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James Patrick Flynn
Iowa State College

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HEATS OF SOLUTION AND RELATED THERMOCHEMICAL PROPERTIES OF SOME RARE EARTH METALS AND CHLORIDES

by

James Patrick Flynn

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I. INTRODUCTION

Modern physical and chemical theories indicate that a chemical element or compound is fully defined only when its thermodynamic, structural, spectroscopic, and nuclear properties are known. An experimenter making a systematic study of such a physical or chemical property for a group of elements or compounds is usually confronted with numerous variables beyond his control. Simultaneous variations in oxidation states, bond angles, interatomic and interionic distances, and so forth, serve only to complicate or even make impossible an intelligent interpretation of experimental data. In the case of the rare earth group these simultaneous variations are at a minimum. The chemical properties of the fifteen elements comprising the group are similar; the usual valence state is three; and bond angles change only slightly in a series of compounds. The increase in atomic number is provided for by the filling in of the 4f shell which makes up part of the central core of the atom. The energies released in ordinary chemical reactions are usually insufficient to influence these inner electrons and, therefore, they play only a minor role in determining the chemical properties of the rare earths.

The increase in nuclear charge throughout the rare earth series tends to draw the electron shells closer to the nucleus thereby causing a regular decrease in atomic and ionic radii as the series is traversed from lanthanum to lutetium. In the case of the ions the decrease in ionic radii results in an increase in surface charge density since the ionic charge remains the same. Thus, one can study the effect of ionic size while the valency, bond angles, crystal structure, and so forth, do not change or vary only slightly. This unique series should serve as a check point for theories of solution and atomic and molecular structure.

Until relatively recently the rare earths were not available in large amounts for extensive experimental work on their properties and much of the earlier work was done with impure materials. Now that the rare earths are available in the oxide and metallic forms in high purity and in large quantities (1, 2, 3, 4, 5, 6), the research can be done.

The purpose of this thesis is to extend the knowledge of the thermodynamic properties of the rare earths as part of a planned program underway at the Institute for Atomic Research at Iowa State College. The work presented here is concerned with calorimetric measurements of the heat changes accompanying the solution of some rare earth metals and chlorides and the thermodynamic quantities derivable therefrom.

It may be said that the ultimate goal of thermochemical investigations is to tabulate the free energies, heats, and entropies of formation of all chemical compounds. The free energy change of a process is of utmost importance from the standpoint of the chemist, not only because it is the true measure of the direction of the reaction, but also because it is thermodynamically related to the equilibrium constant and the reversible e.m.f. of the given reaction. At ordinary temperatures the most important contribution to the free energy of formation of most substances is the heat of formation. In many instances the heat of formation of a compound can be conveniently determined from heat of solution data by proper application of Hess's law of constant heat summation. Then, if the entropy of formation is known or can be estimated, it is a simple matter to calculate the free energy of formation.

The crystal energy of an ionic salt such as a rare earth chloride is defined to be equal to the energy per mole required to separate the ions in the solid lattice to gaseous ions an infinite distance apart. When such a salt dissolves in water, the crystal lattice is destroyed and the ions are separated and hydrated. Therefore, differences in the heats of solution at infinite dilution in a series of rare earth trichlorides represent the differences in lattice and hydration energies; thus, such data can be used as part of a Born-Haber thermochemical cycle in evaluating other heat quantities.

A change in crystal structure occurring in a series of salts should manifest itself in a corresponding change in thermodynamic properties. Similarly, when a crystalline substance can exist in more than one crystal system the thermodynamic properties should differ. Accurate thermochemical data would be an invaluable aid in a study of the effects of crystal geometry on physical-chemical properties.

A knowledge of integral heats of solution as a function of concentration would permit calculation of integral heats of dilution in the same concentration range. Since heats of dilution are thermodynamically related to relative partial molar heat contents, these quantities can also be evaluated. In addition, the relative partial molar heat contents are used in expressing the temperature dependence of the activity coefficient.

The only extensive work done in the past on the measurement of the quantities presented in this thesis has been that of Bommer and Hohmann (7, 8). Recent measurements by Spedding and Miller (9, 10) and Lohr and Cunningham (11) indicate significant differences from values reported by Bommer and Hohmann. It, therefore, seemed advisable to extend the work to other members of the rare earth series.

II. GENERAL THERMODYNAMIC THEORY

Thermochemistry is essentially a branch of thermodynamics based on the first law. According to the first law, there exists a property of every thermodynamic system called its energy, E, which is always conserved in an isolated system in every process. The energy may be in the form of thermal, mechanical, potential, or radiant energy, and, although it may be converted from one form to another, it cannot be created nor destroyed. Whenever a quantity of energy of one kind is produced, an exactly equivalent amount of another kind is consumed.

If a system initially has energy equal to E_1 and after a change in energy has an energy E_2, the change in energy is defined by

II-1. $$\Delta E = E_2 - E_1 .$$

If the energy of the system is increased by the addition of a quantity of heat, q, and some of the heat is expended by the system in doing work, w, in one form or another, the final increase in energy of the system is given by the equation

II-2. $$\Delta E = q - w$$

which is a mathematical expression of the first law. The energy change, ΔE, is positive when the internal energy of the system increases; q is positive when the system absorbs heat and w is positive when work is done by the system. The heat and work terms, q and w, differ from the change in energy content in one important regard. The quantity, ΔE, for a given change has a definite value depending only on the initial and final states of the system and is independent of the path taken from the initial to the final state. On the other hand, the values of the heat and work terms vary with the path followed by the system. This is true because q and w are not defined to be thermodynamic properties of the system but only represent different ways in which energy can enter or leave the system.

If the work done by the system is only work of expansion occurring at a constant pressure, P, then $w = P\Delta V$, where ΔV represents the change in volume. The first law can be rewritten as

II-3. $$\Delta E = q - P\Delta V$$

or

II-4. $$q = \Delta E + P\Delta V \ .$$

The thermodynamic heat content function, H, is defined as

II-5. $$H = E + PV$$

and, like the energy content, is independent of path. This is true since both P and V as well as E are properties of the state of the system. Since the energy change ΔE is equal to $E_2 - E_1$ and the volume change, ΔV, is equal to $V_2 - V_1$, Equation II-4 can be written at constant pressure as

II-6. $q = (E_2 + PV_2) - (E_1 + PV_1)$.

Utilizing the definition of H, Equation II-6 becomes

II-7. $q = H_2 - H_1 = \Delta H$

where ΔH represents the change in heat content of the system and q is the observed calorimetric heat of the reaction or process. Thus, for a reaction at constant pressure, the measured increase in heat content is equal to the heat of reaction. In Equation II-7 the sign of q is the same as that of ΔH. The convention among thermochemists is to regard heat absorbed by a system as a negative quantity and heat evolved as a positive quantity. For the thermodynamic development to follow, the convention represented by Equations II-2 and II-7 will be maintained but the thermochemical convention will be used in the presentation of experimental results.

The heat of a chemical reaction is equal to the difference between the total heat content of the products and that of the reactants at constant temperature and pressure. Thus

II-8. $q = \Delta H = \sum_i H_i - \sum_j H_j$

represents the heat change when j reactant molecules react to form *i* product molecules.

The effect of temperature on the heat of reaction at constant pressure can be derived by differentiating Equation II-8 with respect to temperature at constant pressure,

$$\text{II-9.} \quad \left[\frac{d(\Delta H)}{dT}\right]_P = \sum\left(\frac{dH_i}{dT}\right)_P - \sum\left(\frac{dH_j}{dT}\right)_P \quad .$$

The term, $\left(\frac{dH}{dT}\right)_P$, is the rate of change of heat content with temperature at constant pressure and is called the heat capacity and denoted by the symbol, *Cp*. Equation II-9 can therefore be rewritten as

$$\text{II-10.} \quad \left[\frac{d(\Delta H)}{dT}\right]_P = \sum_i C_{Pi} - \sum_j C_{Pj} = \Delta C_P$$

where $\sum C_{Pi}$ and $\sum C_{Pj}$ are the total heat capacities of the products and reactants, respectively, and ΔC_P is the increase in heat capacity accompanying the reaction. To determine the heat of reaction at one temperature if that at another temperature is known, Equation II-10 must be integrated. To perform the integration indicated, the heat capacities should be known as a function of temperature if the integration interval is large. A mean value of ΔC_p is usually taken if the temperature interval is small.

The second law of thermodynamics introduces the concept of the entropy function, *S*. The differential change in entropy for a system is quantitatively equal to the differential heat taken up reversibly by the system divided by the absolute temperature at which the process takes place. A reversible process is one which is carried out in such a manner that the system at all times differs only infinitesimally from the equilibrium condition. For example, the entropy of a substance at a particular temperature can be evaluated from molar heat capacity data since the heat capacity is such a reversible heat effect. Thus, at a temperature, T, the entropy is given by the integral

$$\text{II-11.} \qquad S_T = S_o + \int_o^T \frac{C_P}{T}\, dT$$

where the integration constant, S_o, is the value of the entropy at the absolute zero of temperature. According to the so-called third law of thermodynamics, the value of the integration constant is zero for pure crystalline substances. The entropy change of a chemical reaction is equal to the difference between the total entropy of the products and that of the reactants. Reaction entropies may be calculated from heat capacity data on the products and reactants as indicated above. If the reaction under consideration can be harnessed in a reversible galvanic cell the reaction entropy can be obtained from the temperature coefficient of the generated e.m.f. by means of the relation

$$\text{II-12.} \qquad \Delta S = n \mathcal{F} \frac{dE}{dT}$$

where n is the number of electrons involved in the reaction and $\mathcal{F}$ the value of the faraday. In addition, if the equilibrium constant for the given reaction is known as a function of temperature, the standard entropy change is given by

II-13. $$\Delta S = RT \frac{d\ln K}{dT} - R\ln K$$

where K is the equilibrium constant and R the gas constant.

The true measure of the direction of a chemical reaction is determined by the free energy change of the reaction. At constant temperature and pressure the chemical reaction will proceed spontaneously if the free energy change is negative; if positive, work must be expended to effect the reaction. The free energy function, F, is defined as

II-14. $$F = H - TS$$

where H is the heat content, S the entropy, and T the absolute temperature. The free energy, like the heat content, is a thermodynamic property of the system and its value depends only on the state of the system and not on the path followed by the system in reaching its final state. For a macroscopic change, at constant temperature and pressure, the equation

II-15. $$\Delta F = \Delta H - T\Delta S$$

gives the change in free energy for the process. If the heat and entropy changes for a reaction are known, the free energy change may be calculated from Equation II-15. Alternatively, if the equilibrium constant for the reaction is known, or if the reaction can be made to produce current in a reversible galvanic cell, the free energy change can be calculated from the relationships

II-16. $$\Delta F = - RT\ln K$$

or

II-17. $$\Delta F = - n\mathcal{F}E$$

where the symbols have the significance aforementioned.

In dealing with the heat effects in systems of variable composition it becomes necessary to define a new function called the partial molar heat content. In general, the change in heat content for such a system is given by the total differential

II-18. $$dH = \left(\frac{\partial H}{\partial T}\right)_{P,N} dT + \left(\frac{\partial H}{\partial P}\right)_{T,N} dP + \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_j} dn_i \,.$$

At constant temperature and pressure this becomes

II-19. $$dH = \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_j} dn_i = \bar{H}_i dn_i$$

where $\underline{n_i}$ is the number of moles of component $\underline{i}$ and $\underline{n_j}$ the number of moles of all other components except the $\underline{i\text{-th}}$ one considered in the differentiation. The term $\underline{\bar{H}_i}$ is the rate of change of the heat content of the system with respect to a change in the moles of component _i_ at constant pressure, temperature, and n_j and is called the partial molar heat content of the _i-th_ component. In the case of the binary systems considered in this thesis, the change in heat content is

II-20. $$dH = \overline{H}_1 dn_1 + \overline{H}_2 dn_2$$

where n_1 is the moles of solvent and n_2 the moles of solute. General integration of Equation II-20 gives

II-21. $$H = n_1\overline{H}_1 + n_2\overline{H}_2$$

as the total heat content of the system at constant temperature and pressure. Since it is not yet possible to determine heat contents in an absolute sense, values must be considered relative to a reference state. For the solvent the reference and standard states are identical, _viz._, pure liquid at one atmosphere pressure; for the solute the reference state is the infinitely dilute solution at one atmosphere pressure. Designating the values of the partial molar heat contents in the reference states as $\overline{H}_1^{\circ}$ and $\overline{H}_2^{\circ}$, the relative partial molar heat contents become

II-22. $$\overline{L}_1 = \overline{H}_1 - \overline{H}_1^{\circ}$$

for the solvent, and

II-23. $$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^{\circ}$$

for the solute. Combining Equations II-22 and II-23 with Equation II-21,

II-24. $$H - (n_1\bar{H}_1^{\circ} + n_2\bar{H}_2^{\circ}) = n_1\bar{L}_1 + n_2\bar{L}_2 \; .$$

Since the quantity $n_1\bar{H}_1^{\circ} + n_2\bar{H}_2^{\circ}$ is the reference value for the total heat content of the system, the left-hand side represents the total relative heat content, L, that is,

II-25. $$L = n_1\bar{L}_1 - n_2\bar{L}_2 \; .$$

Partial molar thermal properties are most often evaluated from experimental heats of solution and dilution. When one chemical substance dissolves in another, as a crystalline salt in water, the change in heat content is given by

II-26. $$\Delta H = H - (n_1H_1 + n_2H_2)$$

where H is the heat content of the solution and H_1 and H_2 are the molar heat contents of the pure solvent and solute. The value of ΔH divided by n_2 so as to give the value per mole of solute is called the integral heat of solution. In general, as the ratio n_1/n_2 increases, the molar value of ΔH approaches a limit called the integral heat of solution at infinite dilution. This quantity is a property of the particular solute and solvent at a specified temperature and pressure. The integral heat of dilution is the change in heat content per mole of solute when a solution is diluted from one concentration to another and is equal to the difference between the integral heats of solution in the initial and final states. The differential heat of solution is obtained by differentiating Equation II-26 with respect to n_2 while the temperature, pressure, and n_1 are maintained constant. Hence,

II-27. $$\left[\frac{\partial(\Delta H)}{\partial n_2}\right]_{T,P,n_1} = \left(\frac{\partial H}{\partial n_2}\right)_{T,P,n_1} - H_2 \quad .$$

By definition, the first term on the right is the partial molar property, $\bar{H}_2$, and therefore

II-28. $$\left[\frac{\partial(\Delta H)}{\partial n_2}\right]_{T,P,n_1} = \bar{H}_2 - H_2 \quad .$$

The quantity, $\bar{H}_2 - H_2$, is the differential heat of solution of the solute and represents the increase in heat content per mole of solute when it is dissolved in a large volume of solution so that there is no appreciable change in concentration. If the term, $\bar{H}_2^{\circ}$, is added and subtracted from Equation II-28, the corresponding relative property is obtained, that is,

II-29. $$\bar{H}_2 - H_2 = (\bar{H}_2 - \bar{H}_2^{\circ}) - (H_2 - \bar{H}_2^{\circ})$$

or

II-30. $$\overline{H}_2 - H_2 = \overline{L}_2 - L_2 ,$$

where $\overline{L}_2$ is the relative partial molar heat content of the solute in the solution and L_2 the differential heat of solution at infinite dilution.

Apparent molar properties, although having no thermodynamic significance of their own, are useful in evaluating partial molar properties since they are more closely related to actual experiment (12). In the case of the heat content, the apparent property, ϕ_H, is defined as

II-31. $$\phi_H = \frac{H - n_1\overline{H}_1^{\circ}}{n_2}$$

at constant temperature and pressure and is understood to refer to the solute. In the reference state of infinite dilution Equation II-21 becomes

II-32. $$H^{\circ} = n_1\overline{H}_1^{\circ} + n_2\overline{H}_2^{\circ}$$

or, in terms of the apparent heat content

II-33. $$H^{\circ} = n_1\overline{H}_1^{\circ} + n_2\phi_H^{\circ}$$

showing that

II-34. $$\phi_H^{\circ} = \overline{H}_2^{\circ} .$$

In terms of the relative apparent property,

II-35. $$L = H - H^{o} = n_1\overline{H}_1^{o} + n_2\phi_H - n_1\overline{H}_1^{o} - n_2\phi_H^{o}$$
$$= n_2(\phi_H - \phi_H^{o}) = n_2\phi_L$$

where ϕ_L is the relative apparent molar heat content. From this relation it is seen that ϕ_L is equal in magnitude but opposite in sign to the heat of dilution to infinite dilution. The relation can be restated as

II-36. $$L = n_1\overline{L}_1 + n_2\overline{L}_2 = n_2\phi_L \quad .$$

The evaluation of the partial molar property is illustrated by differentiation of Equation II-36 with respect to n_2 at constant temperature, pressure, and n_1 so that

II-37. $$\left(\frac{\partial L}{\partial n_2}\right)_{T,P,n_1} = \overline{L}_2 = \phi_L + n_2\left(\frac{\partial \phi_L}{\partial n_2}\right)_{T,P,n_1} \quad .$$

Therefore, from a plot of ϕ_L versus n_2 one can determine the slope $d\phi_L/dn_2$ and thereby the value of $\overline{L}_2$ at a given concentration. If this value of $\overline{L}_2$ is substituted in Equation II-36 one obtains

II-38. $$\overline{L}_1 = -\frac{n_2^2}{n_1}\left(\frac{\partial \phi_L}{\partial n_2}\right)_{T,P,n_1}$$

so that the relative partial molar heat content of both components can be determined from the same data.

The apparent molar heat content is useful also in dealing with reactions in solution where it is necessary to consider the complete heat content contribution of each dissolved substance. If Equation II-26 is combined with Equation II-31 it is seen that

$$\text{II-39.} \qquad \phi_H = \frac{\Delta H + n_2 H_2}{n_2}$$

where H_2 is the molar heat content of the solute, *viz.*, its heat of formation, and ΔH its heat of solution.

A simultaneous extension of the Debye-Huckel interionic attraction theory by Adams (13) and Bjerrum (14) predicts the heat of dilution of very dilute solutions of strong electrolytes. Bjerrum showed that the sign of the limiting heat of dilution depends upon the dielectric properties of the solvent, and that all salts dissolved in dilute aqueous solutions should liberate heat on infinite dilution. The amount of heat depends upon the properties of the solvent and the valence type of the salt. Scatchard (15) pointed out that the heat of dilution at constant pressure also involves the thermal expansibility of the solvent. He showed that the limiting law at low concentrations for the electrical contribution to the relative apparent molal heat content of a strong electrolyte is

$$\text{II-40.} \qquad \phi_L = -A\left(1 + \frac{d\ln D}{d\ln T} + \frac{1}{3}\alpha T\right)\frac{\left(\sum \nu_i z_i^2\right)^{3/2}}{D^{3/2}\,T^{1/2}} \quad c^{1/2} \; .$$

In this equation, $A = (N^3\epsilon^6/1000\,k)$, N is Avogadro's number, ϵ the charge of the electron, k is Boltzmann's constant, D is the dielectric constant of the solvent, T the absolute temperature, α the coefficient of thermal expansibility of the solvent, ν_i the number of ions of the *i-th* kind, with charge z_i, and C is the molarity. The term, $(\sum \nu_i z_i^2)^{3/2}$, is the valence factor.

III. THE CALORIMETRIC METHOD

A. Introduction

Heats of formation and of reactions are usually determined by a calorimetric method. The reaction to be investigated is carried out in an apparatus of known heat capacity, the calorimeter, so that the heat effect is measured by the change in temperature during the reaction.

