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Chapter 1.

INTRODUCTION

High temperature thermodynamic property measurements are of particular interest from the point of view of chemists, as their basic importance is in calculating the thermodynamic feasibility of a specific chemical process at elevated temperatures. Enthalpy is a basic property of a material and at a certain temperature and pressure has a fixed value, which is the sum of the enthalpies of each constituent, minus any heat evolved in the process of bringing them together. Changes in enthalpy are defined as differences between the initial and final states of the system only, i.e.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$  \hspace{1cm} (1-1)

For a chemical reaction,

$$\Delta H = \sum_i (H_i)_{\text{products}} - \sum_j (H_j)_{\text{reactants}}$$  \hspace{1cm} (1-2)

or, for a physical change from $P_1T_1$ to $P_2T_2$, where $T_2 > T_1$, one measures $(H_{T_2} - H_{T_1})$, the enthalpy increment. In practice one measures the change in enthalpy of a substance and the absolute value is not known. It is conventional to take enthalpy at 298°K arbitrarily as zero when the substances are in their standard states.

From the variation of $(H_{T_2} - H_{T_1})$ with temperature, one defines

$$C_p = \left(\frac{dH}{dT}\right) = \text{ the heat capacity at constant temperature and thus,}$$

$$H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p(T) \cdot dT$$  \hspace{1cm} (1-3)
Statistical mechanics furnishes an exact approach to the calculation of thermodynamic properties of gases, for which detailed energy level information is available from spectroscopic studies. For solids, the situation is more complex (1).

An ideal solid may be regarded as a space lattice of independent particles vibrating about their equilibrium positions. Heat capacity arises as these particles move and acquire kinetic energy as well as potential energy, increasing with temperature increase. For harmonic oscillators, equipartition principles predict that the energy content of such a system is

$$E = 3kT$$  \hspace{1cm} (1.4)

so that the heat capacity at constant volume is given by,

$$C_v = \frac{\partial E}{\partial T} = 3R$$  \hspace{1cm} (1.5)

The heat capacity of many solids (per atom) is found to be approximately this value and the principle of equipartition of energy provides a theoretical explanation of the empirical Dulong and Petit rule (2). This rule states that the atomic heat capacity is about 6.2 cals./gm. atom/deg. Certain light elements, for example Be and C, show significant departure from these values and further, the heat capacities tend towards zero as the temperature approaches absolute zero.

Einstein (3) was the first to apply the idea of the quantum theory to the problem of the heat capacities of solid materials. He considered the solid as an ideal space lattice of independent atoms vibrating about their mean equilibrium position. On the assumption of the harmonic oscillator he derived the following expression:

$$C_v = 3Nk(h\nu/kT)^2 \cdot \frac{e^{h\nu/kT} - 1}{h\nu/kT} \cdot \frac{e^{h\nu/kT}}{e^{h\nu/kT}} \cdot 2$$  \hspace{1cm} (1.6)
where \( k \) = the Boltzmann constant

\( h \) = the Planck constant

\( \nu \) = oscillator frequency

The Einstein equation predicts that the heat capacity should be equal to the classical value of \( 3R \) at high temperatures and approach zero as the temperature approaches zero. Einstein's theory is a definite improvement, but it is found that the theoretical heat capacities of most solid elements do not conform quantitatively.

Debye (4) improved Einstein's approach on the assumption that atoms are vibrating with a broad spectrum of frequencies but with a definite maximum. A solid containing \( N \) atoms will have \( 3N \) coupled oscillators and will have \( 3N \) different frequencies. He assumed that the distribution of the frequencies is that of an isotropic elastic medium and is equivalent to elastic waves like sound waves in a continuous medium. The number of modes of vibrations \( dn \), vibrating in one direction and lying between the range \( \nu + d\nu \) is given by,

\[
\text{dn} = \frac{4\pi \nu^2}{c^3} \cdot d\nu
\]  

(1-7)

where \( c \) is the velocity of light and \( \nu \) is the volume of the solid.

The waves have three components vibrating in three mutually perpendicular fields. These consist of one longitudinal wave vibrating in the direction of propagation with velocity \( c_1 \) and two transverse waves vibrating with velocity \( c_t \). Then expression (1 - 7) becomes

\[
\text{dn} = \frac{4\pi \nu}{c_1^3 + 2/c_t^3} \cdot \sqrt{\nu} \cdot d\nu
\]  

(1-8)
The total number of vibrations, which is $3N$ for a system containing $N$ atoms, can be obtained by integrating equation (1-8) between the limits 0 and the frequency $v_m$

$$3N = 4\pi\nu (1/c_1^3 + 2/c_1^3) \int_0^{v_m} v^2 dv$$

$$= \frac{h\pi\nu}{3} (1/c_1^3 + 1/c_T^3) v_m^3 \tag{1-9}$$

The number of modes of vibrations in three directions between the range $v + dv$ is

$$dn = 9N \frac{\sqrt{v}}{v_m^3} \cdot dv \tag{1-10}$$

Using the quantum mechanical value of the mean energy of a harmonic oscillator, the total internal energy of oscillators can be represented by

$$E = \frac{9N}{v_m^3} \int_0^{v_m} \left( \frac{hv}{h\nu/kT} + \frac{hv}{2} \right) v^2 dv \tag{1-11}$$

Defining the Debye characteristic temperature as

$$\Theta = \frac{h\nu_m}{k}$$

and expressing $h\nu/kT$ as $x$, we have as the energy expression,

$$E = \frac{9NkT}{\Theta} \left( \frac{T}{\Theta} \right)^3 \int_0^{\frac{T}{\Theta}} \left( \frac{x^3}{e^{x} - 1} \right) \cdot dx + \frac{9Nk}{\Theta} \Theta \tag{1-12}$$

Differentiation of the above expression with respect to temperatures gives the equation for $C_v$, i.e.,

$$C_v = 3Nk \left\{ 12\left( \frac{T}{\Theta} \right)^3 \int_0^{\frac{T}{\Theta}} \left( \frac{x^3}{e^{x} - 1} \right) dx - \left( \frac{3}{e^{\frac{T}{\Theta}} - 1} \right) \left( \frac{\Theta}{T} \right) \right\} \tag{1-13}$$
This expression can be integrated as an infinite series and integrating term by term for moderate or high temperature, then the expression for \( C_v \) becomes

\[
(\text{a}) \quad C_v = 3Nk \left\{ 1 - \frac{1}{20} \left( \frac{\theta}{T} \right)^2 + \frac{1}{560} \left( \frac{\theta}{T} \right)^4 \right\} \quad (1 - 14)
\]

\[
(\text{b}) \quad \text{for low temperatures}
\]

\[
C_v = 3Nk \left\{ \frac{4}{5} \cdot \pi^4 \left( \frac{T/\theta}{3} \right)^3 - \cdots \right\} \quad (1 - 15)
\]

\[
= 464.4 \left( \frac{T}{\theta} \right)^3 \approx aT^3 \quad (1 - 16)
\]

From the above equations it can be concluded that \( C_v \) is a function of \((\theta/T)\) only. The Debye equations give a better agreement for real solids than the Einstein equations, and are particularly useful in the low temperature region. At low temperatures, \( C_v \) is proportional to \( T^3 \) and goes to zero at absolute zero. This \( T^3 \)-law is found to be very useful for extrapolating heat capacities to absolute zero, and for establishing entropies from the thermal data.

Later Born and Von Karman (5,6) postulated a more exact theory than Debye's but it requires a knowledge of interatomic forces and elastic constants which are not generally available. They calculated the frequencies of a simple cubic lattice and the total heat capacity is the sum of the contributions of individual vibrations,
\[ C_v = \sum E(hv/kT) \]  \hspace{1cm} (1-17)

If \( f_T(v) \) is the vibrational spectrum, then, the heat capacity can be expressed as

\[ C_v = \int f_T(v) \cdot E(hv/kT) \]  \hspace{1cm} (1-18)

The distribution of frequencies can be represented by

\[ f_T(v) = \frac{72N}{\pi^3v_m} \left( \sin^{-1} \frac{\sqrt{2}/v_m}{v/\sqrt{2}} \right)^2 \]  \hspace{1cm} (1-19)

where \( N \) is the number of atoms.

However, their theory makes a significant contribution toward the theoretical calculation of the heat capacity of solids and crystals.

Later Thirring (7) extended the work of Born and Von Karman and derived a more general equation for the heat capacity which can be applied to any crystal. Blackman (8) computed values of Debye characteristic temperatures and found that it is not constant but varies with temperature.

Recently, distributions of lattice vibrations for Na have been calculated on Born and Von Karman's theory (9). Force constants have been evaluated from the inelastic neutron scattering experiments and specific heats and Debye temperatures have been calculated from the results. The results indicate a variation of the Debye temperature below 40°K. In a recent paper, Foreman (10) discusses in detail the high temperature contribution toward lattice specific heat of a solid, i.e., correction to Dulong and Petit's value of 3k per atom, due to anharmonicity (11-15).
For solids, experimental data are currently more reliable than calculated values. From experimental enthalpy increments or heat capacity data, one can derive the following relationships:

(a) Free energy functions:

\[
\left( \frac{F^0_T - H^0}{T} \right)_T = -S^0_T + \frac{H^0_T - H^0}{T} \tag{1-20}
\]

(b) Entropy:

\[
S_T = \int_0^T \frac{C_p}{T} \, dT + \int_{T_1}^{T_2} \frac{\Delta H^0}{T} \, dT + \int_{T_1}^{T_1} \frac{C_p}{T} \, dT + \ldots \tag{1-21}
\]

(c) Enthalpy functions:

\[
\left( \frac{H_T - H_0}{T} \right) = \frac{1}{T} \left[ \int_0^{T_1} C_p \, dT + \int_{T_1}^{T_2} \Delta H^0 \, dT + \int_{T_1}^{T_1} C_p \, dT \right] + \ldots \tag{1-22}
\]

These functions are extremely useful. For example, one can examine the feasibility of a chemical reaction at various temperatures, when free energy functions and heats of formation are known, through the equations:

\[
\Delta (\text{free energy function}) = \left( \frac{F^0_T - H^0}{T} \right)_{\text{products}} - \left( \frac{F^0_T - H^0}{T} \right)_{\text{reactants}}
\]

\[
\Delta (\text{fef}) = \frac{\Delta F^0}{T} - \frac{\Delta H^0}{T}
\]

\[
= -R \ln K_{eq} - \frac{\Delta H^0}{T} \tag{1-23}
\]
Free energy functions are now compiled for a large number of compounds in the temperature range 298°C to 3000°C (16).

