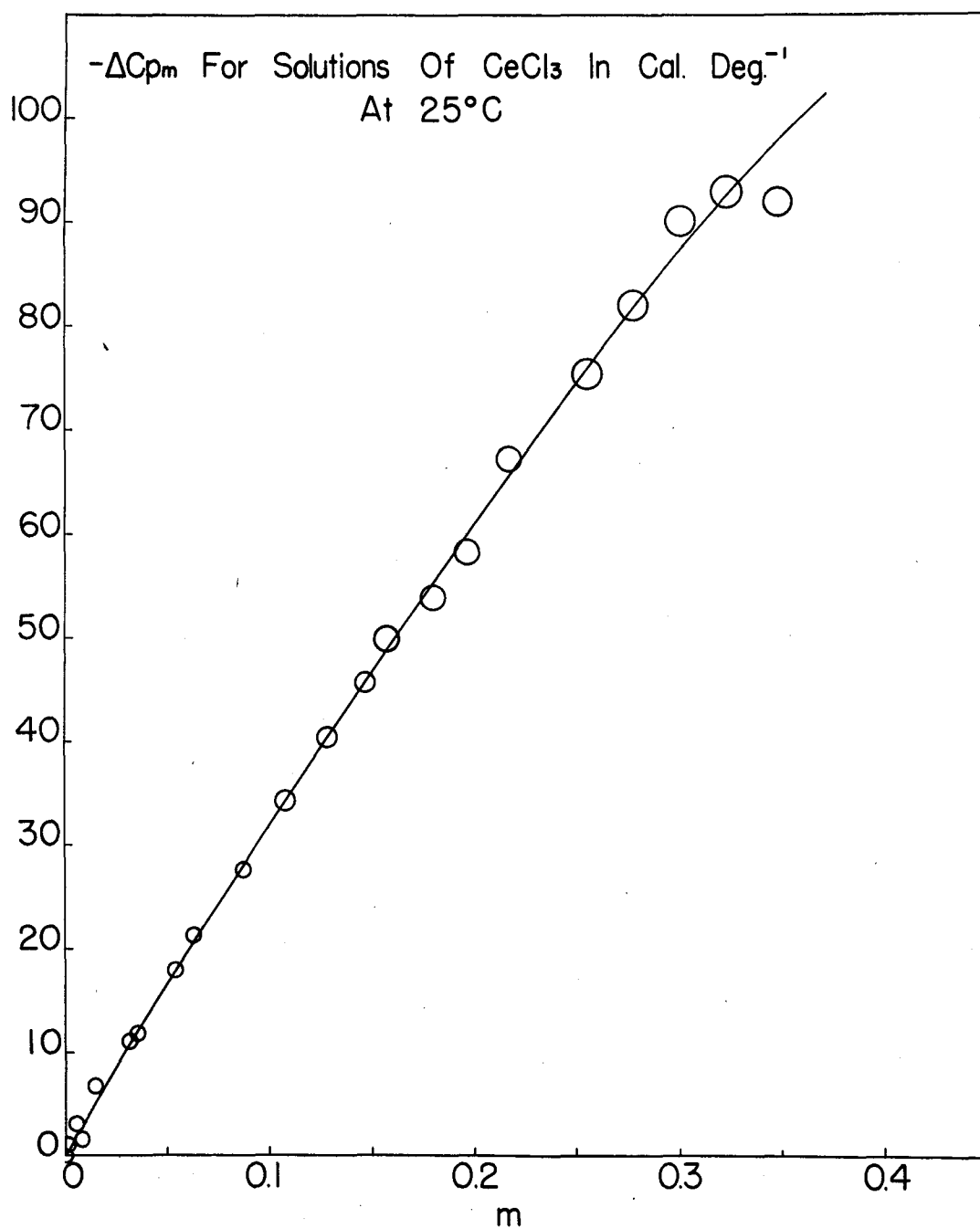
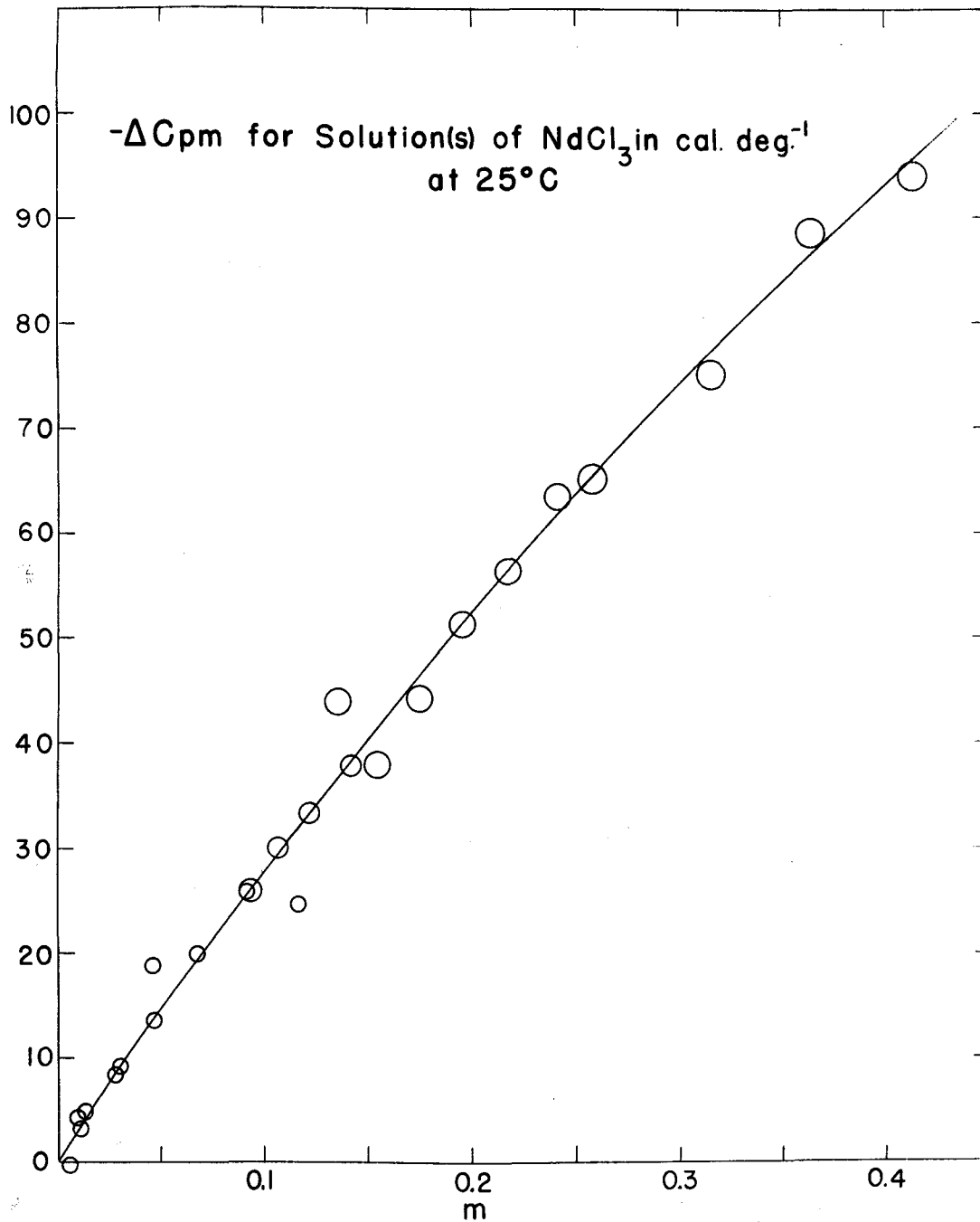Figure 11. Molal Heat Capacity of Solutions
of Cerium Chloride.

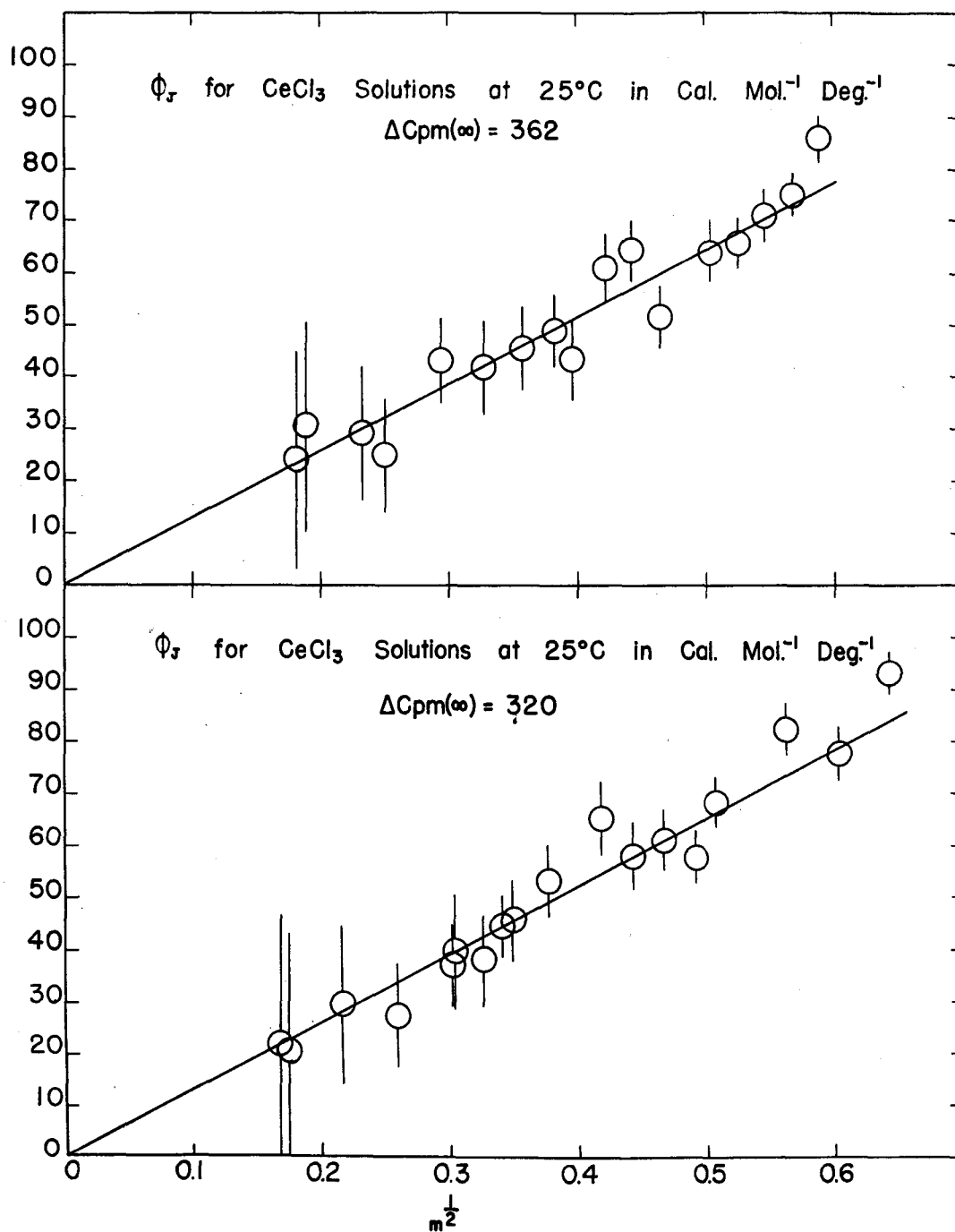Figure 12. Molal Heat Capacity of Solutions

of Neodymium Chloride.

Figure 13. Relative Apparent Molal Heat Capacity for
Solutions of Cerium and of Neodymium Chlorides.

Table 9

Heats of Solution of Cerium Chloride at 25°C

$m^{\frac{1}{2}}$	W	$\Delta\varepsilon_c$	δq_0^{25}	q_0^{25}	q_M	q_m	Q_m	Q_M
0.04014	0.433754	161.7	+0.04	70.18	33672	54.25	54.25	33762
0.05840	0.433404	180.0	----	78.01	33512	60.30	114.55	33587
0.07542	0.433049	226.8	-0.03	98.19	33320	75.90	190.45	33480
0.09322	0.432694	298.0	-0.04	128.92	33206	99.65	290.10	33386
0.1217	0.447095	1456.0	-0.93	650.05	33279	493.21	493.21	33279
0.1812	0.444960	1751.8	-1.08	778.38	32776	590.58	1083.79	33003
0.1887	0.449739	3448.0	-1.33	1549.36	32976	1174.71	1174.71	32976
0.2318	0.442407	2025.1	-1.72	894.20	32505	678.46	1762.24	32809
0.2498	0.446818	2566.2	-1.96	1144.66	32379	867.87	2042.58	32720
0.2943	0.444502	2316.8	-0.37	1029.44	32264	780.52	2823.10	32592
0.3273	0.445957	2151.1	-0.43	958.86	32165	742.20	3476.43	32447
0.3573	0.444019	1910.1	+0.20	848.32	32029	656.64	4133.06	32380
0.3823	0.442020	1722.6	-0.15	761.28	31846	589.26	4722.33	32312
0.3956	0.434487	3610.4	-2.96	1565.73	31813	1203.71	5048.59	32266
0.4230	0.432602	2143.3	-0.56	926.63	31731	712.38	5760.97	32199
0.4424	0.431176	1608.9	+0.14	693.87	31805	533.44	6294.42	32165
0.4642	0.429137	1944.6	-0.09	834.42	31794	641.49	6935.90	32130
0.4814	0.425080	3535.7	-2.31	1500.63	31828	1183.19	7430.66	32059
0.5043	0.423363	2128.8	-0.18	901.29	31588	710.63	8141.29	32017
0.5262	0.421270	2140.0	-0.39	901.14	31366	710.54	8851.84	31964
0.5474	0.419135	2149.3	-0.65	900.22	31236	709.78	9561.61	31909
0.5607	0.417429	2272.7	-0.41	948.15	30905	747.61	10309.2	31834
0.5897	0.415726	2248.6	-0.53	934.28	30849	736.65	11045.9	31766

($\underline{\Delta\varepsilon_c}$ is the corrected temperature rise in microvolts)

80

Table 10

Heats of Solution of Neodymium Chloride at 25°C

$m^{\frac{1}{2}}$	W	$\Delta\varepsilon_c$	δq_0^{25}	q_0^{25}	q_M	q_m	Q_m	Q_M
0.05238	0.444897	299.4	+0.05	133.27	36768	100.88	100.88	36768
0.07580	0.444545	325.6	+0.05	144.80	36520	109.60	210.48	36638
0.09608	0.444114	376.4	+0.03	167.21	36310	126.56	337.04	36514
0.1041	0.456800	1162.4	+0.09	531.06	36471	395.25	395.25	36471
0.1154	0.443621	439.2	-0.01	-194.82	36180	147.46	484.51	36412
0.1208	0.455571	1559.8	+0.49	711.08	36385	530.78	530.78	36385
0.1679	0.454726	1845.9	-0.43	838.95	35997	624.40	1019.66	36179
0.2141	0.452758	1870.5	-0.82	846.04	35678	629.68	1649.34	35986
0.2157	0.452117	1722.6	+0.19	779.00	35672	581.47	1673.32	35963
0.2589	0.450488	2239.7	-1.23	1007.73	35384	750.02	2399.36	35796
0.3020	0.448308	2558.1	-1.10	1145.71	35234	852.71	3252.07	35647
0.3040	0.450499	1334.0	-0.49	600.49	35518	454.45	3292.21	35612
0.3262	0.449090	1459.7	-0.75	653.16	35446	494.30	3786.51	35590
0.3404	0.445653	2599.2	-2.21	1156.11	35280	870.46	4122.53	35569
0.3483	0.447908	1564.4	-0.45	700.28	35456	529.96	4316.48	35574
0.3674	0.444933	1734.1	-0.85	770.73	35134	587.91	4783.95	35450
0.3760	0.445855	2076.8	-1.28	924.66	34947	699.77	5016.24	35485
0.3926	0.443075	1991.5	-1.40	880.99	35050	672.02	5455.97	35400
0.4175	0.441707	2106.7	-0.64	929.89	35166	709.32	6165.29	35373
0.4419	0.439587	2190.8	-1.60	961.44	35014	733.39	6898.69	35334
0.4662	0.438135	2309.4	-0.78	1011.06	34872	771.24	7669.93	35287
0.4912	0.436211	2499.3	-1.05	1089.16	34669	830.82	8500.75	35226
0.5079	0.435363	4320.6	-3.56	1877.48	34675	1453.76	9078.98	35195
0.5617	0.430670	5969.2	-7.72	2563.03	34498	1984.58	11063.6	35068
0.6033	0.428060	5030.1	-2.62	2150.58	34358	1665.22	12728.8	34973
0.6426	0.424684	5110.0	-3.25	2166.87	34273	1677.83	14406.6	34890

