HEAT CONTENT OF LIQUID CERIUM
BY LEVITATION CALORIMETRY

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M. S. Thesis Submitted to Iowa State University

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by levitation calorimetry

by

Lyle K. Kuntz

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INTRODUCTION

Levitation calorimetry is a recent thermodynamic experimental technique which has great potential in liquid state structure and property studies. These studies involve the thermodynamics related to structure transformations from solid to liquid phase changes and the resulting liquid structure to temperatures 1000° above the solid melting point. The electronic configuration as related to possible order changes between solids and liquids regulates the magnitude of energy transformations in and between phases. These energy transformations occurring between solids and liquids are constrained by the first and second laws of thermodynamics. From these laws a vast network of equations exist which allow scientists and engineers to investigate various reactions and processes. In order to apply these laws to materials, extensive physical property research must be performed. This research will then continually add new dimensions to theories concerning the transformations and structures.

Previous work concerning liquid metals has been hampered by the lack of accurate thermodynamic data. The liquid phase estimation procedures are more complex than those concerning solids and gases. Predicted results for liquids have usually been inaccurate and rare. The technique of levitation calorimetry has so far proven both its reliability and accuracy concerning the determination of thermodynamic properties of liquid metals. This method has now just begun to fill some of the voids associated with liquid metal properties.

Present theories have indicated that significant advances have been made concerning liquid state properties. General rules have been established concerning the liquid phase systems. First it is believed that the heat capacities of liquid metals should range from 7 to 8 cal. per mole per degree. Second the heat capacity of liquid metals appears to be approximately constant and third, the heat capacity tends to decrease with increasing temperature. The need for further evaluating these theories dictates extended work with liquid metals. This work was undertaken to add information which would help to improve the theories on liquid state structures.

The levitation calorimetry technique is a version of the popular drop calorimetry method. The heat content of a given sample material is determined from the temperature rise of a calibrated calorimeter. The heat capacity, entropy, enthalpy function, and free energy function may then be calculated from the heat content data. This particular technique is both interesting and unique in that samples are actually levitated in an electromagnetic field with an inert gas as the surrounding medium. The interest is generated from the standpoint of accomplishing experimental work which is new and unusual.

The future contribution of levitation calorimetry to thermodynamic studies of liquid metals is very encouraging. The vast amount of work required concerning elements in the liquid phase is endless. Future problems where levitation calorimetry is most useful involve the evaluation of the heat content of liquid binary and multicomponent alloys. Studies of this nature could yield important correlations between heat capacity and alloy composition.

The parameters associated with levitation calorimetry make it a useful tool in assembling thermodynamic data. This work will indirectly yield significant information that will help solve future energy shortages. Nuclear systems involving high temperature operations illustrate the need for more thermodynamic data of materials above their melting temperatures.

PREVIOUS WORK

Three general methods are in use for the experimental determination of high temperature heat contents and heat capacities. These are drop calorimetry, adiabatic calorimetry and data derived from thermal analysis and phase diagram studies. Thermodynamic data for cerium has been obtained using the three methods, with slight variations to each.

The following section has been divided into three categories emphasizing the method used to determine the thermodynamic functions of cerium. Each category includes a synopsis of experimental work performed with cerium and the corresponding results.

Drop Calorimetry

Drop calorimetry procedures are differentiated by furnace and calorimeter structures. Both resistance and electromagnetic furnaces have been used to heat samples. Two common calorimeter systems are copper block calorimeters and ice calorimeters. Liquid argon calorimeters have also been used for calorimetry work, but will not be discussed in this thesis.

The first calorimeter system uses a furnace to heat an incased sample to a known temperature. The incased sample is then dropped into a copper block calorimeter. Copper block calorimeters are used because of quick temperature recovery and ease of assembly. The heat content of the sample is related to the temperature rise of the copper block. This particular arrangement is closely related to levitation calorimetry in that the only difference is the furnace. Levitation

calorimetry simultaneously heats the sample inductively, while in a levitated position. This procedure then eliminates the need for any type of crucible to contain the sample in the liquid phase.. The accuracy of this system is based on the electric calibration of the calorimeter substantiated by copper evaluation experiments of Stretz (1) and Bonnell (2). The copper evaluation experiments authenticate the heat loss corrections and sample temperature measurement calculations. The results of this type of experimental work concerning cerium are given in the results section of this thesis.

A second "drop" method uses a regular resistance furnace to heat an incased sample to be dropped into an ice calorimeter. This process melts the ice which is in thermal equilibrium with the water resulting in a decrease in total volume. This decrease in volume is measured by a mercury displacement method. The volume change is then related to the amount of heat required to melt the ice. This type system was used by McKeown (3) for his work with cerium, praseodymium, neodymium and samarium. The accuracy of this method depends to a large extent on the purity of the water and mercury, the ability to maintain a constant volume calorimetric system and the ability to accurately measure heat loss corrections caused by convection and radiation.

McKeown's (3) work indicates the liquid phase heat content for cerium to be

$$H_T - H_O = 9.345(t) + 680 \text{ cal/mole} \quad (1)$$

where t is in degrees Celsius. Converting this to the 298.15 °K reference state gives

$$H_T - H_{298.15} = 9.345T - 2033 \text{ cal/mole} \quad (2)$$

where T is in degrees Kelvin. The heat capacity of cerium is 9.345 cal per mole per degree and the heat of fusion is 1238 cal per mole. These values were determined from four experimental values above the melting point of 1077 °K. The four values were taken in the temperature range 1084 °K to 1374 °K.