In this thesis, a drop-type copper-block calorimeter has been used to determine enthalpy increments of various refractory compounds, including several trifluorides of the rare earth elements. The heat contents and heat capacities of these compounds are not available in the literature and results of this sort make up part of a comprehensive effort to study the thermodynamic properties of refractory materials, especially transition element fluorides.
Chapter 2.

CALORIMETRIC TECHNIQUES

Introduction

Heat capacity and heat content data are generally available only up to $1500^\circ$K, but for over 50 years it has been possible to operate furnaces at much higher temperatures, up to $3000^\circ$K, or higher. However, there are many problems -- structural materials, control and measurement of the furnace temperature, etc. Drop-calorimeters are commonly used in the higher temperature regions but an adiabatic calorimeter can be applied up to $\sim 1000^\circ$C. In addition to these methods, differential calorimeters and transient techniques can also be utilized for calorimetric measurements. In this section, a short description of these various methods as applied to heat content and heat capacity measurement will be presented. There are several recent and comprehensive reviews (17, 18).

Adiabatic Calorimetry

The adiabatic method for determination of heat capacities is based on the elimination of heat exchange between the calorimeter proper and the surroundings, so that energy supplied goes solely to increase the temperature of the sample. If the heat exchange between the calorimeter and jacket is zero, (as in the ideal case), or negligible, heat capacity can be calculated from the energy input, $\Delta H$, and the temperature increase of the sample, $\Delta T$, i.e. $C_p = \Delta H / \Delta T$. Heat capacity is directly determined
in this method and the results are often of great accuracy. The advantages of this method have been discussed in great detail by White (19) and Sturtevant (17). To mention a few of these advantages, corrections for heat exchange by radiation or convection are reduced to a minimum, and the apparatus is capable of running continuously from the lowest to highest temperature. This method has found wide application in the study of phase transitions and order-disorder phenomena since one may study a sample over arbitrarily small energy and temperature increments.

The adiabatic calorimeter finds its widest application for heat capacity measurements in the regions of low temperature. Several low temperature adiabatic calorimeters have been recently described (20,22).

At higher temperatures, adiabatic conditions are difficult to maintain and the problems of the high temperature adiabatic calorimeter have been discussed by West and Westrum (18). The thermal head between the calorimeter and jacket is kept to a minimum by making arrangements to heat the calorimeter at a constant rate and making the shield follow closely. A differential thermocouple relay circuit can be used as a controller (23), and recently Stansbury, Nauman and Brooks (24) reported a modified thermocouple comparator circuit. West and Ginnings (25) have described an adiabatic calorimeter which can be used up to 600° and a temperature differential of ±0.001° can be maintained between the calorimeter and jacket automatically. Only a few adiabatic calorimeters which can be operated above 500° can be found in the literature (26, 29). Backhurst described an automatically controlled adiabatic
calorimeter for the study of Ti and various steels up to 1600° (30).

**Drop Calorimetry**

The measurement of enthalpy increments $H_T - H_{T_{\text{ref}}}$ where $T_{\text{ref}}$ is usually 298°K, by means of a drop calorimeter is readily performed and particularly suitable for high temperature studies. This method is reliable for slowly varying heat capacities, but is less suitable for locating anomalies as, for example, transitions with small heat effects.

In the drop method a weighed sample is heated in the isothermal zone of a furnace and then dropped into a calorimeter of known heat capacity. The enthalpy content of the sample can easily be calculated from the rise in the temperature of the calibrated calorimeter block as measured with a resistance thermometer (Pt, Cu or Ni), a thermocouple, a thermistor or most conveniently with a quartz thermometer. In the ice or diphenyl ether calorimeter, the amount of liquid formed is a measure of the amount of heat transferred from the sample to the calorimeter. Heat losses from the container plus contents during the fall tends to cancel out as the system is calibrated by dropping standard samples (Al$_2$O$_3$ in the container, or the empty container). The heat capacities may be calculated from the slope of the $(H_T - H_{T_{\text{ref}}})$ vs temperature curve and with proper precautions they are accurate to within a few tenths of a per cent.

One of the major problems in high temperature-drop calorimetry is the design and construction of a furnace to provide a reasonably extended zone of uniform temperature. Electrical resistance methods are found to
be the most suitable and easy to control. Excellent discussions on the construction of high temperature furnaces are found in the literature (30). Kanthal- or Pt-wound furnaces are commonly used for calorimetric experiments up to 1400-1500°C and 80% Pt-20% Rh wire-wound furnaces can be operated up to 1700°C. Russian workers (32a,b) have used a tungsten-resistance furnace for heat content measurements on W, SiC and BeO, while Hoch and Johnston (33,34) used an induction heater for the measurements of heat contents of W and Ta (up to 3000°C) and Al₂O₃ and ThO₂ (up to 2500°C), by the drop technique. Levinson (35,36) used a graphite furnace for enthalpy measurements on refractory carbides up to 2700°C using a copper-block calorimeter. West and Ishiara (37) measured the enthalpy of graphite from 1200-2600°C by a slightly different technique in which a hot sample was lifted into an adiabatic calorimeter which operated between 30 and 65°C. An induction furnace was used to heat the cylindrical graphite tube which acted as a susceptor. Conway and Hein (38) employed a split tungsten-tube furnace to determine the enthalpies of Re, Nb and Cr up to 2400°C by dropping the sample into a modified Parr adiabatic calorimeter; and Glasser (39) has described a solar imaging furnace for measuring enthalpies by dropping a hot sample into a copper calorimeter block.

Accurate measurement of temperature poses no particular problem in the range 1200-1800°C. Chromel-Alumel and Pt vs Pt-10% Rh thermocouples are commonly used for the measurement of temperature up to 1200-1300°C, while Pt-20% Rh vs Pt-40% Rh have been successfully used up to 1800°C.
Some other thermocouples -- W vs Ir, Mo vs Re, and W vs Re (40) -- have been used to measure temperatures up to 2700° or higher. In an optical pyrometer, the temperature is determined by comparing the brightness of the hot body with a calibrated sample and this is found to be convenient to measure temperatures beyond 3000°C. The automatic photo-electric pyrometer is the most promising instrument in the field of high temperature measurement, having the advantage of eliminating the personal factor in the measurement and furthermore providing precision (±0.01°) and accuracy (±0.1°C) not previously approached at temperatures above 1000°C (41).

Calibration of the calorimeter is often accomplished by passing a measured amount of electric current through a standard resistance to the calorimeter heater. From the energy input and temperature rise, the calorimeter constant can be calculated. It is conventional in drop calorimetry to check such a calibration against a reference Calorimetry Conference sample (42). Alternatively the calorimeter can be calibrated by dropping α-Al₂O₃, the heat capacity of which is known very accurately and accepted as a calorimetry standard and then one can check the reliability of the calibration by measuring the enthalpy content of a sample whose value is known. A detailed description of the calibration process is available (43).

The temperature change of the calorimeter may be followed by a sensitive thermometer and the temperature rise established to ±0.0005° or better. Pt, Cu and Ni resistance thermometers have been used to measure the temperature rise in calorimeters, although in recent years a number
of workers have used thermistors as temperature sensing devices (44,45). A quartz thermometer, recently developed and now available commercially is especially convenient (46). This latter instrument relates changes in the resonant frequency of a quartz crystal to temperature and has both linearity and stability in line with calorimetric requirements for accuracy. The crystals are hermetically sealed in stainless steel cases and are available in various shapes and sizes. Typical temperature ranges are -40 to 230°C. Three different resolutions, 0.01, 0.001 and 0.0001°C are available and the temperatures are visually displayed for different lengths of time depending on the resolution, or they may be put on cards or tape for computer processing of data. It is easier to follow rapid temperature changes, particularly during reaction periods or immediately after a drop than with bridge-type instrumentation. Quartz thermometers have been successfully used in high precision bomb calorimetry and drop calorimetry (47,49).

A bath, the temperature of which can be controlled to within a fraction of a degree, is of great importance for a drop calorimeter and with modern electronic devices the temperature of the bath can be controlled to within ±0.001°C. Recently thermistors have become very popular for control of bath temperatures and they are more sensitive than bimetallic sensors or expanding liquid sensors. A detailed discussion of the temperature control of baths has been presented by Weber (50), Sturtevant (51) and Skinner et al (52).
Among the various types of drop calorimeters one finds the isothermal aneroid calorimeter consisting of a huge metal block (usually Cu or Al), with a receiving well of proper design for the sample which is in a container of non-reacting material like Au, Pt or Pt-10% Rh. Another form of calorimeter is filled with a stirred liquid within a metallic shell. An isothermal phase-change calorimeter is one where heat change is measured by the amount of liquid formed. The Bunsen ice-calorimeter and diphenyl-ether calorimeter are examples of this type.

**Transient Calorimetric Techniques**

All of the previous methods described are limited to \(2500^\circ K\) or in certain cases up to \(3000^\circ K\). This limitation is because of problems concerning the container, temperature measurement methods, enviroment, and reactions between container and sample and not necessarily a limitation of the methods. To avoid these problems, one can utilize transient techniques in which a sudden pulse of energy raises the sample to a very high temperature. The temperature is measured as a function of time and energy input for a period ranging from a few milliseconds to seconds. Typical accuracy of such transient measurements is about \(\pm 5\%\). The sample may be heated suddenly from \(T_{ref}\) to \(T\), or, one may use a capacitor method with a steady state furnace by which the temperature of the sample is raised to a certain high temperature before a pulse of current is passed through the sample to heat it still further. An electric-pulse technique can be used for an electrically-conducting
sample or an arc image furnace; a bright light flash or a laser beam, may be used for heating a non-conducting sample (53,55). Temperature can be determined for conductors from the resistance-temperature relationship as a function of time or a photo-electric pyrometer may be used. This simultaneous and rapid measurement of current, voltage and resistance can be done with precision by an oscilloscope and other electronic devices.