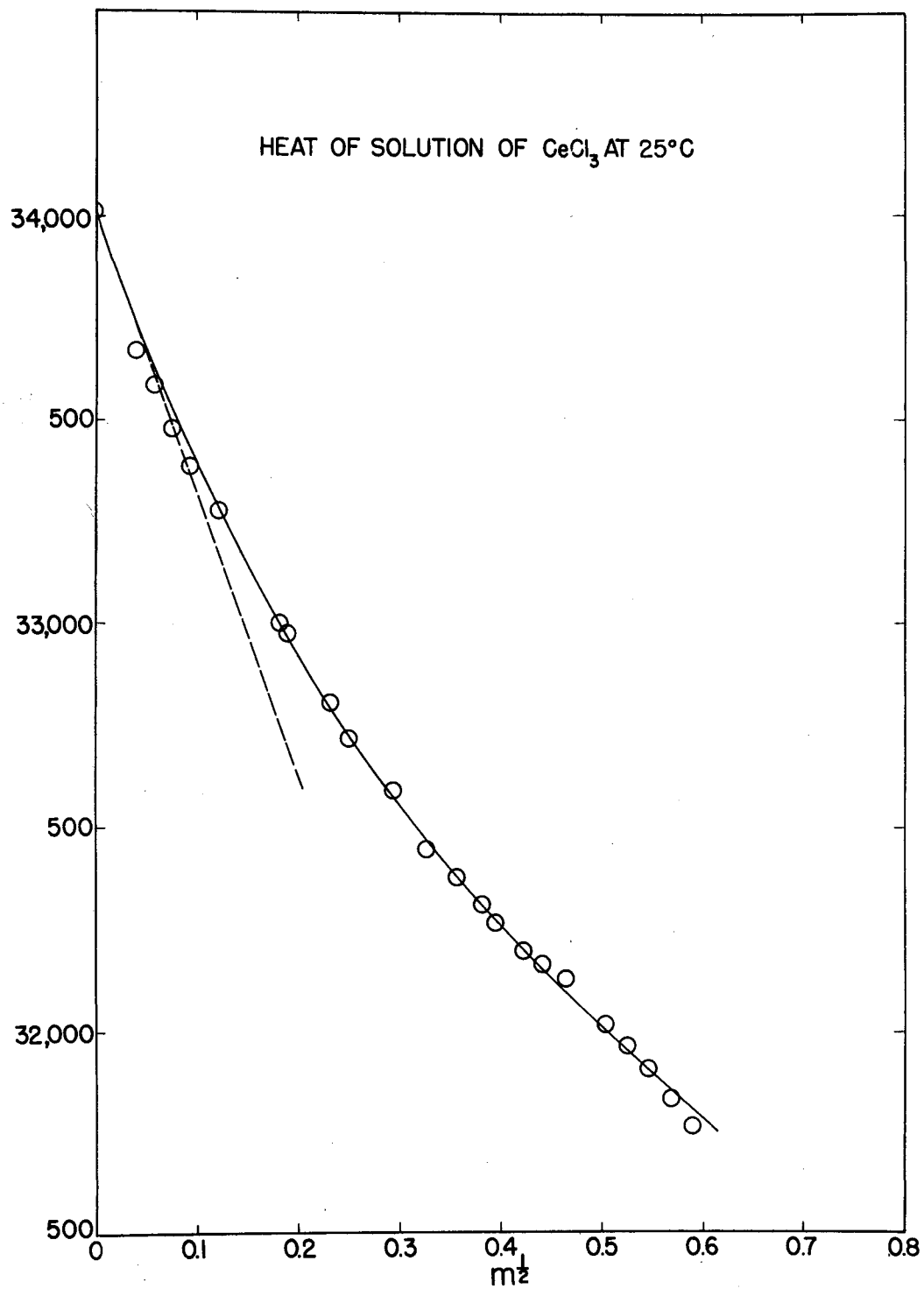($\Delta\varepsilon_c$ is the corrected temperature rise in microvolts)
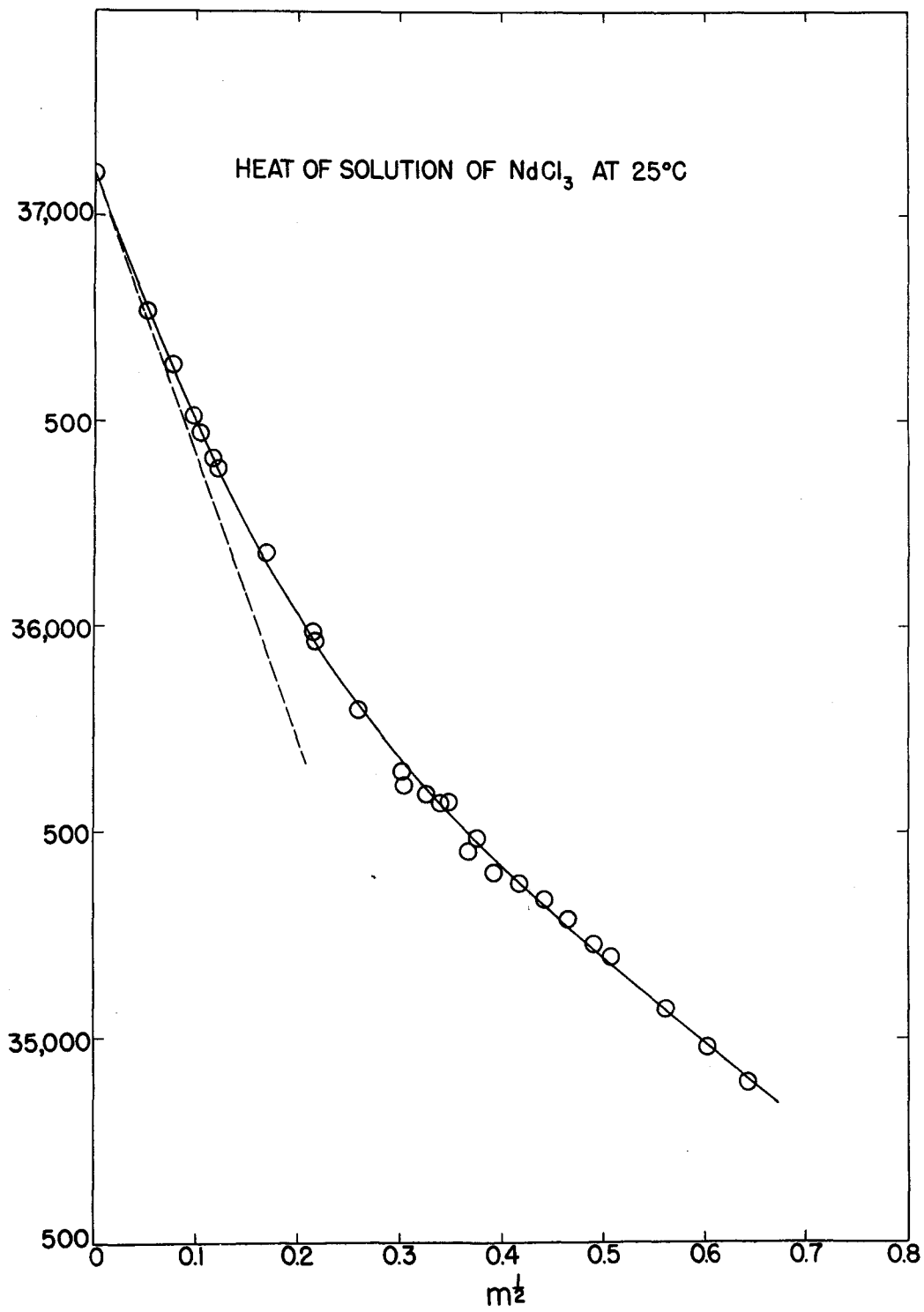
Figure 14. Heat of Solution of Cerium Chloride.

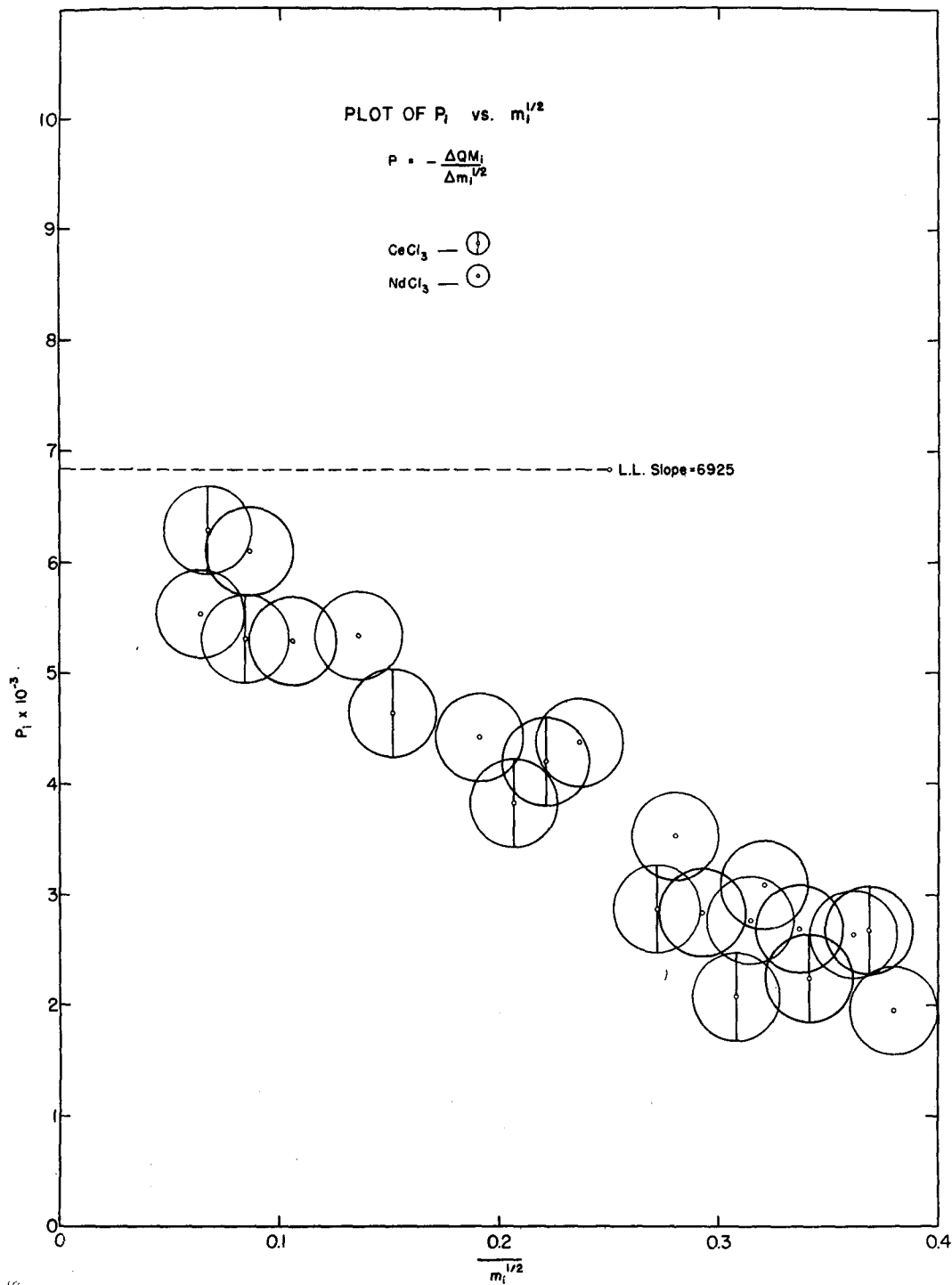Figure 15. Heat of Solution of Neodymium Chloride.

Figure 16. Slopes of the Heats of Solution
by the Chord Method.

to an error of 0.16 calorie in the experimental value of
the heat measurement. An analysis of the errors in the
experimental determinations of the heats of solution by
a least squares treatment showed that the expected devi-
ations of the heat measurements were nearly independent
of sample size; the largest contributing factor to the
probable error of a measurement was the uncertainty in
the determination of the time of heat input used in the
calculation of the electrical energy for the calibration
experiments. Further analysis showed that the probable
deviations in Q_M were proportional to $1/m$ and approxi-
mately proportional to $n^{\frac{1}{2}}$ in which n is the number of
experiments in a series. Therefore, the values of Q_M
in the very dilute range where $1/m$ is large would not be
expected to be as valid as those for higher concentrations.
The high concentration values near the end of the curve
were not weighted as heavily as those in the center con-
centration region since the last few experimental values
at the highest concentrations were not duplicated experi-
ments. The average deviation of the calculated values
from the experimentally determined values of Q_M for cerium
chloride was 10 calories per mole.

The values of the heat of solution at the more dilute
extremity of the curve for the heat of solution of neo-
dymium chloride fit the calculated curve and were used in

the determination of the constants for Equation (134).
The average deviation of the experimental values from
those calculated was 14 calories per mole.

The probable deviation of the integral heat of so-
lution, Q_M, was calculated by least square methods to be
60 to 70 calories per mole at a concentration of 0.01
molal and to be two to four calories per mole at a con-
centration of 0.4 molal for a single experimental determi-
nation. The values of two to four calories per mole for
a single experiment were increased by a factor of about
five to six when the number of experiments required to
reach a concentration of 0.4 molal was taken into account.
The error involved in the curve-joining, in which one
series of experiments overlapped part of the concentration
range of another series of experiments, was considered to
be the same as that for an experimentally determined value.
The above described treatment gave a calculated average
deviation of very nearly 20 calories per mole for each
value of the integral heat of solution of both electrolytes.
This single value was used in plotting Figures 14 and 15.
However, in Figures 11, 12, and 13, in which the data for
the heat capacities of the solutions of both electrolytes
are plotted, the calculated probable errors were used to
determine the size of the circles or the lengths of the
vertical lines.

Discussion

The heats of solution of chlorides of many of the rare earth elements were determined by Bommer and Hohmann (37, 38). They reported an average value of 32.7 $\pm$ 0.1 kcals/ mole at 20°C for the heat of solution of cerium chloride in which the concentrations of the final solutions varied from about 0.05 to 0.12 molal. For the heat of solution of neodymium chloride they reported a single value of 35.9 kcals/mole at 20°C; Matignon (39,40) had previously measured the heat of solution of neodymium chloride and found it to be 35.4 kcals/mole at 17°C at a final concentration of approximately 0.043 molal. The heat capacities of solutions of rare earth salts have not been reported.

The method used in the present work to obtain the heat capacity of aqueous solutions of the chloride of cerium and neodymium was convenient in that the values of the heat capacity were obtained from the same series of experiments from which the heats of solution were determined. In addition, the sign and magnitude of ΔC_p obtained from two or more similar experiments in which different amounts of the same chemical substance are used, served as an excellent check on systematic errors in the calorimetric apparatus. Since random errors in the heat content measurements are magnified in the values of ΔC_p calculated by

the difference of two large numbers, a series of experiments which show good concordance in the values of ΔC_p can only have systematic errors in the measurement of the electrical energy. The fact that values of the relative apparent and relative partial molal heat capacity of the electrolytes are obtained from the difference of two large numbers is a disadvantage since a precision of only one per cent in the relative apparent molal heat capacity would require a precision of approximately 0.005 to 0.01 per cent in the determination of the heat capacity of the calorimeter system. However, even when the heat capacities of solutions are measured differentially with twin calorimeters, the values of the partial molal heat capacities of the electrolytes cannot be determined with great accuracy in solutions more dilute than 0.01 molal. In the procedure described for the determination of the heat capacities of solution of cerium and neodymium chlorides the changes in the concentrations of the electrolyte were much greater than 0.01 molal; the average change in concentration during a series of experiments was from 0.08 to 0.2 molal. The trend in the values of ΔC_p observed for such changes in concentration is shown in Figures 11 and 12. The plots of the relative apparent molal heat capacity in Figure 13 indicate possible deviations from linearity in concentrations greater than $m^{\frac{1}{2}} = 0.5$; the lines drawn through the values

were derived from the smoothed-curve values of the molal

ΔCp values as plotted in Figures 11 and 12. The equations

which represent the lines are

(135) $\phi_J = 128m^{\frac{1}{2}}$

for cerium chloride solutions, and

(136) $\phi_J = 131m^{\frac{1}{2}}$

for neodymium chloride solutions. The Debye-Hückel limiting

slope, according to the revised calculation of Harned and

Owen (3), is 90. The data of the present work are in better

agreement with the older value of the limiting slope which

was about 132. This difference in the calculated slopes,

which resulted from new data on the temperature variation

of the dielectric constant of water, shows the high sensi-

tivity of the calculation of the partial molal heat capacity

of an electrolyte from the theoretical equations as related

to the value of the dielectric constant of water. Smoothed-

values of the relative apparent molal heat capacity and of

the relative partial molal heat capacity of solutions of

cerium chloride and of neodymium chloride are given in

Table 11.

The heats of solution of the anhydrous chlorides at

infinite dilution are a measure of the differences between

lattice energies of the crystals and of the hydration ener-

gies of the ions in an ideal solution. The lattice ener-

gies which result largely from electrostatic forces have

TABLE 11

Smoothed Values of the Relative Apparent Molal and Partial Molal Heat
Capacities of Solutions of the Chlorides of Cerium
and Neodymium at 25°C

$m^{\frac{1}{2}}$	Cerium Chloride				Neodymium Chloride			
	$-\Delta Cp_M$	$\emptyset_J$	$\bar{J}_2$	$-\bar{J}_1$	$-\Delta Cp_M$	$\emptyset_J$	$\bar{J}_2$	$-\bar{J}_1$
0	362.3	0	0	0	320.3	0	0	0
0.01	361.0	1.3	1.9	$0.0_5 12$	319.0	1.3	2.0	$0.0_5 12$
0.02	359.7	2.6	3.8	$0.0_5 92$	317.7	2.6	3.9	$0.0_5 94$
0.05	355.9	6.4	9.6	$0.0_3 14$	313.7	6.6	9.8	$0.0_3 15$
0.1	349.5	12.8	19.2	$0.0_2 12$	307.2	13.1	19.7	$0.0_2 12$
0.2	336.7	25.6	38.4	$0.0_2 92$	294.1	26.2	39.4	$0.0_2 94$
0.3	323.9	38.4	57.6	0.031	281.0	39.3	59.1	0.032
0.4	311.1	51.2	76.8	0.074	267.9	52.4	78.8	0.076
0.5	298.3	64.0	96.0	0.143	254.8	65.5	98.5	0.148

values which are proportional to inverse functions of the
distance between the ions. It follows that, for a series
of similar crystals, such as those of the chlorides of the
rare earths in which the ionic radius of the rare earth
ion decreases with increasing atomic number, the lattice
energies of a given anion-type salt of the rare earths
should increase with the atomic number of the rare earth.
The heat of hydration of the rare earth ions should also
increase with atomic number since the surface charge density
of the highly charged positive ion increases with decreasing
ion size results in a progressively higher degree of polar-
ization of the water molecules about the ion of each suc-
ceeding rare earth. At infinite dilution, the heat of hy-
dration of the chloride ion for each rare earth chloride
would be the same so that the difference in heats of so-
lution between two rare earth chlorides includes the dif-
ference in the lattice energies of the two salts and the
difference in the hydration energies of the two rare earth
ions. When data on the heats of solution at infinite di-
lution of other rare earth chlorides are available and
when sufficient other data are measured from which an
accurate determination of the lattice energies of the
anhydrous chlorides can be made, it will be possible to
calculate the differences in the hydration energies of the
rare earth ions. These can then be correlated with other
data relating to the hydration effects on the properties

of these ions as well as to their coordination numbers.

The apparent molal heat content data and smoothed-values of the partial molal heat contents of solutions of cerium chloride and of neodymium chloride are given in Table 12 and are plotted in Figure 17. The data for lanthanum chloride solutions obtained by Nathan, Wallace, and Robinson (9) are shown by the dotted lines in Figure 17. The data for the solutions of cerium and neodymium chlorides do not show any discontinuity in the relative apparent molal heat contents or in the partial molal heat contents as do the reported data for lanthanum chloride. The equations which represent the data for $\bar{L}_2$ and $\bar{L}_1$ up to a concentration of 0.35 molal are

(137) $\bar{L}_2 = 1.0387 \times 10^4 m^{1/2} - 1.6970 \times 10^4 m + 1.3003 \times 10^4 m^{3/2}$

and

(138) $\bar{L}_1 = -62.379 m^{3/2} + 15.286 m^2 - 14.056 m^{5/2}$

for cerium chloride solutions, and

(139) $\bar{L}_2 = 1.0387 \times 10^4 m^{1/2} - 1.7905 \times 10^4 m + 1.3650 \times 10^4 m^{3/2}$

and

(140) $\bar{L}_1 = -62.379 m^{3/2} + 16.129 m^2 - 14.755 m^{5/2}$

for neodymium chloride solutions.

Notable differences in the relative heat contents of the two electrolytes appear at concentrations of about 0.05 molal. Since the hydrated chloride ions in solutions of both electrolytes should, according to the simplified

TABLE 12

Smoothed Values of the Relative Apparent Molal and Partial Molal Heat
Contents of Solutions of the Chlorides of Cerium
and Neodymium at 25°C

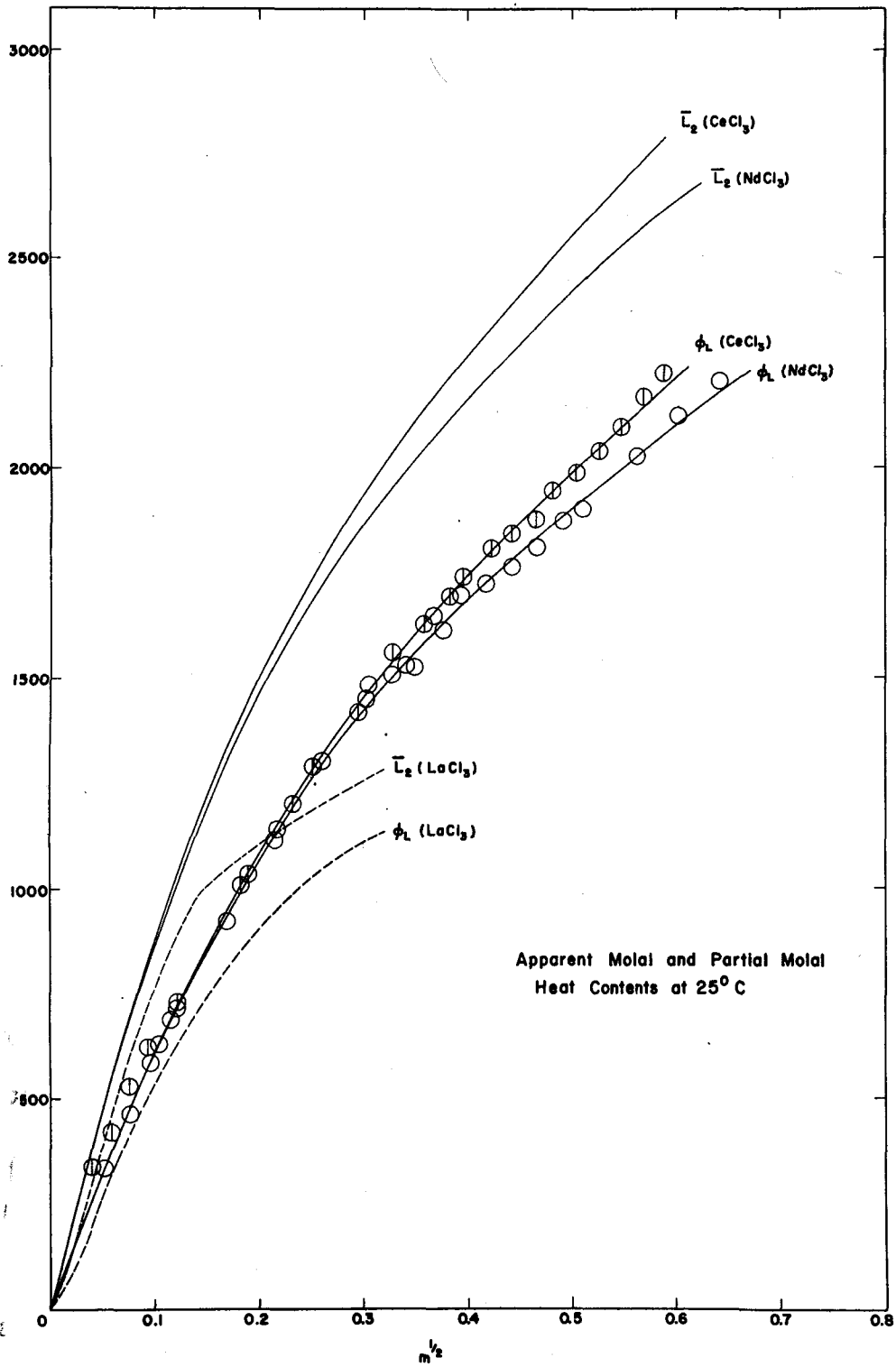| $m^{\frac{1}{2}}$	Cerium Chloride			Neodymium Chloride		
	$\emptyset_L$	$\overline{L}_2$	$-\overline{L}_1$	$\emptyset_L$	$\overline{L}_2$	$-\overline{L}_1$
0	0	0	0	0	0	0
0.01	68	102	0.0_462	68	102	0.0_462
0.02	135	201	0.0_350	135	201	0.0_350
0.05	326	479	0.0_277	324	476	0.0_277
0.1	613	882	0.0610	608	871	0.0609
0.2	1087	1503	0.479	1071	1470	0.478
0.3	1454	1940	1.595	1419	1873	1.589
0.4	1745	2272	3.745	1687	2164	3.428
0.5	1991	2576	7.281	1907	2424	7.250
0.6	2224	2932	12.59	2111	2735	12.53

Figure 17. Heat Contents of Solutions.