Two quantities are determined in all calorimetric experiments, viz., the change in temperature during the experiment and the water equivalent of the calorimeter which is found by calibration. In addition, it is essential to know as precisely as possible what amount of substance takes part in the reaction and to ensure that no secondary reactions occur.

The heat capacity of the calorimeter is determined as its water equivalent. Theoretically this is the sum of the heat capacities of all the constituent parts of the calorimeter. In practice, however, the water equivalent is always determined experimentally. The water equivalent multiplied by the change in temperature, with appropriate corrections, then gives directly the heat change of the reaction.

Calorimeters are of two types; isothermal and adiabatic. In the isothermal method the outer jacket of the calorimeter is kept at a constant temperature and the temperature in the calorimeter vessel is observed at frequent intervals before, during, and after the reaction. In the adiabatic method, the temperature of the calorimeter jacket is controlled as close as possible to that of the calorimeter vessel during the reaction period so that there are no significant heat losses due to radiation and convection.

The design, construction, and advantages and disadvantages of the two types of calorimeter systems have been adequately set forth by White (16) and Swietoslawski (17). In general, comparative rather than absolute measurements are made in either case. The adiabatic method is used when small heat effects are being measured or when the heat effect is one of long duration. Rapid reactions proceeding to completion in less than fifteen minutes are more conveniently run in isothermally jacketed calorimeters. Among the best of modern adiabatic calorimeters designed for measuring very small heat quantities are those of Lange and his co-workers (18, 19, 20) and of Gucker, Pickard, and Planck (21).

The isothermally jacketed calorimeter was used in obtaining the data for this thesis for the following reasons: 1) it is more simple in design and construction than an adiabatic calorimeter of equal precision; 2) the reactions studied were rapid chemical processes proceeding to completion in a few minutes; and 3) the heat effects measured were fairly large in magnitude so that the heat leak corrections in general constituted one percent or less of the total rise in temperature. An adiabatic calorimeter under conditions 2) and 3) simultaneously would be difficult if not impossible to operate satisfactorily.

B. Theory of the Isothermal Calorimeter

The following theory of the isothermally jacketed calorimeter and the heat leak corrections involved is that described by Coops, van Nes, Kentie and Dienske (22), Jessup (23), and King and Grover (24).

If there is a development of heat, $\underline{q_o}$, in the calorimeter occurring between the times $\underline{t_o}$ and $\underline{t_m}$, the total rise in temperature is $\underline{\theta_m - \theta_o}$. Neglecting second order corrections the heat developed may be split up as follows:

III-1. $$W(\theta_m - \theta_o) = q_o + Q_u + Q_r + Q_t$$

where $\underline{Q_u}$ represents the heat exchanged with the surroundings and $\underline{Q_r}$ the heat due to stirring; $\underline{W}$ is the energy equivalent of the calorimeter; and $\underline{Q_t}$ the heat added to the calorimeter due to the passage of electrical current through the windings of the thermometer. In the experimental work performed for this thesis the stirring and thermometer current were maintained constant during both calibration and heat of solution experiments, and it was assumed that their contribution to the heating of the calorimeter was effectively cancelled by calibration. The effect of $\underline{Q_r}$ and $\underline{Q_t}$ will therefore not be given further discussion. The heat exchange with the surroundings, $\underline{Q_u}$, will now be considered in detail.

The calorimeter temperature is assumed to consist of two terms. The first, the heating function, depends in general on the temperature difference between the heat source and the calorimeter fluid. The second, the cooling function, depends on the difference between the calorimeter and jacket temperatures.

III-2. $$\frac{d\theta}{dt} = F(\theta_s - \theta) + f(\theta - \theta_j)$$

where

θ_s = temperature of heat source

θ_j = jacket temperature

θ = calorimeter temperature.

The two functions are expanded in power series:

III-3. $$F(\theta_s - \theta) = h + b(\theta_s - \theta) + \ . \ . \ .$$

III-4. $$f(\theta - \theta_j) = g - G(\theta - \theta_j) + \ . \ . \ .$$

Higher terms are negligible if proper experimental precautions are taken. The constants $\underline{h}$ and $\underline{b}$ depend on the particular experiment. The term, $\underline{- G(\theta - \theta_j)}$, is an expression of Newton's Law of Cooling, the constant $\underline{G}$ being the cooling coefficient. With good calorimeter construction Newton's Law is a fair approximation to the cooling correction. The term, $\underline{g}$, is almost entirely dependent on the heat due to stirring.

Assume that $\underline{g}$, $\underline{\theta_j}$, and $\underline{G}$ are constant and define a temperature, $\underline{\theta_k}$, such that the following relation holds:

III-5. $$f(\theta - \theta_j) = -G(\theta - \theta_k) .$$

The temperature, $\underline{\theta_k}$, is that temperature to which the calorimeter system would converge if left to itself with constant stirring and is called the convergence temperature.

In an experiment the observed rise in temperature is $\underline{\theta_m - \theta_o}$. Since there is a heat exchange with the surroundings the true temperature rise, $\underline{\Delta\theta_t}$, is

III-6. $$\Delta\theta_t = (\theta_m - \theta_o) + C$$

where $\underline{C}$ represents the correction.

Representing the heating function generally by

III-7. $$F(\theta_s - \theta) = F(t)$$

and combining Equations III-2, III-5, and III-7,

III-8. $$\frac{d\theta}{dt} = F(t) - G(\theta - \theta_k) .$$

During the fore period of an experiment, that is, before heat is introduced either electrically or by solution of a sample, $\underline{F(t)} = 0$ and

III-9. $$\frac{d\theta}{dt} = -G(\theta - \theta_k) .$$

Integration of Equation III-9 between limits, $\underline{\theta_1'}$ and $\underline{\theta_2'}$, and $\underline{t_1'}$ and $\underline{t_2'}$, in the fore period gives the following:

III-10. $$\int_{\theta_1'}^{\theta_2'} \frac{d\theta}{(\theta - \theta_k)} = -G \int_{t_1'}^{t_2'} dt ,$$

III-11. $$\ln \frac{\theta_2' - \theta_k}{\theta_1' - \theta_k} = -G(t_2' - t_1') ,$$

III-12. $$\frac{\theta_2' - \theta_k}{\theta_1' - \theta_k} = e^{-G(t_2' - t_1')} .$$

A similar equation can be derived for the after period. Hence, by rearranging

III-13. $$\theta_1' = \theta_k + (\theta_2' - \theta_k)\, e^{\overset{\text{should be } +}{-}G(t_2' - t_1')} .$$

III-14. $$\theta_1'' = \theta_k + (\theta_2'' - \theta_k)\, e^{\overset{\text{should be } +}{-}G(t_2'' - t_1'')} .$$

During the heating period, $\underline{F(t)} \neq 0$, and

III-15. $$\int d\theta_t = \int F(t)dt - \int G(\theta - \theta_k)dt .$$

III-16. $$\Delta\theta_t = \int_{t_o}^{t_m} F(t)dt - \int_{t_o}^{t_m} G(\theta - \theta_k)\, dt$$

where t_o is the time at which the heat was introduced and t_m the time at which the calorimeter first reached a steady state in the after period. If Equation III-16 is integrated from t_o to t_m, the first integral is equal to $\Delta\theta$ and the second integral is equal to the correction term

III-17. $$C = -\int_{t_o}^{t_m} G(\theta - \theta_k)dt \ .$$

In order to evaluate the integral in Equation III-17, θ must be known as a function of t. In the case of an electrical calibration the rise in temperature is linear and can be expressed by an equation

III-18. $$\theta = at + b \ .$$

The slope, a, is

III-19. $$a = \frac{\theta_m - \theta_o}{t_m - t_o}$$

and b can be evaluated by choosing $\theta = \theta_m$ at $t = t_m$:

III-20. $$\theta_m = \frac{\theta_m - \theta_o}{t_m - t_o} \quad t_m + b \ ,$$

III-21. $$b = \frac{\theta_m(t_m - t_o) - (\theta_m - \theta_o)t_m}{t_m - t_o} \ .$$

Therefore, the linear temperature rise during calibrations is given by

$$\text{III-22.} \qquad \theta = \frac{\theta_m - \theta_o}{t_m - t_o}\, t + \frac{\theta_m(t_m - t_o) - (\theta_m - \theta_o)t_m}{t_m - t_o} \; .$$

If the value of θ given in Equation III-22 is put into the integral in Equation III-17 and integration performed between the limits t_o and t_m one obtains

$$\text{III-23.} \qquad C = -G(t_m - t_o)\left\{\frac{\theta_m + \theta_o}{2} - \theta_k\right\} .$$

Therefore, in an electrical calibration experiment the corrected temperature rise is given by

$$\text{III-24.} \qquad \Delta\theta_t = (\theta_m - \theta_o) - G(t_m - t_o)\left\{\frac{\theta_m + \theta_o}{2} - \theta_k\right\} .$$

To use Equation III-24 the cooling constant, G, and the convergence temperature, θ_k, must be known. Both G and θ_k can be evaluated from data on the fore and after periods. From Equation III-9

$$\frac{d\theta'}{dt} = -G(\theta - \theta_k)$$

$$\frac{d\theta''}{dt} = -G(\theta - \theta_k) \; .$$

Therefore, if temperature versus time data ~~is~~ are taken in the fore and after periods, both G and θ_k can be calculated from two simultaneous equations

$$\text{III-25.} \qquad \left(\frac{d\theta'}{dt}\right)_{\theta_1} = g_1 = -G(\theta_1 - \theta_k) \; ,$$

and

III-26. $$\left(\frac{d\theta''}{dt}\right)_{\theta_2} = g_2 = -G(\theta_2 - \theta_k) ,$$

from which

III-27. $$G = \frac{g_1 - g_2}{\theta_2 - \theta_1}$$

and

III-28. $$\theta_k = \frac{g_1\theta_2 - g_2\theta_1}{g_1 - g_2} .$$

In a heat of solution experiment the heat supplied to the calorimeter does not give a linear temperature rise and the mean temperature cannot be used in calculating the correction term. In the method of Dickinson (25) used in this thesis the integral

III-17. $$C = \int_{t_o}^{t_m} G(\theta - \theta_k)dt$$

is evaluated by choosing a time, $\underline{t_x}$, such that

III-29. $$g_1(t_x - t_o) + g_2(t_m - t_x) = G\int_{t_o}^{t_m} (\theta - \theta_k)dt$$

or

III-30. $$G\int_{t_o}^{t_m} (\theta - \theta_k)dt = G\int_{t_o}^{t_x} (\theta - \theta_k)dt + G\int_{t_x}^{t_m} (\theta - \theta_k)dt .$$

This condition will be satisfied if $\underline{t_x}$ is so chosen that the shaded areas in Figure 1 are equal. That is,

$$\text{III-31.} \quad - G \int_{t_o}^{t_x} (\theta_o - \theta_k)dt + G \int_{t_x}^{t_m} (\theta_m - \theta_k)dt = 0 .$$

The temperature correction term is now given by

$$\text{III-32.} \quad C = - g_1(t_x - t_o) - g_2(t_m - t_x)$$

where

g_1 = slope of fore period

g_2 = slope of after period .

The time $\underline{t_x}$ was evaluated by Dickinson (25) by assuming the temperature rise to follow an exponential law of the form

$$\text{III-33.} \quad \theta = 1 - e^{-kt} .$$

From Equation III-33 the time $\underline{t_x}$ may be calculated by imposing the condition that it must produce equal areas as originally postulated. Assume that $\underline{\theta_o} = 0$, $\underline{\theta_k} = 0$, and $\underline{\theta_m} = 1$. For the condition of equal areas

$$\text{III-34.} \quad \int_0^{t_x} (1 - e^{-kt})dt = \int_{t_x}^{\infty} \left[1 - (1 - e^{-kt})\right] dt .$$

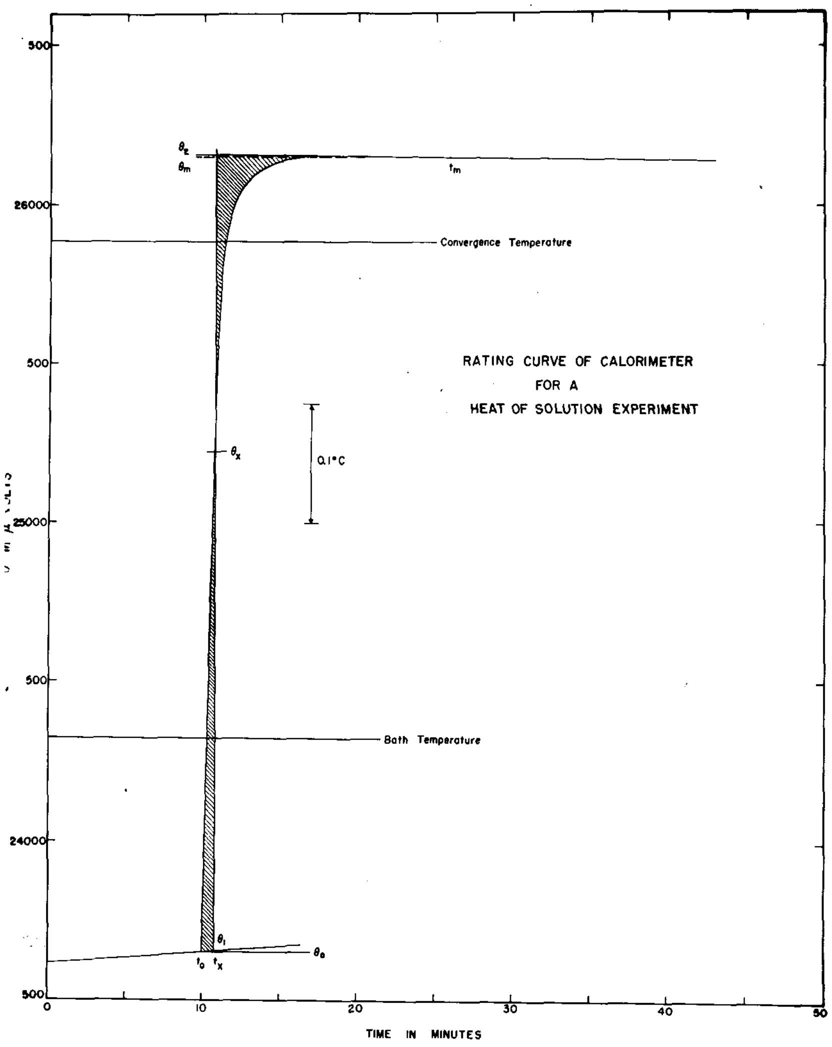


Figure 1. Typical Curve for a Heat of Solution Experiment.

Integration and simplification of Equation III-34 gives

III-35. $$t_x = \frac{1}{k} ,$$

and, therefore,

III-36. $$\theta_x = 1 - e^{-\frac{k}{k}} = 0.63 .$$

Thus, the time observed when the temperature rise has reached 0.63 of its final value can be used as the value of $\underline{t_x}$. The corrected temperature rise for a heat of solution experiment using the method of Dickinson becomes

III-37. $$\Delta\theta_t = (\theta_m - \theta_o) - g_1(t_x - t_o) - g_2(t_m - t_x) ,$$

which, according to Dickinson, introduces an error no greater than 1 part in 10,000 if 0.60 is used rather than 0.63.

C. Apparatus

The calorimeter used in this work was similar to those built by Maier (26) and Southard (27). Figure 2 is a photograph of the apparatus and Figure 3 a schematic diagram. The calorimeter vessel was a two-quart Dewar flask sealed onto a brass flange with Àpiezon-W wax. The wax seal was protected by a layer of Scotch electrical tape. The Dewar flask was held in place by six brass bolts through holes in the brass plate. A second brass plate served as a mount for brass tubes which housed a stirrer shaft, breaker assembly, and

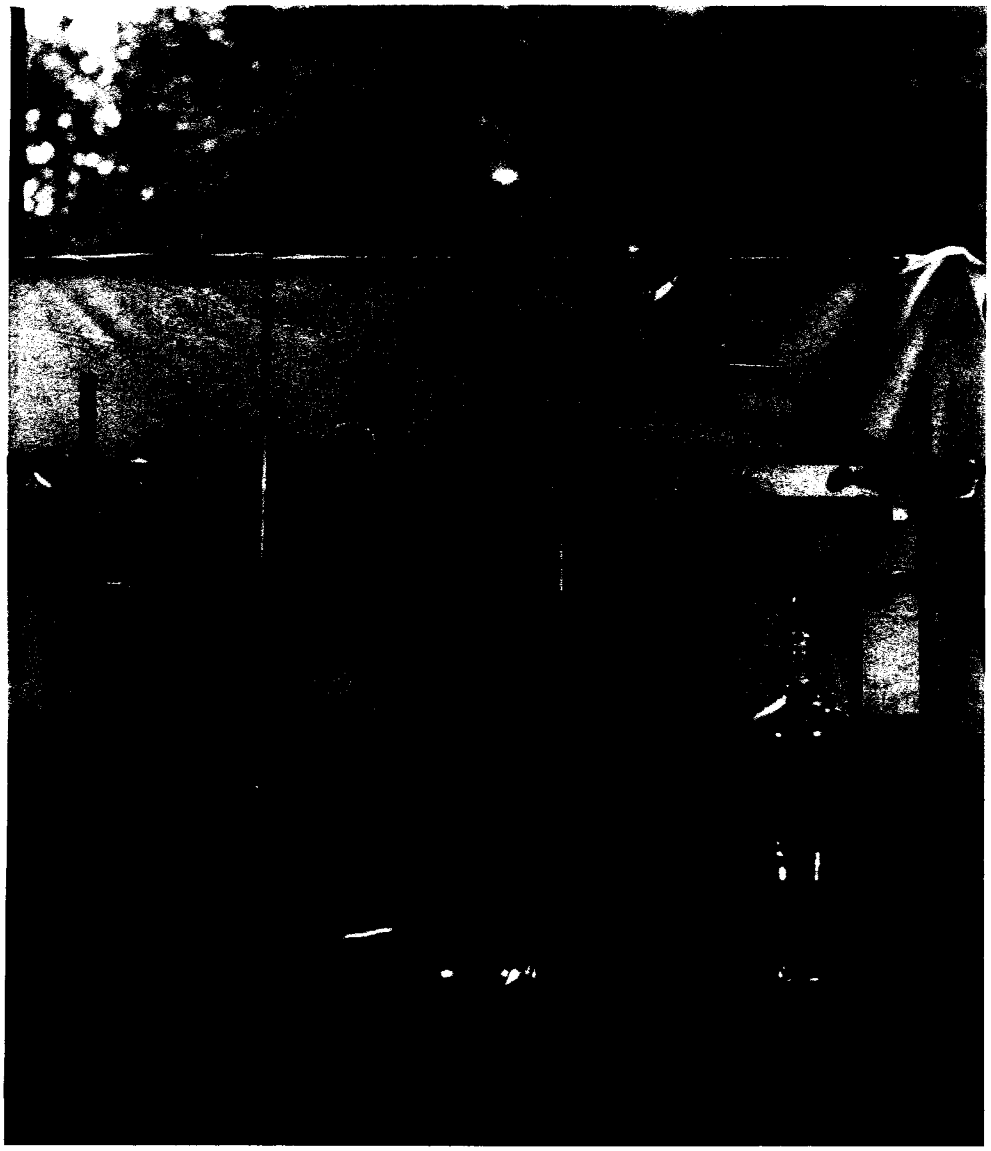


Figure 2. Photograph of Calorimeter and Accessories.