Worthing (56) was first to use the pulse technique for the specific heats of metals, and later Avramescu and others (57,59) used this technique. A comprehensive review of these methods can be found in (60), while Cezairliyan (61) has described simultaneous measurement of heat capacity and electrical resistivity.

**Differential Calorimetry**

The differential calorimeter makes a comparison of the heat absorption or evolution in two identical cells, one of which contains reference material, while the other contains a sample to be characterized. The two cells are heated in such a way that both of them are kept at the same temperature, in spite of exothermic or endothermic transitions. This method is just coming into use for the study of chemical reactions and phase transitions. Sykes (62) and Galenchanko (61) used this type of calorimeter. Recently Oriani (64) studied the heats of formation of the noble metal alloys by this method and Thomassen and Cunningham (65) described an apparatus to study heats of reaction in solid materials up to 1000°C.
A commercial instrument, the differential scanning calorimeter can be used over the range -100°C to 500°C and yield results of \( \sim 1\% \) accuracy on a rapid and routine basis.
Chapter 3.

APPARATUS

The copper-block calorimeter described by Southard (66) was the prototype of this calorimeter. A dropping mechanism is attached to the top of the furnace and the bottom of the furnace is attached to a cylindrical brass tube. At right angles to this tube is attached a side tube of appropriate dimensions and a right angle prism attached to a moveable piston. By viewing through this prism one can measure the surface temperature of the sample container and accurately position the capsule inside the furnace tube. The bottom of the brass tube is attached, through a water-cooled gate, to the calorimeter. The drop tube contains a plunger, from the bottom of which the capsule containing the sample is suspended on a wire into the isothermal zone of the furnace. The furnace is regulated through an SCR regulator. The water gate consists of a clam gate sandwiched between two water cooled plates. The calorimeter proper is contained inside a chromium-plated brass jacket in a well regulated oil bath. After the capsule has attained the equilibrium temperature, it is allowed to fall into the calorimeter. The temperature rise is followed by a quartz thermometer. A more detailed description of different parts of the apparatus will be given in the following sections.

Dropping Mechanism

The function of the drop tube is to allow the sample capsule to fall smoothly into the calorimeter and, when the experiment is complete,
allow one to raise the capsule again into the furnace for the next experiment. The drop tube is a 33-1/3" by 1-1/2" nickel-plated brass tube, which is slotted with 1/8" x 1" holes within a few inches of the bottom. These slots allow air pressure to be released so that the plunger can fall freely, while the unslotted portion acts as an air brake so that the capsule may slip smoothly into the calorimeter well. A slotted stainless steel plunger (1-29/32" by 1-11/32") is located inside the drop tube. A braided wire is attached to the top of the plunger through two pulleys at the top of the tube. The plunger is held in the top by a spring-loaded, solenoid-activated trigger. The plunger is released simultaneously with the opening of the water gate and gate of the calorimeter.

The capsule is suspended from the bottom of the plunger by means of a suitable wire, depending on the temperature range. Kathal, Jeliff alloy K or Chromel can be used up to 1200°C. Pt and Pt-10% Rh wires were used when the temperature was higher than 1200°C but these materials caused considerable trouble by jamming the drop tube.

The drop tube is screwed into the thermocouple support, which in turn is attached to the top of the furnace. A side arm is provided for the introduction of the thermocouple leads.

**Furnace**

The furnace consists of a 1.5" i/d Alundum tube, 20" in length, around which BS-16 Kanthal A-1 wire is wound as suggested by Kingery (31c). The furnace is enclosed inside an 11.5" stainless steel casing and granules of stabilized zirconia are used as insulating material.
Circular transite plates about 1" thick are used as the top and bottom plates of the furnace. Two blowers are used to cool the furnace wall. Proper arrangements were made for the attachment of the drop tube at the top, and a pyrometer port at the bottom.

Power is fed into the furnace through a Barber-Coleman Model 622 SCR controller and a 20 amp Variac is used to regulate the amount of current to the furnace. A control thermocouple along with the temperature measuring thermocouple is fed into the furnace. A silicon controlled rectifier proportions the a-c power to load in a direct relation to the small d-c control signal. The temperature of the furnace can be controlled to within ±1°C up to 1400°C.

The furnace is supported on the flanges of the pyrometer port by means of screws and the lower flange of the pyrometer port is screwed into the water gate.

**Pyrometer Port**

A brass tube 2-1/2" in diameter and 5" long ends with two flanges. A 1-1/4" brass tube is attached at right angles to the main body. A right angle prism is attached to a movable piston and a Vycor window is attached to a flange to allow one to view the capsule for temperature measurement with a pyrometer. The prism can be moved into the drop tube looking directly at the bottom of the capsule for temperature measurement; otherwise, it is pulled out of the path of the capsule.
Water Gate

The water gate consists of nickel-plated brass shutters sandwiched between two water-cooled copper plates. The shutters are operated manually to open or shut the gate.

Bath

The bath consists of a stainless steel tank, 18" in diameter and 18-1/2" in depth. This tank is housed in a 25" x 25" x 22 1/2" wooden box. Vermiculite insulating material is used to pack the air gap between the tank and the box. Transformer oil is the bath liquid and two stirrers are placed on the side to agitate the fluid thoroughly. One of the stirrers is Lightnin Model L, while the other consists of a four bladed propeller on a 5-1/6" shaft, housed inside a 3-1/2" x 1/4" brass tube and is driven by a belt. The driving motor is a 1/20 horsepower, 1800 rpm, Bodine single-phase motor.

The temperature of the bath is controlled by a Precision Temperature Controller Model 123 from the Bailey Instrument Company, Danville, California. The temperature of the bath can be maintained to within ±0.001°C. Cooling water is passed through a copper coil under a constant pressure water head. A Beckman thermometer in a protective aluminium sheath is used to measure the temperature of the bath. The Beckman thermometer is calibrated against an NBS-calibrated thermometer.

The calorimeter and calorimeter jacket are placed on the bottom of the bath on a three-legged aluminium stand. The calorimeter is held on the stand by an aluminium annulus bolted at the top by three sets of
screws. The level of the support is adjusted by levelling screws from the bottom. Photographs of the apparatus are shown in Figs. 1 and 2.

Calorimeter and Calorimeter Jacket

The calorimeter is a massive copper block 5-1/2" in diameter and 8" high. The center receiving well has a gold plated exterior and a rhodium plated interior. A nickel and chromium-plated, tapered outer jacket protects the calorimeter. A hermetically sealed quartz sensor crystal for the quartz thermometer, Model Dy-2801A, manufactured by the DyMec Division of Hewlett-Packard, is used for the measurement of temperature in the calorimeter. The probe is 11/16" in length and about 3/8" in diameter and is attached to a 12 ft. coaxial cable which is permanently sealed to it. A hole is drilled almost on the outer wall of the calorimeter and the probe wrapped with 0.001" Cu-foil so as to fit snugly into the hole. The position of the probe is such that it is almost in the middle of the receiving well. The cable is put inside a copper tube which is in intimate contact with the calorimeter, before it is led out of the calorimeter.

The calorimeter connection to the furnace includes a spring-loaded copper gate, which is mounted on the top of the calorimeter, and is operated from outside by a stainless-steel shaft consisting of two sections, joined by a nylon center section to reduce thermal leakage along the shaft. The calorimeter is supported on a piece of Garolite Bakelite, on which a knife edge is machined for the support and rests on the bottom of the outer jacket.
FIGURE 1
Drop Calorimeter
Fig. 1. Drop Calorimeter

1) Drop Tube Assembly; 2) Furnace;
3) Constant Temperature Oil Bath.
FIGURE 2

Drop Calorimeter Assembly
Fig. 2. Drop Calorimeter Assembly

1) Furnace; 2) Pyrometer Window; 3) Temperature Controller for Constant Temperature Oil Bath; 4) Potentiometer; and 5) Quartz Thermometer.
The outer jacket is made from a nickel and chromium-plated brass cylinder. This consists of two sections and is sealed with a neoprene gasket. A copper coil is soldered at the bottom of the cylinder, and an inert gas is passed through it to maintain an inert atmosphere inside the calorimeter. The top section of the calorimeter jacket has three tubes attached: 1) one tube is for the shaft to the calorimeter closure device; 2) the center tube connects the furnace to the calorimeter receiving well through the water gate; 3) the other tube is for electrical leads.

Capsules

The sample is usually sealed in a capsule made of metal with the specific material used depending on the sample and the temperature range employed. Au, Pt, Pt-10% Rh, stainless steel, tantalum and iridium are among the materials which have been used. The capsule is made in the form of a tapered tube, the body of which is about 1" in length and 3/4" in diameter at the widest part, and the length of the neck is about 3/4". Two ears are provided in the top section to connect with the wire for suspension in the furnace. The reason for making the capsule as a tapered cylinder is to ensure intimate contact with the calorimeter well and, thus, better thermal exchange between the sample capsule and the calorimeter body.

Thermocouples

The temperature of the capsule can be measured by a Pt vs Pt-10%Rh thermocouple. The thermocouple junction is located at the top of the
capsule and slightly to the edge, so that the capsule and thermocouple maintain the same relative position with regard to the furnace wall. The control thermocouple is right beside the temperature-measuring thermocouple.

**Quartz Thermometry**

The Dymec-2801A quartz-crystal thermometer is used to measure the temperature of the calorimeter. This thermometer uses a specially-cut quartz-crystal as the sensor element. The frequency of the crystal changes linearly with temperature. This frequency is compared with the frequency generated from a stable reference source and the output is presented as °C or °F and displayed on a six-digit indicator panel. The sensing crystal is in a hermetically-sealed capsule connected by means of a coaxial cell to the thermometer panel. A complete description of the complex circuitry is available from the manufacturer.

The typical temperature range is -40 to 230°C. The three different resolutions are 0.01, 0.001 and 0.0001°C and the temperature is displayed visually for different lengths of time depending on the resolution. For this measurement the resolution used is 0.0001°C. The linearity of this thermometer is found to be quite good, and compares with the linearity of a conventional platinum resistance thermometer. Maximum variation from reading to reading is only ±0.0002°C and zero drift is about ±0.0°C for a period of one month in absolute scale. Response time to reach 63.2% final value is 1 second.
A calibration curve was provided by the manufacturer and no attempt has been made at further calibration in this laboratory (Fig. 3). However, the thermometer has been checked on a conventional ice-water equilibrium mixture, in the manner suggested by the manufacturer.