Debye-Hückel theory, make identical contributions to the
partial molal heat content for a given concentration of
electrolyte, the observed difference in the thermal proper-
ties of the two electrolytes can be ascribed wholly to the
differences in the two hydrated rare earth ions. The
factors which can cause differences in the thermal proper-
ties of the two rare earth ions are related to the size of
the ion; these factors include: (1) the apparent diameter
of the hydrated ion; (2) the changes in the dielectric
constant of the water caused by a distortion of the water
molecules in the vicinity of the highly charged positive
ion; and (3) the differences in energy contents caused by
concentration changes which involve possible changes in the
polarization of those water molecules which are the most
strongly bonded to the ion. In addition, the number of
coordinated water molecules for different rare earth ions
may change with a change in the size of the ion; it may
also be possible for the rare earth ions with the larger
ionic radii and smaller atomic numbers to have more than
one coordination number. If an equilibrium should exist
between the amounts of two hydrated ions with different
coordination numbers which depends on the concentration
of the electrolyte, then the heat content of solutions of
such rare earths would differ from those which have only
one coordination number. The explanation, on this basis

of the larger relative apparent molal and relative partial
molal heat contents of solutions of cerium chloride, com-
pared to those of neodymium chloride in more concentrated
solutions, is that: (1) the cerium ion has two coordination
numbers and the neodymium ion has only one; (2) both ions
have two coordination numbers but dilute solutions of the
cerium ion contain a relatively greater amount of the ion-
species with the higher coordination number; and (3) the
equilibrium between the amounts of the two ion-species is
shifted in such a manner as to increase the proportion of
the species with lower coordination number as the concen-
tration of electrolyte increases. These phenomena would
lead to a larger observed heat content for solutions of
cerium chloride as compared to that of neodymium chloride.
However, additional thermal data on the solutions of other
rare earth chlorides and other rare earth salts will be
required before any final conclusion can be drawn and before
the above described phenomena can be adequately studied.
The thermal properties of solutions of the rare earth salts
are related to many other physico-chemical properties which
are being studied at the Ames Laboratory. The correlation
of all the data which will be obtained on the properties of
solutions of salts of the rare earths will aid in perfecting
the theories of solutions of electrolytes. Data on the
crystallographic properties of solid compounds of the rare

earths which have a bearing on the properties of their so-
lutions should also be extended; for example, studies of
the structure of the hydrated crystals would give valuable
information regarding the possible coordination numbers of
the ions. The application of the laws of thermodynamics
to such data will be a great contribution to the laws and
theories of electrolytic solutions.

THERMODYNAMICS OF CHEMICAL REACTIONS

Introduction

Thermochemistry is concerned with heat changes which are associated with chemical reactions. According to Hess's Law, which was stated over a century ago, the heat absorbed or evolved for a given chemical reaction is independent of the particular manner in which the reaction takes place. This is in accord with the defined thermodynamic function, H, which has an exact total differential and whose variance, therefore, depends only on the initial and final states of the particular chemical substance under observation. Hence, for a given chemical reaction,

$$(141) \qquad \Delta H = \sum_j n_j H_j - \sum_i n_i H_i$$

in which n_j refers to the number of moles of each of the products and n_i refers to the number of moles of each of the reactants; the reactants are the chemical substances which disappear during the reaction to form the products. Equation (141) is called the Van't Hoff equation. The fact that H, for either the products or the reactants, is unknown but ΔH for the reaction can be measured has led to the defining of a particular state for a given substance in which H is taken to be zero. Such a state called the standard state, has been arbitrarily chosen, so that for any element in its stable form at $25^{\circ}C$ under a pressure

of one atmosphere, $\underline{H}$ is defined to be zero. When the heat
of reaction is measured such that the reactants are elements
in the standard state and the product is the result of their
combination, also at 25°C and one atmosphere pressure, the
measured value of $\underline{\Delta H}$ is written as $\underline{\Delta H^0}$ and is called the
standard heat of formation of the resultant compound. For
example, Muthmann and Weiss (41) used a bomb calorimeter
to determine values of $\underline{\Delta H^0}$ for the reactions

(1) $Ce(s) + O_2(g) = CeO_2$

and

(2) $2Nd(s) + 3/2O_2(g) = Nd_2O_3$
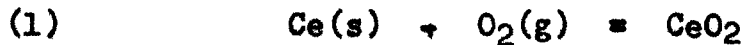
For Reaction (1) they found $\underline{\Delta H^0} = -224.5$ kcals/mole, and
for Reaction (2) $\underline{\Delta H^0} = -434.5$ kcals/mole. Reaction (1)
was later measured by Hirsch (42); Moose and Parr (43);
and Kremers and Beuker (44). They found the values of
$\underline{\Delta H^0}$ to be -243.6, -232.9, and -232.8 kcals/mole, respectively.
However, $\underline{\Delta H^0}$ is not measured directly by the bomb calo-
rimeter; the heat evolved by the reaction, Q_v, is measured
at constant volume and is related to $\underline{\Delta H}$ by the following
thermodynamic equations:

(142) $DQ = dE + PdV$

at constant volume, the above equation is

(143) $DQ = dE$

or

(144) $Q_v = \Delta E$

H is defined by

(145) $$H = E + PV$$

so that

(146) $$\Delta H = \Delta E + \Delta(PV)$$
$$= Q_V + \Delta(PV)$$

For most reactions in the bomb calorimeter $\Delta(PV)$ is small so that the ideal gas law

(147) $$PV = nRT$$

can be used to approximate $\Delta(PV)$. At constant temperature

(148) $$\Delta(PV) = (\Delta n)RT$$

in which Δn is the change in the number of moles of gas which occurs during the course of the reaction. For Reaction (1), Δn is -1, and for Reaction (2) it is -3/2. Further, the oxygen gas in the bomb is not at a pressure of one atmosphere, but is at 20 or 30 atmospheres pressure; hence the value of ΔH must be also corrected to an oxygen pressure of one atmosphere. The methods used to calculate the pressure and other corrections necessary to reduce measurements made by use of the bomb calorimeter to standard conditions have been summarized and put in a useful form by Washburn (45).

The variation of ΔH with temperature is given by the Kirchhoff equation which is

(149) $$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta Cp = \sum_j n_j \left(\frac{\partial H}{\partial T}\right)_P - \sum_i n_i \left(\frac{\partial H}{\partial T}\right)_P$$

or

(150) $\quad \Delta Cp = \sum_j n_j Cp_j - \sum_i n_i Cp_i$

Equation (150) for Reaction (1) is written as

(151) $\quad \Delta Cp = Cp(CeO_2) - Cp(Ce) - Cp(O_2)$

If it is desirable to know ΔH at a different temperature which differs by more than a few degrees from the temperature at which ΔH was measured, the value of Cp for each of the products and reactants should be known as a function of the temperature. The change of heat content, ΔH_T, for the reaction at the new temperature is

(152) $\quad \Delta H_T = \Delta H_T' + \int_{T'}^{T} \Delta Cp\, dT$

in which $\Delta H_T'$ is the known change in heat content for the reaction at the temperature T', and ΔCp is given by Equation (150). Once a standard of heat formation is known for a chemical substance its value can be used to calculate ΔH for other reactions and to aid in determining ΔH^o for other compounds.
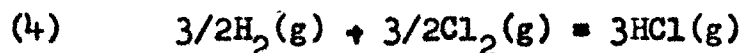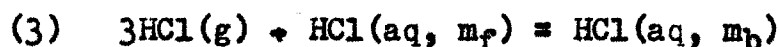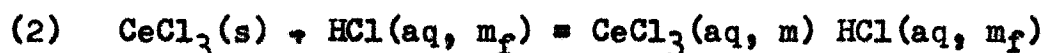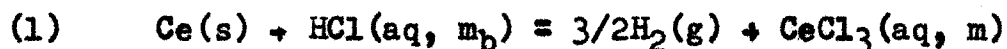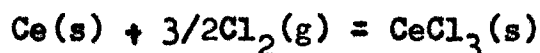
Heats of Formation

Anhydrous chlorides

In order to determine the heat of formation of a substance using a heat of solution calorimeter, the heat of reaction for a number of reactions must be known or measured. The reaction which gives the heat of formation of anhydrous cerium chloride is

$$Ce(s) + 3/2Cl_2(g) / = CeCl_3(s)$$
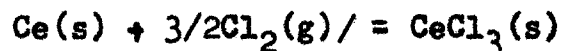
If the changes in heat content for the following reactions are known, Hess's Law can be applied in the following manner:

(1) $Ce(s) + HCl(aq, m_b) = 3/2H_2(g) + CeCl_3(aq, m)$
$$HCl(aq, m_f)$$

(2) $CeCl_3(s) + HCl(aq, m_f) = CeCl_3(aq, m) \ HCl(aq, m_f)$

(3) $3HCl(g) + HCl(aq, m_f) = HCl(aq, m_b)$

(4) $3/2H_2(g) + 3/2Cl_2(g) = 3HCl(g)$

in which $\underline{m_b}$ and $\underline{m_f}$ are the molalities of the hydrochloric acid in the initial and final solutions, respectively in Reaction (1). If Reactions (1), (3), and (4) are added, and Reaction (2) is subtracted from the sum of the other three, the resulting equation is

$$Ce(s) + 3/2Cl_2(g) = CeCl_3(s)$$

If the changes in heat content for each reaction is numbered to correspond to the above reactions and summed in the same manner as were the reactions, then

(153) $\Delta H^O = \Delta H_1 - \Delta H_2 + 3 \Delta H_3 + 3 \Delta H_4^O$

in which $\underline{\Delta H^O}$ is the heat of formation of $\underline{CeCl_3(s)}$.

The heat of Reaction (1) has been measured calorimetically by Sieverts and Gotta (46), Neumann, Kroger and Kunz (47), Biltz and Pieper (48), and by Bommer and Hohmann (37). The last-named investigators measured the

same reaction for neodymium. The data reported by the
above authors are summarized in Table 13.

Bommer and Hohmann's values appear especially high.
Their reported procedure was to first reduce the rare earth
chlorides with potassium in vacuum after which they placed
the crude mass, slag and metal, into the calorimeter.
After the slag had dissolved, they added acid to dissolve
the metal. It would appear that such a procedure would
make it difficult to determine the heat leak corrections
during the reactions which take place. In addition, it is
possible that the uncast metal mass would entrain an
unknown amount of potassium at the low reduction tempera-
tures that were reported; therefore, a reduction which was
less than 100 per cent complete would increase the observed
heat of reaction. The discrepancy is further increased
when increments of heat are added for the endothermic
reaction which takes place when the slag, considered as
pure potassium chloride, is dissolved; the dilution effects
of such a mixture of salts is ill-defined at best. These
investigators also mention that the presence of small
amounts of hydrochloric acid and salts do not effect the
heats of solution of the anhydrous chlorides.

In the present work, the heats of reaction for
Reactions (1) and (2) were determined for cerium and neo-
dymium in such a manner that the end concentrations for a

TABLE 13

Heats of Solution of Cerium and Neodymium
Metals in Hydrochloric Acid

Literature Reference	m_b HCl	t^oC	$-\Delta H$
46	2.1	20	170.0 ± 1.4
47	2.3	?	165.1 ± 0.2
48	2.8	18	164.9
48	1.1	18	166.4
37	0.1	20	173.7 ± 0.7
37	0.1	20	171.4 ± 1.0*

*Value for Neodymium metal (t^oC is the temperature
at which the ΔH values were obtained; ΔH is in
kcals/mole)

given pair of reactions were very nearly the same. It was found that in other than extremely dilute solutions of hydrochloric acid the heats of solution of the chlorides were lower than the corresponding values in pure water. The experimental results found for Reactions (1) and (2) are given in Table 14. The effect of hydrochloric acid on the heats of solution of the anhydrous chlorides is illustrated in Figures 18 and 19. The values of the heats of solution, in calories per mole, were plotted on an arbitrary scale so that the data for both cerium and neodymium chlorides could be put on the same graph. The plot in Figure 19 was used to make corrections for the effect of the acid on the heats of solution of the chlorides.

The heat of formation of gaseous hydrogen chloride was determined by Rossini (49). In the same report, he reviewed all the previously published data on the heats of solution and dilution and on the heat capacity of the solutions of hydrochloric acid; the data were presented as values at 25°C. By combining the proper data from the above article, the change in heat content for Reaction (3) and (4) were computed. The standard heats of formation were found to be

(154) $\Delta H^0 = -250,580 \pm 10$ cals/mole

for $CeCl_3(s)$

and

TABLE 14

Heats of Solution of Cerium Chloride, Neodymium Chloride, Cerium and Neodymium in Hydrochloric acid at 25°C

Compound	$m^{\frac{1}{2}}$	$m_b^{\frac{1}{2}}$ (HCl)	$m_f^{\frac{1}{2}}$ (HCl)	ΔCp_M	$-\Delta H$
$CeCl_3$	0.13271	0.60911	0.60911	-569	31,301
$CeCl_3$	0.19901	0.60911	0.60911	-416	31,450
$CeCl_3$	0.2475	0.60911	0.60911	-410	31,401
$CeCl_3$	0.1324	0.4909	0.4909	-422	32,296
$CeCl_3$	0.15052	0.4909	0.4909	-420	32,194
$NdCl_3$	0.1432	0.4909	0.4909	-423	35,048
$NdCl_3$	0.1885	0.4909	0.4909	-417	34,821
Ce	0.05280	0.4964	0.4879	-376	164,520
Ce	0.06150	0.4993	0.4878	-317	164,410
Nd	0.06062	0.5001	0.4889	-272	160,780
Nd	0.07315	0.5069	0.4907	-267	160,380

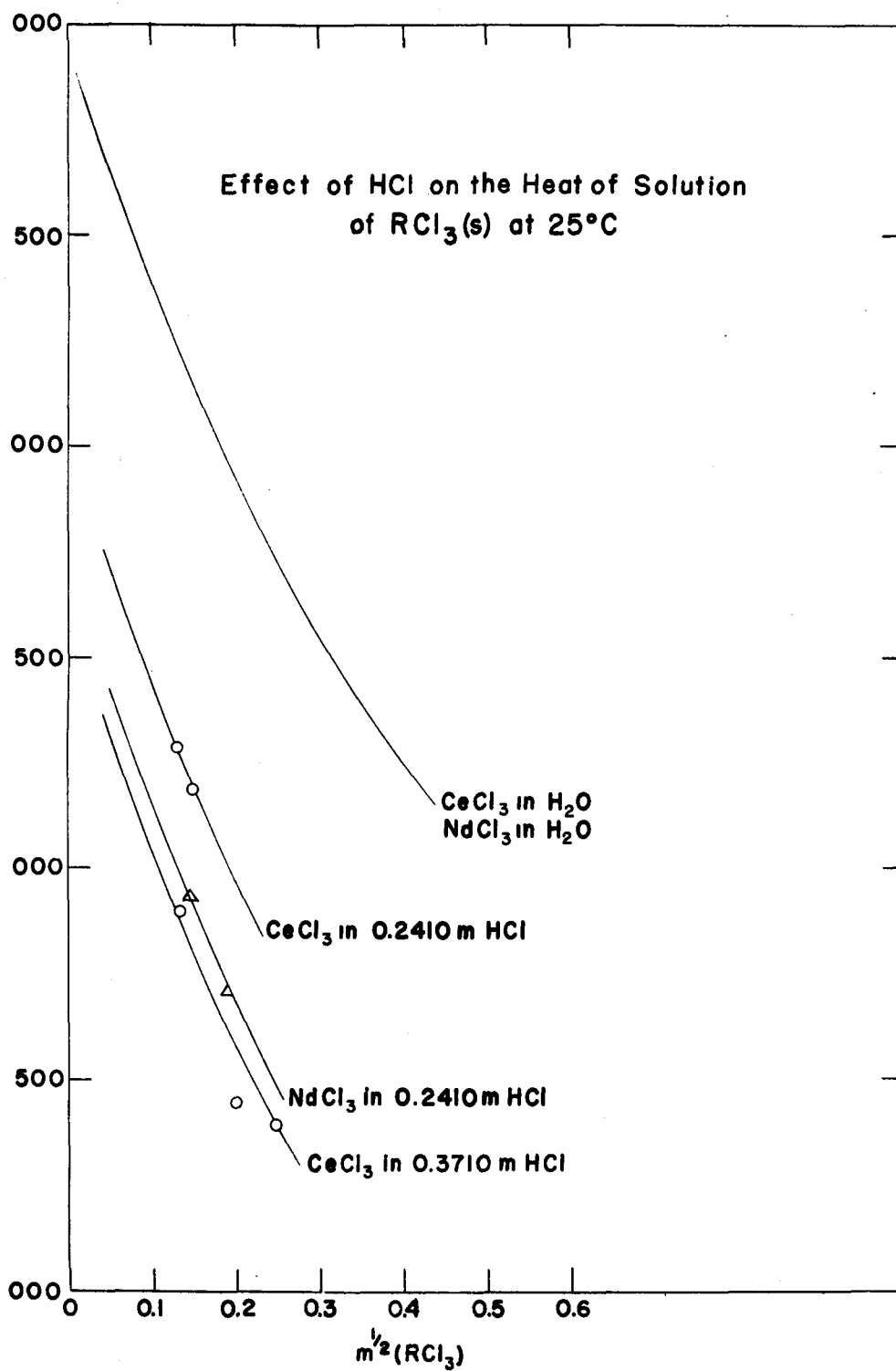(m is the final molality; ΔCp_M is in cal/mole-deg C; and ΔH is in cal/mole)

Figure 18. Heats of Solution in Hydrochloric Acid

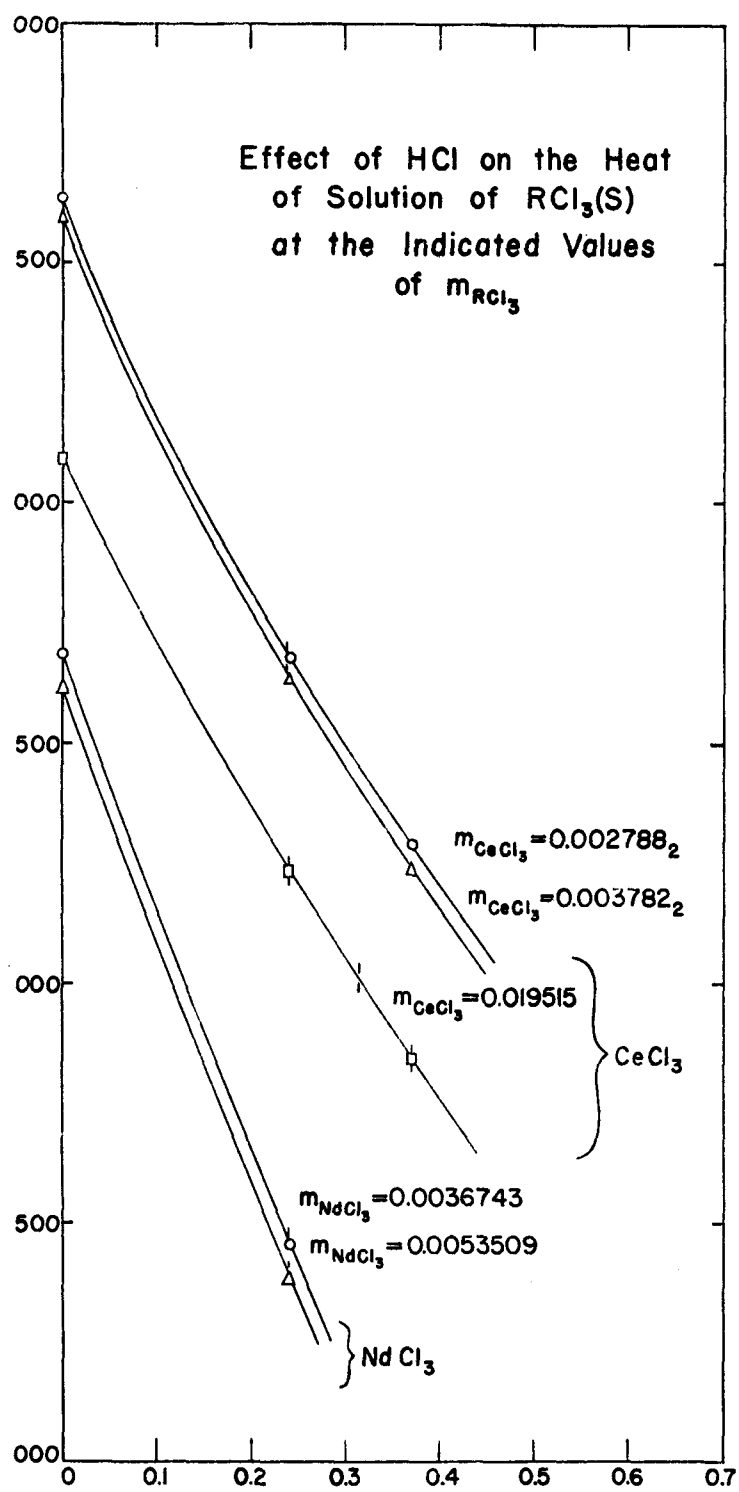Figure 19. Heats of Solution in Hydrochloric Acid

(155) $\Delta H^O = -244,080 \pm 20$ cals/mole

for $NdCl_3(s)$.