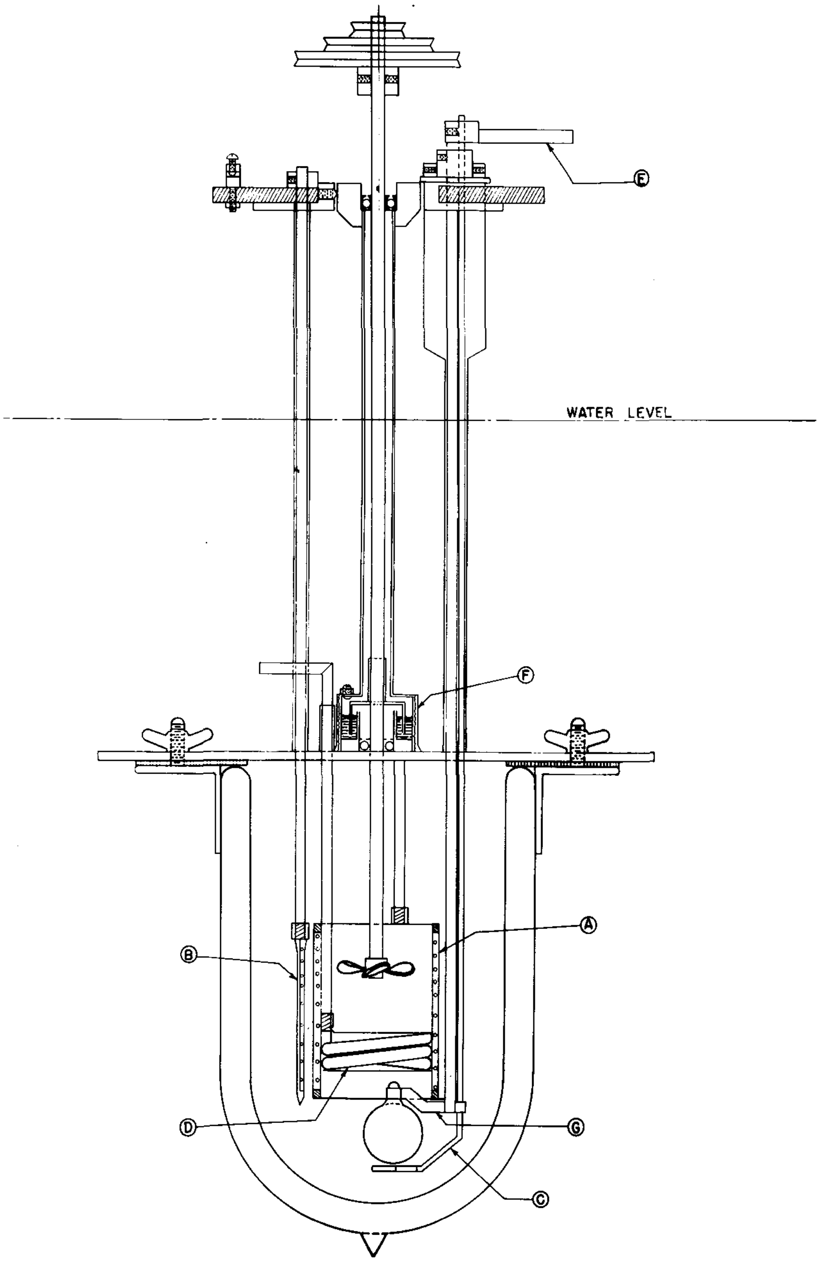
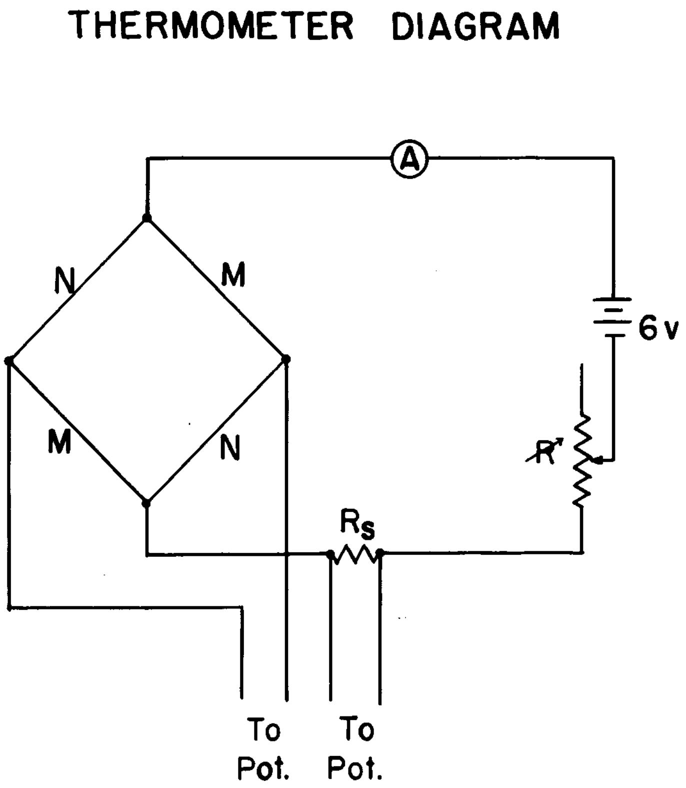


Figure 3. Schematic Diagram of Calorimeter.

cooling coil and electrical leads. The brass tubes were silver soldered to the brass plate. The two brass plates were separated by a one-quarter inch soft rubber gasket. The thermometer (A) was very similar to Maier's transposed bridge type (28). It consisted of four resistances, alternately manganin and nickel. Nickel was used rather than the copper used by Maier because of its greater temperature coefficient of resistivity. Such a bridge arrangement is in balance only at one temperature. The amount of unbalance at other temperatures was measured potentiometrically with a White double potentiometer as an indicator of the temperature rise of the calorimeter. The second circuit of the White double potentiometer was used to maintain a constant current through the thermometric bridge by balancing the drop across a standard 10 ohm resistance against a fixed voltage setting on the potentiometer. Each bridge arm had a resistance of about 250 ohms and a set current of about 5 milliamperes was maintained. The sensitivity of the thermometer was approximately 3×10^{-4} degree per microvolt under these conditions. The e.m.f. across the thermometer was recorded to 0.1 microvolt by utilizing galvanometer deflections. A Leeds and Northrup high-sensitivity galvanometer with a sensitivity of 0.1 microvolt per millimeter deflection was used for temperature measurements. The thermometer was wound with No. 38 AWG enameled manganin wire and No. 36 AWG silk covered nickel wire on a thin-walled copper cylindrical tube previously insulated with a thin layer of bakelite varnish baked at 110° C. A second thin-walled copper tube was soldered over the first through two heavier copper end rings so as to form a jacket for the thermometer windings. The air space left in the thermometer jacket was filled with paraffin to increase the thermal conductivity of the unit. Two drilled and tapped copper lugs were soldered onto the upper copper end ring of the jacket and threaded polystyrene tubes fastened into the lugs. Both potential and current leads from the inner thermometer windings were brought out through the polystyrene tubes. When completely assembled the polystyrene tubes passed up through the brass tubes soldered on the upper brass plate. The thermometer was calibrated by comparing the e.m.f. drop across the thermometer with the temperature indicated by a platinum resistance thermometer. The thermometer circuit diagram is given in Figure 4.

A knife heater (B) of 110 ohms of No. 26 AWG manganin wire was made by winding the wire on a strip of mica and encasing it in a copper sheath. A drilled and threaded polystyrene tube was fastened to a tapped copper lug at the top of the copper sheath to house potential and current leads. The heater was used to add measured amounts of electrical energy to the calorimeter.

For heat of solution experiments a holder (G) was provided for as many as three sample bulbs. Sample bulbs were



N = Nickel
M = Manganin
R = 10,000 decade box plus 1 ohm slide wire
R_s = 10 ohms
A = Milliammeter

Figure 4. Thermometer Circuit Diagram.

fastened to the holder by means of Apiezon-W wax. The sample holder was supported by a three-sixteenths inch stainless steel rod which passed up through one of the brass tubes soldered to the upper brass plate. Sample bulbs were broken by a one-eighth inch stainless steel rod with a crook at the end (C). The breaker rod passed up through the same brass tube as the sample holder rod and was held at the top of the calorimeter by a notched brass lug (E) fastened to the rod by set screws.

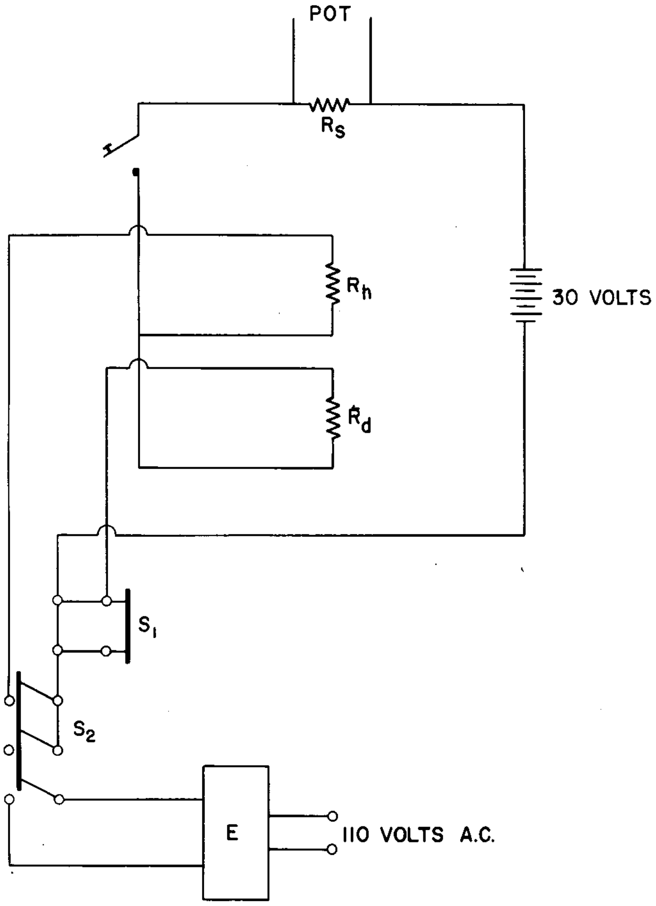
A multivaned propeller was mounted at the end of a one-fourth inch stainless steel rod. The stirrer shaft was supported by oil-seal bearings (F). A constant stirring rate of 540 r.p.m. was provided by an adjustable synchronous motor. A cooling coil (D) of one-fourth inch copper tubing was held in place by two polystyrene tubes which passed to the exterior of the calorimeter through two brass tubes.

All metal parts of the calorimeter assembly were painted with acid-resistant Ajax varnish. The underside of the upper brass plate was tin plated and polished to provide a radiating surface.

The energy input during calibration experiments was measured by reading the e.m.f. drop across a 0.1 ohm Reichsanstalt type standard resistor calibrated by the National Bureau of Standards. The standard resistor was kept in an oil bath at 25° C. Readings of the e.m.f. drop were taken every 25 seconds and the total time of energy input was read off an electronic timer accurate to 0.001 second. The frequency of the crystal oscillator used in the electronic timer was compared to the frequency of the National Bureau of Standards Station WWV. The e.m.f. drop was measured by a Leeds and Northrup type K-2 potentiometer. Direct current was supplied by five Willard storage batteries in series. The electrical circuit is given in Figure 5.

The resistance of the calorimeter heater was measured by comparing it with a 100 ohm standard resistor calibrated by the National Bureau of Standards. The e.m.f. drop across the heater resistance was compared with that across the standard while the same current was flowing through the two in series. In experimental work the resistance of the heater was assumed constant for calculations of energy inputs. The resistance of the heater did not change significantly over long periods of time. An original measurement gave 109.9614± 0.0001 ohms as the resistance value and a second measurement seven months later gave 109.9662±0.0001 ohms representing an increase of 0.005 percent.

A Mueller G-2 type temperature bridge calibrated according to the specifications of the National Bureau of Standards was used in measuring the resistance of the platinum resistance thermometer. The isothermal jacket for the calorimeter was provided by a 100 gallon water bath held



CIRCUIT FOR ELECTRICAL CALIBRATIONS

R_h = CALORIMETER HEATER
R_d = DUMMY HEATER
R_s = STANDARD 0.1 OHM RESISTANCE
POT = K-2 POTENTIOMETER
E = ELECTRONIC TIMER
S_1 = SWITCH; NORMALLY CLOSED
S_2 = SWITCH; NORMALLY OPEN

Figure 5. Circuit Diagram for Electrical Calibrations.

at 25.00±0.01°C.

D. Preparation of Materials

The rare earth metals and oxides used in this work were obtained from the metallurgical and ion exchange sections of this Laboratory under the supervision of Dr. F. H. Spedding. Table 1 gives the results of spectrographic analyses of the rare earth materials.

The hydrated chlorides were prepared by slow crystallization from slightly acid solutions. The solutions were first rapidly evaporated on a hot plate until near saturation was reached. They were then transferred to 250 ml. beakers and placed in a vacuum desiccator. The desiccator was evacuated occasionally until the first crystals appeared. The supernatant liquid was then transferred to another 250 ml. beaker and one of the larger crystals added to seed the saturated solution. The beakers containing the seeded solutions were then placed in desiccators freshly charged with anhydrous calcium chloride and the crystals allowed to grow slowly over a period of from six to ten months. The crystals obtained in this manner were quite large and beautifully formed. A single crystal of samarium chloride measured one and three-fourths inch across and three-fourths of an inch high. The crystals were washed with absolute alcohol to remove excess supernatant liquid and then crushed thoroughly in a porcelain

Table 1. Analysis of Materials

Substance	Spectrographic Analysis*
Yttrium metal	Dysprosium 0.3%; erbium 0.03%; terbium 0.3%; iron and calcium weak; no other rare earths detected.
Yttrium oxide	Dysprosium oxide 0.2%; thorium oxide 0.1%; no other rare earths detected.
Lanthanum metal	Iron 70 p.p.m.; calcium less than 0.04%; no other rare earths detected.
Lanthanum oxide	No other rare earths detected.
Praseodymium metal	Calcium and iron weakly detected; other rare earths not detected.
Praseodymium oxide	Praseodymium oxide greater than 99.9%; other rare earths, iron and calcium weakly detected.
Samarium oxide	Samarium oxide greater than 99.9%; europium oxide 0.04-0.05%; no other rare earths detected.
Gadolinium metal	Dysprosium 0.05%; yttrium 0.03%; no other rare earths or iron detected; calcium less than 0.04%.
Gadolinium oxide	Terbium 0.04%; samarium 0.04%; no other rare earths.
Erbium metal	Faint traces of calcium and magnesium; iron and other rare earths not detected.
Erbium oxide	Erbium oxide greater than 99.9%; no other rare earths detected.
Ytterbium oxide	Ytterbium oxide greater than 99.8%; approx. 0.2% dysprosium and 0.02% terbium.

* The limit of detection of the rare earths was about 0.02 to 0.03 percent; that for common elements about 0.01 percent.

mortar. The crushed crystals were put in a sintered-glass bottomed filtering funnel and dry argon passed through the stem of the funnel and up through the bulk of the crystals. This procedure served to remove any hydrogen chloride and water trapped by the crystals and any alcohol remaining from the washing. The crystals were ground again in the mortar and given a final drying with argon gas before they were sealed in a clean dry jar. The hydrate, $PrCl_3 \cdot 6H_2O$, was prepared by desiccating powdered $PrCl_3 \cdot 7H_2O$ crystals over calcium chloride.

The anhydrous chlorides were prepared by dissolving the oxides in hydrochloric acid, crystallizing the resulting solutions and drying the hydrated crystals in an atmosphere of hydrogen chloride. The formation of oxychlorides during the drying operation became increasingly troublesome as the atomic number of the rare earth increased. Erbium and ytterbium were difficult and yttrium the most difficult to prepare free of oxychloride. To prevent the formation of oxychlorides and obtain pure anhydrous chlorides, the following procedure was used: After solution of the oxide in hydrochloric acid,the chloride solution was evaporated on a hot plate at 60°C to near saturation. A few milliliters of concentrated hydrochloric acid were added at this point to insure the acidity of the solution. The beaker of solution was then placed in a vacuum desiccator which was continually evacuated until a sufficiently large crop of hydrated crystals had formed to make a slurry of crystals and supernate.

The crystal slurry obtained above was transferred to a pyrex drying tube and placed in a resistance furnace for drying. One end of the drying tube was connected to a water trap and thence to a water aspirator by a piece of rubber pressure tubing. The other end of the tube was connected to a series of three traps by means of glass ball and socket joints. The series of traps terminated in a hydrogen chloride generator. The generator was comprised of a three-liter glass bottle and a 500 milliliter glass bulb which fitted onto the top of the bottle by means of a ground glass tapered joint. To charge the generator, two liters of c.p. hydrochloric acid were placed in the glass bottle and 400-500 milliliters of concentrated c.p. sulfuric acid in the glass bulb. Hydrogen chloride was generated by dropping the concentrated sulfuric acid into the hydrochloric acid through a stopcock provided in the stem of the bulb. The generated gas was pulled through a sulfuric acid bubbler and two calcium chloride traps to remove water before it entered the drying tube.

The temperature of the furnace was initially set at 40°C and all excess water from the original slurry of crystals driven off while a flow of hydrogen chloride was maintained. The temperature was then increased to about 80°C and this temperature maintained until no more water was seen condensing in the trap at the end of the drying tube. The temperature was next taken to about 130-140°C and maintained until no more water was being removed. At this time the major portion of the water was removed and only about one water of hydration remained in the crystals. To remove the final water the furnace temperature was increased to 360-400°C. After the temperature of the furnace had reached its upper value, the generation of hydrogen chloride was discontinued and argon gas allowed to pass over the anhydrous chloride while it cooled to room temperature. The argon was cleaned of any hydrocarbons by passing the gas over uranium turnings at 400°C and through a sulfuric acid bubbler. The use of argon during cooling removed excess hydrogen chloride from the salt and maintained a dry inert atmosphere while the salt was cooling. After the salt had cooled to room temperature, the ends of the drying tube were sealed with glass caps and the tube taken to a dry box where the salt was transferred to a clean dry glass jar. Samples for heat of solution measurements were made up from this supply.

The rare earth ions were analyzed by precipitating weighed amounts of the hydrated chlorides or solutions of the chlorides with oxalic acid and igniting the filtered oxalate in porcelain crucibles overnight at 800°C. The chloride contents of the hydrated and anhydrous chlorides and the hydrochloric acid solutions were determined gravimetrically.

The silver chloride procedure recommended by Willard and Furman (29) was used. Either weighed amounts of the salt were dissolved in water or weighed portions of solutions were used. All weighings were corrected to weight in vacuo. Analytical data on the hydrated and anhydrous chlorides are given in Table 2.

Samples for heat of solution measurements were prepared in pyrex glass bulbs with two inch stems blown from six millimeter tubing. The bulbs were rinsed with acetone and dried at 110°C before being used. After weighing, the bulbs were taken to a dry box where they were loaded with sample material in a dry helium atmosphere. Metal samples were prepared from turnings off blocks of metal by using a jeweler's lathe mounted in a dry box with a helium atmosphere. After loading, the bulbs were stoppered, removed from the dry box and sealed off about an inch from the bulb by heating the stem with a gas-oxygen torch. The bulbs were cleaned again before final weighing by dipping them in acetone and drying in air. The weight of material was obtained by difference and corrected to weight in vacuo.