Operation of this thermometer is very simple. The sensor probe is connected to the proper sensor oscillator connector, the proper probe button and resolution button are selected and the power switch turned on. Every time the temperature changes, a neon light flashes and the temperature is recorded from the display panel. The interval between two readings is ten seconds when the 0.0001°C scale is used.
FIGURE 3
Quartz Thermometer
Fig. 3. Quartz Thermometer
Chapter 4.

OPERATING PROCEDURE

In this section a brief description of the operating procedure will be given.

A. Procedure Prior to Run

1) The drop tube is removed from the top of the furnace with the plunger trigger in the off position. Precaution is taken during the removal so that the thermocouple is not damaged.

2) The thermocouple base is removed from the drop tube.

3) An annealed wire is attached to the plunger hook with the plunger trigger in the release position. The thermocouple base is screwed to the drop tube. The length of the wire is adjusted and the capsule is attached to the wire. Two ears or metal hooks of the same material are provided for that purpose. The length is adjusted so that the total length of the wire is 104 cm. from the level of the thermocouple base to the bottom of the capsule, and in the suspension position the length between the same two points is 33.3 cm. This ensures that the capsule is in the most isothermal zone of the furnace.

4) The drop tube assembly is mounted back on the top of the furnace.
B. Procedure During Run

1) Now, the calorimeter is ready for operation, and the bath is set at the proper temperature. The Beckman thermometer reads 3.360 which is about 24.90°C.

2) The furnace is turned on and set at the proper temperature.

3) The thermometer probe is connected to the thermometer panel.

4) The cooling water for the water gate is turned on.

5) Helium gas is passed through the calorimeter at the rate of about 26 ml./minute.

6) The capsule is pulled into position when the temperature is attained.

7) The calorimeter temperature is set so that the final temperature after the capsule is dropped always reaches a certain value.

8) The temperature is taken at intervals of 10 seconds.

9) At 600 seconds the calorimeter gates are opened and the capsule is dropped; then, immediately the gate is closed. The exact time of the drop is determined from an electric stop watch. About 4-6 seconds are necessary and the temperature is extrapolated to find the beginning of the main period.

10) Temperatures are noted as before at intervals of 10 seconds till the system is in equilibrium. The total length of an experiment from start to finish is about 50 minutes.
Chapter 5.

CALIBRATION

The energy equivalent of the calorimeter can be determined by two methods: 1) from the rise in temperature when a known amount of electrical energy is fed into the system, or 2) from the rise in temperature produced by dropping a standard sample. In the first method, one uses high-precision, calibrated electrical instrumentation but derives an absolute and very accurate calibration. The second method actually gives comparable values since there are some very pure substances whose heat contents are accurately known and, in addition, extra apparatus (other than that which is normally used), is not needed. $\alpha$-Al$_2$O$_3$ has been accepted as the standard sample for calorimetric calibration. Heat content values have been accurately determined by Furukawa, Douglas, McCoskey and Ginnings (42) at the National Bureau of Standards and pure $\alpha$-Al$_2$O$_3$ can be obtained from NBS for this calibration purpose. The copper-block calorimeter has been calibrated with standard $\alpha$-Al$_2$O$_3$ in this laboratory.

Determination of Corrected Temperature rise.

In isothermal calorimetry, the experiment can be divided into three periods: 1) the initial period in which the temperature rise is entirely due to thermal exchange between the calorimeter and its surroundings, and the heat of stirring; 2) the main period in which the change in temperature occurs as a result of heat input from the
sample and heat exchange from the surroundings; and 3) the final period in which the temperature change in the calorimeter is again due only to heat exchange with the surroundings and heat of stirring.

The relation between the temperature, $T$, of the calorimeter and the time, $t$, in which the hot sample is dropped is illustrated in Figure 4, in which the regions 'a b', 'b e', and 'e f' represent the initial, main and final periods, respectively. $T_j$ represents the temperature of the calorimeter jacket and $T_0$ is the convergence temperature, i.e. the temperature it would attain at infinite time. The lengths of the initial and final periods are between 10-20 minutes and the temperature is measured at equal intervals during these periods.

The length of the main period depends upon the lag of the calorimeter and should be long enough so that a steady rate of change of temperature is established. The length should be greater by a factor of 10 than the time required for the temperature rise to attain two thirds of its final value. During the main period the temperature should be read within intervals of 10-15 secs.

Now if $T_b$ and $T_e$ are the temperatures at the beginning and end of the main period, then the temperature rise is $T_e - T_b$. This value should be corrected for the heat of stirring and the heat exchange between the calorimeter and surroundings to get the correct temperature rise. On the assumption that Newton's law of cooling is valid for thermal exchange between the calorimeter and jacket, then the rate of temperature rise due to thermal leakage and stirring is given by

$$\frac{dT}{dt} = u + k(T_j - T) \quad (5 - 1)$$
FIGURE 4

Time Temperature Curve for Isothermal Calorimeter
Fig. 4  Time Temperature Curve for Isothermal Calorimeter
where \( k \) is the Newton's law constant and \( u \) is the constant rate of temperature rise due to the constant rate of stirring.

Now when \( T = T_\infty \), \( \frac{dT}{dt} = 0 \), then from equation (1)

\[
T_j = T_\infty - \frac{u}{k} \quad (5-2)
\]

Substituting the value of \( T_j \) in equation (1)

\[
\frac{dT}{dt} = k(T_\infty - T) \quad (5-3)
\]

Now if \( R_i \) and \( R_f \) are the initial and final rates at mean temperatures \( T_i \) and \( T_f \), then from equations (1) and (2) one gets

\[
k = \frac{R_i - R_f}{T_f - T_i} \quad (5-4)
\]

\[
u = R_f + k(T_f - T_j) \quad (5-5)
\]

\[
T = \frac{R_f}{k} + T_f = \frac{R_i T_f - R_f T_i}{R_i - R_f} \quad (5-6)
\]

Again combining the equation

\[
R_f = u + k(T_j - T_f) \quad (5-7)
\]

with equation (1), one finds,

\[
\frac{dT}{dt} = R_f + k(T_f - T) \quad (5-8)
\]

which does not involve \( u \).

Now the correction \( \Delta T \) must be added to the observed temperature rise, \( T_f - T_b \), to get the true temperature rise for the calorimetric process. The value of \( \Delta T \) can be obtained by integrating any of the equations (5-1), (5-5), or (5-8). The resulting expressions are (5-9), (5-10) and (5-11) respectively.
\[ \Delta T = -u(t_e - t_b) - k \int_{t_b}^{t_e} (T_j - T) \, dt \]
\[ = \left[ u + k(T_j - T_m) \right] (t_e - t_b) \quad \ldots \ldots \quad (5 - 9) \]
\[ \Delta T = -k \int_{t_b}^{t_e} (T \Delta - T) \, dt \]
\[ = -k (T_m - T) (t_e - t_b) \quad \ldots \ldots \quad (5 - 10) \]
\[ \Delta T = -R_f (t_e - t_b) - k \int_{t_b}^{t_e} (T_f - T) \, dt \]
\[ = -[R_f + k(T_f - T_m)] (t_e - t_b) \quad \ldots \ldots \quad (5 - 11) \]

\( T_m \) is the average temperature of the calorimeter in the main period.

No simple analytical formula to calculate this value of \( T_m \) is derived and the Regnault-Pfaundler method (43) is used when there are \( n \)-temperature readings, \( T_r \) is measured at equal intervals \( \Delta t \) in the main period. Then \( T_m \) is given by
\[ T_m = \left\{ \sum_{r=2}^{n-1} T_r + \frac{T_b + T_e}{2} \right\} \frac{\Delta t}{t_e - t_b} \quad (5 - 12) \]
\[ = \left\{ \sum_{r=2}^{n-1} T_r + \frac{T_b + T_e}{2} \right\} \frac{1}{n - 1} \quad \ldots \ldots \quad (5 - 13) \]

So, the corrected temperature rise is given by
\[ \Delta T_{\text{correct}} = T_e - T_b + \Delta T \quad \ldots \ldots \quad (5 - 14) \]

This method of calculating \( \Delta T \) is valid if air is the only insulating material between the calorimeter and jacket, and if the thickness of the air-space is not more than 12 mm. For a maximum temperature difference of 3° between the calorimeter and jacket.
Calibration of Thermocouples

The Pt vs Pt-10%Rh thermocouples are made from the thermocouple-grade wires purchased from Engelhard Industries. Approximately 3.5 ft. lengths of each wire are welded without flux and the thermocouples are strung on alundum tubes.

The thermocouples were calibrated against a NBS, Text No. G-30774 Pt vs Pt-10%Rh thermocouple, and the emf of the thermocouple was determined at gold point (1063°C) silver point 960.8°C, 630.5°C and 419.5°C (zinc point) with reference junction at 0°C. The uncertainties are not more than 2 micro volts. The standard thermocouple and the test thermocouple were tied together, with the bead of the test thermocouple placed very close to the standard thermocouple. A Kanthal-furnace was used with both ends closed, and an ice bath served as the cold junction. A clean-glass U-tube filled with purified mercury provided the cold junction contact between the thermocouple and the copper wire.

The furnace was regulated by a Barber and Coleman Model 622 SCR-controller and the temperature was taken at intervals of 50-75°C with a Minneapolis Honeywell Model 2745 potentiometer. The difference between the standard thermocouple and the unknown thermocouple was determined from the calibration charts provided by the NBS and the difference is plotted against temperature (in microvolts) for reference and correction of individual temperature measurements (Fig. 5).
FIGURE 5

Calibration Curve for Thermocouple
Calibration of the Calorimeter with $\text{Al}_2\text{O}_3$

The calorimeter was calibrated by dropping a synthetic sapphire sample, prepared by the National Bureau of Standards, into the calorimeter. The $\text{Al}_2\text{O}_3$ is 99.9% pure with a trace of impurities and this sample is accepted as a standard calorimetric substance.

The usual practice in drop calorimetry is to make two measurements, one with the empty (or partially-filled) capsule and a second with the capsule plus more sample under the same conditions. The idea behind this is to cancel out heat loss during the fall of the capsule from the furnace to the calorimeter. This second practice has been followed for all experimental measurements in this thesis.