The corresponding values given by Bommer and Hohmann (37) are -259,800, and -254,300, approximately 10 kcals/mole higher than those given by Equations (154) and (155); this discrepancy is due to the fact that their reported values for the heat of solution of the metals, of cerium and neodymium were about 10 kcals higher than those given in Table 14.

Hydrated chlorides

The determination of the heats of solution of the hydrated chlorides of cerium and neodymium, along with the reported values of the heats of solution and dilution of the anhydrous chlorides, would make possible the calculation of the heats of hydration of the chlorides as given by the reactions

$$CeCl_3(s) + 7H_2O(l) = CeCl_3 \cdot 7H_2O(s)$$

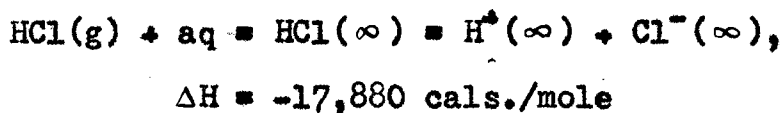and

$$NdCl_3(s) + 6H_2O(l) = NdCl_3 \cdot 6H_2O(s)$$
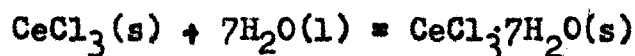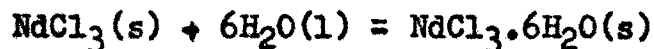
The heats of formation of the two hydrates can be calculated by use of the values of the heats of formation of the anhydrous chlorides as given by Equations (154) and (155) and the value for the heat of formation of water.

The heat of solution of $CeCl \cdot 7H_2O(s)$ has not been reported. Matignon (40, 50) reported the heat of solution of $NdCl_3 \cdot 6H_2O(s)$ to be -7.6 kcals/mole at $15^{\circ}C$; however, since the final concentration was not given, this value cannot be compared with the present data. The heats of solution, the standard heats of formation, and the heats of hydration of the hydrates of the chlorides of cerium and neodymium obtained in the present work are given in Table 15. The value used for the heat of formation of water was -68,313 ± 10 cal/mole as given by Bichowsky and Rossini (51).

Ions

The standard heat of formation of an ion is based on the conventional definition that, at infinite dilution, the standard heat of formation of hydrogen ion is zero. The standard state of any ion is taken at infinite dilution at a given temperature and the standard heat of formation of the ion is relative to the hydrogen ion in its standard state. The thermal data of Rossini (49) on hydrochloric acid are

$$HCl(g) + aq = HCl(\infty) = H^+(\infty) + Cl^-(\infty),$$
$$\Delta H = -17,880 \text{ cals./mole}$$

and for

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g),$$
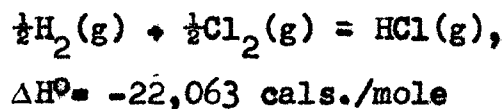$$\Delta H^{\circ} = -22,063 \text{ cals./mole}$$

TABLE 15

The Heats of Solution; Heats of Formation; and
Heats of Hydration of the Hydrates of Cerium
and Neodymium Chloride at 25°C

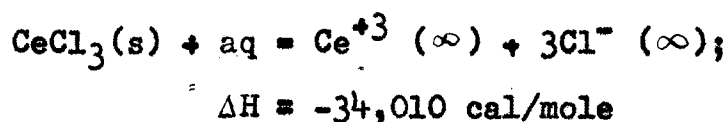| Hydrate	$m^{\frac{1}{2}}$	ΔC_{PM}	$-\Delta H$	$-\Delta H^O$	$-\Delta H(hyd)$
$CeCl_3 \cdot 7H_2O$	0.09908	-382	6,336	755,830	27,070
$CeCl_3 \cdot 7H_2O$	0.20557	-380	5,854	755,810	27,050
			Average	755,820±10	27,060±10
$NdCl_3 \cdot 6H_2O$	0.1659	-356	8,319	681,810	27,850
$NdCl_3 \cdot 6H_2O$	0.1435*	-362	----	----	----
$NdCl_3 \cdot 6H_2O$	0.2490	-355	7,912	681,770	27,750
			Average	681,790±20	27,800±50

*Second heat of dilution was done with this initial
concentration of neodymium chloride (ΔH is the heat
of solution, ΔH⁰ is the heat of formation, and
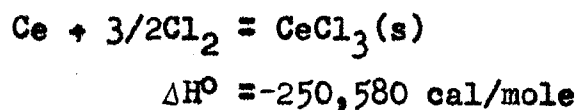ΔH(hyd) is the heat of hydration in cals/mole)

Adding the two equations gives

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = H^+(\infty) + Cl^-(\infty),$$

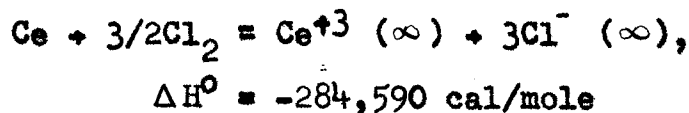$$\Delta H^0 = -39,943 \text{ cals/mole}$$
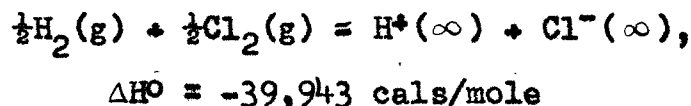
Since by previous conventions, the heat contents of the two substances on the left side of the above equation were taken to be zero, and the heat of formation of the hydrogen ion at infinite dilution is also taken as zero, it follows that -39,943 cals/mole is the heat of formation of the chloride ion. It has been found that for

$$CeCl_3(s) + aq = Ce^{+3}(\infty) + 3Cl^-(\infty);$$

$$\Delta H = -34,010 \text{ cal/mole}$$

and for

$$Ce + 3/2Cl_2 = CeCl_3(s)$$

$$\Delta H^0 = -250,580 \text{ cal/mole}$$

Adding the two equations gives

$$Ce + 3/2Cl_2 = Ce^{+3}(\infty) + 3Cl^-(\infty),$$

$$\Delta H^0 = -284,590 \text{ cal/mole}$$

Hence

(156) $\Delta H^0 = -284,590 - 3(-39,943) = -164,760$ cal/mole

for $Ce^{+3}(\infty)$. Similarly

(157) $\Delta H^0 = -281,180 - 3(-39,943) = -161,350$ cal/mole

for $Nd^{+3}(\infty)$.

The above calculations give the heats of formation of the cerium and neodymium ions in their standard states.

Entropy and Free Energy

It would be of great interest to know, in addition
to heats of formation of the compounds and ions of cerium
and neodymium, their entropy and free energy of formation.
If either one of the latter is known, in addition to the
heats of formation, the other can be calculated from the
Gibbs-Helmholtz equation

$$(158) \qquad \Delta F^O = \Delta H^O - T \Delta S^O$$

since the same conventions regarding the standard state of
the compounds and ions are used for their entropies and free
energies. It would be of particular interest if the standard
entropy of the ions were measured since there is no known
equilibrium reaction in aqueous media in which active metals
like the rare earths can participate reversibly and from
which the electro-motive force or free energy can be de-
termined. Furthermore, there are few reliable heat capacity
data on rare earth metals and compounds from which the abso-
lute entropy could be calculated. Spectroscopic data on the
rare earths are very difficult to analyze; even if the
entropy of the metal vapors were estimated by the Sacker-
Tetrode equation, the heats of sublimation at $25^O C$, and
therefore, the entropies of sublimation, are not available
for any of the rare earth metals with exception of cerium.
The entropy of cerium metal at $25^O C$ was reported by Lewis

and Gibson (52), Lewis, Gibson, and Latimer (53). These
values can be calculated by utilizing an empirical method
of estimating entropies of solid compounds as recently
presented by Latimer (54). By use of this method, values
of the entropies of cerium and neodymium and a few of
their compounds were calculated and are listed in Table 16.

The solubilities of some of the rare earth halides
have been determined in water and aqueous acid solutions
by Williams, Fogg, and James (55), and by Newton and Hale
(56). Newton and Hale's data give, for $NdCl_3 \cdot 6H_2O$ at 25^oC,
a concentration of approximately 3.85 molal in Nd^{+3}.
Saturated solutions of rare earth chlorides in pure water,
however, tend to give solid phases which are not pure hy-
drates but a mixture of hydrate, hydroxide, and oxychloride.
To grow and maintain a pure hydrated crystal solid, acid
must be present. But even if the solubilities are known,
the activity coefficients of the rare earth chlorides have
not been determined for the saturated solutions and there-
fore the free energy of the ions cannot be calculated.

The free energy of the reversible reaction

$$R_2(C_2O_4)_3 \cdot XH_2O = 2R^{+++} + 3C_2O_4^{=} + XH_2O$$

in which $\underline{R}$ is a rare earth, has been determined for cerium
and neodymium by Crouthamel and Martin (57) at the Ames
Laboratory. They give $\Delta F_1^o = 39.87$ kcals/mole for the

solubility reaction of cerium oxalate, and $\Delta F^0 = 42.43$

kcals/mole for neodymium oxalate. Latimer (58) gives,

for $C_2O_4^=$, the values, $\Delta F^0 = -158,660$ cals/mole,

$\Delta H^0 = -195,160$ cals/mole, $\Delta S^0 = -122.4$ e.u., and

$S^0 = 9.6$ e.u.

Table 16

Calculated Values of Absolute Entropies

at 25° C

Substance	S^0
Ce	13.8
Nd	13.9
$CeCl_3$	34.5
$NdCl_3$	34.6
$CeCl_3 \cdot 7H_2O$	100.3-102.3
$NdCl_3 \cdot 6H_2O$	91.0- 93.0
$Ce_2(C_2O_4)_3 \cdot 9H_2O$	154 - 156
$Nd_2(C_2O_4)_3 \cdot 10H_2O$	164 - 166

(S^0 is in cal/deg. which is the same as S^0 in e.u.)

Therefore, if the estimated values of the absolute entropies

of the oxalates are taken to be 155 and 165 for cerium oxa-

oxalate and neodymium oxalate, respectively, the corresponding entropies of formation of the two compounds are -677 e.u. and -723 e.u., respectively. Latimer's (58) value for the entropy of water was used in the calculations.

Heat of formation of the oxalates

Since the free energy of the above reaction for cerium and neodymium is known, the entropy change for the reaction can be calculated if the heat of the reaction is known. The heat of reaction could be determined from a measurement of the equilibrium constant for the reaction at different temperatures, but it can better be determined from a direct calorimetric measurement of the heat of precipitation of the oxalate providing the calorimetric measurement is carried out in such a manner that heat of formation of the oxalate precipitate can be determined accurately. The entropy change for the reaction can then be calculated from

$$(159) \quad \Delta S^o = \frac{\Delta H^o - \Delta F^o}{T} = 2S_+^o + 3\ S_-^o + XS(H_2O) - S^o(s)$$

in which

S_+^o is the standard entropy of the rare earth ion

S_-^o is the standard entropy of the oxalate ion

$\underline{S^o(H_2O)}$ is the absolute entropy of water

$\underline{S^o(s)}$ is the absolute entropy of the solid oxalate salt

Heat of solution of oxalic acid. Before the heats of pre-
cipitation of the oxalates of cerium and neodymium could
be applied to Equation (159), it was necessary to recheck
the standard heat of formation of oxalic acid hydrate and
to determine the heats of solution and dilution of oxalic
acid.

The heat combustion of anhydrous oxalic acid was
measured by Berthelot (59), Louguinine (60), Stohmann,
Kleber, and Langbein (61), and Verkade, Hartman, and Coops
(62). The Washburn correction was applied to the values
reported by the last two investigators. Stohmann and his
coworkers reported an average value for the heat of com-
bustion of -60,100 cal/mole at 18°C; their value, when
corrected to 25°C under standard conditions, was found to
be -59,850 ± 190 cal/mole; the value, -60,100 cal/mole,
for the heat of combustion at 20°C, given by Verkade and
his associates, was found to be -59,690 ± 90 cal/mole at
25°C and standard conditions. The value, -59,690 cal/mole,
for the heat of combustion of anhydrous oxalic acid was
used for subsequent calculations presented in this thesis.
The heat of combustion of hydrated oxalic was reported by

Jorissen and van de Stadt (63) to be -53,700 cal/mole at 18°C; this value, corrected to standard conditions at 25°C, was found to be -53,300 cal/mole. Therefore at 25°C and one atmosphere pressure,

$$(COOH)_2(s) + \tfrac{1}{2}O_2(g) = 2CO_2(g) + H_2O(l)$$
$$\Delta H^o = -59,690 \text{ cal/mole}$$

and
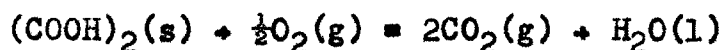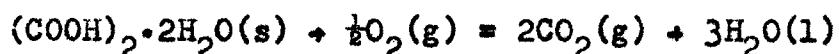
$$(COOH)_2 \cdot 2H_2O(s) + \tfrac{1}{2}O_2(g) = 2CO_2(g) + 3H_2O(l)$$
$$\Delta H^o = -53,300 \text{ cal/mole}$$

The heat of combustion of diamond given by Bichowsky and Rossini (51) was corrected to 25°C; when the heat of transition of diamond to β-graphite as given by Latimer (58) is added, the heat of formation of carbon dioxide from β-graphite is found to be -94,200 cal/mole. When the value for the heat of formation of carbon dioxide is combined in the above equations, the heat of formation of the anhydrous oxalic is calculated to be -197,030 cal/mole and the heat of formation of the hydrated oxalic acid to be -340,000 cal/mole. The heat of hydration of anhydrous oxalic was determined by Jorissen and van de Stadt (63) to be -6200 and -6330 cal/mole at 18°C, by Jorissen (64) to be -6,260 cal/mole at 18°C, and by Becker and Roth (65) to be -6,590 cal/mole at 20°C. Bichowsky and Rossini prefer Jorissen's value; corrected to 25°C, it was found

to be -6360 cal/mole. When Jorissen's value for the heat of hydration of the anhydrous oxalic acid is used along with the above heat of formation of the anhydrous acid, the heat of formation of the hydrated acid is -340,020 cal/mole. The latter value for the heat of formation of oxalic acid hydrate will be used in subsequent calculations presented in this thesis.

The heat of solution and dilution of the hydrated oxalic acid at 25°C has not been reported. Berthelot (59) reported a single value, 8,490 cal/mole, for the heat of solution at 18°C. Thomsen (65) gave a value of -2,260 cal/mole for the heat of solution of the anhydrous acid at 18°C. The data on the heat of solution and dilution of oxalic acid hydrate at 25°C, obtained in the present work are given in Table 17 and are plotted in Figure 20; although the extrapolation to infinite dilution may be some-what in error, the use of the dilutions in subsequent calculations will not be affected since the heats of di-lution used in those calculations pertain only to dilutions within the concentration ranges of the measured heats of solution and dilution as shown in Figure 20.

TABLE 17

The Heats of Solution and Dilution of
Oxalic Acid Hydrate at 25°C

$m^{\frac{1}{2}}$	ΔCp_M	$\emptyset_{cp}$	ΔH	$\emptyset_L$
0	(124)	(170)	(8,495)	0
0.1799	136	182	8,700	202
0.2765	142	188	8,783	295
0.3524	147	193	8,848	350

(m is the final molality; ΔCp_M is the change in heat
capacity in cal/mole°C; $\emptyset_{cp}$ is the apparent molal heat
capacity in cal/mole°C; ΔH is the heat of solution in
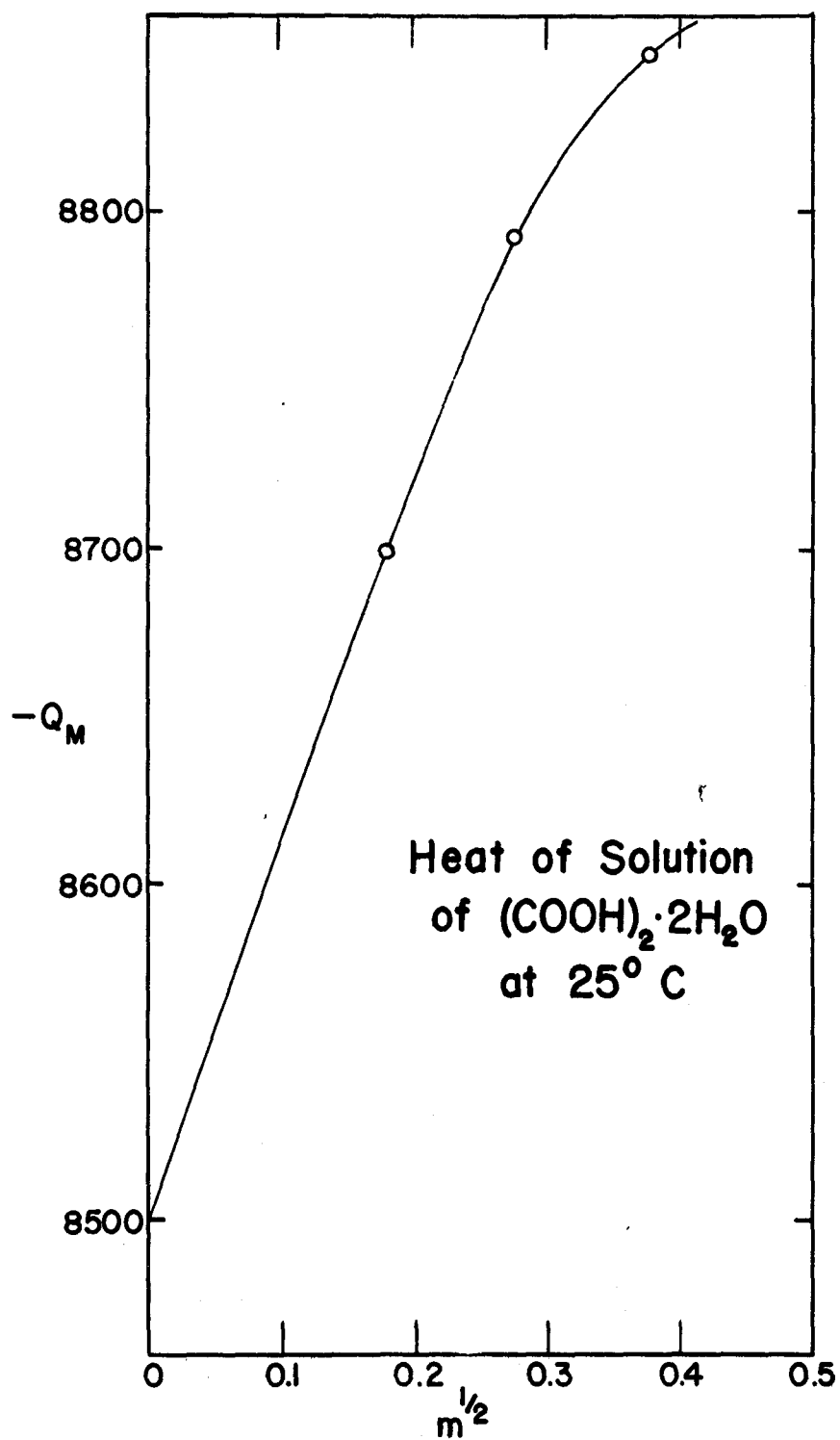cal/mole; and $\emptyset_L$ is the relative molal heat content in
cal/mole)

Figure 20. Heat of Solution of Oxalic Acid Hydrate.