E. Experimental Procedure

For an actual experiment the sample bulbs were waxed onto the sample holder and the unit assembled to the calorimeter proper. The notched brass terminal of the breaker rod

Table 2. Analysis of Rare Earth Salts

Material	Cl/R	H_2O/RCl_3
YCl_3	3.002±0.003	- - -
$YCl_3 \cdot 6H_2O$	- - -	5.98±0.01
$LaCl_3$	3.004±0.002	- - -
$LaCl_3 \cdot 7H_2O$	- - -	7.06±0.01
$PrCl_3$	2.997±0.003	- - -
$PrCl_3 \cdot 6H_2O$	- - -	6.15±0.02
$PrCl_3 \cdot 7H_2O$	- - -	7.03±0.01
$SmCl_3$	3.002±0.003	- - -
$SmCl_3 \cdot 6H_2O$	- - -	6.03±0.01
$GdCl_3$	2.998±0.001	- - -
$GdCl_3 \cdot 6H_2O$	- - -	5.99±0.01
$ErCl_3$	3.001±0.001	- - -
$ErCl_3 \cdot 6H_2O$	- - -	6.07±0.01
$YbCl_3$	2.996±0.003	- - -
$YbCl_3 \cdot 6H_2O$	- - -	6.07±0.01

was set so as to bring the breaker into position under the first bulb. About 1100 to 1200 grams of distilled water weighed to the nearest milligram were then delivered to the two quart Dewar flask and the flask immediately bolted to the upper brass plate to complete the assembly. The calorimeter unit was then immersed in the constant temperature bath, all electrical connections made, and stirring commenced. The calorimeter fluid was brought to a few tenths of a degree below 25°C by passing warm or cold water as required through the copper coil inside the Dewar vessel. The calorimeter was then allowed to stand in the water bath for 15 to 30 minutes to establish temperature equilibrium between the bath and calorimeter.

An electrical calibration was performed first by passing a measured quantity of electrical energy through the calorimeter heater. Readings of temperature in microvolts were taken at half-minute intervals for ten minutes to determine the fore slope, $\underline{g_1}$, used later in heat leak corrections. During this ten minute period, the battery current was allowed to pass through a dummy heater of approximately the same resistance as the calorimeter heater. This permitted the battery current to level out to a fairly constant value before it was passed into the calorimeter heater. The measurements of the current were thereby made much more precise than they would be if the dummy heating were not used. On the tenth minute the calorimeter heater was switched into the battery circuit, the same switching action removing the dummy heater from the circuit. One operator took readings every 25 seconds of the e.m.f. drop across the 0.1 ohm standard resistance in the calorimeter heater circuit while a second operator took temperature readings at 30 second intervals. Electrical energy input intervals were usually from 300 to 600 seconds, the actual period being more or less regulated so as to make the temperature rise during calibrations correspond nearly to that produced in a heat of solution experiment. After the electrical energy input was terminated, temperature measurements were taken until the temperature of the calorimeter contents reached a constant decrease or increase depending upon whether the final temperature was above or below the convergence temperature. These latter readings determined the after slope, $\underline{g_2}$, used in the heat leak calculations.

After the last temperature reading in the after period was taken, the calorimeter was cooled to approximately the beginning temperature of the calibration experiment. Ten minutes of temperature versus time data were recorded as before and at the tenth minute the first sample bulb was broken by pulling up on the breaker rod. The temperature rise was followed at half minute intervals until solution of the sample was complete and a steady state was again reached. The calorimeter was again cooled to nearly the same starting temperature and a second calibration experiment performed. This procedure was continued until the last bulb was broken. A final calibration experiment was made after solution of the last sample. In the case of measuring the heat of solution of a rare earth metal only one sample was mounted in the calorimeter and two calibration experiments performed, one before, and one after, solution of the metal. The acid solutions used in metal experiments were previously saturated with hydrogen gas.

After all heat of solution experiments were run, the calorimeter was removed from the water bath and the Dewar flask unfastened. The contents of the vessel were examined for any evidence of incomplete solution. The solution was filtered free of broken glass and stored in a stoppered flask for analytical work. A thorough rinse with distilled water was given the metal parts of the calorimeter.

F. Treatment of Data

The electrical energy input during a calibration is given by

$$\text{III-38.} \qquad Q_{el} = \frac{R_h}{4.184\ R_s^2} \int_0^t E^2 dt$$

where

R_h = resistance of calorimeter heater

R_s = 0.1 ohm standard resistance

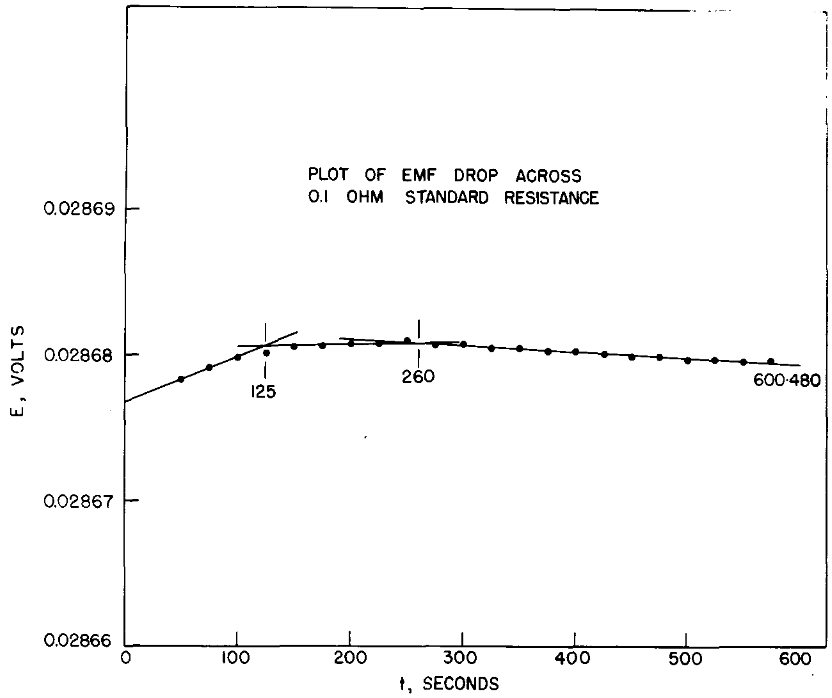
E = e.m.f. drop across R_s

t = time in seconds

Q_{el} = electrical energy in calories.

To evaluate the integral in the above expression a plot was made of $\underline{E}$ versus $\underline{t}$. Points on the plot were connected by a series of short chords and the midpoints of the chords taken as the average value of $\underline{E}$ for the time interval represented by the chord. The products, $\underline{\bar{E}^2 \Delta t_i}$, were then summed to obtain the total value of the integral. This procedure was compared to the more laborious trapezium method given by Worthing and Geffner (30) and no significant difference was found. A typical graphical integration is indicated in Figure 6.

The temperature change, $\underline{\theta_m - \theta_o}$, and the heat leak correction term, $\underline{C}$, were determined from plots of the e.m.f. of the thermometer in microvolts against the time in minutes. The slopes, $\underline{g_1}$, and $\underline{g_2}$, and the initial and final temperatures were taken from plots of the fore and after periods on a scale of 0.1 microvolt per division along the temperature axis, and 0.05 minutes per division along the time axis. The times, $\underline{t_o}$, $\underline{t_m}$, and $\underline{t_x}$, were taken from plots on a scale of 0.05 minutes per division along the time axis and five microvolts per division along the temperature ordinate.



$\overline{E}$	Δt	$\overline{E}^2 \Delta t$
0.0286787	125.0	0.102808
0.0286806	135.0	0.111048
0.0286802	340.480	0.280063
SUM	600.480	0.493919

$R_h / R_s^2 = 10,995.9_2$

$Q_{el} = 5431.09$ ABS. JOULES

$Q_{el} = 1298.06$ CALS.

Figure 6. Graphical Integration of Typical Electrical Energy Input.

The lag of the heater and thermometer produced a displacement of the observed temperature curve from that of the true calorimeter temperature. The combined heater and thermometer lag is represented by the quantity, $\frac{1}{2}(\Delta t - t_h)$, in which $\Delta t = t_m - t_o$ and t_h is the exact time of heat input. The heater lag is negligibly small and the time lag was attributed to the thermometer. The thermometric lag was not considered in calculating the heat equivalent of the calorimeter since the same lag was present during heat of solution experiments (16). The times t_o and t_m for calibration experiments were determined by extrapolation of the fore and after slopes to the linear portion of the main temperature rise. Using the values of g_1 and g_2, and one temperature from the steady state regions of the fore and after periods, the values of θ_o and θ_m were calculated. In heat of solution experiments t_o was taken as the time the bulb was broken and t_m as the time at which the calorimeter first reached the steady state in the after period. The value of θ at t_m was taken as θ_m.

Tables 3, 4, and 5 contain the data and calculations for a set of heat of solution experiments in which three samples of anhydrous samarium chloride were used. Numbers I, III, V, and VII refer to electrical calibrations, and II, IV, and VI to heat of solution experiments. The values of G, θ_k, and the temperature correction, C, were calculated by

Table 3. Calorimeter Rating Data; Heat of Solution of Samarium Chloride in Samarium Chloride Solution

No.	t_o, θ_o	t_m, θ_m	g_1, g_2	$G \times 10^4$	θ_k	$\bar{\theta}$, or t_x, θ_x	C	$\Delta\theta_t$
I	10.55	20.57	3.626	14.525	26,602.7	25,393.7=$\bar{\theta}$	17.6	2557.3
	24,106.3	26,681.2	-0.114	- -	- -	- -	- -	- -
II	10.00	28.00	3.638	13.803	26,766.7	10.65=t_x	23.4	1734.2
	24,131.0	25,888.6	1.212	- -	- -	25,185.6=θ_x	- -	- -
III	10.56	17.65	3.722	13.917	26,743.0	24,984.7=$\bar{\theta}$	17.4	1814.9
	24,068.6	25,900.9	1.172	- -	- -	- -	- -	- -
IV	10.00	25.00	3.589	14.427	26,715.6	10.46=t_x	13.9	1888.1
	24,227.9	26,129.9	0.845	- -	- -	25,369.1=θ_x	- -	- -
V	11.05	17.74	3.615	15.560	26,500.1	25,040.9=$\bar{\theta}$	15.2	1712.9
	24,176.9	25,905.0	0.926	- -	- -	- -	- -	- -
VI	10.00	45.00	3.679	14.091	26,761.5	10.81=t_x	1.3	2644.7
	24,150.7	26,796.7	-0.050	- -	- -	25,738.3=θ_x	- -	- -
VII	10.57	20.60	3.475	14.056	26,644.1	25,462.7=$\bar{\theta}$	16.6	2565.3
	24,171.8	26,753.7	-0.154	- -	- -	- -	- -	- -

($\underline{\theta}$ is in microvolts and $\underline{t}$ in minutes; $\underline{\Delta\theta_t}$ is the corrected temperature rise.)

Table 4. Electrical Calibration Data; Heat of Solution of Samarium Chloride in Samarium Chloride Solution

No.	Q_{el}, in calories	$\Delta\theta_t$ μvolts	W cals/μvolt	$\bar{\theta}$ μvolts	dt/d$\bar{\theta}$ x 10^4
I	1261.67	2557.3	0.493359	25,393.7	3.6867
III	892.13	1814.9	0.491558	24,984.7	3.6883
V	839.81	1712.9	0.490286	25,040.9	3.6881
VII	1259.68	2565.3	0.491044	25,462.7	3.6864

No.	C_P, in cals/°C	$-(C_{Pi}-C_{Po})$	$-(C_{Pi}-C_{Po})'$	C_{Po}'	C_P (Smoothed)
I	1338.21	0	0	1338.21	1339.38
III	1332.75	5.46	5.47	1338.22	1333.91
V	1329.37	8.84	8.03	1337.40	1331.35
VII	1332.04	6.17	11.63	1343.67	1327.75

Table 5. Heat of Solution Data; Heat of Solution of Samarium Chloride in Samarium Chloride Solution

No.	n_i moles	m molality	$\bar{\theta}$ μvolts	$dt/d\bar{\theta}$ x 10^4	$\Delta\theta_t$ μvolts
II	0.02209	0.04329	25,009.8	3.6882	1734.2
IV	0.02405	0.06340	25,178.9	3.6875	1888.1
VI	0.03379	0.09165	25,473.6	3.6864	2644.7

No.	W_I, W_F	ΔW_i	q_i	$\theta_{25}-\theta_o$	Δq_i
II	0.493990 0.491973	0.002017	853.18	1331.0	2.68
IV	0.491879 0.490935	0.000944	926.93	1234.1	1.16
VI	0.490789 0.489462	0.001327	1294.48	1311.3	1.74

No.	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
II	855.86	38737	715.60	1682.09	38859
IV	928.09	38592	775.99	2458.08	38774
VI	1296.22	38363	1083.79	3541.87	38647

(Value of θ at 25°C = 25,462.0 μvolts; for this experiment m_o = 0.02481 and Q_{mo}= 966.49 cals.)

Equations III-23, III-27, III-28, and III-32; the corrected temperature rise, $\underline{\Delta\theta_t}$, was calculated from Equations III-24 and III-37; $\underline{\bar{\theta}}$ is the mean temperature of the experiment in microvolts. The initial heat equivalent, $\underline{W_o}$, of the calorimeter was calculated from

III-39. $$W_o = \frac{Q_{el}}{\Delta\theta_t} .$$

The heat equivalent can be divided as follows:

III-40. $W_o = W(n_1+n_2+n_3 \text{ moles salt})+W(H_2O)+W(\text{calorimeter})$.

The second calibration, III, determined a second heat equivalent, $\underline{W_1}$, where

III-41. $W_1 = W(n_2+n_3 \text{ moles salt})+W(\text{soln. } m_1)+W(\text{calorimeter})$.

Subtraction of Equation III-40 from Equation III-41 gives

III-42. $W_1-W_o = \Delta W_1 = W(\text{soln. } m_1)-W(n_1 \text{ moles salt})-W(H_2O)$.

Succeeding calibrations V and VII permitted calculation of two more $\underline{\Delta W}$ values,

III-43. $\Delta W_2 = W(\text{soln. } m_2)-W(n_1+n_2 \text{ moles salt})-W(H_2O)$,

and

III-44. $\Delta W_3 = W(\text{soln. } m_3)-W(n_1+n_2+n_3 \text{ moles salt})-W(H_2O)$.

Thus, the changes in $\underline{W}$ are a measure of the change in heat capacity for the reaction indicated. This is not exactly true, however, since the four experimental values of W were not determined at exactly the same temperature.

The experimental quantity, W, was measured in calories per microvolt. For convenience in further treatment of data, W was changed to C_p in calories per degree by applying the calibration formula of the thermometer at the mean temperature of the calibration experiment. The thermometer calibration for temperature, T, as a function of e.m.f. in microvolts was

III-45. $$T = a + b\bar{\theta} + c\bar{\theta}^2 ,$$

and

III-46. $$\frac{dT}{d\bar{\theta}} = b + 2c\bar{\theta} .$$

Hence,

III-47. $$W \Big/ \frac{dT}{d\bar{\theta}} = C_p$$

where $\bar{\theta}$ is the mean temperature of the calibration experiment. These calculations for the samarium chloride experiment are given in the 4-th, 5-th, and 6-th columns of Table 4. The heat capacities calculated in this manner are average values for each experiment. The values of ΔC_{p_1} calculated for each heat of solution experiment were used for smoothing the heat capacity data by plotting them against the molality of the final solution. The best straight line was drawn through the ΔC_{p_1} values and smoothed values taken off the curve. The smoothed values, indicated as $-(C_{p_1}-C_{p_0})'$ in Table 4, were added to $\underline{C_{Pi}}$ and the sums, $\underline{C_{Po}}'$, averaged with $\underline{C_{Po}}$ to obtain a new average value for $\underline{C_{Po}}$. The smoothed values, $\underline{-(C_{Pi}-C_{Po})'}$, were then successively subtracted from the new $\underline{C_{Po}}$ to obtain

$$C_{Po} = C_{Po}\ (\text{avge.})$$

$$C_{P1} = C_{Po}\ (\text{avge.}) - \Delta C_{P1}$$

$$C_{P2} = C_{Po}\ (\text{avge.}) - \Delta C_{P2}$$

$$C_{P3} = C_{Po}\ (\text{avge.}) - \Delta C_{P3}\ .$$

These latter calculations are shown in the last four columns of Table 4.

The heat capacity data served also to indicate systematic or random errors in the calibrations since for solutions of strong electrolytes one would expect the heat capacity to decrease regularly with increasing concentration (32). The experiment selected to describe the treatment of data was chosen to illustrate a random error in the final calibration.

For the heat of solution experiments in Table 5, the smoothed values of $\underline{C_P}$ before and after each measurement were converted to $\underline{W}$ values at the mean temperature of the heat of solution experiment by use of Equation III-47. Table 5 gives $\underline{W_I}$ and $\underline{W_F}$ as the initial and final heat equivalents for each experiment calculated in this manner. The heat equivalent of the final solution, $\underline{W_F}$, was used in each case to calculate the raw heat value, $\underline{q_i}$,[1] by the equation

---

[1] For what follows, the running number, $\underline{i}$, takes on the values 1, 2, and 3 for the three heat of solution experiments.

III-48.
$$q_i = W_F \Delta\theta_t$$

where

III-49.
$$q_i = -\Delta H$$

so that q_i was positive for heat evolved.

The difference, $\Delta W_i = W_I - W_F$, was used to correct q_i to its value at 25°C in the following manner. Since $q_i = -\Delta H$, and

III-50.
$$\left[\frac{d(\Delta H)}{dT}\right]_P = \Delta C_P$$

then

III-51.
$$\left(\frac{dq_i}{d\theta}\right)_P = f\, \Delta W_i \quad ,$$

or

III-52.
$$\Delta q_i = f \int_{\theta_o}^{\theta^{25}} (\Delta W_i)\, d\theta$$

where θ_o is the initial temperature of the heat of solution experiment and θ^{25} is the e.m.f. across the thermometer at 25°C. Integration of Equation III-52 gives

III-53.
$$\Delta q_i = f\, \Delta W_i(\theta^{25} - \theta_o) \; .$$

The initial temperature, θ_o, was used as the lower limit since the heat equivalent of the final system was used in calculating q_i (31). The experimental heat corrected to 25°C is thus given by

III-54. $$q_i^{25} = q_i + \Delta q_i \; .$$

The remaining heat quantities used in Table 5 are defined as follows:

III-55. $$q_i^{25} = W_F(\Delta\theta_t) + \Delta q_i$$

is the heat given off at 25°C by n_i moles of salt dissolving in X x 10^3 grams of water containing $\underline{n_j}$ moles of salt where

III-56. $$n_j = \sum_{o}^{i-1} n_i \; .$$

III-57. $$q_M = \frac{q_i^{25}}{n_i}$$

is the heat given off per mole of salt when dissolved in sufficient water or solution to give the same final molality, $\underline{m_i}$, which was reached in the given experiment;

III-58. $$q_{mi} = \frac{q_i^{25}}{X} = \Delta m_i q_M$$

is the heat given off at 25°C by $\underline{n_i/X}$ moles of salt dissolving in 1000 grams of water or a solution containing 1000 grams of water;

III-59. $$Q_m = \sum_i q_{mi}$$

is the molal heat of solution; and

III-60. $$Q_M = \frac{Q_m}{m} = - \Delta H$$

where m is the molality, gives the total or integral heat of solution.

When a set of heat of solution experiments was run beginning with a solution of molality, m_o, as in the illustration presented, the points were connected to those obtained when water alone was used in the following manner. A plot was made of q_M versus $m^{\frac{1}{2}}$ for all data and the best smooth curve drawn through the points; then, Q_m was calculated through all the points by means of Equations III-58 and III-59 to determine the best value of Q_{mo} . This was done because for any set of experiments not starting with water Equation III-59 was changed to

III-61. $$Q_m = Q_{mo} + \sum_i q_{mi} \quad .$$

The integral heat of solution was then calculated by Equation III-59.