The sample was contained in gold capsules. Experiments were performed at four different temperatures, 999.3°, 1050.5°, 1091.4° and 1149.3°K and for each temperature two experiments were performed. For each temperature the average value of the temperature rise was assumed and energy input calculated from the work of Furukawa et al. (42), and hence, an energy equivalent was calculated. The value found was 1965.35 cal deg.⁻¹ with an average deviation of ±0.3%, comparable with typical modern calorimetric measurements.

Comparison with $\text{CeO}_2$

To check the reliability of the $\text{Al}_2\text{O}_3$ calibration, one can make measurements on a substance whose enthalpy-content is known and compare with the values obtained. $\text{CeO}_2$ was chosen in this work for two reasons: 1) both low temperature and high temperature data for $\text{CeO}_2$
were available (67, 68) and 2) this was a good compound with which to compare the enthalpies of the rare earth fluorides. The CeO₂ sample was obtained from Johnson and Matthey and was a spectro-chemical grade compound, i.e., 99.9⁺% purity. The sample was checked by x-ray diffraction and no impurities were indicated in the diffraction pattern. The amount of sample taken was 6.78718 g. (vacuo) and a platinum capsule was used for the measurement. The results are presented in Table 1. The accuracy is comparable with results normally reported in high temperature work, including absolute measurement on α-Al₂O₃. The enthalpy-temperature data for CeO₂ are presented in Fig. 6.
Table I

High Temperature Enthalpy Increments for CeO$_2$

<table>
<thead>
<tr>
<th>Temperature $^{\circ}$K</th>
<th>$H^0_T - H^0_{298.15}$ (this work) cal.mole$^{-1}$</th>
<th>$H^0_T - H^0_{298.15}$ (literature) * cal.mole$^{-1}$</th>
<th>% deviation of this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>573.3</td>
<td>4619.3</td>
<td>4588.1</td>
<td>+ 0.68</td>
</tr>
<tr>
<td>674.8</td>
<td>6392.7</td>
<td>6388.1</td>
<td>+ 0.07</td>
</tr>
<tr>
<td>776.4</td>
<td>8203.0</td>
<td>8247.8</td>
<td>- 0.54</td>
</tr>
<tr>
<td>875.2</td>
<td>10063.8</td>
<td>10111.6</td>
<td>- 0.47</td>
</tr>
<tr>
<td>975.3</td>
<td>12033.5</td>
<td>12055.7</td>
<td>- 0.18</td>
</tr>
<tr>
<td>1074.8</td>
<td>13969.5</td>
<td>14043.7</td>
<td>- 0.53</td>
</tr>
<tr>
<td>1174.9</td>
<td>16083.1</td>
<td>16099.7</td>
<td>- 0.10</td>
</tr>
<tr>
<td>1272.9</td>
<td>18143.7</td>
<td>18167.4</td>
<td>- 0.13</td>
</tr>
</tbody>
</table>

* See reference (67)
FIGURE 6

Enthalpy-Temperature Data for CeO$_2$
Chapter 6.

RESULTS AND DISCUSSION

The elements from atomic number 58 to 71 are known as the rare earths and have a unique position in the periodic table of elements. Lanthanum and yttrium have chemical properties similar to these elements and are also found along with the rare earths; they are, therefore, often included with the rare earths. The rare earths have been known for about 150 years but until recently little was known about their chemical and physical properties. One of the reasons for this has been the non-availability of high purity elements and compounds. Obviously, their properties are generally similar since the basic differences in their electronic configurations involve the 4f-electrons in the second-from-outermost energy shell.

The rare earth elements and their compounds are now available in high purity, and there is a great deal of scientific interest in the determination of the physical and chemical properties of these elements and their compounds. It was the lack of quantitative thermodynamic data for the rare earth fluorides that led to this study of the high temperature thermodynamic properties of the rare earth trifluorides. Heats of sublimation and appearance potentials for the rare earth trifluorides are being studied in this laboratory by microbalance and mass spectrometric methods, while the present dissertation deals with the determination of high temperature enthalpy increments. From these measurements, various thermodynamic functions can be derived for use
## Table II

**Analysis Report of Rare Earth Trifluorides**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Metal Content %</th>
<th>Fluorine Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Analysis</td>
</tr>
<tr>
<td>CeF$_3$</td>
<td>71.99</td>
<td>71.78</td>
</tr>
<tr>
<td>PrF$_3$</td>
<td>71.45</td>
<td>71.55</td>
</tr>
<tr>
<td>NdF$_3$</td>
<td>71.68</td>
<td>71.70</td>
</tr>
<tr>
<td>GdF$_3$</td>
<td>73.37</td>
<td>73.08</td>
</tr>
<tr>
<td>DyF$_3$</td>
<td>74.03</td>
<td>73.76</td>
</tr>
</tbody>
</table>
in high temperature calculations.

Materials

The compounds studied were the trifluorides of Ce, Pr, Nd, Gd, Dy and Yb. PrF$_3$ and NdF$_3$ were purchased from Semi-Elements Inc., Saxonburg, Pennsylvania, while the rest of the trifluorides were supplied by Gallard-Schlessinger, New York, New York. These compounds are 99.9% pure and no further purification was made before use, although they were carefully examined by x-ray diffraction to confirm their identity; no impurities were indicated from the diffraction pattern. All of the fluorides except YbF$_3$ were analyzed for metal and for fluorine content by microanalytical methods performed by the Schartzkopf Microanalytical Laboratory of New York and the results are listed in Table II. Samples weighing from 5 to 8 gms. were used.

YbF$_3$ was not analyzed for metal and fluorine content but a careful x-ray examination did not indicate any impurities. These compounds were again examined by x-ray after the measurements were completed to see if there was any oxide or oxyfluoride formation (from hydrolysis) but no lines due to oxides or oxyfluorides were observed. The capsules were also examined but no reaction of the samples with the Pt was observed.

Results

The experimental results and smoothed thermodynamic functions for the trifluorides of Ce, Pr, Nd, Gd, Dy and Yb are presented in Tables III
Table III

Experimental Results for CeF₃
Weight of CeF₃ used = 6.53882 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$H_T^0 - H_{298}^0$ (cal. mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>575.3</td>
<td>6217.3</td>
</tr>
<tr>
<td>675.0</td>
<td>8739.0</td>
</tr>
<tr>
<td>774.8</td>
<td>11310.3</td>
</tr>
<tr>
<td>876.5</td>
<td>13933.4</td>
</tr>
<tr>
<td>975.5</td>
<td>16606.1</td>
</tr>
<tr>
<td>1075.1</td>
<td>19322.6</td>
</tr>
<tr>
<td>1173.0</td>
<td>22097.2</td>
</tr>
<tr>
<td>1273.8</td>
<td>24915.4</td>
</tr>
<tr>
<td>1378.3</td>
<td>27781.5</td>
</tr>
</tbody>
</table>
FIGURE 7

Enthalpy-Temperature Data for CeF₃
Table IV

High Temperature Thermodynamic Functions for CeF₃

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$H^0_T - H^0_{\text{H}_2\text{O}}$</th>
<th>$S^0_T - S^0_{\text{H}_2\text{O}}$</th>
<th>-$\frac{(F^0_T - H^0_{\text{H}_2\text{O}})}{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>(4425.0)</td>
<td>(11.24)</td>
<td>(30.25)</td>
</tr>
<tr>
<td>600</td>
<td>6486.3</td>
<td>15.65</td>
<td>31.78</td>
</tr>
<tr>
<td>700</td>
<td>9356.5</td>
<td>15.52</td>
<td>33.69</td>
</tr>
<tr>
<td>800</td>
<td>11937.9</td>
<td>22.96</td>
<td>35.58</td>
</tr>
<tr>
<td>900</td>
<td>14580.8</td>
<td>26.08</td>
<td>37.42</td>
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<tr>
<td>1000</td>
<td>17279.5</td>
<td>28.92</td>
<td>39.18</td>
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<tr>
<td>1200</td>
<td>22830.4</td>
<td>33.98</td>
<td>42.42</td>
</tr>
<tr>
<td>1300</td>
<td>25678.5</td>
<td>36.25</td>
<td>44.04</td>
</tr>
<tr>
<td>1400</td>
<td>(28573.1)</td>
<td>38.40</td>
<td>(45.53)</td>
</tr>
</tbody>
</table>

*$S^0_{\text{H}_2\text{O}}$ is measured as $27.54 \pm 0.5$ eu (68)

$H^0_T - H^0_{\text{H}_2\text{O}} = 23.53 T + 2.11 \times 10^{-3}T^2 + 4.90 \times 10^5T^{-1} - 8846$ cal.mole⁻¹

($\pm 0.15\%$, 575°K to 1372°K)

$C_p^0 = 23.53 + 4.22 \times 10^{-3}T - 4.90 \times 10^5T^2$ cal.mole⁻¹ deg⁻¹
Table V

Experimental Results for PrF₃

Weight of PrF₃ used = 6.03412 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$^0_{HT}$ $^0_{Ho88.15}$ cal. mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>727.1</td>
<td>10871.1</td>
</tr>
<tr>
<td>799.8</td>
<td>12602.5</td>
</tr>
<tr>
<td>875.7</td>
<td>14602.5</td>
</tr>
<tr>
<td>952.0</td>
<td>17016.6</td>
</tr>
<tr>
<td>1026.3</td>
<td>18964.9</td>
</tr>
<tr>
<td>1099.5</td>
<td>21155.5</td>
</tr>
<tr>
<td>1168.2</td>
<td>22991.0</td>
</tr>
<tr>
<td>1243.2</td>
<td>24965.1</td>
</tr>
<tr>
<td>1324.1</td>
<td>27042.6</td>
</tr>
</tbody>
</table>
FIGURE 8

Enthalpy-Temperature Data for PrF₃
Fig. 8 ENTHALPY-TEMPERATURE FOR PRASEODYMIUM FLUORIDE
Table VI

High Temperature Thermodynamic Functions for PrF$_3$

<table>
<thead>
<tr>
<th>Temperature $^\circ$K</th>
<th>$H_T^0 - H_{298.15}^0$ cal.mole$^{-1}$</th>
<th>$S_T^0 - S_{298.15}^0$ eu</th>
<th>$-(F_T^0 - H_{298}^0)/T$ cal.mole$^{-1}$deg.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>(4991.1)</td>
<td>12.76</td>
<td>30.32</td>
</tr>
<tr>
<td>600</td>
<td>(7538.1)</td>
<td>17.40</td>
<td>32.38</td>
</tr>
<tr>
<td>700</td>
<td>10133.9</td>
<td>21.40</td>
<td>34.47</td>
</tr>
<tr>
<td>800</td>
<td>12778.3</td>
<td>24.93</td>
<td>36.54</td>
</tr>
<tr>
<td>900</td>
<td>15471.6</td>
<td>28.10</td>
<td>38.48</td>
</tr>
<tr>
<td>1000</td>
<td>18213.5</td>
<td>30.99</td>
<td>40.32</td>
</tr>
<tr>
<td>1100</td>
<td>21004.2</td>
<td>33.65</td>
<td>42.10</td>
</tr>
<tr>
<td>1200</td>
<td>23843.5</td>
<td>36.12</td>
<td>43.80</td>
</tr>
<tr>
<td>1300</td>
<td>26731.8</td>
<td>38.43</td>
<td>45.41</td>
</tr>
<tr>
<td>1400</td>
<td>29668.6</td>
<td>40.61</td>
<td>46.96</td>
</tr>
</tbody>
</table>

*$S_{298}$ is estimated as 27.54 ± 0.5 eu.