Heat of precipitation of oxalates. The following heats of
reaction in the determination of the standard heats of
formation for the oxalates of cerium and neodymium are in-
volved: (1) the reaction of the solid anhydrous chloride
with an oxalic solution to form the precipitated oxalate
and aqueous hydrochloric acid; (2) the dilution of the oxalic
acid and the removal of the excess oxalic acid from solution;
and (3) the removal of the hydrochloric acid from the final
solution. The effect of oxalic acid on the heat of solution
of hydrogen chloride, or the effect of hydrochloric acid
on the heat of solution and dilution of oxalic acid, has not
been taken into consideration. The heat of precipitation
of the oxalates was measured in the calorimeter by dis-
solving the anhydrous chlorides in previously determined
concentrations of oxalic acid so that the final oxalate
concentration would correspond to the oxalate concentrations
which Crouthamel and Martin (57) give for the minimum solu-
bility of the oxalates of cerium and neodymium.

The experimental data for the heats of precipitation
of the oxalates of cerium and neodymium obtained in the
present work are summarized in Table 18. The summation of
the above described reactions gives

$$2CeCl_3(s) + 3(COOH)_2 \cdot 2H_2O(s)$$
$$+ 3H_2O(l) = Ce_2(C_2O_4)_3 \cdot 9H_2O(s) + 6HCl(g)$$
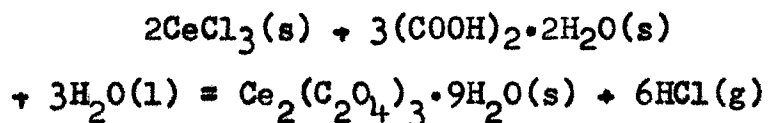
for cerium chloride. By using the data given in Tables 17 and 18 and the heats of formation of the compounds given previously, the heat of formation of cerium oxalate was found to be $-1,545.4 \pm 0.2$ kcal/mole.

The summed reaction for neodymium chloride is

$$2NdCl_3(s) + 3(COOH)_2 \cdot 2H_2O(s) + 4H_2O(l) = $$
$$Nd_2(C_2O_4)_3 \cdot 10H_2O(s) + HCl(g)$$
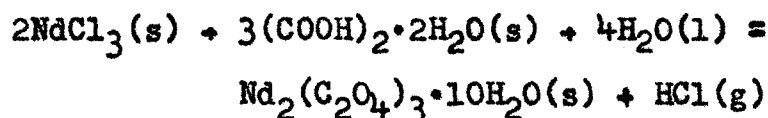
The heat of formation of the neodymium oxalate was found to be $-1,607.2 \pm 0.2$ kcal/mole.

The reason that these heats of formation are so large is that the heat of formation of oxalic acid hydrate is large and that each molecule of precipitate contains a large number of waters of hydration. It was assumed that the hydrated form, shown in the equations above, is the one obtained in the experiments since precipitation would not occur before the complete crystal is formed and the extra waters of adsorption on the crystal would not contribute appreciably to the energy of precipitation. In fact, the indicated number of water molecules are not strongly bonded because these precipitates, when warmed, easily lose their waters of hydration.

All the data necessary for calculating the entropy for the reaction

$$R_2(C_2O_4)_3 \cdot XH_2O(s) = 2R^{+++} + 3C_2O_4^{=} + XH_2O(l)$$
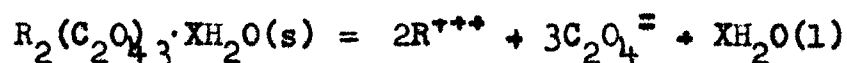
TABLE 18

The Heats of Precipitation of the Oxalates of Cerium and Neodymium at 25°C

Compound	moles	ΔCp_M	$-\Delta H$	m_b (oxalic)	m_f (oxalic)	m_f (HCl)
$CeCl_3$	0.01212	-230	42,363	0.03079	0.01264	0.03635
$CeCl_3$	0.01409	-230	42,184	0.03376	0.01264	0.04233
$NdCl_3$	0.01734	-230	45,597	0.03846	0.01247	0.05210
$NdCl_3$	0.01928	-230	54,321	0.04155	0.01264	0.05795

(m_b and m_f are the beginning and final concentrations, respectively; ΔCp_M is the change in heat capacity in cal/mole°C; ΔH is the heat of solution in cal/mole)

124

were combined to give, for the solubility reaction of
cerium oxalate, ΔH^o = 15,580 cal/mole, and ΔS^o =-81.47
e.u.; and for the solubility reaction of neodymium oxalate,
ΔH^o = 15,840 cal/mole, ΔS^o = -89.18 e.u. By the use of
Equation (159), the standard entropies of the ions are
calculated to be -53.0 e.u., and -60.3 e.u. for cerium and
neodymium, respectively.

Results

The remaining calculations for the entropy of formation
and free energies of formation, along with the measured heats
of formation and calculated entropies, for the compounds
and ions of cerium and neodymium under investigation are
given in Table 19.

From the standard free energy of formation of the two
rare earth ions, it is possible to calculate $\underline{E^o}$ for the two
metals by use of the electrode equation

(160) $E^o = - \Delta F^o / nF$

in which $\underline{n}$ is three, and $\underline{F}$ is 23,066 cal/volt-equivalent.
The electrode reactions are:

$$Ce(s) = Ce^{+++} + 3e^-, \qquad E^o = 2.294_9$$

$$Nd(s) = Nd^{+++} + 3e^-, \qquad E^o = 2.213_9$$
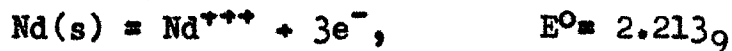
TABLE 19

The Free Energies of Formation; Heats of Formation;
Entropies of Formation; and Calculated Entropies of
Compounds and Ions of Cerium and Neodymium at 25°C

Compound or Ion	ΔF^O	ΔH^O	ΔS^O	S^O
$CeCl_3$	-232.90	-250.58	-59.3	34.5
$NdCl_3$	-226.40	-244.08	-59.3	34.6
$CeCl_3 \cdot 7H_2O$	-641.62	-755.82	-383.0	101
$NdCl_3 \cdot 6H_2O$	-581.52	-681.79	-336.3	92
$Ce_2(C_2O_4)_3 \cdot 9H_2O$	-1,343.6	-1,545.4	-677	155
$Nd_2(C_2O_4)_3 \cdot 10H_2O$	-1,391.6	-1,607.2	-723	165
Ce^{+++}	-158.80	-164.76	-20.0	-53.0
Nd^{+++}	-153.20	-161.35	-27.3	-60.3

(ΔF^O and ΔH^O are in kcal/mole; ΔS^O and S^O are in entropy units)

Discussion

The values of the standard free energy of formation of the compounds and ions are given in Table 19 and the standard electrode potentials of cerium and neodymium are based on the estimation of the entropies of the solids; these values would be subject to revision when a more accurate determination of the entropies are made. However, the $T \Delta S^O$ contribution to the standard free energy of the two rare earth ions is about four per cent of the value of the free energy so that it is possible that any revision would not change the values of E^O appreciably. Yost, Russell, and Garner (66) estimate the E^O values for cerium and neodymium to be 2.3 and 2.2 volts, respectively.

The heats of solution of the chlorides of cerium and neodymium are definitely affected by the presence of other electrolytes in solution. The effect of hydrochloric acid was to reduce the value of the heat of solution; it was measured only for the purpose of determining the heats of formation of the anhydrous chlorides by a procedure which eliminated any estimations of dilution effects and in which the initial and final states of all the substances involved were known. A more complete set of measurements of the effects of other electrolytes on either the heat of solution

or on the heat of dilution of a series of rare earth salts should furnish the type of data necessary for a study of association in electrolytic solutions.

The thermodynamic requirements for the determination of the entropy of a reaction has been discussed. The necessary data required to extend the calculation of the free energy of formation to additional compounds and ions of all the rare earth elements and the calculation of their electrode potentials are: (1) the heat capacity data for the solid crystalline salts and metals over the temperature range from near zero degrees absolute to room temperature; (2) the equilibrium constant for a reversible reaction of each rare earth element at $25^{\circ}C$ which involves a rare earth ion and a solid salt for which the data for (1) are known; and (3) the changes in heat content of the reactions for which the data for (2) above are known. If the oxalates of the rare earths, for example, are chosen for further extension of these thermodynamic data, their heat capacities and solubility products would be of prime interest. The data presented in this thesis have demonstrated that these insoluble salts are well-suited for the above types of thermodynamic treatment. Since the thermal data on oxalic acid hydrate have been critically reviewed and additional experimental data have been presented, the calorimetric

measurements of (3) above for additional oxalate salts can be readily accomplished.

The accuracy of all the measurements was about 0.1 per cent. The interpretation of the calorimetric data in some of the reactions was complicated by what appeared to be simultaneous exothermic and endothermic reactions which proceeded at different rates; in order to minimize errors in the measurement of the net heat evolved, the post-rating curves were extended for a greater length of time. No attempt was made to correlate the shape of the temperature-curves with the processes which occurred in the calorimeter-vessel, but the evidence of such phenomena suggests the possible use of the calorimeter as an aid to the study of the kinetics of chemical reactions.

HEAT CAPACITY OF SOLIDS

Introduction

The heat capacity is one of the most useful thermal quantities for applying the laws of thermodynamics to chemical substances. Its measurement and application through thermodynamic relations requires no special theory. By use of the values of the heat capacity of a substance as a function of the temperature, from very nearly zero degrees absolute to a given temperature, the entropy; heat content; energy content; and free energy of the substance can be determined at any temperature to which the heat capacity is known. Heat capacity measurements to very low temperatures have given the basic experimental evidence supporting the third law of thermodynamics (67), and, in addition, heat capacity data are an aid to the development of theories of crystal structure and of atomic structure.

The energy absorbed by the crystal, upon the addition of heat, is used up in large part to cause the atoms to vibrate or oscillate more vigorously about their equilibrium positions. In some cases the increased vibrations are such that the atoms prefer a new arrangement among themselves and when enough energy has been supplied they will shift to new

positions. At the temperature where this occurs the crystal absorbs a large amount of energy, and when the new arrangement is accomplished the atoms vibrate about their new positions. This rearrangement is called a phase change; in the heat capacity curve it is called an anomaly. If sufficient heat is added to most solids, the resulting increase in temperature causes the atoms to vibrate so energetically that they slide past each other and the crystal melts. At low temperatures, for some crystals like those of the rare earth metals and their compounds, it is possible to observe the small amounts of energy required to excite the lower lying electronic levels when the ground state is not a single state. Such splitting of the ground state is also observed by means of absorbtion spectra. As the higher energy levels become more heavily populated, the crystal absorbs more energy per degree rise in temperature which causes a hump in the heat capacity curve. After these states have reached their equilibrium ratio the crystal again utilizes further additions of heat mainly in the form of vibrational energy and its heat capacity, although higher, is a continuous function of the temperature. At higher temperatures the above phenomenon is not so noticeable in the heat capacity curves because the excitation of the lower lying electronic energy levels requires only a small

amount of energy so that a hump is not observed at these temperatures; the increased number of states that absorb given amounts of energy do so at different temperatures so that their combined effect is smoothed-out in the observed heat capacity curve. Extremely high temperatures are usually required to excite the electrons in the inner shells of the atoms to higher electronic states.

There are other contributing factors to the heat capacity such as that due to the "free" electrons in a metal; these will be mentioned specifically in the next section.

Theory

The thermodynamic definition of heat capacity is given by the following equations:

$$(161) \qquad C_V = \left(\frac{DQ}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

is the heat capacity at constant volume;

and

$$(162) \qquad C_p = \left(\frac{DQ}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

is the heat capacity at constant pressure. The heat content is defined by

$$(163) \qquad H = E + PV$$

and

$$(164) \qquad \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = C_p$$

and

(165)
$$C_p - C_V = P \left(\frac{\partial V}{\partial T}\right)_P$$

is the difference between the two. This difference is small for solids at ordinary temperatures.

According to statistical theory (68), the contributions of various kinds of energy to the total energy content of an atom, molecule, or to the crystalline agglomerate of atoms and molecules are considered to be independent of each other whenever they are responsible for an extension of phase space and represent a given state in that space. Hence it is possible to write the total energy content of the solid as

(166) $E = E_t + E_v + E_r + E_{ei} + E_{eo} + E_n + E_m + E_{cc}$

in which

E_t is the contribution of the translational energy

E_v is the contribution of the vibrational energy

E_r is the contribution of the rotational energy

E_{ei} is the contribution of the internal electronic
energy

E_{eo} is the contribution of the energy of "free" electrons

E_n is the contribution of the nuclear energy due to
interaction of the nuclear moments in crystalline
fields

E_m is the contribution of the magnetic energy due to
interaction of the magnetic moments in crystalline
fields

E_{cc} is the contribution of the energy of crystalline
transformations

For solids, the term E_t is not considered since the
average positions of the atoms in a crystal are fixed rela-
tive to the crystal. In addition, for the cases of a metal
or ionic crystal, the term E_r can be neglected. Although
the metallic-type bond is considered to have some of the
characteristics of the covalent-type bond, in most metals
the bonds are considered to be equally shared between
neighboring atoms which are the same distance apart rather
than as being a paired-electron bond between two atoms.
Since only a small part of the bonding between the atoms
of most ionic crystals is of the covalent-type (8), neither
the metallic-type bonds nor the ionic type bonds between
atoms in a crystal give molecular structures which contribute
to the rotational energy.

If an ideal elementary solid is pictured as a space
lattice of independent atoms which do not interact with
each other and are vibrating about their equilibrium positions
in a simple harmonic manner, then the contribution of each
of the three possible modes of vibration to the energy is
kT since each harmonic mode contains two quadratic terms in

the energy equation for a harmonic oscillator. The total energy is $3kT$ per atom or $3RT$ per mole; therefore C_V is $3R$, which is very nearly 6 cal mole^{-1} deg.$^{-1}$ This is the empirical value of C_V found by Dulong and Petit (2) for the atomic heat capacities of many of the common elements at room temperature which means that the main contributing factor to the heat capacity of a metal crystal is its capacity to convert the absorbed heat into a corresponding increase in its vibrational energy. However, it soon became evident that such a rule was not sufficient because the specific heats of practically all simple solids approach zero as the absolute temperature approaches zero. Einstein (69) made the first attempt, on the basis of quantum theory, to show that if a crystal was an aggregate of atomic oscillators all vibrating at some mean frequence the heat capacity would approach zero as the absolute temperature approaches zero.

Although Einstein's equation was qualitatively correct it neglected the fact that closely placed atoms could have an effect on the oscillations of each other. Debye (70) improved the Einstein equation by assuming that the atoms perform more complex oscillations based on the crystal as a whole; that all of the N atomic oscillators are coupled; and that the simple harmonic vibrations of these oscillators will have $3N$ frequencies. The lowest frequency of

the oscillators was assumed to be zero and the maximum
frequency was given a definite limit. In order to solve
the equation for the energy, the solid was considered to
be a homogeneous elastic medium. Two equations were ob-
tained when the contributions of all these possible oscil-
lators were summed by integrating the equation to the maxi-
mum frequency; one applicable to low temperature heat
capacity and one applicable to moderate and high temperature
heat capacity. The more outstanding result of the two
equations was the prediction that the heat capacity ap-
proaches zero as a function of T^3 near the absolute zero of
temperature, or,

$$(167) \qquad Cv = AT^3$$

At higher temperatures, the equation for the heat capacity
was

$$(168) \qquad C_V = 3R\left[1 - \frac{1}{20}\left(\frac{\Theta}{T}\right)^2 + \frac{1}{560}\left(\frac{\Theta}{T}\right)^4 - \cdots\right]$$

in which

$$(169) \qquad \Theta = \frac{h\nu_m}{k}$$

defined the characteristic temperature in terms of the
maximum frequency. Born and von Karman improved upon
Debye's method by treating only those $3N$ degrees of free-
dom that correspond to intermolecular vibrations by the
continuum method of Debye and the remaining $3(N - 1)$ sets

by $3(N - 1)$ Einstein functions. They also took a slightly
different value for the maximum frequency. Blackman directly
computed the frequency-distribution functions for the normal
modes of vibration for some simple lattices and applied the
results to heat capacities. All the above mentioned theories
are given in some detail by Sietz (71). In all the theories
it is assumed that interatomic forces obey Hooke's law.
While the theories are adequate for qualitative estimations
of the heat capacities of solids, in many cases they do not
satisfactorily describe the details of experimentally deter-
mined heat capacity curves. Some of the vibrations in the
solid may be anharmonic; ionic crystals, for instance,
which have some degree of covalent bonding between the ions
so that the ions may not prove to be simple harmonic oscil-
lators in all directions.

The additional factors contributing to the energy
content of a solid which are not included in the theoretical
equations of Einstein and Debye, are the remaining terms
E_{ei}, E_{ev}, E_n, E_m, and E_{cc}. The internal electronic energy
term E_{ei}, is the energy absorbed in exciting the low energy-
level electronic states at very low temperatures and higher
levels at higher temperatures. A hump in the heat capacity
is observed at the temperature at which these electronic
states respond in absorbing the proper amounts of heat; the

absorbed energy causes an excitation of the inner electrons
(4f electrons in the rare earths) in addition to causing
an increase in the vibrational energy. The energy of the
outer or "free" electrons of an atom in a metal, E_{eo}, is
that given by Fermi-Dirac statistics. Although the valence
electrons of a metal atom are considered in a sense to be
free as far as motion through the solid metal is concerned,
they are restricted by the Pauli principle; application of
the Fermi-Dirac statistics shows that even up to room
temperatures the electrons are still practically all in
their lowest states. A simple explanation is that even at
low temperatures, the kinetic energy of the electrons is
very great compared with kT, and only when T is very large
the contribution of energy to the heat capacity by the
electrons is observed since only at the high temperatures
is their kinetic energy altered by an appreciable amount.
The contribution of the free electrons to the heat capacity
has been found to be linear with temperature. So that

(170) $$C_v = aT$$

in which a is the order of 10^{-4}; this is much smaller than
would be expected if electrons behaved like ordinary gase-
ous molecules. The energy due to thermal motion in un-
coupling nuclear moments would be very small; since it would
be less than experimental error, it is neglected. The

magnetic energy term also would not contribute appreciably
to the heat capacity of the solid since the magnetic fields
about the atoms in the solid are not changed to any great
extent by the addition of heat.