The treatment of data described above assumes that the heat capacity, C_p, is a constant in each case. Such an assumption is valid when it is considered that the rise in temperature in any heat of solution experiment was always less than one degree; any error introduced into the final heat values because of the assumption of no variation of the heat capacity with temperature is negligible compared to other sources of error.

IV. EXPERIMENTAL RESULTS

A. Calorimeter Precision and Accuracy

An error analysis by the method of propagation of precision indexes set forth by Worthing and Geffner (30) indicated the calorimeter should give a precision of from 1 to 2 parts per 1000 in the range of concentrations studied. The error in heat of solution experiments is approximately proportional to $1/m$ where m is the final molality of the experiment. For example, in the heat of solution experiments described in Tables 3, 4, and 5, the errors in the successive heat measurements were approximately 21, 14, and 10 cals/mole.

The calorimeter and the method of treating data were tested by measuring the heats of solution of potassium nitrate in water, extrapolating the data to infinite dilution, and comparing the results with those of other investigators. Table 6 contains the values of L_2 obtained by previous authors converted to $25^\circ C$ by use of the heat capacity and relative apparent molal heat content data given by Harned and Owen (32). Equations II-26, II-35, and III-49 were used to make the correction to standard conditions. Table 7 lists the data obtained in this work for the heat of solution of potassium nitrate. A set of three samples was run and each value of Q_M converted to L_2 by adding the corresponding ϕ_L value for the final concentration of the experiment. The results are

Table 6. Heats of Solution at Infinite Dilution of Potassium Nitrate by Other Investigators Corrected to 25°C

Investigators	Reference No. and Date	t°C	L_2
Cohen and Kooy	33(1928)	20	8314
Lange and Monheim	34(1930)	12.5	8375
		25	8376
Roth and Eymann	35(1929)	21	8332
Colson	36(1915)	18.5	8526
		20	8514
Haigh	37(1912)	20.5	8323
Thomsen	38(1908)	18	8434
		20	8377
		Average:	8397±63

L_2 is in cals/mole at 25°C; t°C is the temperature of the measurements.

Table 7. Heats of Solution of Potassium Nitrate at 25°C

m	$m^{\frac{1}{2}}$	Q_M	ϕ_L	L_2
0.04239	0.2059	-8394.4	10.4	8384
0.09904	0.3147	-8329.5	-36.5	8366
0.1588	0.3985	-8320.3	-82.7	8403
			Average:	8384 ± 12

$\underline{Q_M}$ is the heat of solution in cals/mole at the final molality $\underline{m}$; $\underline{\phi_L}$ is the relative apparent molal heat content and $\overline{L_2}$ is the heat of solution at infinite dilution in cals/mole.

in reasonable agreement with the overall average of those in Table 6 and agree within experimental error with the adiabatic work of Lange and Monheim (34).

B. Heats of Solution

The data of other investigators on the heats of solution of anhydrous rare earth chlorides in water and rare earth metals in hydrochloric acid solution are given in Tables 8 and 9. The only data found in the literature on the heats of solution of hydrated rare earth chlorides are those measured by Matignon (39) who reported $\underline{Q_M} = 5.3$ Kcals/mole for $PrCl_3 \cdot 7H_2O$ and $Q_M = 28.9$ Kcals/mole for $PrCl_3 \cdot H_2O$.

Table 8. Heats of Solution of Rare Earth Chlorides by Other Investigators

Chloride	Investigators	Reference No. and Date	t°C	Q_M
$LaCl_3$	Bommer and Hohmann	8(1939)	20	31.6 ±0.05
	Matignon	39(1906)	17	31.4
$PrCl_3$	Bommer and Hohmann	8(1939)	20	33.9 ±0.05
	Matignon	39(1906)	17	33.5
$SmCl_3$	Bommer and Hohmann	8(1939)	20	39.0 ±0.05
	Matignon	40(1906)	17	37.4
$GdCl_3$	Bommer and Hohmann	8(1939)	20	42.4 ±0.05
$ErCl_3$	Bommer and Hohmann	8(1939)	20	49.55±0.05
$YbCl_3$	Bommer and Hohmann	8(1939)	20	50.95±0.05
YCl_3	Bommer and Hohmann	8(1939)	20	52.3 ±0.05
	Matignon	39(1906)	17	45.4

$\underline{Q_M}$ is in Kcals/mole; t°C is the temperature of the measurements.

Table 9. Heats of Solution of Rare Earth Metals in Hydrochloric Acid by Other Investigators

Metal	Investigators	Reference No. and Date	HCl Conc.		t°C	Q_M
Y	Bommer and Hohmann	7(1941)	0.12	normal	20	168.3 ±0.7
La	Sieverts and Gotta	41(1938)	1	normal	20	164.27
	Sieverts and Gotta				17	164.72
	Neumann, Kroger and Kunz	42(1932)	2.8	molal		167.72±0.31
	Bommer and Hohmann	7(1941)	0.12	normal	20	176.5 ±0.7
	Lohr and Cunningham	11(1951)	1.5	normal	25	167.0 ±1.4
Pr	Bommer and Hohmann	7(1941)	0.12	normal	20	172.9 ±0.7
	Lohr and Cunningham	11(1951)	1.5	normal	25	165.3 ±0.9
	Sieverts and Gotta	41(1928)	2	normal	18	168.87
Gd	Bommer and Hohmann	7(1941)	0.12	normal	20	168.8 ±0.7
Er	Bommer and Hohmann	7(1941)	0.12	normal	20	162.6 ±0.7

$\underline{Q_M}$ is in Kcals/mole; $\underline{t}$°C is the temperature of the measurements.

For this work the heats of solution of the anhydrous and hydrated chlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, yttrium, and ytterbium were measured. The data are given in Tables 10, 11, 12, 13, 14, 15, 16, and 17. In addition, the heats of solution of some rare earth metals and anhydrous chlorides in hydrochloric acid were determined. These data are given in Table 18.

For the heat of solution data on the anhydrous chlorides in water, an equation of the general form

$$\text{IV-1} \qquad Q_M = a + bm^{\frac{1}{2}} + cm$$

was formulated by an approximate least squares method to represent the heat of solution, $\underline{Q_M}$, as a function of the molality. The constant, $\underline{b}$, was taken as the theoretical limiting slope of Equation II-40 for a 3-1 electrolyte. The limiting value was assumed in the equation for the following reason. In a metal experiment the final rare earth concentration was always much lower than any reached in the chloride experiments. As will be shown presently, the heat of solution of the anhydrous chloride was required at the same final concentration reached in the metal experiment in order to make heat of formation calculations. This condition necessitated an extrapolation of the chloride data. It was believed that the extrapolation would be more accurate if the limiting slope of the Debye-Huckel theory were used. This procedure is justified to some extent on the basis of work on conductances, transference numbers, and activity coefficients of rare earth halides at high dilutions by Spedding, Porter, and Wright (43, 44, 45) and Spedding and Yaffe (46). The data of these investigators indicates approach to the limiting laws of the Debye-Huckel theory for these salts. The extrapolated constant, a, represents the absolute value of $\underline{L_2}$, the heat of solution at infinite dilution. Table 19 lists the values of the constants in Equation IV-1 for the chlorides studied in this work. The data on the heats of solution of the anhydrous chlorides are plotted in Figures 7, 8, 9, 10, 11, 12, and 13.

Table 10. Heats of Solution of Lanthanum Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.09287	0.320695	1074.0	0.58	345.00	32306	278.61	278.61	32306
0.1343	0.320081	1161.3	0.72	372.43	31977	300.77	579.38	32134
0.1745	0.319236	1524.6	1.08	487.78	31728	393.92	973.29	31969
0.1106	0.322750	1523.3	0.28	491.92	32261	394.57	394.57	32260
0.1640	0.321773	1798.2	0.67	579.29	31658	464.64	859.21	31932
0.2071	0.319595	1289.6	0.57	412.72	31687	332.02	1359.01	31687
0.2085	0.316110	1800.8	1.33	570.58	31671	463.35	1378.09	31711
0.2423	0.315042	1864.7	1.51	588.97	31588	478.28	1856.36	31622
0.2797	0.313661	2371.2	2.22	745.97	31256	605.77	2462.13	31476
0.2320	0.318568	1332.8	1.33	425.92	31461	344.6	1700.05	31581
0.2596	0.318196	1636.2	0.28	520.92	31099	421.48	2121.52	31485
0.2584	0.317874	1699.7	0.33	540.62	31136	437.42	2558.94	31425

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

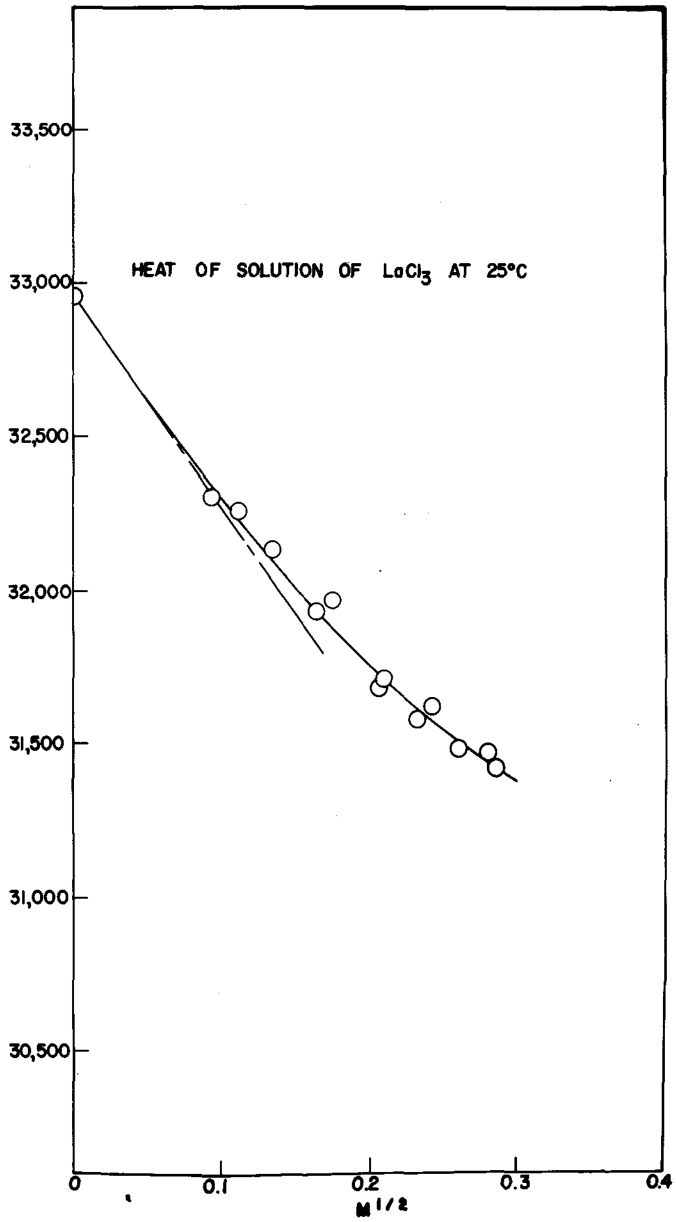


Figure 7. Integral Heats of Solution of Lanthanum Chloride in Calories Per Mole.

Table 11. Heats of Solution of Praseodymium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.1020	0.322735	1404.1	0.39	453.55	35045	364.82	364.82	35045
0.1544	0.322058	1786.7	0.50	575.92	34522	463.25	828.07	34750
0.1976	0.321299	2026.8	0.55	651.76	34475	524.25	1352.32	34643
0.1425	0.325759	2726.7	0.84	889.09	34824	706.89	706.89	34824
0.1705	0.328259	3907.4	2.08	1284.72	34622	1006.44	1006.44	34622
0.2109	0.327276	2047.4	1.02	671.49	34141	526.04	1532.48	34455
0.1904	0.511916	1512.1	0.80	774.87	34271	617.15	1252.55	34559
0.2247	0.511495	1191.3	0.38	609.72	34116	485.62	1738.17	34433
0.2490	0.317748	1789.2	1.35	569.86	34009	461.86	2125.32	34290
0.2804	0.317284	2179.6	0.31	691.86	33705	560.74	2686.05	34166
0.3058	0.316936	1967.6	0.32	623.93	33929	505.68	3191.73	34129

$\underline{\Delta\theta_t}$ is the corrected temperature rise in microvolts; $\underline{W_F}$ is the heat equivalent in cals/μvolt; $\underline{Q_M}$ is the integral heat of solution in cals/mole.

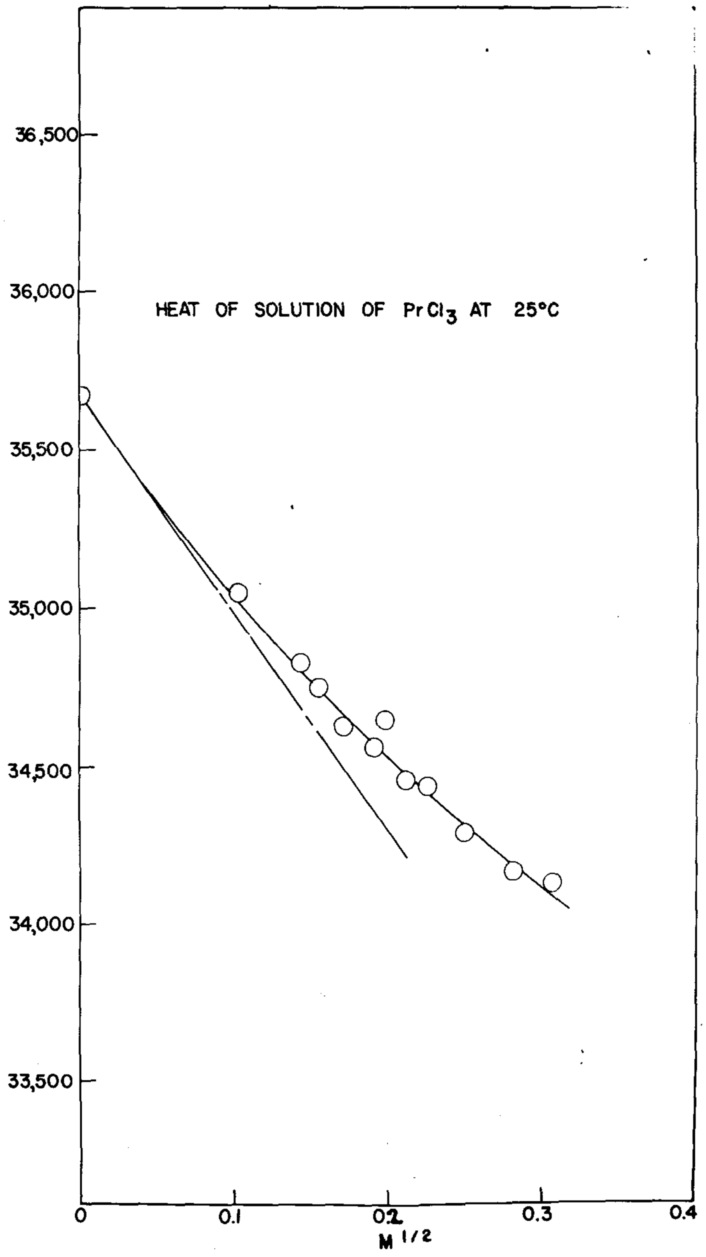


Figure 8. Integral Heats of Solution of Praseodymium Chloride in Calories Per Mole.

Table 12. Heats of Solution of Samarium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.07119	0.502322	482.9	1.53	244.10	39.490	200.12	200.12	39490
0.1154	0.500409	782.4	2.27	393.80	39.133	322.85	522.96	39270
0.1575	0.497767	1086.1	2.84	543.46	38.755	445.53	968.49	39030
0.1258	0.508864	1494.7	1.96	762.56	39.204	615.33	615.33	39204
0.1775	0.508106	1494.6	0.79	760.21	38.760	613.44	1228.77	38981
0.2251	0.507423	1805.5	0.75	916.90	38.636	739.88	1968.65	38851
0.2081	0.491973	1734.2	2.68	855.86	38.737	715.60	1682.09	38859
0.2518	0.490935	1888.1	1.16	928.09	38.592	775.99	2458.08	38774
0.3027	0.489462	2644.7	1.74	1296.22	38.363	1083.79	3541.87	38647

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

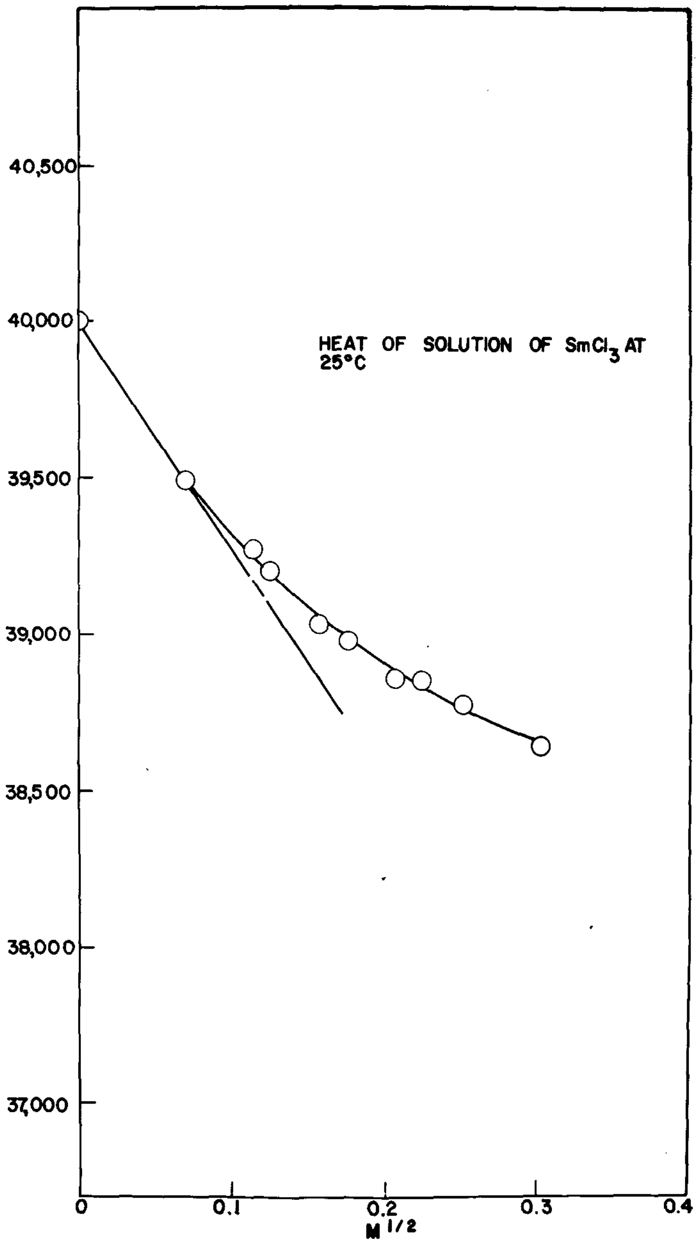


Figure 9. Integral Heats of Solution of Samarium Chloride in Calories Per Mole.