$H_T^0 - H_{298.15}^0 = 22.79 T + 2.44 \times 10^{-3}T^2 - 7013$ cal.mole$^{-1}$

($\pm 0.5\%$, $727^\circ$K $\leq T \leq 1324^\circ$K)

$C_P^0 = 22.79 + 4.88 \times 10^{-3}T$ cal.mole$^{-1}$deg.$^{-1}$
Table VII
Experimental Results for NdF₃
Weight of NdF₃ used = 7.82129 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$^0\text{H}<em>T - ^0\text{H}</em>{298.15}$ cal.mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>726.5</td>
<td>10423.6</td>
</tr>
<tr>
<td>797.1</td>
<td>12298.2</td>
</tr>
<tr>
<td>876.7</td>
<td>14238.1</td>
</tr>
<tr>
<td>950.5</td>
<td>16433.1</td>
</tr>
<tr>
<td>1027.4</td>
<td>18587.8</td>
</tr>
<tr>
<td>1099.4</td>
<td>20541.1</td>
</tr>
<tr>
<td>1174.4</td>
<td>22659.6</td>
</tr>
<tr>
<td>1247.0</td>
<td>24742.5</td>
</tr>
<tr>
<td>1324.0</td>
<td>26999.8</td>
</tr>
</tbody>
</table>
FIGURE 9

Enthalpy-Temperature Data for NdF₃
Fig. 9  ENTHALPY-TEMPERATURE DATA OF NEODYMIUM FLUORIDE
Table VIII

High Temperature Thermodynamic Functions for NdF₃

<table>
<thead>
<tr>
<th>Temperature 0°C</th>
<th>( \Delta H_{0}^{\circ} - \Delta H_{298.15}^{\circ} ) cal.mole⁻¹</th>
<th>( \Delta S_{0}^{\circ} - \Delta S_{298.15}^{\circ} ) eu</th>
<th>( -\left( \frac{\Delta H_{0}^{\circ} - \Delta H_{298}^{\circ}}{T} \right) ) cal.mole⁻¹deg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>(4642.7)</td>
<td>11.82</td>
<td>30.07</td>
</tr>
<tr>
<td>600</td>
<td>7128.9</td>
<td>16.35</td>
<td>32.01</td>
</tr>
<tr>
<td>700</td>
<td>9693.1</td>
<td>20.30</td>
<td>33.99</td>
</tr>
<tr>
<td>800</td>
<td>12322.5</td>
<td>23.81</td>
<td>35.95</td>
</tr>
<tr>
<td>900</td>
<td>15009.9</td>
<td>26.97</td>
<td>37.83</td>
</tr>
<tr>
<td>1000</td>
<td>17751.5</td>
<td>29.86</td>
<td>39.65</td>
</tr>
<tr>
<td>1100</td>
<td>20544.3</td>
<td>32.52</td>
<td>41.38</td>
</tr>
<tr>
<td>1200</td>
<td>23386.5</td>
<td>34.99</td>
<td>43.04</td>
</tr>
<tr>
<td>1300</td>
<td>26277.0</td>
<td>37.31</td>
<td>44.64</td>
</tr>
<tr>
<td>1400</td>
<td>29214.9</td>
<td>39.49</td>
<td>46.16</td>
</tr>
</tbody>
</table>

\( \Delta S_{298}^{\circ} \) is estimated as 27.54 ± 0.5 eu

\( \Delta H_{0}^{\circ} - \Delta H_{298.15}^{\circ} = 23.62 \, T + 2.22 \times 10^{-3} T^2 + 3.55 \times 10^{5} T^{-1} - 8427 \) cal.mole⁻¹

\( \pm 0.25\%, 727^\circ K \leq T \leq 1324^\circ K \)

\( \Delta C_{p}^{\circ} = 23.62 + 4.44 \times 10^{-3} T - 3.55 \times 10^{5} T^{-2} \) cal mole⁻¹deg⁻¹
### Table IX
Experimental Results for GdF$_3$

Weight of GdF$_3$ used = 5.35782 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature $^\circ$K</th>
<th>$H^0_T - H_{298.15}^0$ cal. mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>576.0</td>
<td>6830.4</td>
</tr>
<tr>
<td>676.0</td>
<td>9408.9</td>
</tr>
<tr>
<td>774.4</td>
<td>12048.2</td>
</tr>
<tr>
<td>875.6</td>
<td>14745.0</td>
</tr>
<tr>
<td>975.3</td>
<td>17510.4</td>
</tr>
<tr>
<td>1074.0</td>
<td>20325.6</td>
</tr>
<tr>
<td>1174.5</td>
<td>23197.2</td>
</tr>
</tbody>
</table>
FIGURE 10

Enthalpy-Temperature Data for GdF₃
Fig. 10 ENTHALPY-TEMPERATURE FOR GADOLINIUM FLUORIDE
Table X

High Temperature Thermodynamic Functions for GdF$_3$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$H_T^0 - H_{298.15}^0$ (cal.mole$^{-1}$)</th>
<th>$S_T^0 - S_{298.15}^0$ (eu)</th>
<th>$-(F_T^0 - H_{298}^0)/T$ (cal.mole$^{-1}$deg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\circ$K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>4921.1</td>
<td>12.57</td>
<td>30.28</td>
</tr>
<tr>
<td>600</td>
<td>7453.6</td>
<td>17.19</td>
<td>32.31</td>
</tr>
<tr>
<td>700</td>
<td>10048.3</td>
<td>21.19</td>
<td>34.38</td>
</tr>
<tr>
<td>800</td>
<td>12705.4</td>
<td>24.74</td>
<td>36.40</td>
</tr>
<tr>
<td>900</td>
<td>15425.0</td>
<td>27.93</td>
<td>38.34</td>
</tr>
<tr>
<td>1000</td>
<td>18206.7</td>
<td>30.87</td>
<td>40.20</td>
</tr>
<tr>
<td>1100</td>
<td>21050.8</td>
<td>33.58</td>
<td>41.98</td>
</tr>
<tr>
<td>1200</td>
<td>23957.3</td>
<td>36.11</td>
<td>43.68</td>
</tr>
</tbody>
</table>

* $S_{298}^0$ is estimated as $27.54 \pm 0.5$ eu.

$H_T^0 - H_{298.15}^0 = 21.90 \ T + 3.12 \times 10^{-3}T^2 - 6806$ cal.mole$^{-1}$

($\pm 0.1\%$, $575^\circ K < T < 1175^\circ K$)

$C_p^0 = 21.90 + 6.24 \times 10^{-3}T$ cal.mole$^{-1}$deg$^{-1}$
Table XI
Experimental Results for DyF$_3$

Weight of DyF$_3$ used = 6.73391 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$K)</th>
<th>$^\circ$H$<em>T$ - $^\circ$H$</em>{298.15}$ cal. mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>576.6</td>
<td>6419.8</td>
</tr>
<tr>
<td>676.3</td>
<td>8956.7</td>
</tr>
<tr>
<td>775.5</td>
<td>11547.4</td>
</tr>
<tr>
<td>877.2</td>
<td>14187.0</td>
</tr>
<tr>
<td>975.2</td>
<td>16872.4</td>
</tr>
<tr>
<td>1075.7</td>
<td>19607.4</td>
</tr>
<tr>
<td>1173.2</td>
<td>22402.0</td>
</tr>
</tbody>
</table>
FIGURE 11

Enthalpy-Temperature Data for DyF$_3$
Fig. II  ENTHALPY - TEMPERATURE FOR DYSPROSIUM FLUORIDE
Table XII
High Temperature Thermodynamic Functions for DyF₃

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>H°ₜ - H°ₑₑₑₑ·₁₅</th>
<th>S°ₜ - S°ₑₑₑₑ·₁₅</th>
<th>-(H°ₜ - H°ₑₑₑₑ)/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>4565.7</td>
<td>11.62</td>
<td>30.03</td>
</tr>
<tr>
<td>600</td>
<td>7021.2</td>
<td>16.02</td>
<td>31.93</td>
</tr>
<tr>
<td>700</td>
<td>9555.4</td>
<td>19.99</td>
<td>33.88</td>
</tr>
<tr>
<td>800</td>
<td>12158.5</td>
<td>23.47</td>
<td>35.81</td>
</tr>
<tr>
<td>900</td>
<td>14822.1</td>
<td>26.61</td>
<td>37.68</td>
</tr>
<tr>
<td>1000</td>
<td>17542.1</td>
<td>29.41</td>
<td>39.47</td>
</tr>
<tr>
<td>1100</td>
<td>20315.5</td>
<td>32.11</td>
<td>41.18</td>
</tr>
<tr>
<td>1200</td>
<td>23140.6</td>
<td>34.57</td>
<td>42.83</td>
</tr>
</tbody>
</table>

*E₂ₑₑₑₑ is estimated as 27.54 ± 0.5 eu

H°ₜ - H°ₑₑₑₑ·₁₅ = 23.22 T + 2.31 x 10⁻³T² + 3.64 x 10⁵T⁻¹ - 8347 cal.mole⁻¹

(±0.16%, 576°K < T < 1173°K)