The last term, E_{cc}, is the energy required for crystal-
line modification as evidenced in a phase change. While
it is true that after a phase change occurs the vibration
modes and frequencies would be different, no theory as yet
attempts to predict when the atoms, with a given set of
vibrational modes in a given lattice, will prefer a differ-
ent arrangement with respect to position and modes of oscil-
lation. However, the present theories are applicable to
each allotropic form separately so that it is not necessary
that the above mentioned phenomenon which is a unique
property of a given substance be predicted by the accepted
general theory.

Studies on the paramagnetism, resistivity, and the
heat capacities of all the rare earth metals and salts
should furnish a large source of data by means of which the
theories presented above can be further clarified and ex-
tended. Since, from lanthanum to lutetium, as the $4f$ shell
is gradually filled, the number of humps in the heat capaci-
ty curve would be different for each succeeding element de-
pending on the allowed splitting of the ground state the

internal electronic effects can be studied from low temperature heat capacity measurements. The energy contributions of the vibrational energy-levels should be nearly the same for solid crystals of the same structure; the outer or free electrons of the rare earth elements should contribute about the same amount to the heat capacity since each has three valence electrons. When the values of heat capacities of lanthanum, gadolinium, and lutetium, in which the inner electrons should not give the anomalous humps in the heat capacity curves, have been determined from nearly absolute zero of temperature to higher temperatures the above factors can be subtracted from the heat capacity values of the other 12 elements and the electronic contributions to the heat capacity can be studied independently.

Methods of Measurement

The first use of the ice-water phase system to measure heat quantities was reported by Black; a block of ice with a small hole in it was used as a calorimeter. The amount of ice that melted after a warm body had been inserted into the hole and had cooled to $0^{o}C$ was determined by the gain in weight of a blotter used to absorb the water formed during the experiment. Lavoisier and Laplace later made a more complicated device to measure heats by the use of the ice-water change of state, but their calorimeter was not a

great improvement on Black's simple method. Preston (11)
discusses these calorimeters in some detail.

In 1870, Robert Bunsen (72) constructed the first
satisfactory ice calorimeter. The best models of the ice
calorimeter of the present time, such as those described
by Ginnings and Corruccini (73) and by Ginnings, Douglas,
and Ball (74), are modifications of the calorimeter de-
scribed by Bunsen; all the models are operated with ice-
water and water-mercury phases in contact. In each case
the amount of ice melted by the introduction of a quantity
of heat which causes a contraction of the three-phase
system is measured by the amount of mercury intake into
the calorimeter. The calibration factor, K, of the ice
calorimeter is

$$(171) \qquad K = L/(v_i - v_w)d_m$$

in which

    L is the heat of fusion of ice

    v_i is the specific volume of ice

    v_w is the specific volume of water

    d_m is the density of mercury

The calibration factor is independent of the amounts of ice,
water, or mercury present in the calorimeter vessel and
therefore is independent of the size of the vessel; however,
the combined quantities of ice, water, and mercury must be
confined in a vessel at constant volume.

The advantages of the ice calorimeter are: (1) no temperature measuring devices are required to determine heat quantities; (2) the calibration factor, K, should be the same for all ice calorimeters if materials of equal purity are used in them and if the external pressures are about the same; (3) the calorimeter possesses a high sensitivity and can be used for micro-calorimetric measurements; and (4) its heat leak is small when it is operated in an ice bath. Since the ice calorimeter can only be used at $0^{o}C$, its application is limited to the measurement of the heat of reactions which can be performed at that temperature or to the measurement of changes in heat content of substances which are dropped into it from higher temperatures. The latest models of the ice calorimeter are constructed so that they can be used in conjunction with the latter type of heat experiment.

Experimental

Preparation of materials

The neodymium metal was furnished by the metallurgy section of the Ames Laboratory rare earth group under the direction of Dr. F. H. Spedding. A large cast cylinder of very pure metal was trimmed under mineral oil on a lathe.

After dissolving the oil from the metal with benzene, the metal cylinder was placed in a special pyrex container which was then sealed with Apiezon-wax and evacuated; purified helium was then passed into the container up to atmospheric pressure. The helium prevented the metal from being oxidized and permitted storage until ready for use.

Two types of samples for heat capacity measurements were prepared; the first type consisted of those which were sealed in quartz bulbs. Since it was found impossible to seal a 3/4-inch quartz tube containing a solid cylinder of metal under a helium atmosphere without contaminating the quartz, the samples were prepared as follows: (1) a 3/4-inch quartz tube about 12 inches long was sealed at one end; (2) a tantalum-foil crucible was fabricated and placed in the quartz tube; (3) the tube was flushed with helium gas and a short length of the tube just above the top of the tantalum-foil crucible was narrowed by pulling while it was heated in the flame of an acetylene torch; (4) small rods of the metal were made and allowed to slide down the quartz tube through the narrow neck into the tantalum-foil crucible; (5) the tube was evacuated, filled with helium, and the narrowed-neck was sealed. As the sample-bulb was sealed, a small closed loop of quartz was formed by means of which the sample could be attached to a wire for suspension in a furnace. The bulbs were made from

clear commercial-grade quartz tubing. A dummy quartz
sample-bulb containing no metal was prepared for measuring
the heat capacity of the quartz; a sample-bulb containing
a tantalum-foil crucible packed with strips of tantalum-
foil for measuring the heat capacity of tantalum was also
prepared. The tantalum and neodymium metals were weighed
separately in each case and the weight of the quartz was
found by difference.

The second type of sample consisted of those which
were sealed in metal jackets. By use of a procedure of
arc-welding tantalum-foil developed by Daane (75) it was
possible to make a sample of a solid cylinder of metal
which had been turned down to fit tightly into a prefabri-
cated 10-mil tantalum-foil crucible. A lid was formed by
pressing a piece of the foil in a die of the proper di-
mension; with the metal cylinder in the tantalum crucible,
the lid was welded on in an argon atmosphere. To protect
the tantalum from air-oxidation, the sealed samples were
next welded into platinum jackets made from 15-mil pure
platinum-foil. All the tantalum was boiled in aqua regia
before use. The two samples are pictured in Figure 21.
It was desirable, for two reasons, to change over to the
use of all-metal samples: (1) the metal-to-metal contact
with the calorimeter allows a faster transfer of heat from
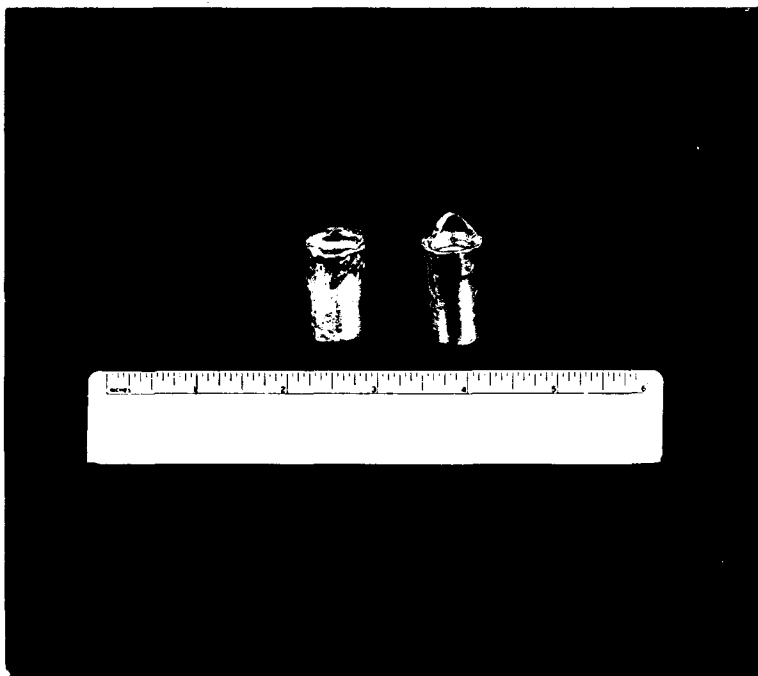the sample to the calorimeter thus cutting down the time

Figure 21. Samples of Tantalum (left) and
Neodymium in Platinum Jackets.

required to reach equilibrium; and (2) the metals transport
an amount of heat from the furnace to calorimeter roughly
in proportion to their weight while the quartz transports
a very much larger proportion of the heat. Tantalum
jackets were used to keep the hot metal from reacting with
the quartz in the one case and to prevent it from alloying
with the platinum in the other. It had been found that
neodymium vapor readily corrodes platinum thermocouple
wires even in extremely low pressure near the melting-
point of the neodymium metal, but that it does not attack
tantalum at temperatures considerably above its melting-
point (75). The weights of the samples and the purity of
the neodymium metal used are given in Table 20. The tanta-
lum-foil was supplied by the Fansteel Corporation.

Apparatus

Two ice calorimeters were constructed from a design
which followed very closely the models built by Ginnings
and Corruccini (73) and by Ginnings, Douglas, and Ball (74).
Their reports explain in great detail the calibration and
operation of the calorimeter. The first model used for
the work presented in this thesis had a copper-well with a
pyrex section interposed between the copper-well and the
first brass plate by means of two pyrex-copper seals
instead of a continuous metal tube. The later model which

is more identical to the model of Ginnings, Douglas, and Ball is shown in ^{F}igures 22 and 23. In the schematic drawing, $\underline{A}$ is the outside one of the two concentric pyrex jars sealed with Apiezon-wax to the upper brass plates. $\underline{B}$ is a pyrex tube which carries the mercury column to the outside; it extends to the bottom of the mercury pool, $\underline{D}$, in the inner chamber. The center well, $\underline{C}$, is a tapered thin-walled monel tube of one-inch inside diameter at the top and of 3/4-inch diameter at the bottom. Numerous copper-foil vanes were welded on the tapered portion of the main-well to help carry the heat out into the ice-mantle. A 1/8-inch copper tube leads out of the bottom of the well and to the outside through a coil in the ice bath, $\underline{I}$; helium was passed through this tube into the well to keep moisture from collecting in the monel tube and to aid in transferring the heat from the sample to the calorimeter-well. The bath vessel was a large pyrex jar. It was first wrapped with tin-foil, then with a layer of thick wool felt, $\underline{F}$, and finally with another layer of tin-foil. Dikalite insulation filled the remaining space, $\underline{E}$, in the plywood box. It was found advantageous to use the stirrer, $\underline{J}$, for experiments which were carried out in warm weather in order to keep the heat leaks from increasing towards the end of a long experiment. The gate, $\underline{G}$, was opened only while the sample was being dropped but was immediately closed after

TABLE 20

Samples for Heat Capacity Measurements and Purity of Neodymium Metal

Sample Number	Quartz (grams)	Tantalum (grams)	Platinum* (grams)	Neodymium (grams)
1	6.0659	0	0	0
2	7.6804	5.3084	0	0
3	6.7591	18.0846	0	0
4	0	27.8557	19.9376	0
5	4.9167	3.2219	0	8.3368
6	0	6.5949	30.1504	25.2861

Purity of Neodymium

5   No other rare earths or tantalum detected by emission spectrography; faint traces of calcium and magnesium; iron, 0.0095 per cent.

6   No other rare earths or tantalum detected by emission spectrography; faint traces of calcium and magnesium; iron, 0.02 per cent.

*does not include the platinum discs
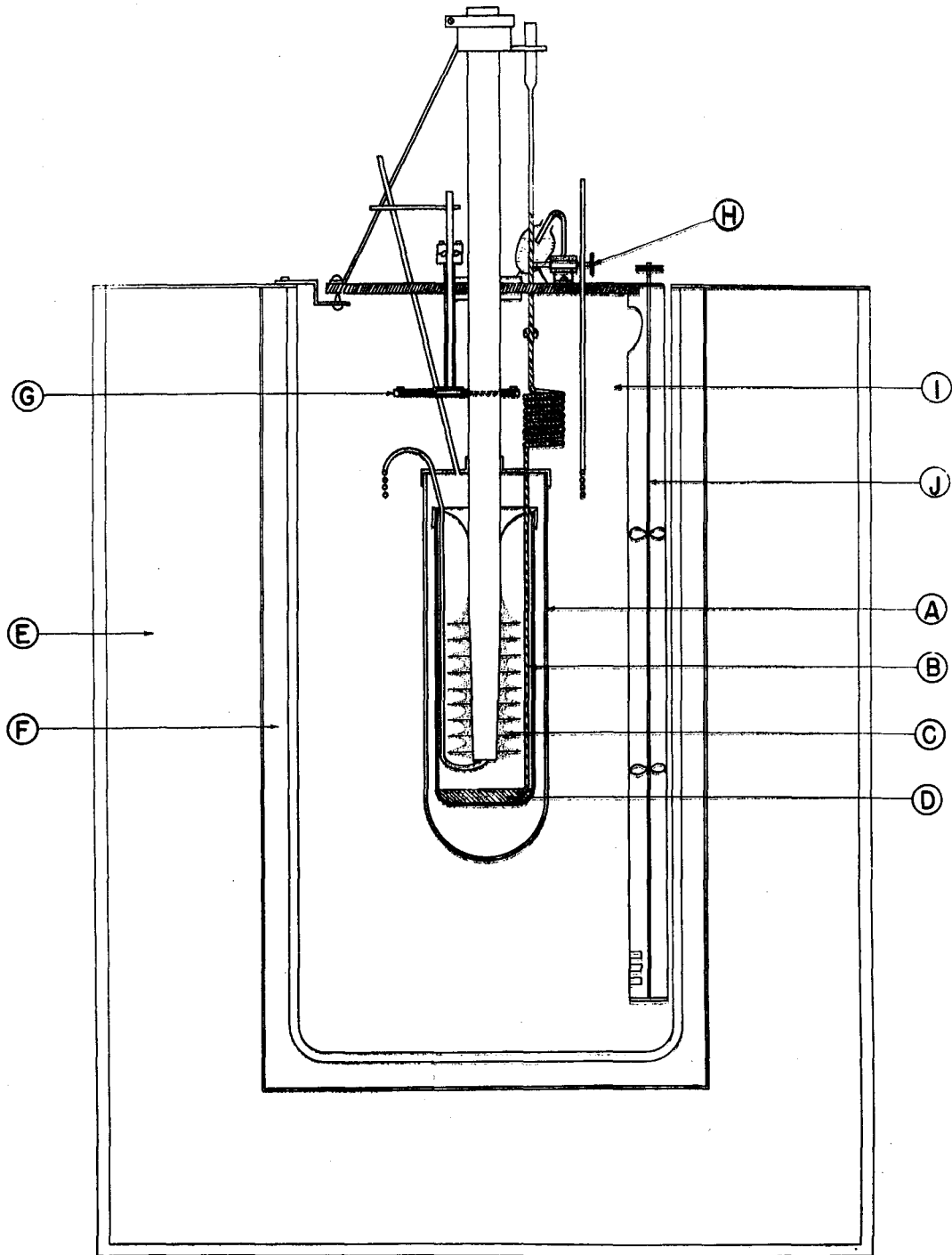
Figure 22. Ice Calorimeter.

Figure 23. Schematic Diagram of the Ice Calorimeter.

the sample had been dropped. The gate, in the closed position, held the wire to which the sample was attached against the side of the monel tube to shunt off any heat flowing down the wire from the furnace into the gate housing and to the ice bath. The gate was tin-plated and polished to reflect heat radiation in both directions. The needle valve, $\underline{H}$, had a sharp-pointed steel-needle which seated into a soft iron core; it was sealed with paraffin-soaked packing.

In order to observe the heat leak of the calorimeter, mercury was pulled from the flask into the glass capillary-tube by means of a short rubber tube and bulb; the needle-valve was then closed and the movement of the mercury down the capillary was followed by means of a cathetometer which could be read to 0.05 millimeter. The capillary was calibrated over its whole length. An electric-timer was used to follow the rate of fall of the height of the mercury column in the capillary; the observed rate of fall was proportional to the heat leak of the calorimeter. Readings of the height of the mercury column, $\underline{R}$, were observed over a period of time prior to the dropping of a sample. The value of the rate of fall of the column, $\underline{\Delta R/\Delta t}$ in milli-meters per second, was used as an indication of whether or not the calorimeter was in a steady state condition so that the sample could be dropped and was also used as an aid

in determining when the sample, after being dropped, had come to equilibrium with the calorimeter. The observed heat leak at equilibrium should be the same as that of the initial rate.

If the weight of the flask of mercury prior to dropping the sample is M_1 and the height of the mercury column at a given time is R_1, then the total weight of mercury and flask relative to an arbitrary zero on the capillary at this time, is

(172) $$W_1 = M_1 + KR_1$$

in which K is the calibrated value of the capillary in grams of mercury/millimeter. At some later time, δt_1 the total weight will be

(173) $$W_1 = M_1 + KR_1 - K\left(\frac{\Delta R}{\Delta t}\right)\delta t_1$$

Similarly, after the sample has been dropped, the total weight relative to the same arbitrary zero on the capillary tube is

(174) $$W_2 = M_2 + KR_2 - K\left(\frac{\Delta R}{\Delta t}\right)\delta t_2$$

if $\Delta R/\Delta t$ has the same value for the whole experiment. It follows that the total intake of mercury due to the quantity of heat carried into the calorimeter by the sample is

(175) $$-\Delta W = W_1 - W_2 = M_1 - M_2 + K\left[R_1 - R_2 - (\Delta R/\Delta t)(\delta t_1 - \delta t_2)\right]$$

However, it was found more convenient to plot the R readings before and after the drop against the time and to

extrapolate the graph to the drop-time. If $\Delta R/\Delta t$ is linear and has the same value over both the initial and final rating periods it makes no difference to which time the readings are extrapolated; however, if the post-rating becomes linear at a different rate from the initial one, the time, or times, at which the rate changes is in question since the true heat leak from the surroundings cannot be observed until the sample has cooled to $0^{\circ}C$ and is in equilibrium with the calorimeter. However, the only time at which the calorimeter experiences an abrupt change of atmosphere is when the gate is opened and the sample is dropped; therefore, the dropping-time was taken as the most reasonable time for a change of heat leak. In order to substantiate the above assumption, two additional methods were tried by which $-\Delta W$ was calculated for a set of two or three experiments in which a sample had been dropped from the furnace at a given temperature, and in which the value of the post-rate differed from that of the pre-rate. For these, the readings of the two rating periods were extrapolated to a time midway between the dropping-time and the time at which the post-rating curve indicated that the sample and calorimeter had reached equilibrium. In one of the methods an average of the two heat leaks was used for the extrapolation; in the other the actual extrapolated values of the readings were used. However, neither

of these two methods gave as high a precision in the calculated value of $-\Delta W$ as did the method of extrapolating both rating-curves to the drop time. The corrected reading from an extrapolation of the graph is given by

(176) $$R_{D1} = R_{01} - \Delta R_1$$

in which R_{D1} is the reading at the drop-time, R_{01} is the reading at zero time, and ΔR_1 is the difference between the first observed reading at zero time and the reading at the drop-time as taken from a smoothed curve drawn through all the plotted readings. Similarly, the extrapolated post-rate reading, R_{D2}, at the drop-time is given by

(177) $$R_{D2} = R_{02} - \Delta R_2$$

in which R_{02} is the first reading on the post rating-curve. The change in the weighed mass of mercury for an experiment is

(178) $$\Delta M = M_1 - M_2$$

The correction to the change in the weighed mass of mercury due to the heat leak and to the difference in the height of the mercury column in the capillary before and after dropping the sample is

(179) $$K(R_{D1} - R_{D2}) = K \Delta R_D$$

All the values of $-\Delta W$ were calculated by this method. The value of K for the capillary-tube was 0.01520 ± 0.00005 grams of mercury per millimeter.