Table 13. Heats of Solution of Gadolinium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.1026	0.320229	1710.3	0.10	547.79	42356	445.50	445.50	42356
0.1470	0.321417	1784.1	0.09	573.53	42067	466.44	911.94	42177
0.09126	0.322343	1360.2	-0.04	438.42	42392	353.07	353.07	42392
0.1696	0.321029	3295.3	-0.14	1057.75	41718	851.85	1204.92	41913
0.1041	0.322378	1730.4	-0.80	557.05	42277	458.03	458.03	42477
0.1556	0.333966	1501.7	-0.56	500.96	41879	399.87	1014.13	41879
0.1991	0.348902	1522.1	-3.93	527.14	41523	399.22	1655.55	41780
0.2235	0.350021	1599.2	-0.90	558.86	41023	423.25	2078.80	41623
0.2520	0.351509	2085.1	-1.31	731.63	40798	554.09	2632.89	41477
0.1947	0.320473	1602.3	-0.22	513.27	41638	416.61	1586.19	41830
0.2198	0.320131	1649.5	-0.12	527.94	41200	428.51	2014.71	41694
0.2461	0.319731	1931.0	-0.18	617.22	40962	500.98	2515.69	41546

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

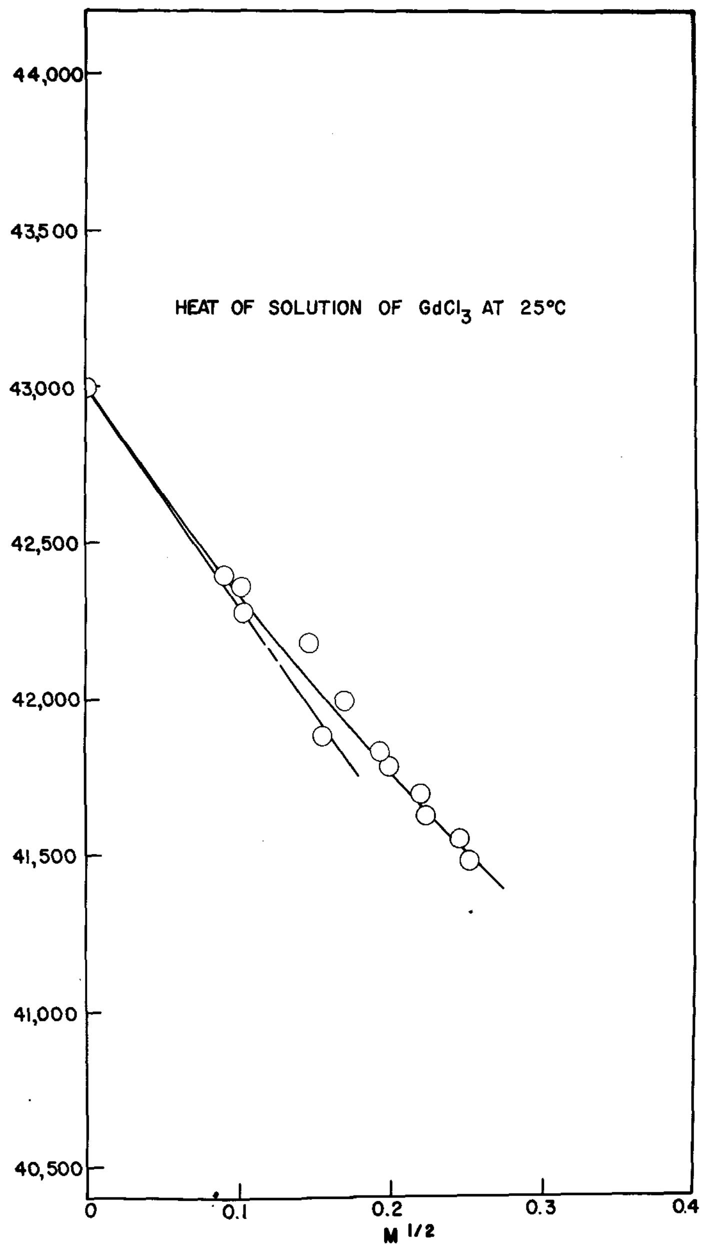


Figure 10. Integral Heats of Solution of Gadolinium Chloride in Calories Per Mole.

Table 14. Heats of Solution of Erbium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.09904	0.316298	1859.0	0.42	588.42	49138	481.99	481.99	49138
0.1486	0.315666	2316.3	0.49	731.67	48817	599.33	1081.32	48960
0.1895	0.314987	2601.4	0.55	819.96	48530	671.65	1752.97	48794
0.09964	0.324489	1896.7	0.41	615.87	49270	489.10	489.10	49270
0.1515	0.323919	2464.1	0.41	798.58	48644	634.21	1123.31	48914
0.1951	0.323669	2854.3	0.05	923.90	48560	733.73	1857.05	48773
0.2135	0.313122	1933.0	0.68	605.94	47961	499.97	2215.97	48611
0.2384	0.312303	2109.5	0.75	659.56	48344	544.21	2760.18	48558
0.2610	0.311877	2104.6	0.32	656.70	48124	541.85	3302.04	48486

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

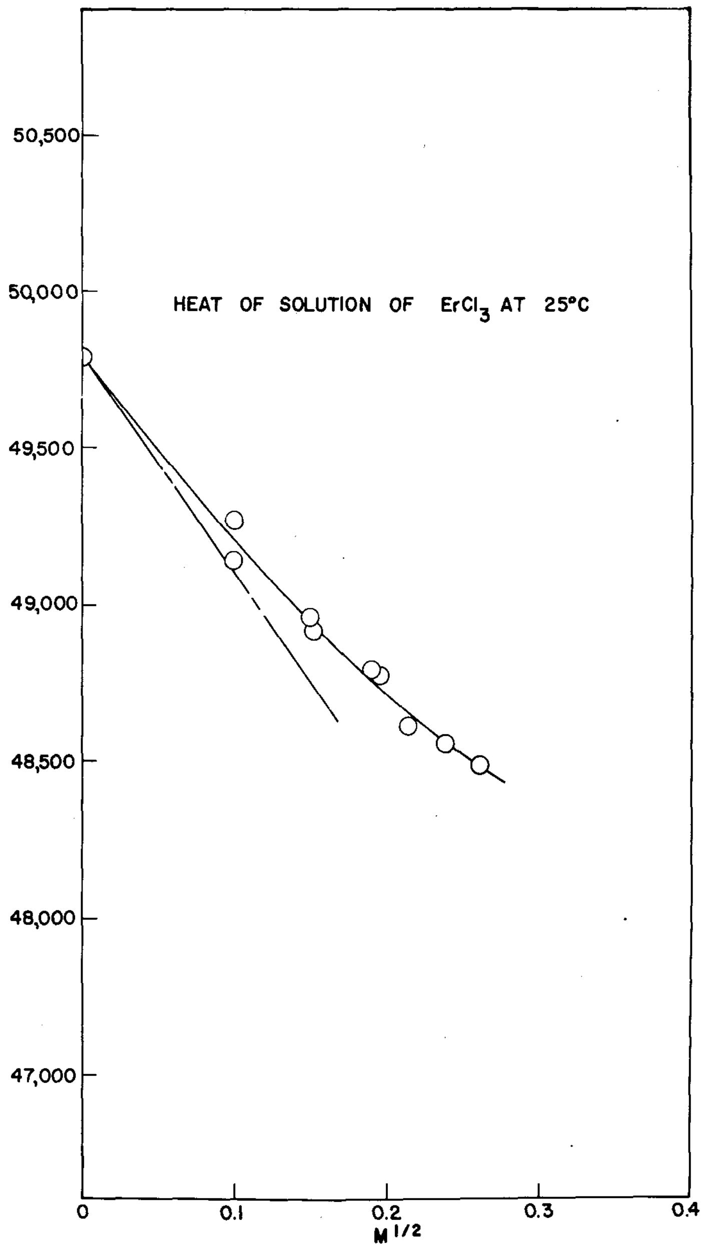


Figure 11. Integral Heats of Solution of Erbium Chloride in Calories Per Mole.

Table 15. Heats of Solution of Ytterbium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_1	q_1^{25}	q_M	q_{mi}	Q_m	Q_M
0.1120	0.506862	1557.2	3.21	792.50	50922	639.11	639.11	50922
0.1663	0.505929	1866.8	0.91	945.37	50501	762.40	1401.51	50691
0.2149	0.504794	2285.9	1.10	1155.01	50286	931.46	2332.97	50529
0.1191	0.488830	1760.9	1.13	861.91	50880	722.25	722.25	50880
0.1733	0.487757	1943.2	1.19	948.99	50230	795.22	1517.47	50537
0.2178	0.486536	2143.7	1.26	1044.25	50236	875.04	2392.51	50427
0.2458	0.483598	1575.3	1.05	762.86	50099	650.04	3035.29	50230
0.2693	0.483545	1477.6	0.10	714.59	50259	608.90	3644.19	50234
0.2969	0.483348	1859.2	0.10	898.74	48988	765.82	4410.01	50014

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

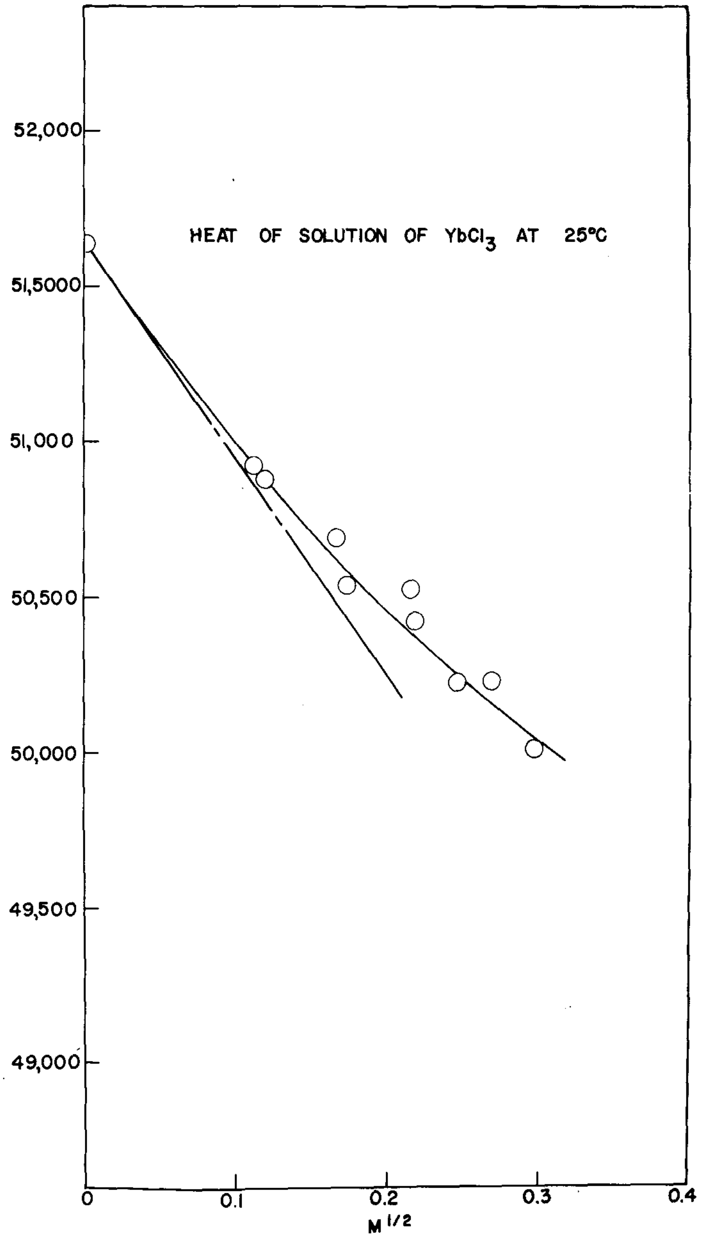


Figure 12. Integral Heats of Solution of Ytterbium Chloride in Calories Per Mole.

Table 16. Heats of Solution of Yttrium Chloride in Water at 25°C.

$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_M	q_{mi}	Q_m	Q_M
0.08684	0.502185	879.6	0.71	442.42	48145	363.10	363.10	48145
0.1167	0.509887	1594.1	0.11	812.92	47945	652.37	652.37	47945
0.1712	0.509448	1818.1	0.09	926.33	47385	743.39	1395.76	47645
0.2114	0.509128	1779.7	0.14	906.22	47228	727.25	2123.01	47502
0.09528	0.505477	1059.6	2.44	538.04	48052	436.18	436.18	48052
0.1324	0.504755	983.5	0.71	497.12	47631	403.01	839.19	47850
0.1598	0.503999	924.1	0.75	466.48	47302	378.17	1217.36	47678
0.1020	0.512123	1212.0	0.75	621.44	48148	500.45	500.45	48148
0.1459	0.511643	1248.2	0.35	638.99	47276	514.58	1015.03	47701
0.2681	0.503126	1474.8	0.07	742.09	46843	604.65	3398.76	47270
0.2907	0.502663	1410.5	0.09	709.11	45945	577.78	3976.54	47073

$\Delta\theta_t$ is the corrected temperature rise in microvolts; W_F is the heat equivalent in cals/μvolt; Q_M is the integral heat of solution in cals/mole.

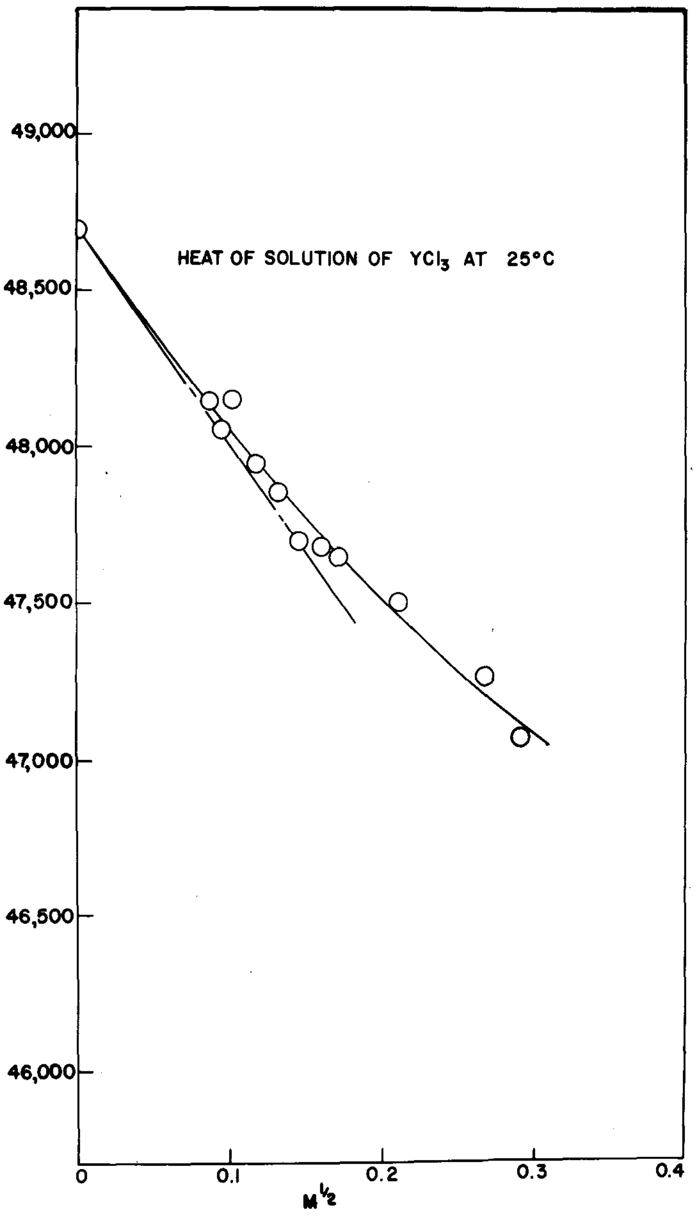


Figure 13. Integral Heats of Solution of Yttrium Chloride in Calories Per Mole.

Table 17. Heats of Solution of Hydrated Chlorides in Water at 25°C.

Hydrate	$m^{\frac{1}{2}}$	W_F	$\Delta\theta_t$	Δq_i	q_i^{25}	q_{mi}	Q_m	Q_M
$LaCl_3 \cdot 7H_2O$	0.1277	0.471366	254.3	2.69	122.56	107.71	107.71	6596
	0.1703	0.469704	197.5	2.20	94.96	83.45	191.16	6566
	0.2067	0.467753	211.7	2.18	101.20	88.94	280.10	6520
$PrCl_3 \cdot 7H_2O$	0.1267	0.489225	247.5	1.06	122.14	102.28	102.28	6374
	0.1731	0.488301	206.6	0.89	101.78	85.23	187.51	6256
$PrCl_3 \cdot 6H_2O$	0.1078	0.309696	404.9	0.43	125.83	105.63	105.63	9097
	0.1582	0.309152	451.1	0.29	139.74	117.31	222.94	8912
	0.1968	0.308621	457.9	0.17	141.49	118.78	341.72	8821
$SmCl_3 \cdot 6H_2O$	0.1277	0.508457	343.3	0.32	174.87	141.17	141.17	8656
	0.1782	0.508193	283.7	0.40	144.57	116.71	257.88	8123
	0.2188	0.507693	288.5	0.36	146.83	118.53	376.41	7862
$GdCl_3 \cdot 6H_2O$	0.1211	0.465088	271.3	0.90	127.08	112.86	112.86	7701
	0.1737	0.464330	285.4	0.94	133.46	118.52	231.38	7672
$YCl_3 \cdot 6H_2O$	0.1371	0.501121	476.1	0.51	239.10	196.18	196.18	10434
	0.2004	0.500725	522.8	0.47	262.25	215.17	411.35	10244
	0.2408	0.500226	432.0	0.61	216.71	177.80	589.15	10160
$ErCl_3 \cdot 6H_2O$	0.1703	0.499226	739.9	1.40	371.05	306.77	306.77	10574
	0.2203	0.498005	488.0	1.36	244.39	202.05	508.82	10484
$YbCl_3 \cdot 6H_2O$	0.1285	0.494909	404.2	1.17	201.21	167.66	167.66	10161
	0.1789	0.493973	360.9	1.06	179.33	149.43	317.09	9909

$\underline{\Delta\theta_t}$ is the corrected temperature rise in microvolts; $\underline{W_F}$ is the heat equivalent in cals/μvolt; $\underline{Q_M}$ is the integral heat of solution in cals/mole.

Table 18. Heats of Solution of Metals and Chlorides in Hydrochloric Acid at 25°C.

Substance	$m^{\frac{1}{2}}$	$m_B^{\frac{1}{2}}$(HCl)	$m_F^{\frac{1}{2}}$(HCl)	Q_M
La	0.05282	0.5196	0.5115	168.62
	0.04743	0.5196	0.5131	168.72
$LaCl_3$	0.1213	0.5014	0.5014	31.277
	0.1767	0.5014	0.5014	30.994
Pr	0.04229	0.5196	0.5145	168.28
	0.05083	1.2122	1.2090	165.59
$PrCl_3$	0.1005	0.5014	0.5014	34.130
	0.1611	0.5014	0.5014	33.855
	0.1074	1.2122	1.2122	30.209
	0.1704	1.2122	1.2122	29.804
Gd	0.04748	0.5196	0.5131	163.69
	0.05103	0.5196	0.5121	163.08
$GdCl_3$	0.07905	0.5014	0.5014	41.719
	0.1232	0.5014	0.5014	41.641
	0.1522	0.5014	0.5014	41.451
Er	0.06251	1.2114	1.2065	157.97
	0.05469	1.2134	1.2097	157.99
	0.05459	1.2134	1.2097	158.29
$ErCl_3$	0.09173	1.2134	1.2134	46.301
	0.1316	1.2134	1.2134	46.118
Y	0.07223	1.2103	1.2038	161.97
	0.09106	1.2100	1.1997	162.15
YCl_3	0.09057	1.2134	1.2134	46.777
	0.1359	1.2134	1.2134	46.827
	0.1791	1.2134	1.2134	46.244

m_B and m_F are initial and final acid molalities; m is the molality of the rare earth chloride; Q_M is the integral heat of solution in Kcals/mole.