C°ₚ = 23.22 + 4.62 x 10⁻³T - 3.64 x 10⁵T⁻² cal.mole⁻¹deg⁻¹
Table XIII
Experimental Results for YbF₃

Weight of YbF₃ used = 6.46324 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( H_T^0 - H_{298.15}^0 ) (cal.mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>577.2</td>
<td>6571.4</td>
</tr>
<tr>
<td>675.5</td>
<td>9087.7</td>
</tr>
<tr>
<td>775.9</td>
<td>11656.8</td>
</tr>
<tr>
<td>875.1</td>
<td>14274.6</td>
</tr>
<tr>
<td>976.4</td>
<td>16942.1</td>
</tr>
<tr>
<td>1075.1</td>
<td>19657.4</td>
</tr>
<tr>
<td>1174.5</td>
<td>22427.5</td>
</tr>
</tbody>
</table>
FIGURE 12

Enthalpy-Temperature Data for YbF₃
| Temperature \( ^\circ\text{K} \) | \( \Delta H_T^0 - \Delta H_{298.15}^0 \) cal.mole\(^{-1}\) | \( \Delta S_T^0 - \Delta S_{298.15}^0 \) eu | \( -(\Delta F_T^0 - \Delta H_{298}^0)/T \) cal.mole\(^{-1}\)deg\(^{-1}\) |
|----------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 500            | 4693.2          | 11.96           | 30.11          |                 |                 |                 |                 |                 |
| 600            | 5918.0          | 14.30           | 31.99          |                 |                 |                 |                 |                 |
| 700            | 9692.2          | 20.36           | 34.05          |                 |                 |                 |                 |                 |
| 800            | 12280.6         | 23.82           | 36.01          |                 |                 |                 |                 |                 |
| 900            | 14920.9         | 26.92           | 37.90          |                 |                 |                 |                 |                 |
| 1000           | 17610.4         | 29.76           | 39.69          |                 |                 |                 |                 |                 |
| 1100           | 20347.5         | 32.37           | 41.41          |                 |                 |                 |                 |                 |
| 1200           | 23130.9         | 37.06           | 43.05          |                 |                 |                 |                 |                 |

\( \Delta S_{298} \) is estimated as \( 27.54 \pm 0.5 \) eu

\( \Delta H_T^0 - \Delta H_{298.15}^0 = 23.07T + 2.14 \times 10^{-3}T^2 + 2.29 \times 10^5T^{-1} - 7837 \) cal. mole\(^{-1}\)

\( \pm 0.18\% \), \( 575^\circ\text{K} \leq T \leq 1174^\circ\text{K} \)

\( C_p = 23.07 + 4.28 \times 10^{-3}T - 2.29 \times 10^5T^{-2} \) cal. mole\(^{-1}\)deg\(^{-1}\)
through XIV, with the elements arranged in the order indicated. There are two tables for each compound, the first contains the experimental data and the second contains the smoothed thermodynamic functions along with the fitted equation. Figures 7-12 present the plots of $H^O_T - H^O_{298}$ for these compounds against temperature.

Errors and Corrections

Some of the possible errors and corrections that may be associated with these types of measurements are discussed in the following paragraphs.

Temperature measurements by a Pt-wtPt-10% Rh thermocouple may be in error because of changing calibration or deterioration, depending upon use, environment, handling and time. They are stable and reliable under the conditions used in these experiments, but frequent checks against the NBS-calibrated thermocouple should eliminate such error. The possible error of temperature measurement should not be greater than $\pm 1^\circ C$ at $1200^\circ C$.

In a drop-type calorimeter it is assumed that the heat loss by the empty capsule and full capsule is the same. As the enthalpy is calculated from the difference of two measurements, some of the errors cancel out. Grimley (69) has considered this problem. He found that the assumption is reasonable and that the error involved is insignificant compared with the accuracy of this type of measurement. This is further supported by the fact that there is excellent agreement between drop calorimeter data and adiabatic calorimeter data for many compounds.
Thermodynamic data are conventionally referred to a standard temperature of \(298.15^\circ\text{K}\). Experimentally, one determines the quantity \(H_T^0 - H_{T_f}^0\), where \(T_f\) is the final temperature of the calorimeter. If it is close to the reference temperature and the corrections are small they can be made by means of the following equation:

\[
(H_T - H_{298.15}) = (n_1 \cdot C_{p1} + n_2 \cdot C_{p2} + \ldots \ldots) (T_f - 298.15)
\]

where \(C_p\) is the heat capacity and \(n_i\) is the number of moles of component \(i\).

Enthalpy increments and heat capacities are usually reported for substances at the standard state pressure of one atmosphere. In most cases usually reported, however, the capsule has to be sealed to prevent losses due to sample evaporation and to minimize oxidation. Loss of material can be detected by frequent checks on the weight. In heating the capsule from room temperature to \(1200^\circ\text{C}\), the pressure is increased about 5-fold. The variation of heat capacity with pressure can be represented by:

\[
\left( \frac{\partial C_p}{\partial p} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_p
\]

Now the coefficient of thermal expansion is

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p
\]

Substituting \(\alpha = a + bT\) where \(a, b\) are constants, we have

\[
\left( \frac{\partial C_p}{\partial p} \right)_T = -TV (\alpha^2 + b)
\]
This expression can be evaluated using standard tables and the effect on $C_p$ found to be negligible.

**Discussion of Results**

The rare earth elements are unique in their position and chemical behavior among the elements in the periodic table. After La which has the outer electronic configuration of $5d^1\ 6s^2$, electrons are added to the 4f shell until 14 electrons are added, but there is also a tendency for the $5d^1$ electron to drop into the 4f-level (70), so that one may represent the generalized electronic configuration of the outermost rare earth shells as $4f^n\ 5d^0\ 6s^2$, with the exception of Gd and Lu which have the configurations $4f^7\ 5d^1\ 6s^2$ and $4f^{14}\ 5d^1\ 6s^2$ respectively. The chemistry of the rare earths is almost exclusively that of their tri-positive state, but, in addition, Ce forms Ce (IV)-compounds and Eu and Yb exhibit a valence state of (II). The chemistry of all of these elements shows the close relationship and there are also similarities with other Group III-elements like scandium, yttrium and lanthanum.

One finds an internal periodic behavior in these elements. As 4f-electrons are added with increasing atomic number there is a general contraction (71) and the atomic volume decreases gradually with a discontinuity at the $4f^7$ configuration. The 4f-electrons play an important part in some physical properties of the elements, but do not have much influence on the chemical behavior of their compounds. For example, the oxidation potentials show a gradual decrease from Ce to Yb which reflects their decreasing basicity in the same order, and the same
conclusion can be drawn from the atomic volume relationship (70).

The heats of vaporization of the metals and the dissociation energies of the monoxides show a double periodicity (73, 75). The heats of sublimation of the trifluorides of these elements show similar variations (76), but available measurements of the heats of formation of the trifluorides indicate little difference in the $\Delta H_f$-values for the different compounds (77, 79). The $C_p$-values of all the compounds measured are very similar to each other, as one would expect them to be.

The standard heats of sublimation of the solid rare earth fluorides can be calculated, if the free energy functions of both condensed and gaseous-phases of these compounds are known, from vapor pressure measurements provided that the trifluoride is the main product and no disproportionation or dissociation reactions take place. $\Delta H_{sub}^0$ can be calculated from the free energy functions in the following manner:

\[
\Delta \left( \frac{F^0 \text{ or } H^0}{T} \right)_{\text{reaction}} = \Sigma \left( \frac{F^0 \text{ or } H^0}{T} \right)_{\text{products}} - \Sigma \left( \frac{F^0 \text{ or } H^0}{T} \right)_{\text{reactants}}
\]

\[
= \left( \frac{\Delta F^0}{T} \right)_{\text{reaction}} - \left( \frac{\Delta H^0}{T} \right)_{\text{reaction}}
\]

From the above equation, either $\Delta F^0_T$ or $\Delta H^0_{sub}$ can be calculated if one or the other is known.

Free-energy functions for the solid rare earth fluorides have been calculated from the enthalpy measurements reported here. $\Delta H^0_T$ for rare earth fluoride sublimations have been determined either by microbalance
or mass spectrometric methods. Recently, free-energy functions of
gaseous CeF₃ and LaF₃ have been estimated (80, 81). The values of
the free-energy functions of the gaseous species are very similar,
and so are the values for the solid state which have been calculated
from the enthalpy measurements of this work. By combining the values
of the free energy functions (65) for gaseous CeF₃ or LaF₃ and the
corresponding solid rare earth fluorides in this work, one can cal-
culate third law values for $\Delta H^0_{\text{sub},298}$ . The vapour pressures have been
taken from the literature and heats of sublimation calculated from
the free energy functions in Table XV.

Within the limits of the assumptions, agreement between the
second and third law values are generally within the uncertainties of
the vapour pressure measurements, although the difference for DyF₃
is too large.

Low temperature heat capacity values for CeF₃ are known and
Fig. 13 shows the plot of $C_p$ against temperature. The low temperature
and high temperature curves seem to join smoothly with one another.
Table XV

Comparison of Heats of Sublimation of Rare Earth Fluorides

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^0_{s,298}^{(2nd\ law)}$</th>
<th>$\Delta H^0_{s,298}^{(3rd\ law)^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal.mole$^{-1}$</td>
<td>kcal.mole$^{-1}$</td>
</tr>
<tr>
<td>LaF$_3$</td>
<td>$107.5 \pm 4$ (81)</td>
<td>$103.5 \pm 4$ (81)$^{**}$</td>
</tr>
<tr>
<td></td>
<td>$108 \pm 5$ (82)</td>
<td>$105.0 \pm 5$ (82)</td>
</tr>
<tr>
<td>NdF$_3$</td>
<td>$95.5 \pm 5$ (83)</td>
<td>$99.4 \pm 5$ (83)</td>
</tr>
<tr>
<td>DyF$_3$</td>
<td>$115 \pm 5$ (84)</td>
<td>$104.0 \pm 5$ (84)</td>
</tr>
<tr>
<td>YbF$_3$</td>
<td>$95 \pm 5$ (85)</td>
<td>$100.5 \pm 5$ (85)</td>
</tr>
</tbody>
</table>

* Based on estimated free energy functions for gaseous MF$_3$ species (80, 81).