The furnace used for heating the samples is shown
schematically in Figure 24; it is similar to a furnace
described by Scheider and Hollies (76). The main heating
element $\underline{G}$, was approximately two ohms of No. 16 AWG plati-
num (10% rhodium) wire. The wire was wound in a bifilar
manner on a one-inch inside-diameter alundum tube on which
four separate grooves had been cut at a pitch of $2\frac{1}{2}$ threads
per inch; the tube was 18 inches in length. The heating
element was wound on the grooved-tube starting at angles
of 0° and 180°; a controller resistance thermometer of
No. 32 AWG pure platinum wire was wound on starting at 90°
and 270°. At the bottom of the tube, the heavy wire was
doubled back through notches filed in the ridges on the
alundum tube; the controller wire was doubled back at 180°
from the bend in the heavier wire and was insulated from
the heating element by a strip of mica. Another alundum
tube was ground-out to fit over the first alundum tube and
served to hold the wires in place. At each end, the space
between the outer and inner tubes was sealed with a small
amount of alundum cement to hold them firmly in place;
this small amount of cement could be easily chipped off in
case the heating element or controller-wire later required
repair. The two end-heaters, $\underline{C}$, which were wound on the
outside of the larger alundum tube, were also covered with
a thin layer of alundum cement. By adjusting the ratio of

the current between the main and end heaters it was possible
to increase the linear portion of the temperature distri-
bution about the position of the sample in the center of
the furnace. The space, E, around the heating elements,
was filled with dikalite insulation. Two concentric sheet-
metal cylindrical shells, which were separated by the dead
air space, D, were held in place by a series of transite
discs, H. A low-fired magnesia plug B, was inserted in the
top of the alundum tube to restrict convection currents
upward through the furnace. The plug had three small holes
through it; a hole through the center for a No. 30 AWG ni-
chrome "A" wire which was fastened to the sample, and two
holes near one edge for the thermocouple wires. The tip of
the thermocouple, which was made of No. 26 AWG platinum and
platinum (13% rhodium) wires, was fused into a 10-mil plati-
num-foil cylinderical shell, E, which completely surrounded
the sample. The top end of the nichrome wire was fastened
to a brass piston, A, which fitted into the brass pipe at
the top of the furnace; the pipe was slit down the length
of one side to within six inches from the bottom. The
bottom of the pipe was closed by its supporting brass plate
except for a hole just large enough to pass the nichrome
wire. The brass piston, which is shown in the down position
by the dotted lines in Figure 24, was actually held at the
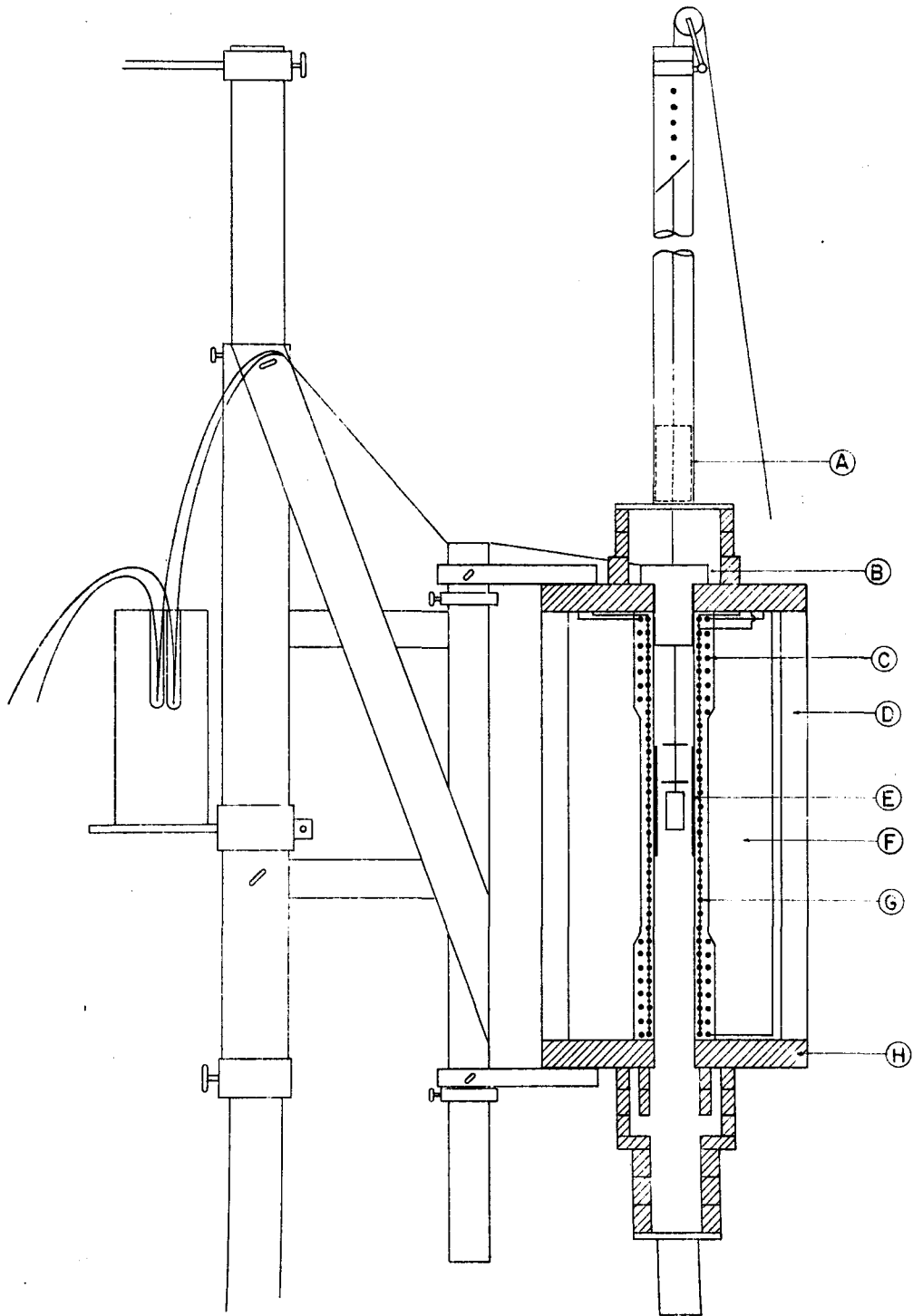top of the brass pipe when the sample was at the position

Figure 24. Schematic Diagram of the Platinum-wound Furnace.

shown; when it was released, the sample and piston fell
freely until the piston reached the end of the slit in the
brass pipe; from this point the rate of fall of the two was
reduced by action of an air-cushion which formed under the
falling piston. The fall of the sample was therefore re-
tarded just after it had entered the calorimeter-well so
that it did not crash onto the bottom of the well. The
picture of the furnace and calorimeter with one of the
switchboards is shown in Figure 25.

The temperature controller circuit is shown in
Figure 26. The legend is as follows:

<u>V.R.</u> is a 5KVA Stabiline voltage regulator

<u>K</u> is a set of two 28 amp Powerstats

<u>S</u> is a variable one ohm resistor of 25 amp capacity

<u>T</u> is a variable one ohm shunt resistor of 25 amp
capacity

<u>R</u> is a power relay

<u>P</u> is a Worner photo-cell relay and photomultiplier
(model 62-R)

<u>L</u> is a light source

<u>G</u> is a Leeds and Northrup type HS Galvanometer with
a sensitivity of 0.1 $\mu V/mm$ at one meter

<u>B</u> is either a Wheatstone or Mueller temperature bridge

<u>Q</u> is 35 ohms of No. 32 AWG pure platinum wire

<u>N</u> is 2.0 ohms of No. 16 AWG platinum (10% rhodium) wire
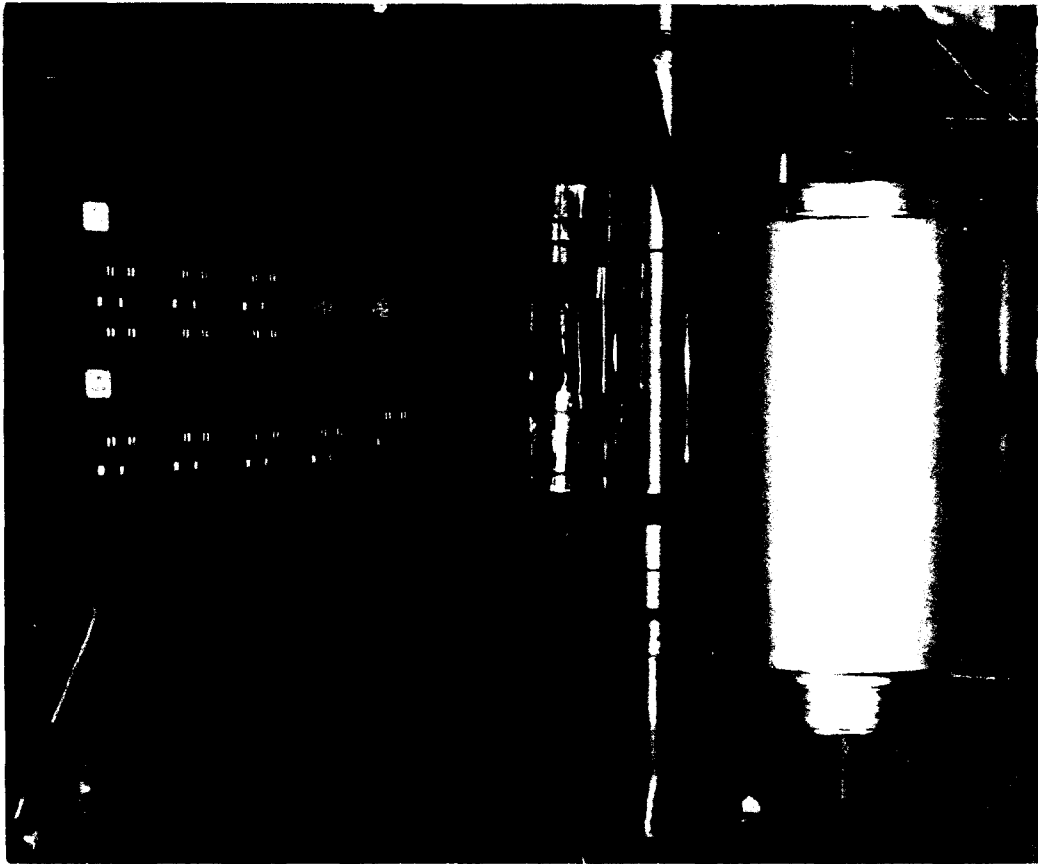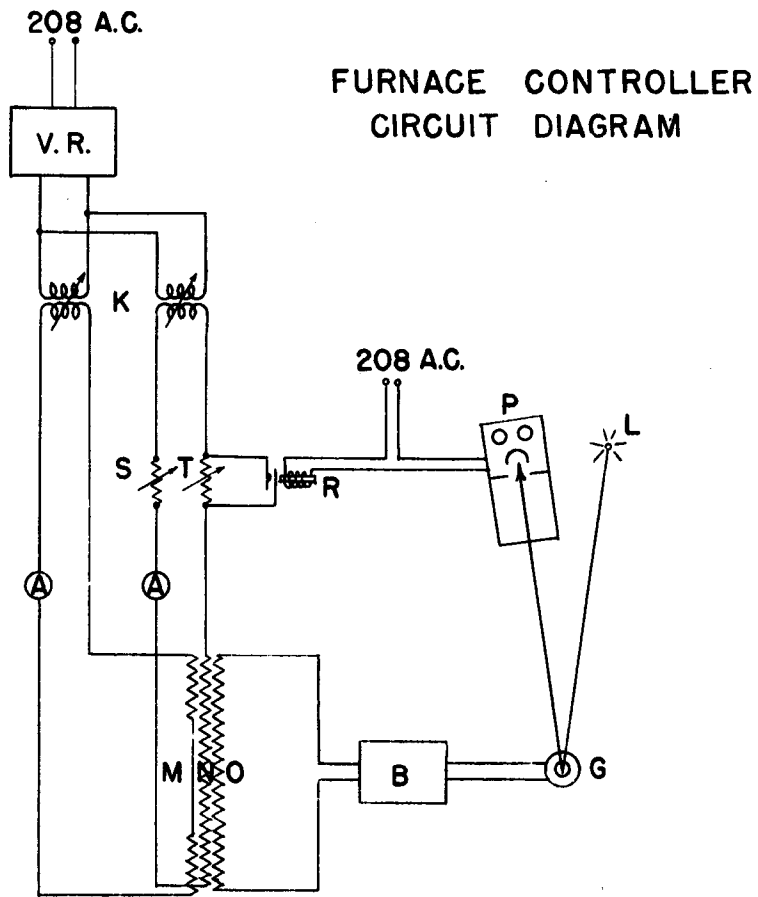
Figure 25. Furnace and Ice Calorimeter Assembly.

208 A.C.

FURNACE   CONTROLLER
CIRCUIT   DIAGRAM

V. R.

K

208 A.C.

P

L

S   T

R

A   A

M   O

B

G

Figure 26.   Furnace Controller Circuit Diagram.
(see page 157 for legend)

$\underline{M}$ is 1.2 ohms of No. 16 AWG platinum (10% rhodium) wire

The advantage of the type of controlling circuit shown in Figure 25 is that the controlling mechanism permits a wide range in the sensitivity of the resultant temperature control. By the use of a 12-foot optical path between the light-source and photo-cell in conjunction with a G-2 type Mueller temperature bridge set at a sensitivity of three milliamps, it was possible to reduce the temperature fluctuations of the thermocouple to about 0.002°C over the temperature range of 25°C to 300°C for a sufficiently long period of time to complete an experiment. From day to day, however, the temperature of the furnace drifted a few tenths of a degree; since the drift was not always in the same direction it is possible that the load on the line to the regulator as well as fluctuations in the room temperature affected the inertia of the whole electrical system. One disadvantage to the use of this type of temperature-controller for drop-calorimetry is that it has to be shut off and the temperature of the furnace has to be readjusted to controlling range each time a sample is either dropped from or raised into the furnace. After the controller was put into operation, the temperature of the sample and furnace, in the range of 0°C and 450°C, was measured on a platinum resistance thermometer; the emf of the thermocouple was noted on the White double potentiometer; for successive

experiments at the same temperature, the controller was
adjusted by use of the bridge to give the recorded emf.
When one series of experiments was completed for a given
temperature, the furnace current was changed to give a
different temperature and the whole procedure repeated.

The above described controller-system was not put
into operation until after the second ice calorimeter had
been constructed. Practically all the data to be reported
were obtained from the samples which were sealed in quartz
bulbs by the use of the first model of ice calorimeter.
For these, the furnace was controlled by the variacs which
were connected directly to the voltage regulator. The
furnace temperature drifted from day to day, but was suf-
ficiently steady during the course of an experiment so that
the recorded emf of the thermocouple could be used as a
measure of the temperature of the sample. The thermocouple
was calibrated by comparing its emf with the temperature
read on a platinum resistance thermometer placed in the
core of the furnace so that its tip rested between the
sample and the thermocouple. The temperature of the sample
was estimated, in the temperature range of $0^\circ C$ to $450^\circ C$,
from the thermocouple calibration formula

(180) $t^\circ C = (\varepsilon \times 10^3)/[5.5785 + 0.7452 \times 10^{-5}t(1403.68 - t)]$

in which $\underline{\varepsilon}$ is the emf of the thermocouple in millivolts.

Results

The data on the heat contents for commercial quartz, tantalum, and neodymium metal are summarized in Tables 21, 22, and 23. The data for quartz are represented as a function of the temperature, $t^{o}C$, by the following equations:

(181) $\Delta H_{o}^{t} = 2.718 \times 10^{-3} t + 1.676 \times 10^{-6} t^2 - 1.793 \times 10^{-10} t^3$

in grams mercury/gram quartz, and as

$$\Delta H_{o}^{t} = 0.1773 t + 0.1093 \times 10^{-3} t^2 - 0.0109 \times 10^{-6} t^3$$

in cal/gram when the calibration factor 65.234 cal/gram of mercury is applied; ΔH_{o}^{t} is the change in heat content between $0^{o}C$ and $t^{o}C$. The molar heat capacity is given by

(182) $Cp_{o}^{t} = 19.65 + 13.13 \times 10^{-3} t - 1.970 \times 10^{-6} t^2$

in cal/mole ^{o}C. The above equations are valid in the temperature range from $0^{o}C$ to $400^{o}C$.

The data for tantalum are represented by the equations

(183) $\Delta H_{o}^{t} = 5.006 \times 10^{-4} t + 6.185 \times 10^{-8} t^2$

in grams mercury/gram tantalum, and as

$$\Delta H_{o}^{t} = 3.265 \times 10^{-2} t + 4.034 \times 10^{-6} t^2$$

in cal/gram tantalum, and as

(184) $Cp_{o}^{t} = 5.906 + 1.460 \times 10^{-3} t$

in cal/mole ^{o}C for the temperature range of $0^{o}C$ to $400^{o}C$. The values of the heat capacities, calculated from Equations (182) and (184), checked well with those calculated from equations given by Kelley (77). The measurements on the

TABLE 21

Heat Content Data for Quartz

t°C	− ΔW (total)	− ΔW (Pt)	− ΔW (quartz)	− Δw (quartz)
		First Calorimeter		
51.6	0.9029	0.0231	0.8798	0.1450
54.5	1.0520	0.0246	1.0274	0.1694
95.9	1.7033	0.0431	1.6602	0.2737
96.6	1.7224	0.0434	1.6790	0.2768
100.6	1.7963	0.0458	1.7505	0.2886
103.5	1.8538	0.0660	1.7878	0.2947
104.4	1.8970	0.0666	1.8304	0.3018
105.3	1.8929	0.0672	1.8257	0.3010
144.8	2.6842	0.0654	2.6188	0.4317
146.1	2.7287	0.0660	2.6627	0.4390
146.3	2.6650	0.0661	2.5989	0.4284
146.6	2.7043	0.0663	2.6380	0.4349
185.4	3.5184	0.1195	3.3989	0.5603
186.8	3.5516	0.0849	3.4667	0.5715
196.9	3.7624	0.0896	3.6728	0.6055
197.2	3.7909	0.0897	3.7012	0.6102
205.5	3.8975	0.1328	3.7647	0.6206
239.9	4.6544	0.1097	4.5447	0.7492
263.5	5.1658	0.1208	5.0450	0.8317
263.7	5.2299	0.1209	5.1090	0.8422
299.2	5.9250	0.1377	5.7873	0.9541
300.0	5.9472	0.1381	5.8091	0.9577
308.1	6.1804	0.1419	6.0385	0.9955
311.1	6.3373	0.2035	6.1338	1.0112
311.2	6.2068	0.2035	6.0033	0.9897
352.5	7.2190	0.1631	7.0559	1.1632
353.6	7.2026	0.1636	7.0390	1.1604
353.7	7.1988	0.1637	7.0351	1.1598
409.8	8.6473	0.2707	8.3766	1.3809
424.2	9.0227	0.2807	8.7420	1.4412
425.2	9.0700	0.2813	8.7887	1.4489
438.3	9.3231	0.2045	9.1186	1.5032
443.8	9.3830	0.2073	9.1757	1.5127

(− ΔW is in grams of mercury; − Δw is in grams of mercury per gram quartz)

TABLE 22

Heat Content Data for Tantalum

t°C	− ΔW (total)	− ΔW (Pt)	− ΔW (quartz)	− ΔW (Ta)	− Δw (Ta)
First Calorimeter					
54.6	1.3569	0.0244	1.1776	0.1549	0.02918
94.2	2.3122	0.0423	2.0792	0.1906	0.03590
94.8	2.3818	0.0426	2.0950	0.2442	0.04600
147.2	3.8327	0.0665	3.3469	0.4193	0.07899
147.2	3.8499	0.0666	3.3480	0.4353	0.08200
148.0	3.8539	0.0670	3.3673	0.4196	0.07904
187.9	5.7293	0.1221	3.8447	1.7625	0.09746*
190.2	5.7502	0.1228	3.8971	1.7303	0.09568*
196.8	5.2644	0.0896	4.5982	0.5766	0.1086
197.1	5.3009	0.0897	4.6049	0.6063	0.1142
239.6	6.5585	0.1095	5.7228	0.7262	0.1368
240.0	6.5709	0.1097	5.7324	0.7288	0.1373
282.4	8.8889	0.1842	6.0659	2.6388	0.1459*
298.9	8.3584	0.1375	7.3530	0.8679	0.1635
300.0	8.3531	0.1380	7.3840	0.8311	0.1566
301.5	8.4016	0.1388	7.4269	0.8359	0.1575
354.8	10.1288	0.1643	8.9676	0.9969	0.1878
413.6	13.5778	0.2734	9.4509	3.8535	0.2131*
417.4	13.7984	0.2760	9.5552	3.9672	0.2194*
420.5	13.9097	0.2781	9.6400	3.9916	0.2207*
422.8	12.4864	0.2796	11.0256	1.1812	0.2225
Second Calorimeter					
88.9	2.1301	0.8835		1.2466	0.04475
90.7	2.1789	0.9021		1.2768	0.04584
90.7	2.2035	0.9021		1.3014	0.04672
90.7	2.1796	0.9021		1.2768	0.04586
99.3	2.3990	0.9879		1.4111	0.05066
99.3	2.3850	0.9879		1.3971	0.05015
201.4	4.8132	1.9883		2.8249	0.1014