Table 19. Values of the Constants in Equation IV-1

Chloride	a	b	c	Δ	Highest molality studied
$LaCl_3$	32,933	-6925	5640	35	0.08145
$PrCl_3$	35,672	-6925	5774	21	0.09351
$SmCl_3$	39,932	-6925	8949	15	0.09163
$GdCl_3$	42,992	-6925	4027	39	0.06350
$ErCl_3$	49,792	-6925	7873	40	0.06812
$YbCl_3$	51,638	-6925	5433	50	0.08815
YCl_3	48,690	-6925	5223	40	0.08451

Δ is the average deviation in cals/mole of calculated from experimental values of $\underline{Q_M}$.

C. Derived Thermochemical Quantities

1. Heats of hydration

The energy required to hydrate a compound may be calculated as the difference between the heat of solution of the hydrated compound and the heat of solution of the anhydrous form. Consider the equations

IV-2. $RCl_3(s) + XH_2O = RCl_3(m_F) + \Delta H_1$

IV-3. $RCl_3 \cdot YH_2O(s) + (X-Y)H_2O = RCl_3(m_F) + \Delta H_2$

where $\underline{m_F}$ is the same final molal concentration in each case. Subtraction of Equation IV-3 from Equation IV-2 yields

IV-4. $RCl_3 + YH_2O = RCl_3 \cdot YH_2O + (\Delta H_1 - \Delta H_2)$

where $\underline{\Delta H_1 - \Delta H_2}$ is the energy required to hydrate the compound $\underline{RCl_3(s)}$. In this manner the heats of hydration of lanthanum, praseodymium, samarium, gadolinium, erbium, yttrium, and ytterbium chlorides were calculated. The results are given in Table 20 and plotted in Figure 14.

2. Heats of formation

a. Anhydrous chlorides. The heat of formation of a compound is defined to be the increase in heat content when one mole of the compound is formed from its elements at a given temperature and pressure. The standard heat of formation, designated as $\underline{\Delta H_f^o}$, is the increase in heat content when the elements and the compound

Table 20. The Heats of Hydration; Heats of Formation; and Estimated Entropies and Free Energies of Formation of Some Rare Earth Hydrates at 25°C

Hydrate	$-\Delta H$(hyd.)	$-\Delta H_f^\circ$	$-\Delta S_f^\circ$	$-\Delta F_f^\circ$
$LaCl_3 \cdot 7H_2O$	25.37±0.02	759.27±0.20	383.5	645.0
$PrCl_3 \cdot 7H_2O$	28.45±0.06	759.69±0.16	383.5	645.4
$PrCl_3 \cdot 6H_2O$	25.81±0.06	688.73±0.16	337.2	588.2
$SmCl_3 \cdot 6H_2O$	30.92±0.06	- - -	337.2	- -
$GdCl_3 \cdot 6H_2O$	34.38±0.04	684.24±0.15	337.2	583.7
$ErCl_3 \cdot 6H_2O$	38.22±0.05	679.10±0.25	337.2	578.6
$YbCl_3 \cdot 6H_2O$	40.67±0.01	- - -	337.2	- -
$YCl_3 \cdot 6H_2O$	37.28±0.08	681.63±0.12	337.2	581.1

$\underline{\Delta H\text{(hyd.)}}$, $\underline{\Delta H_f^\circ}$, and $\underline{\Delta F_f^\circ}$ are in Kcals/mole; $\underline{\Delta S_f^\circ}$ is in entropy units.

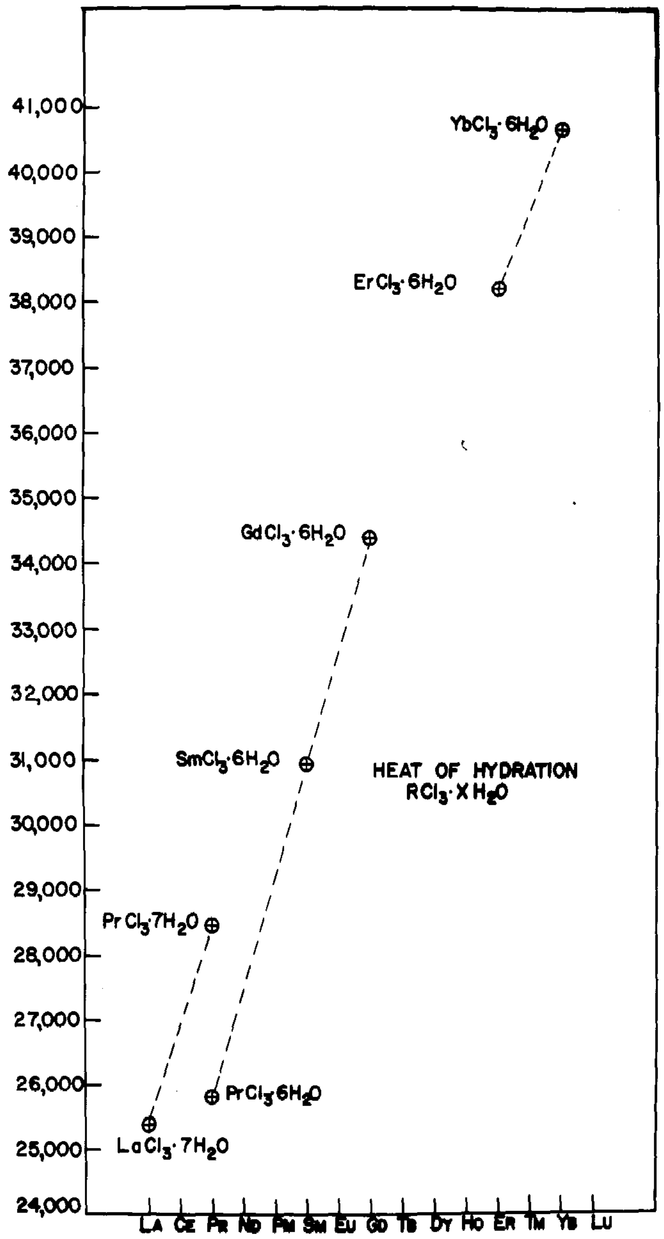


Figure 14. Heats of Hydration of the Rare Earth Trichlorides in Calories Per Mole.

are in their standard states at 25°C and one atmosphere pressure. The standard states of liquids and solids are generally taken as the stable forms at 25°C and one atmosphere pressure; for gases the ideal gas at one atmosphere is postulated. Consider the formation of liquid water at 25°C from hydrogen and oxygen in their standard states;

$$\text{IV-5.} \qquad H_2(g,1\ \text{atm.}) + \tfrac{1}{2}O_2(g,1\ \text{atm.}) = H_2O(1)\ .$$

The standard heat of formation of water becomes

$$\text{IV-6.} \qquad \Delta H_f^o = H^o(H_2O) - H^o(H_2) - \tfrac{1}{2}H^o(O_2)\ .$$

Since the heat content of substances cannot be known in an absolute sense it is permissible to choose any convenient reference scale for the heat content; the choice of a reference scale does not change the value of $\underline{\Delta H_f^o}$. The thermochemical convention is to set the heat content of elements equal to zero in their standard states at all temperatures. Thus the heat of formation of water indicated by Equation IV-6 becomes equal to the heat of Reaction IV-5.

It is not usually possible to measure directly the heat of formation of an inorganic compound from its elements and recourse must be had to indirect methods. In the present work the heats of formation of some rare earth chlorides were calculated from data on the heats of solution of the metals and chlorides in hydrochloric acid solution. Additional data on the heat of formation in solution of hydrogen chloride were required. Consider the following equations:

IV-7. $mR(s) + HCl(m_B) = mRCl_3 \cdot HCl(m_F) + 3/2mH_2(g) + m\Delta H_1^o$

IV-8. $mRCl_3(s) + HCl(m_F) = mRCl_3 \cdot HCl(m_F) + m\Delta H_2^o$

IV-9. $3/2m\ H_2(g) + 3/2m\ Cl_2(g) = 3m\ HCl(g) + 3m\Delta H_3^o$

IV-10. $3m\ HCl(g) + HCl(m_F) = HCl(m_B) + 3m\Delta H_4^o$

where m̲ is the number of moles of compound or element per 1000 grams of water and R̲ is a rare earth. Addition of Equations IV-7, IV-9, and IV-10, and subtraction of Equation IV-8 yields, after division by m̲,

IV-11. $R(s) + 3/2Cl_2(g) = RCl_3(s) + \Delta H_1^o + 3\Delta H_3^o + 3\Delta H_4^o - \Delta H_2^o$

where

$$\Delta H_1^o + 3\Delta H_3^o + 3\Delta H_4^o - \Delta H_2^o = \Delta H_f^o$$

is the standard heat of formation from the elements of the compound $\underline{RCl_3(s)}$.

The heat of formation and heats of solution and dilution of hydrogen chloride used in evaluating the changes in heat content in Reactions IV-9 and IV-10 were taken from a review by Rossini (47). The heat effects indicated by Reactions IV-7 and IV-8 were measured in the present work. In evaluating the change in heat content in Reaction IV-8 the following procedure was adopted. Sets of two or three anhydrous chloride samples were dissolved in a solution of hydrochloric acid whose concentration was very nearly equal to the final acid concentration attained during a metal experiment and the values of $\underline{Q_M}$ calculated. From the rare earth chloride concentrations reached in these acid experiments the corresponding values of $\underline{Q_M}$ in water at the same concentrations were calculated from Equation IV-1 using the appropriate constants for the rare earth chloride concerned. By subtraction of the $\underline{Q_M}$ values in acid from those in water an average lowering effect on the heat of solution of the chloride was observed. This average lowering effect was then applied to all $\underline{Q_M}$ values calculated from Equation IV-1 at the rare earth concentrations attained during metal experiments. The standard heats of formation of the chlorides of lanthanum, praseodymium, yttrium, gadolinium, and erbium are given in Table 21 and plotted in Figure 15.

b. Hydrated chlorides. The heats of formation of the hydrated rare earth chlorides may be calculated as the sum of the following reactions:

IV-12. $R(s) + 3/2Cl_2(g) = RCl_3(s) + \Delta H_1^o$

IV-13. $RCl_3(s) + XH_2O\ (l) = RCl_3 \cdot XH_2O(s) + \Delta H_2^o$

IV-14. $XH_2(g) + X/2\ O_2(g) = XH_2O\ (l) + X\Delta H_3^o$

Table 21. The Heats of Formation and Estimated Entropies and Free Energies of Formation of Some Rare Earth Chlorides and Ions at 25°C

Compound or ion	$-\Delta H_f^o$	$-\Delta S_f^o$	$-\Delta F_f^o$
$LaCl_3$	255.68±0.18	59.3	241.0 238.0
$PrCl_3$	253.02±0.10	59.3	235.4
$GdCl_3$	239.96±0.11	59.3	222.3
$ErCl_3$	231.00±0.20	59.3	213.3
YCl_3	234.47±0.04	59.3	216.8
La^{+++}	168.82±0.18	--	--
Pr^{+++}	168.86±0.10	--	--
Gd^{+++}	163.12±0.11	--	--
Er^{+++}	160.97±0.20	--	--
Y^{+++}	163.33±0.04	--	--

$\underline{\Delta H_f^o}$ and $\underline{\Delta F_f^o}$ are in Kcals/mole; $\underline{\Delta S_f^o}$ is in entropy units.

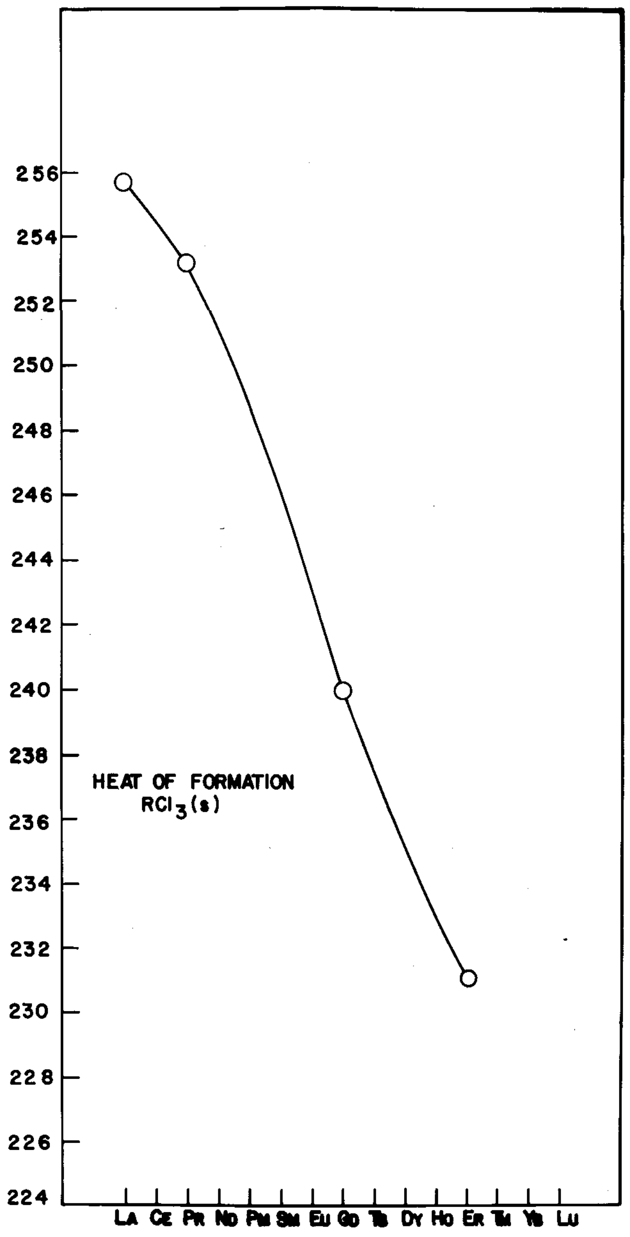


Figure 15. Heats of Formation of the Rare Earth Trichlorides in Kilocalories Per Mole.

where $\underline{\Delta H_2^o}$ is the heat of hydration. The summation of Reactions IV-12, IV-13, and IV-14 yields

IV-15. $R(s) + 3/2Cl_2(g) + XH_2(g) + X/2\ O_2(g) = RCl_3 \cdot XH_2O(s)$

and

IV-16. $\Delta H_f^o = \Delta H_1^o + \Delta H_2^o + X \Delta H_3^o$.

The heat of formation, $\underline{\Delta H_1^o}$, and the heat of hydration, $\underline{\Delta H_2^o}$, have been calculated. The heat of formation of liquid water, $\underline{\Delta H_3^o}$, was taken as -68,313 cals/mole as given by Bichowsky and Rossini (48). The standard heats of formation of the hydrates calculated in this manner are given in Table 20.

<u>c. Rare earth ions</u>. The standard heat of formation of aqueous rare earth ions may be calculated from the foregoing thermal data. The heat of formation of gaseous hydrogen chloride and the heat of solution of hydrogen chloride at infinite dilution are given by Rossini (47) as -22,063 cals/mole and -17,880 cals/mole, respectively. Thus, for the sum of the reactions

IV-17. $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) = HCl(g)$

IV-18. $HCl(g) + aq. = H^+(aq.) + Cl^-(aq.)$

the standard heat content change is -39,943 cals/mole. If the convention is adopted that the standard heat of formation of the aqueous hydrogen ion is zero, then, since the heat content of the elements are also taken as zero, the standard heat of formation of the aqueous chloride ion is -39,943 cals/mole. Hence, since the standard heat content changes for the reactions

IV-11. $R(s) + 3/2Cl_2(g) = RCl_3(s) + \Delta H_f^o$

and

IV-1. $RCl_3(s) + aq. = R^{+++}(aq.) + 3Cl^-(aq.) + \Delta H^o(\infty)$

are known, the standard heat of formation of the aqueous rare earth ion can be calculated. The sum of Reactions IV-1 and IV-11 is

IV-19. $R(s) + 3/2Cl_2(g) + aq. = R^{+++}(aq.) + 3Cl^-(aq.) + \Delta H_f^o + \Delta H^o(\infty)$

and the heat of formation of $\underline{R^{+++}(aq.)}$ becomes

IV-20. $\Delta H_f^o\ (R^{+++}) = \Delta H^o(\infty) + \Delta H_f^o - 3\Delta H_f^o\ (Cl^-)$.

The standard heats of formation of the rare earth ions calculated in this work are given in Table 21 and plotted in Figure 16.

3. Estimated entropies and free energies of formation

The free energy of formation of a compound is the change in free energy accompanying its formation from the elements.

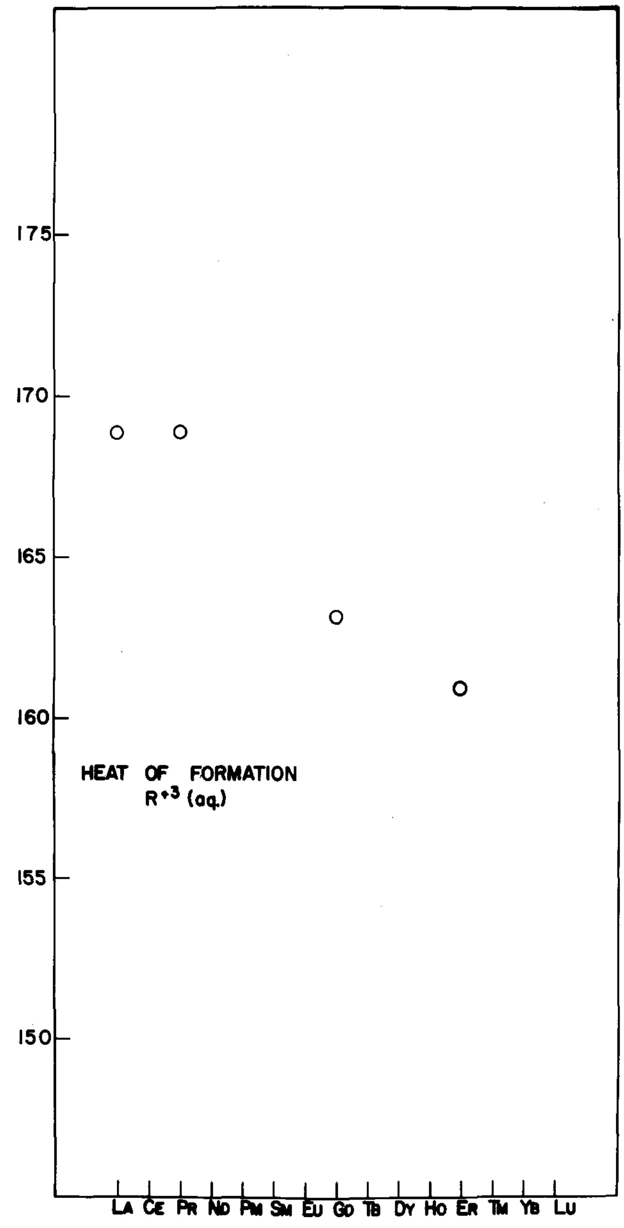


Figure 16. Heats of Formation of Aqueous Rare Earth Ions in Kilocalories Per Mole.

This free energy change becomes the standard free energy of formation when the elements and the compound are in their standard states. As in the case of heat contents, the free energies of the elements are taken as zero in their standard states. Therefore, the free energy of the reaction

IV-21. $R(s) + 3/2Cl_2(g) = RCl_3(s)$

at standard conditions of temperature and pressure becomes the standard free energy of formation, $\underline{\Delta F_f^o}$, of the compound, $\underline{RCl_3(s)}$.