** Literature value.
FIGURE 13

Comparison of Heat Capacity of CeF$_3$ with Low Temperature Data
Fig. 13 COMPARISON OF HEAT CAPACITY FOR CERIUM FLUORIDE DATA
SUGGESTIONS FOR FUTURE WORK

In the absence of reliable theoretical methods for calculating or estimating thermodynamic properties of solids over wide ranges of temperature, the determination of enthalpy increments or heat capacities by calorimetric methods is the main source of such data. The goal of the thermodynamicist is to have sufficient thermodynamic data to predict the behavior of any chemical system at any temperature. From time to time, new representations for thermodynamic functions have been tried. Equations have been suggested which combine the Einstein and Debye approaches (86, 87). However, these only apply over restricted ranges.

Thermodynamic data for solids and liquids at 2500°K are still very scarce. Induction heaters and electron bombardment furnaces have successfully been utilized for a small number of measurements at 2000°K, and higher; and it is likely that such apparatus can provide satisfactory thermodynamic data for refractory materials. Transient techniques seem, however, to be more promising in this field. At present, the results are far from satisfactory but they can be improved substantially with more sophisticated instrumentation. The fact that transient measurements do not require any container is of great importance, as in high temperature work it is difficult to find non-reactive substances and the number of high-melting substances that can be used is very limited.
In the field of temperature measurement, the photo-electric pyrometer should be a boon to calorimetrists. Large portions of the error involved in present day measurements come from uncertainty in the temperature measurement. With this new instrument, temperature can be measured to at least \( \pm 1^\circ \) at 2000\(^\circ\)K, as compared to \( \pm 10^\circ \), or higher, with an optical pyrometer or refractory metal thermocouple. Quartz thermometers similarly eliminate some of the personal factors involved in the measurement of the temperature rise of the calorimeter. The precision and accuracy of the quartz thermometer meets the demands necessary in such a measurement and the output can be directly transmitted to a computer.

Thermodynamic data for refractory carbides, silicides, borides, nitrides, etc. are not currently available. Such data has pure scientific interest from the point of view of correlating the structures of such materials with their properties. In addition, these refractory materials have a wide variety of industrial and technological applications.
APPENDIX I.
ENTHALPY INCREMENTS FOR URANIUM PHOSPHIDE

This work was done in the Calorimetry Laboratory of the Chemical Engineering Division of Argonne National Laboratory. The method of measurement is the same as has been described previously, but there is a small difference in the instrumentation. A brief description of the apparatus will be given and a more detailed description can be found elsewhere (88).

The furnace is a vacuum operated molybdenum-core furnace. It consists of four elements, a bottom shield, main shield, outer shield and a floating shield which helps to prevent radiation loss from the furnace proper. The internal cavity is 3" long and 7/8" in diameter. The temperature of the shield is maintained by a tantalum-wire heating element and controlled by a differential thermocouple. A tantalum sheathed Pt-10% Rh vs Pt thermocouple is installed to monitor the cavity temperature. A Leeds and Northrup Series 60 CAT Control Unit along with a Barber Coleman 622 SCR-Power Controller is used to control the furnace temperature. The sample is suspended by a tantalum wire and a tantalum capsule is used for the measurement.

The calorimeter proper is similar to that in the Rice calorimeter and consists of: 1) a calorimeter block; 2) a constant temperature jacket through which thermostatted water is passed; 3) a central connecting tube to the furnace; 4) two manually operated shutters which are opened briefly to drop the sample capsule. A pyrometer port is provided between the calorimeter and furnace for temperature measurement.
and a black body hole at the bottom of the capsule is for the same purpose. Fig. 14 illustrates the arrangement of the different parts of the calorimeter.

The temperature of the calorimeter can be followed by a Cu or Pt resistance thermometer. For the experiments reported, a copper resistance thermometer was used. Both the Cu and Pt-resistance thermometers were calibrated against an NBS-calibrated resistance thermometer. A Mueller bridge was used to measure the resistance of the thermometer.

The pyrometer was calibrated by comparison with a NBS-calibrated tungsten-filament lamp and checked at the melting point of pure copper. A correction for the glass window and prism was applied to determine the correct temperature of the capsule. The temperature of the furnace was controlled to within ±0.1°C and the uncertainty of the temperature of the capsule was ±1°C. See Fig. 15 for the pyrometer connection curve.

The calorimeter was calibrated electrically and checked against α-Al₂O₃. The reproducibility of the electrical calibration was ±0.02%. The error in the precision of the enthalpy should be of the order of a few tenths of a percent at the most. The calorimeter block was calibrated by passing a constant current through the heater coil and the voltage drop across a standard resistance was measured by a Leeds and Northrup K-3 potentiometer. An electronic time counter, capable of measuring 10⁻⁴ seconds was used to measure the time. Fig. 16 illustrates the circuit used for the electrical calibration, and the results are given in Table XVI. The calorimeter constant has an uncertainty of ±0.07%. The absolute calibration has been previously checked by a
different worker and was found to be within $\pm 1\%$ of the value reported by Furukawa et al. (29).

**Material**

UP has been prepared by the Stanford Research Institute for the Argonne National Laboratory. The compound is synthesized by reacting phosphine with finely divided uranium hydride at 385°C and calcined in a graphite crucible at 1400°C. The major impurity in the compound is oxygen in the form of UO$_2$ and the amount is 0.1%.

Uranium phosphide is grey in color and is metallic in appearance. It has the rock-salt type of crystalline structure. The melting point of this compound is $2540^\circ$C. It has good oxidation resistance and is non-hygroscopic. Uranium phosphide is used as a nuclear fuel in the temperature region 700-2000°C. Thermodynamic data are currently available in the literature.

The enthalpy of this compound has been measured from 1150°K to 1500°K and the results are reported in Tables XVII and XVIII. A plot of $H_T^0 - H_{02}\text{g}^0$ vs temperature is given in Fig. 17.
FIGURE 14

1500° Drop Calorimeter (ANL)
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FIGURE 15

Calibration Curve for Optical Pyrometer (ANL)
Fig. 15 CALIBRATION CURVE FOR PYROMETER
FIGURE 16

Electrical Calibration Circuit for Calorimeter (ANL)
TABLE XVI.

Electrical Calibration of Argonne Calorimeter

<table>
<thead>
<tr>
<th>Energy Input cals.</th>
<th>Temperature rise ohms</th>
<th>E/cal cal/ohm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3083.5784</td>
<td>0.253540</td>
<td>12162.08</td>
</tr>
<tr>
<td>3399.7268</td>
<td>0.279724</td>
<td>12153.86</td>
</tr>
<tr>
<td>3559.1727</td>
<td>0.292787</td>
<td>12156.18</td>
</tr>
<tr>
<td>3915.3081</td>
<td>0.321800</td>
<td>12166.90</td>
</tr>
<tr>
<td>4117.5260</td>
<td>0.338985</td>
<td>12146.63</td>
</tr>
<tr>
<td>4278.5669</td>
<td>0.351500</td>
<td>12172.31</td>
</tr>
<tr>
<td>4477.9995</td>
<td>0.368517</td>
<td>12151.40</td>
</tr>
<tr>
<td>4419.7603</td>
<td>0.363999</td>
<td>12142.23</td>
</tr>
</tbody>
</table>

Average = 12157.34 ± .07% cals/ohm.
Table XVII

Experimental Results for UP

Weight of UP used = 11.1776 gms. (vacuo)

<table>
<thead>
<tr>
<th>Temperature $^\circ K$</th>
<th>$H^\circ_T - H^\circ_{298.15}$ cal.mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1154.2</td>
<td>11434.0</td>
</tr>
<tr>
<td>1203.1</td>
<td>12124.5</td>
</tr>
<tr>
<td>1253.2</td>
<td>12837.8</td>
</tr>
<tr>
<td>1298.6</td>
<td>13488.0</td>
</tr>
<tr>
<td>1339.4</td>
<td>14075.4</td>
</tr>
<tr>
<td>1386.2</td>
<td>14752.8</td>
</tr>
<tr>
<td>1436.0</td>
<td>15477.8</td>
</tr>
<tr>
<td>1513.6</td>
<td>16616.2</td>
</tr>
<tr>
<td>1530.7</td>
<td>16868.5</td>
</tr>
</tbody>
</table>
FIGURE 17

Enthalpy-Temperature Data for UP
Table XVIII
High Temperature Thermodynamic Functions for UP

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>$H^0_T - H^0_{298.15}$ cal.mole$^{-1}$</th>
<th>$C_p^o$ cal.mole$^{-1}$deg.$^{-1}$</th>
<th>$S^o_T - S^o_{298.15}$ eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>(10671.2)</td>
<td>14.01</td>
<td>17.18</td>
</tr>
<tr>
<td>1150</td>
<td>(11374.0)</td>
<td>14.10</td>
<td>17.80</td>
</tr>
<tr>
<td>1200</td>
<td>12081.3</td>
<td>14.19</td>
<td>18.40</td>
</tr>
<tr>
<td>1250</td>
<td>12792.9</td>
<td>14.28</td>
<td>18.98</td>
</tr>
<tr>
<td>1300</td>
<td>13508.9</td>
<td>14.36</td>
<td>19.55</td>
</tr>
<tr>
<td>1400</td>
<td>14954.0</td>
<td>14.54</td>
<td>20.62</td>
</tr>
<tr>
<td>1450</td>
<td>15683.2</td>
<td>14.63</td>
<td>21.13</td>
</tr>
<tr>
<td>1500</td>
<td>16416.7</td>
<td>14.71</td>
<td>21.63</td>
</tr>
<tr>
<td>1550</td>
<td>17154.6</td>
<td>14.80</td>
<td>22.11</td>
</tr>
<tr>
<td>1600</td>
<td>17895.9</td>
<td>14.89</td>
<td>22.58</td>
</tr>
</tbody>
</table>

\[
H^0_T - H^0_{298.15} = 12.08 T + 8.77 \times 10^{-4} T^2 - 3681 \text{ cal.mole}^{-1}
\]

\[
\text{(± 0.1%, } 1150^\circ K < T < 1550^\circ K )\]

\[
C_p^o = 12.08 + 17.55 \times 10^{-4} T \text{ cal. mole}^{-1} \text{deg}^{-1}
\]
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