*second Ta sample in quartz bulb
(− Δw is in grams Hg/gram Ta)

TABLE 23

Heat Content Data for Neodymium

t°C	$-\Delta W$	$-\Delta W$ (Pt)	$-\Delta W$ (quartz)	$-\Delta W$ (Ta)	$-\Delta W$ (Nd)	ΔH_o^t	$\Delta H_o^t/t°C$
First Calorimeter							
23.8	0.5091	0.0106	0.3223	0.0384	0.1378	1.08	0.04535
52.8	1.1518	0.0236	0.7283	0.0857	0.3142	2.46	0.04659
94.5	2.1061	0.0424	1.3364	0.1543	0.5730	4.48	0.04743
143.9	3.2784	0.0650	2.0919	0.2363	0.8852	6.93	0.04812
194.8	4.5644	0.0886	2.9100	0.3218	1.2440	9.73	0.04996
195.6	4.5873	0.0890	2.9228	0.3231	1.2524	9.80	0.05010
196.1	4.5879	0.0892	2.9307	0.3239	1.2441	9.74	0.04965
229.6	5.4982	0.1048	3.4929	0.3809	1.5196	11.89	0.05178
248.2	5.9275	0.1136	3.8107	0.4125	1.5907	12.45	0.05016
252.3	6.0452	0.1155	3.8828	0.4196	1.6273	12.73	0.05046
302.9	7.3078	0.1394	4.7801	0.5068	1.8815	14.72	0.04860
302.9	7.3531	0.1395	4.7804	0.5069	1.9263	15.07	0.04976
303.0	7.3421	0.1395	4.7823	0.5070	1.9133	14.97	0.04940
334.3	8.1689	0.1544	5.3558	0.5614	2.0973	16.41	0.04909
334.9	8.1666	0.1547	5.3661	0.5624	2.0834	16.30	0.04868
357.8	8.7738	0.1657	5.7975	0.6027	2.2079	17.28	0.04830
359.2	8.8624	0.1664	5.8223	0.6050	2.2687	17.75	0.04943
Second Calorimeter							
99.3	3.6396	1.4730		0.3317	1.8349	4.718	0.04753

(ΔH_o^t is in cal/gram Nd)

first sample of tantalum gave a large spread in the values
of the mean heat capacity due to the fact that more than 85
per cent of the total heat was carried into the calorimeter
by the quartz; even for the second tantalum sample in which
the weight ratio of tantalum sample in which the weight
ratio of tantalum to quartz was increased to nearly three
to one, the quantity of heat due to the quartz was 70 per
cent of the total measured heat. About the same conditions
held for the measurements on neodymium; however, the spread
in the values of the mean specific heat was not nearly so
great as for the first tantalum sample since the neodymium
sample in the quartz bulb contributed only about 20 to 25
per cent of the total heat. The data on neodymium show a
decrease in the mean specific heat in the temperature range
of 250°C to 350°C; however, it was impossible to check
these measurements with the second and larger sample of
metal by the use of the second model of the ice calorimeter
since the calorimeter and furnace were urgently needed for
other purposes. The measurements were therefore terminated
after the single value at about 100°C had been measured.

Discussion

The amount of heat contributed by the platinum discs and sample containers for each experiment was calculated from the equations for the heat content of platinum relative to 0°C as given by Jaeger and Rosenbohm (78) who report measuring over a 1000 values of the high-temperature heat content of platinum. The heat capacity of neodymium metal in the temperature range 300°C to 600°C has been reported by Jaeger, Bottema, and Rosenbohm (79). They describe the difficulties that they have encountered in attempting to measure the specific heat of some of the rare earth metals in which hysteresis effects occur at the temperature at which an allotropic change takes place. Their values of the mean specific heat of neodymium have been corrected so that the lower limit of the temperature is zero degrees centigrade. This was done by calculating, from the data given in Table 23, the change in heat content per gram of metal from 0°C to the reported final temperature of each of their experiments and by adding it to their reported values of the change in heat content. The amounts added were all near one calorie per gram. The values of the mean specific heat, $\Delta H_0^t/t$, of neodymium are plotted in Figure 27; the values from 0°C to 250°C are taken from Table 23, and the data given by Jaeger, Bottema, and Rosenbohm. The equations which represent the combined data for
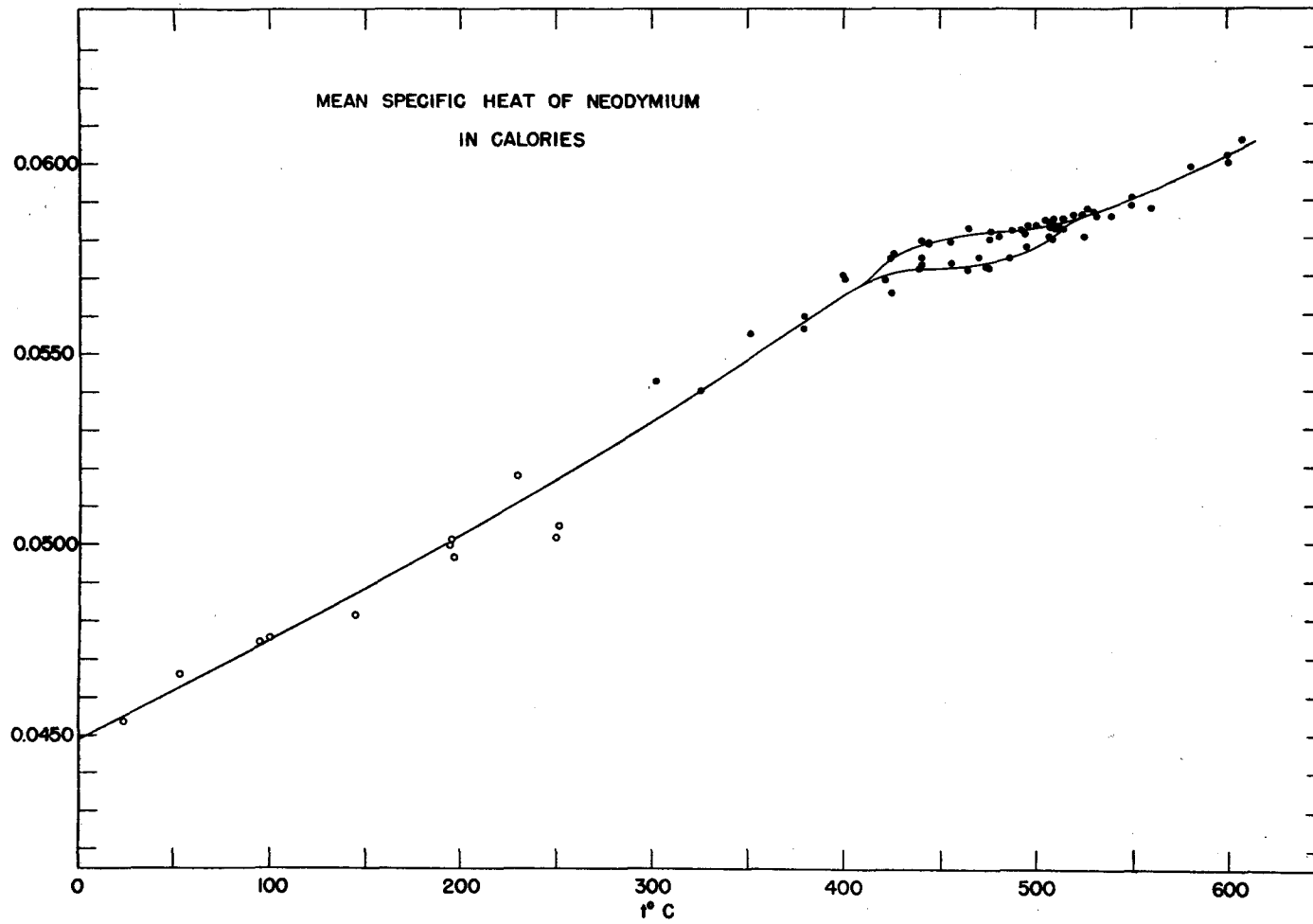
Figure 27. Mean Specific Heat of Neodymium.

neodymium metal from 0°C to 400°C are

$$(185) \quad \Delta H_0^t = 0.04491t + 2.445 \times 10^{-5} t^2 + 1.064 \times 10^{-8} t^3$$

in cal/gram neodymium, and

$$(186) \quad Cp_0^t = 6.479 + 7.065 \times 10^{-3} t + 4.463 \times 10^{-6} t^2$$

in cal/gram atom-deg.C.

SUMMARY AND CONCLUSIONS

Summary

1. The heats of solution and dilution of the anhydrous chlorides of cerium and neodymium in aqueous solutions have been measured for concentrations up to 0.35 and 0.40 molal, respectively; the accuracy of all measurements was within 0.1 per cent. Treatment of the data by the chord method of analysis showed that, within the limits of experimental error, the limiting slope given by the Debye-Hückel equation was approached. Similar agreement with the Debye-Hückel theory had been reported for data on the activity coefficients of these two electrolytes as recently determined at the Ames Laboratory (4). The data for the heats of solution at 25°C for cerium chloride are represented by

(133) $Q_M = 34,010 - 6,925m^{1/2} + 8,485m - 5,201m^{3/2}$

in cal/mole with an average deviation of 10 cal/mole.
The data for the heats of solution at 25°C for neodymium chloride are represented by

(134) $Q_M = 37,100 - 6,925m^{1/2} + 8,953m - 5,460m^{3/2}$

in cal/mole with an average deviation of 14 cal/mole.

2. The heat capacities of aqueous solutions of the chlorides of cerium and neodymium have been determined from measurements of the change in heat capacities of the re-

actions accompanying the solution of the anhydrous chlorides.
The average accuracy of the derived values of the relative
apparent molal heat capacity was about 10 per cent while
the accuracy of the measurements of the total heat capaci-
ty of the calorimeter and its contents was within 0.1 per
cent. The equations which represent the data for the rela-
tive apparent molal heat capacities at $25^{\circ}C$ up to concen-
trations of about 0.30 molal are:

$$(135) \qquad \phi_J = 128 \ m^{\frac{1}{2}}$$

in cal/mole$^{\circ}C$ for cerium chloride, and

$$(136) \qquad \phi_J = 131 \ m^{\frac{1}{2}}$$

in cal/mole$^{\circ}C$ for neodymium chloride. The data for the
change in the molar heat capacities at $25^{\circ}C$ for the re-
actions accompanying the solution of the anhydrous chlorides
are represented by

$$(187) \qquad \Delta Cp_M = -362.3 + 128m^{\frac{1}{2}}$$

in cal/mole$^{\circ}C$ for cerium chloride, and

$$(188) \qquad \Delta Cp_M = -320.3 + 131m^{\frac{1}{2}}$$

in cal/mole$^{\circ}C$ for neodymium chloride. These data are in
better agreement with the unrevised value of the limiting
Debye-Hückel slope, as given by Harned and Owen (3), than
with the revised value based on a revision of the equation
relating the dielectric constant of water to the temperature.

3. The heats of solution of the metals and anhydrous
chlorides of cerium and neodymium in aqueous hydrochloric

acid solutions have been measured. The heats of formation
at 25°C of the anhydrous chlorides were calculated from
the data obtained and were found to be -250,580 ± 10
cal/mole for anhydrous cerium chloride and -244,080 ± 20
cal/mole for anhydrous neodymium chloride. The entropies
of the two chlorides were calculated (54) to be 34.5 e.u.
for cerium chloride and 34.6 e.u. for neodymium chloride.
Hence the free energy of formation was calculated to be
-232,900 cal/mole for cerium chloride and -266,400
cal/mole for neodymium chloride. In addition, the heats
of solution of the anhydrous chlorides were found to be
lower in hydrochloric acid solutions than they were for
water solutions. The heats of solution of neodymium
chloride were decreased more than those of cerium chloride
at the same concentration.

4. The heats of solution of the hydrated chlorides
of cerium and neodymium in aqueous solutions have been
measured. From the data obtained, the heats of hydration
at 25°C were calculated to be -27,060 ± cal/mole for
$CeCl_3 \cdot 7H_2O$ and -27,800 ± 50 cal/mole for $NdCl_3 \cdot 6H_2O$.
The heats of formation at 25°C were calculated to be
-755,820 ± 10 cal/mole for $CeCl_3 \cdot 7H_2O$ and -681,790 ± 20
cal/mole for $NdCl_3 \cdot 6H_2O$. The entropies (54) and the free
energies of formation at 25°C were calculated to be 101 e.u.
and -641,620 cal/mole for $CeCl_3 \cdot 7H_2O$, and 92 e.u. and

-581,520 cal/mole for $NdCl_3 \cdot 6H_2O$.

5. The heats of solution and dilution of oxalic acid hydrate in aqueous solutions have been measured over a limited range of concentrations in order to determine the effects of the dilutions which occurred during the precipitation of the rare earth oxalates. The thermal date leading to the calculation of the heat of formation of oxalic acid hydrate were reviewed, and a more accurate value of its heat formation at 25°C was calculated to be -340,020 cal/mole. The heat of formation at 25°C of anhydrous oxalic acid was calculated to be -197,030 cal/mole; the heat of hydration at 25°C was calculated to be -6,360 cal/mole.

6. The heats of precipitation of the oxalates of cerium and neodymium in aqueous solutions of oxalic acid have been measured. From these data, the heats of formation at 25°C were calculated to be -1,545.6 ± 0.2 kcals/mole for $Ce_2(C_2O_4)_3 \cdot 9H_2O$ and -1,607.2 ± 0.2 kcals/mole for $Nd_2(C_2O_4)_3 \cdot 10H_2O$. The entropies (54) and the free energies of formation at 25°C were calculated to be 155 e.u. and -1,343.6 cal/mole for $Ce_2(C_2O_4)_3 \cdot 9H_2O$, and 165 e.u. and -1,391.6 cal/mole for $Nd_2(C_2O_4)_3 \cdot 10H_2O$. From the data given in (1) above, the heats of formation at 25°C of the ions were calculated to be -164,760 cal/mole for Ce^{+++} and -161,350 cal/mole for Nd^{+++}. By the use of literature values for the standard free energy changes of the solubility reactions of the two oxalates (57) the

standard free energies of formation at 25°C of the two ions were calculated to be 158,770 cal/mole for Ce^{+++} and -153,150 cal/mole for Nd^{+++}. Hence, the standard electrode potentials are given by

(189) $Ce(s) = Ce^{+++} + 3e^{-}$, $E^{o} = 2.2949 \pm 0.0005$

and

(190) $Nd(s) = Nd^{+++} + 3e$, $E^{o} = 2.2139 \pm 0.0006$

7. The heats of solution and dilution of potassium chloride in aqueous solution have been measured. The values were corrected to infinite dilution by use of the relative apparent molal heat contents of potassium chloride, as given by Harned and Owen (3), to give $4,144 \pm 3$ cal/mole for the heat of solution at infinite dilution. A review of literature values for the same quantity showed agreement with the above value obtained by the use of the present methods.

8. The heat capacity of tantalum metal has been measured in the temperature range from 0°C to 425°C; the data are presented by

(184) $Cp_{o}^{t} = 5.906 + 1.460 \times 10^{-3}t$

in cal/mole°C.

9. The heat capacity of neodymium metal has been measured in the temperature range from 0°C to about 250°C. When these data were combined with data from the literature (79) for higher temperatures, the equation which represents

the combined data up to 400°C is

(186) Cp_0^t = 6.479 + 7.056x10^{-3}t + 4.463x10^{-6}t^2

in cal/mole°C.

Conclusions and Comments

1. For solutions of the chlorides of cerium and neodymium more concentrated than about 0.05 molal, the relative apparent molal and partial molal heat contents of cerium chloride were found to be higher than those of neodymium chloride. A tentative explanation can be made on the basis that a second coordination may become possible as the rare earth ions become larger with decreasing atomic number and that an equilibrium may be set up between the two hydrated ion-species which have different coordination numbers (4); a shift in the equilibrium between the different species in the direction of the hydrated ion of lower coordination number, as the concentration increases, should be accompanied by an increase in the observed heat contents of cerium chloride over those of neodymium chloride. This additional increase in the heat contents could be attributed partly to a decrease in the distance of closest approach of the ions as the equilibrium shifts and partly to the change in heat content of the equilibrium reaction. However, at the present time, insufficient data are available for any definite conclusions to be made; the data which would be most useful for correlation with the thermal properties of the rare

earth ions in solution are: (1) additional crystallographic data on the hydrated salts from which more information concerning the coordination numbers of the hydrated ions would be obtained; (2) accurate data on the densities of solutions of the salts as a function of temperature; and (3) further extension of the measurements on the thermal properties of the solutions of other salts of the rare earths such as those presented in this thesis. Such data would aid in making a critical analysis of the present theories of electrolytic solutions as well as in bringing light to bear on the factors which cause the properties of one rare earth ion to differ from those of another.

2. The heats of solution of the anhydrous chlorides of the rare earths increase with increasing atomic number (38); this phenomenon could be due to any increase in the energy of hydration of the rare earth ions through the formation of either larger or more thermodynamically stable solvated ions as the rare earth ions decrease in size with increasing atomic number. Data on the compressibilities of the crystalline salts of the rare earths, along with crystallographic data, would permit an accurate calculation of the lattice energies (80). The combination of such calculations with the heats of solution at infinite dilution of the rare earth salts would give much of the information necessary for a detailed study of the factors

involved in the hydration energies of ions.

3. The equation for the relative partial molal heat capacity of an electrolyte, as given by the extended Debye-Hückel theory (3), gives the partial molal heat capacity as dependent on a sensitive function with temperature of the dielectric constant of water and on the volume expansion of the solution. Therefore a correlation of accurate data on the heat capacities and volume expansions for solutions of a complete series of rare earth salts should provide the basis for a study of the dielectric properties of electrolytic solutions.

4. The effects of hydrochloric acid on the heats of solution of the anhydrous chlorides were determined in this work only for the purpose of facilitating an accurate calculation of the desired heats of formation. However, a more complete and independent set of data on the effects of other electrolytes on the thermal properties of the rare earth salts would aid in the development and extension of the thermodynamics of strong electrolytes. In addition, if the data are obtained for solutions to high ionic strength, the factors affecting association might be determined.

5. A more accurate determination of the standard free energies of formation of the compounds and ions of cerium and neodymium will only be possible after sufficient experi-

mental data are available for a more accurate calculation
of the entropies of the solid compounds. The measurements
of the heat capacities of a group of solid compounds of the
rare earths, together with a careful thermochemical study
of the reversible reactions of these compounds such as the
solubility reactions of the two oxalates which were chosen
for this work, is required in order to place the chemistry
of the other rare earths on a firm thermodynamic basis.

6. The calorimetric apparatus, described in this
thesis, was applied successfully to a great variety of
thermal measurements in initiating the studies on the
thermal properties of the rare earth metals, salts, and
aqueous solutions of the salts. For specialized studies
of a given individual thermal property, another type of
calorimeter might have been preferred. An adiabatic calo-
rimeter employing differential methods of measurement, for
example, would be best suited for the measurement of heats
of dilution only; and specially designed twin-calorimeters
would give some improvement on the accuracy with which the
partial molal heat capacities of the electrolytes could be
measured. However, the consistency of the measured values
of the changes in the heat capacities of the reactions which
occurred in the described isothermal calorimeter showed
that the calorimetric apparatus and methods of treating the
data involved no systematic errors.

7. The precise measurements of some of the thermal properties of the metals and compounds of cerium and neo-dymium and their aqueous solutions, presented in this thesis, are of real significance in furnishing the data which are useful in applying the laws of thermodynamics to these substances. The data were obtained as a part of an extensive program for the accumulation of accurate data on the physical and chemical properties of all the rare earth metals and salts in progress at the Ames Laboratory; it is hoped, when this program is completed, that such data will furnish a background for a better understanding of the nature of the forces operating in solids and in aqueous solutions.

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