The standard entropy change of Reaction IV-21 is given by

IV-22. $\Delta S_f^o = S^o(RCl_3) - S^o(R) - 3/2S^o(Cl_2)$

where $\underline{S^o}$ is the value of the absolute entropy at standard conditions. Standard entropy values of substances are usually evaluated by integrating the equation

IV-23. $$S^o = \int_0^{298.16} \frac{C_p}{T} dt .$$

Parkinson, Simon, and Spedding (49) have measured the heat capacity of lanthanum, cerium, praseodymium, and neodymium from 2 to 180°K and extrapolated their data to calculate values of $\underline{S^o}$. They obtained for $\underline{S^o}$ the values 13.64, 16.68, 17.49, and 17.54 entropy units, respectively. Recent work on gadolinium by Griffel, Skochdopole, and Spedding (50) in the range 15-300°K gave 15.75 entropy units as the value of $\underline{S}^{o}$. In spite of the entropy values available for the elements, a precise calculation of the entropy change in Equation IV-22 is not possible because of the lack of $\underline{S}^{o}$ values for the chlorides. The entropies of the compounds were estimated by the method set forth recently by Latimer (51, 52). From these entropy estimates the entropies of formation of the chlorides were calculated by Equation IV-22; the free energies of formation were then calculated from Equation II-15. These results are given in Tables 20 and 21.

If the free energies of formation of the aqueous rare earth ions were available, it would be possible to calculate the entropies of formation. Free energies of formation of aqueous ions can be calculated from reversible electrode potentials by Equation II-17. The only rare earth electrode process that has been studied is the deposition potentials of the rare earth cations at a dropping mercury electrode by Noddack and Brukl (58). These deposition potentials were used by Yost, Russell, and Garner (59) as rough estimates of the reversible electrode potentials. However, since deposition potentials are essentially irreversible processes and not thermodynamically related to the free energy, they were not used in entropy calculations.

D. Discussion

In general, the data reported in this work on the heats of solution of the anhydrous chlorides in water agree reasonably well with those of Bommer and Hohmann (8) and Matignon (39, 40). The plot in Figure 17 of the heats of solution at infinite dilution indicates a linear relationship from lanthanum to gadolinium. The values for cerium and neodymium chlorides obtained by Spedding and Miller (9) were drawn in for comparison. Erbium chloride is somewhat higher than an extension of the straight line would indicate; the difference cannot be accounted for by experimental error. Ytterbium chloride does fall on the extension of the straight line through the lighter rare earths. A plot of the data of Bommer and Hohmann shows a similar behavior. These investigators reported the trichlorides to exist in $\underline{\alpha}$, $\underline{\beta}$, and $\underline{\gamma}$ forms; the crystals were not further identified. From their work, the chlorides of lanthanum through gadolinium have the $\underline{\alpha}$ form, terbium chloride the $\underline{\beta}$ form, and the remaining members of the series and yttrium chloride, the $\underline{\gamma}$ form. Dysprosium was found to be dimorphic, having both $\underline{\beta}$ and $\underline{\gamma}$ forms, the $\underline{\gamma}$ form having a heat of solution about three kilocalories higher than the $\underline{\beta}$ variety. Zachariasen (53) reported the chlorides of lanthanum, cerium, praseodymium, and neodymium as isostructural having hexagonal type lattices; the crystal system of cerium chloride was confirmed by

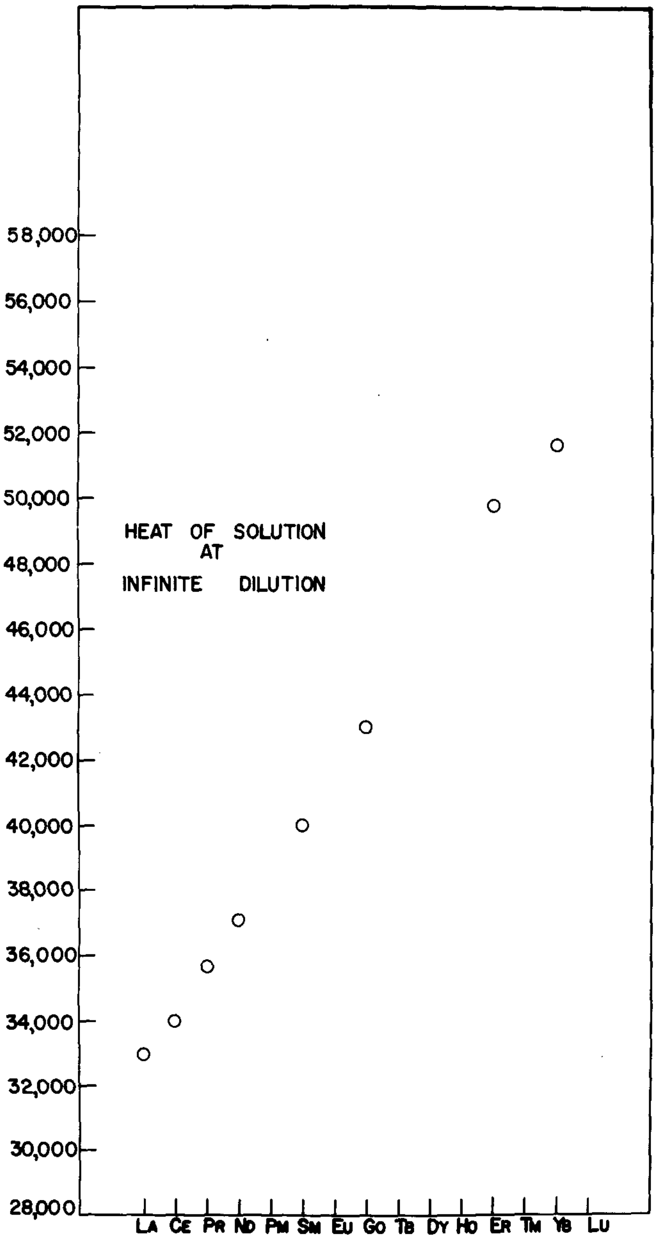


Figure 17. Heats of Solution at Infinite Dilution of the Rare Earth Trichlorides in Calories Per Mole.

Kojima, Inoue, and Ishiyama (54). Recently, Carter (55) identified the γ form as monoclinic by working out the crystal structure of yttrium chloride in detail using single crystals. By comparing X-ray powder diffraction patterns of the trichlorides of dysprosium through lutetium with a powder diagram of yttrium chloride, Carter showed these chlorides to be isostructural. The lattice constants of dysprosium, holmium, erbium, and thulium chlorides decrease almost linearly with increasing atomic number in accordance with the lanthanide contraction. Marked expansions of the *a* and *c* axes of ytterbium and lutetium chlorides were observed while the *b* axis continued to shrink as expected; the total volume of the unit cell increased correspondingly. Although powder diagrams of the chlorides used in the present work are not yet available, it is believed that their structures should be identical with those studied by the aforementioned authors. The crystallographic observations are in qualitative agreement with the heat of solution data presented here. Thus, one would predict a regular relationship from lanthanum to gadolinium since these chlorides are isostructural. Erbium and ytterbium chlorides would not be expected to fall on a line with the lighter rare earths because of the change from hexagonal to monoclinic structures. That ytterbium chloride breaks back sharply towards the straight line through the light rare earths is in qualitative agreement with the sudden change in volume of the unit cell observed by Carter.

The semi-empirical equation

$$\text{IV-1.} \qquad Q_M = a + bm^{\frac{1}{2}} + cm$$

which was formulated to represent the heat of solution data of the chlorides can be used to calculate the relative apparent molal heat content, $\underline{\phi_L}$. Subtraction of the constant, $\underline{a}$, gives

$$\text{IV-25.} \qquad \phi_L = -(bm^{\frac{1}{2}} + cm)$$

in the concentration range studied. Since the data presented here was obtained primarily to calculate other heat quantities, the concentration range studied was relatively small, viz., 0.01-0.09 molal. Furthermore, the data was obtained in a concentration range too high to be used to check the theoretical limiting laws given by the Debye-Huckel theory. To check these limiting laws these studies must be extended to much more dilute solutions than those investigated for this thesis. In these more dilute ranges relative apparent molal heat contents determined from heat of solution data are not very accurate since they represent the difference between two large numbers; they are more precisely determined at very low concentrations from heat of dilution experiments in which a solution of known concentration is diluted in a calorimeter (32). Therefore, since calculations of the relative partial molal heat contents from the data reported here would be for a very limited and relatively uninteresting concentration range, they were not made. However, the data presented in the tables may be used to extend heat of dilution data to higher concentrations.

A few remarks on oxychlorides are in order since their presence in the original materials or their formation by hydrolysis would lead to low results. Final solutions obtained from rare earth chloride experiments showed no obvious evidences of insolubility and Tyndall light tests indicated the absence of colloidal oxychloride particles. This was not true in the case of yttrium chloride; final solutions showed Tyndall effects due to the scattering of light by insoluble oxychloride particles. The anhydrous salt was prepared three times by the procedure described earlier and each time the final solutions gave Tyndall cones. To eliminate the Tyndall effect it was found necessary to run the experiments in solutions made to a pH of about three with hydrochloric acid. Since the analytical results were good and the presence of oxychloride was observable only in the Tyndall cone, it was believed that the oxychloride content was very small. No corrections were applied to the measured data since it was not clear whether the oxychloride was present originally or was produced by hydrolysis. If the oxychloride were present originally, then the acid served to dissolve the colloidal oxychloride which, by estimation, has a heat of solution of the same order of magnitude as does the anhydrous chloride in water; if the presence of acid prevented hydrolysis, no extra heat is involved since the heat effects of hydrolysis and solution are equal in magnitude and opposite in sign. The increase in ionic strength due to the presence of the hydrochloric acid had a negligibly small effect on the heat of solution of yttrium chloride.

The data presented in this work on the heats of solution of the rare earth metals in hydrochloric acid solutions are in better agreement with the results of Lohr and Cunningham (11), Neumann, Kroger, and Kunz (42), and Sieverts and Gotta (41), than with those of Bommer and Hohmann (7). Bommer and Hohmann prepared their metal samples by reduction of the anhydrous chlorides with potassium metal in vacuo. The resultant slag and metal were placed in a calorimeter and after the potassium chloride slag dissolved, hydrochloric acid was added from a burette to dissolve the metal. Complete reduction of the rare earth chloride was assumed in the calculations. It would seem that such a technique would reduce the accuracy of heat leak corrections; furthermore, potassium dissolved or occluded by the rare earth metals would lead to high results. The presence of varying amounts of oxides in the metals used by the other authors would explain the differences in their results; the lanthanum metal used by Sieverts and Gotta was only 84 percent pure. The metals used in the present work were prepared by reducing the anhydrous fluorides with calcium; the reductions were made in tantalum containers in an inert atmosphere. Since precautions were taken to keep oxygen out of the reactant materials and away from the reduction reaction, it is believed the metals contained a minimum of this element. Oxide impurities would produce lower results in the data reported here. The heats of solution of the oxides were estimated to be about 30 percent of the heats of solution of the metals per gram atom of rare earth. Unfortunately, a reliable method for the determination of oxygen in rare earth metals is not presently available; for this reason, the oxide content of the metals used in this work are not reported in Table 1 although it was believed to be very low.

In general, the heats of formation of the rare earth chlorides and ions studied in this work decrease with increasing atomic number of the rare earth. The heat of formation of the aqueous praseodymium ion is nearly equal to that of lanthanum making a sharp break in the plot in Figure 16. Assuming the metals to be completely free of oxides, this equality of the heats of formation of the aqueous ions indicates that the increase in the metal bond energy from lanthanum to praseodymium is just offset by an increase in hydration energy. This break is not as sharply manifested when the heats of formation of the chlorides are considered; the reason for this is that the heat of solution of the anhydrous chloride, which enters into the calculations, is greater for praseodymium chloride than it is for lanthanum chloride. The heats of formation given in the present work do not agree with those given in the tabulations of the National Bureau of Standards (57) since the values reported there were calculated on the basis of the heat of solution data of Bommer and Hohmann (7, 8).

The free energies of formation of the compounds given in Tables 20 and 21 are based upon estimates of the entropies of the compounds. These values are subject to revision as more accurate entropy values for the compounds become available.

Only Matignon (40) has reported the heat of solution of a hydrated rare earth chloride. His value of $\underline{Q_M}$ = 5.3 Kcals/mole for $PrCl_3 \cdot 7H_2O$ cannot properly be compared with those given in this thesis because his final concentration was not specified. The plot in Figure 18 of the heats of solution of the hydrates shows some interesting features of these compounds. Praseodymium chloride forms the most stable seven-hydrate and gadolinium chloride the most stable six-hydrate under ordinary laboratory conditions. There is a regular decrease in $\underline{Q_M}$ with atomic number in the case of

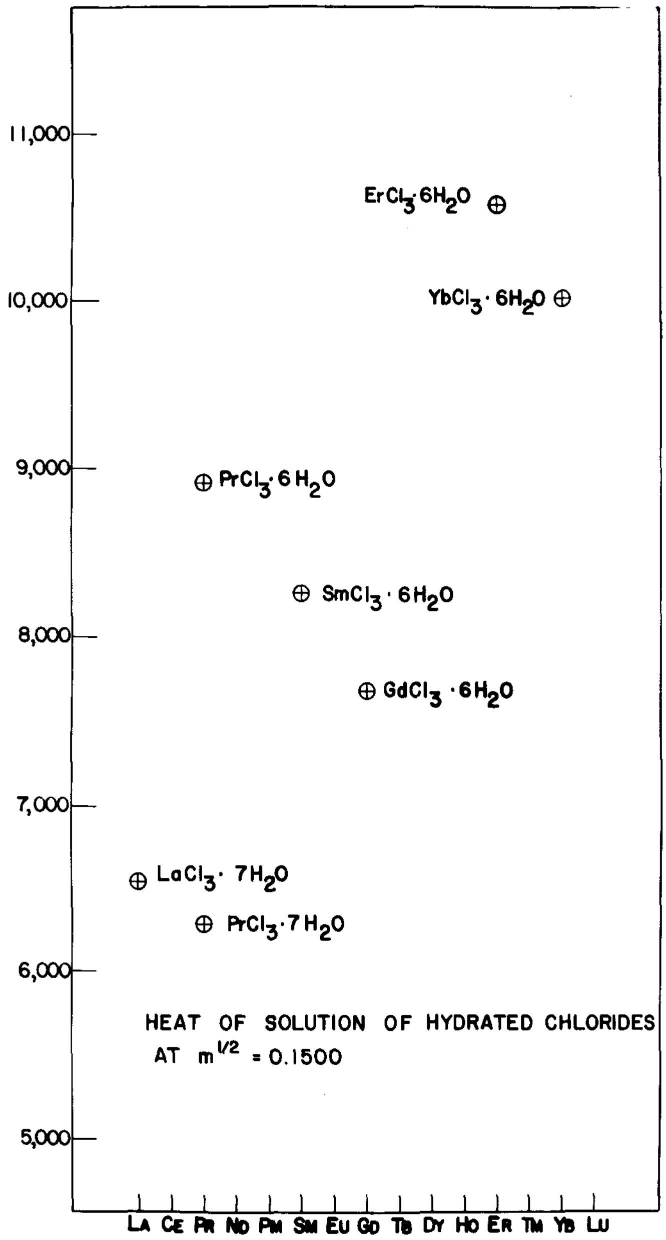


Figure 18. Integral Heats of Solution of the Hydrated Rare Earth Trichlorides at $m^{\frac{1}{2}} = 0.1500$ in Calories Per Mole.

$PrCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$ and $GdCl_3 6H_2O$. That $ErCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ were observed to have higher heats of solution than expected indicates a possible structural change. Changes in crystal systems have been reported in the case of the hydrated chlorides by Iveronova, et al (60); both $NdCl_3 \cdot 6H_2O$ and $SmCl_3 \cdot 6H_2O$ were reported as monoclinic and $LaCl_3 \cdot nH_2O$ and $PrCl_3 \cdot nH_2O$ as triclinic; the number n was not specifically identified. One would expect a structural change and, therefore, a heat of solution change, in the case of going from a crystal with seven waters of crystallization to one with only six; thus, the break at erbium in the heat of solution plot suggests there is a change in crystal form occurring here which is probably brought about by changes in packing due to the smaller erbium ion. An X-ray study of the structures of the hydrated chlorides of the rare earths is presently underway at this Laboratory; when completed, the anomalous behavior in the thermal data reported here may be resolved.

The total hydration energy of the chloride ion should be the same at infinite dilution for the series of compounds studied in this work; for this reason, the differences in the heats of solution of the anhydrous chlorides at infinite dilution are a measure of the differences in lattice energies of the crystals and total hydration energies of the cations. On the basis of the lanthanide contraction one would predict that the lattice energy would increase positively for the seven hexagonal rare earth chlorides. Since the heats of solution increase negatively for the same group it is seen that the differences in total hydration energies are greater than the differences in lattice energies. The same observation is true in the case of erbium and ytterbium. A quantitative measure of these differences will be possible once the lattice energies have been calculated.

V. GENERAL SUMMARY

An isothermally jacketed calorimeter has been constructed to measure the changes in heat content accompanying the solution of some rare earth metals and compounds. To check the performance of the apparatus, the integral heats of solution of potassium nitrate in water at 25°C have been measured. The values corrected to infinite dilution by use of the relative apparent molal heat content data given by Harned and Owen (32) give 8384±12 cals/mole. The result agrees well with the adiabatically measured value of Lange and Monheim (34).

The integral heats of solution in water of the anhydrous chlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, ytterbium, and yttrium, have been measured at 25°C. For each salt empirical equations of the general form

$$\text{IV-1.} \qquad Q_M = a + bm^{\frac{1}{2}} + cm$$

have been formulated to represent the experimental data in the concentration range studied. The constant, b, has been taken as the theoretical value given by the Debye-Huckel theory. The values of the constants, a and c, are given in Table 19. The plot in Figure 17 of the heats of solution at infinite dilution gives a smooth curve for the chlorides from lanthanum through gadolinium. That erbium and ytterbium do not form part of the smooth curve is explained on the basis of the change in crystal structure from hexagonal to monoclinic.

The relation of heats of solution to lattice and hydration energies has been discussed. Once the lattice energies of the rare earth chlorides have been calculated the hydration energies of the rare earth cations can be determined from the data presented here.

A brief discussion of the thermodynamics of binary solutions has been presented and the relationship of partial molal and apparent molal heat quantities to heats of solution and dilution is indicated. The data presented here can be used to extend heat of dilution data at low concentrations to the intermediate concentration range studied for this thesis.

The integral heats of solution of the metals and anhydrous chlorides of yttrium, lanthanum, praseodymium, gadolinium, and erbium, have been measured in hydrochloric acid solutions at 25°C. These data have been used to calculate the standard heats of formation of the anhydrous chlorides and aqueous rare earth ions given in Table 21.

The integral heats of solution of the hydrated chlorides of yttrium, lanthanum, praseodymium, samarium, gadolinium, erbium, and ytterbium, have been measured in water at 25°C. These data, together with the heats of solution of the anhydrous chlorides in water, have been used to calculate the heats of hydration given in Table 20.

The standard heats of formation of the hydrated chlorides of yttrium, lanthanum, praseodymium, gadolinium, and erbium, have been calculated from the data on the heats of hydration and heats of formation of the anhydrous chlorides. These results are given in Table 20.

From estimates of the entropies of the elements and compounds by the method of Latimer (51, 52), the standard entropies of formation of the anhydrous and hydrated chlorides of yttrium, lanthanum, praseodymium, gadolinium, and erbium, have been approximated. Using the standard entropies and heats of formation, the standard free energies of formation of the same compounds have been calculated. These results are given in Tables 20 and 21.

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