Adiabatic Calorimetry

The adiabatic calorimetry technique is the second type of calorimetric studies used in the thermodynamic studies of liquid cerium. This method involves the repetitive heating of an incased sample within an adiabatic calorimeter. A known amount of heat is applied to the sample, resulting in a higher temperature. Several commercial adiabatic calorimeters work by this principle. The sample is heated from an internal resistance heater at constant wattage while under adiabatic conditions. The sample is incased in tantalum which is incased in platinum. Surrounding this platinum container is a nickel sphere at which adiabatic conditions exist. The sample temperature was measured on the external surface of the tantalum crucible by a thermocouple. This temperature and the temperature of the surrounding nickel sphere are automatically controlled to give an ideally zero temperature difference. The zero difference is maintained by the heating of the nickel sphere by an external furnace. This equipment type was used by Chiotti et al. (4) for the experimental determination of the heat of fusion of cerium and several other elements and compounds. Possible drawbacks to the accuracy

of this type of system include the maintaining of near uniform adiabatic conditions at the nickel sphere, the possibilities of thermal gradients within the sample and the temperature measurements of the sample from the external surface of the crucible. The results of their work yielded a heat of fusion for cerium equal to 1305 cal. per mole which is in good agreement with McKeown's (3) work. No heat capacity measurements were made.

Thermal Analysis and Phase Diagram Studies

The thermal analysis technique involves the estimation of the heat capacity and heat of fusion by analyzing the heating and cooling curves of a given sample. These results are then compared to similar results for a sample of known heat capacity and heat of fusion.

Cavallaro (5) applied this technique to the evaluation of the heat of fusion for cerium and praseodymium. The heat of fusion for cerium was reported as 5500 cal. per mole.

This method while being most rapid to perform requires intensive precautions to obtain reproducible data.

Phase diagram studies involve determining the heat of fusion for various materials through the use of binary phase change studies. Freezing point data has been used to establish reasonable estimates of the heat of fusion for many different elements. Kelley (6) has presented the format for calculating the heats of fusion through the use of binary systems.

For cerium, Kelley (6), referred to the work of Vogel (7). Vogel's (7) work consists of freezing point studies concerning the cerium-iron system. From Vogel's (7) data Kelley (6) determined the heat of fusion for cerium to be 2120 cal per mole. Kelley (6) believed this value to be slightly low and referred to 2200 cal per mole in a revised publication (8) in 1960. Kelley (8) gives the heat capacity of liquid cerium to be 8.00 cal per mole per degree, referring to the estimate given by Stull and Sinke (9).

The disadvantages of these calculated values are given by Kelley (6) as the lack of available information concerning activity coefficients, molecular species present in solutions, accurate analysis of separated solid components upon cooling and the lack of thermal equilibrium upon heating and cooling.

Kojima and Kikuchi (10) have employed the phase diagrams of cerium-gold, cerium-silver, cerium-copper, and cerium-thallium systems to evaluate the heat of fusion for cerium. Their values are 3030, 2520, 2340 and 4490 cal per mole, respectively. An average value of 3090 cal per mole was given as a good estimate of the heat of fusion for cerium.

The work of Chiotti et al. (4) supports that of McKeown (3) in establishing the heat of fusion for cerium to be approximately 1300 cal per mole. This however does not prove the reliability of McKeown's (3) work above the melting temperature of 1077 °K. Heat content values above 1077 °K could be slightly low due to previously discussed disadvantages of the ice calorimeter technique.

The heat of fusion estimates of Cavallaro (5), Kelley (6) and Kojima and Kikuchi (10) seem to be approximately 1000 cal per mole too

large. This could be accounted for by the 700 cal. per mole heat of transition at 1000 °K. Their results could include both heats of transition and fusion since the work is empirical.

Further insight is readily available as demonstrated by the recent work of Sommer (11). Analysis of changing binding conditions caused by charge transfers and strain energies in liquid phases have yielded enthalpy of mixing calculations. These quantitative calculations have been done by means of a pseudo potential theory. This relates to the clustering effect of metal atoms in liquid phases as presented by Stretz (1). This clustering of atoms could produce unusual results concerning the thermodynamic evaluation of liquid metals.

The previously reported work demonstrates the need for further work on the thermodynamic properties of liquid cerium.

METHOD AND THEORY

The continued use of levitation calorimetry has been justified by the relative ease of taking data in the temperature region where it is otherwise impossible and by the accuracy of the data obtained. The technique involves a copper block calorimeter subjected to a constant temperature surrounding and an electromagnetic levitation melting apparatus serving to regulate the temperature of a liquid sample. The copper block calorimeter was chosen due to ease of operation while maintaining a relatively high degree of accuracy in the overall method (usually better than $\pm 0.5\%$). The electromagnetic levitation of liquid samples is well suited especially when these samples are highly reactive. Past work involving the use of crucibles has been difficult due to the dissolution of the crucible material into the liquid sample (12, 13). The levitation technique does away with the crucible, eliminating sample contamination. Levitation calorimetry has been successfully employed to evaluate the heat contents of liquid copper and platinum by Chaudhuri et al. (14), copper, platinum, niobium and zirconium by Bonnell (2) and lanthanum, praseodymium, neodymium and yttrium by Stretz (1). Treverton and Margrave (15, 16) have reported successful work with cobalt, palladium, iron, titanium and vanadium. A more detailed description of the method is given in the following sections.

Calorimeter

The technique involved is simply that of a constant temperature block in a constant temperature surroundings. The calorimeter is heated by a sample of known weight to a final temperature while constantly being subjected to the initial surrounding temperature. The temperature rise of the block is recorded as a function of time. After heat usage corrections are made, the heat content of the sample is calculated from the relation

$$H_T - H_{T_j} = (MC_p \Delta T)/m \quad (3)$$

where $(H_T - H_{T_j})$ is the change in heat content of a given sample from T_j , the reference temperature, to T , the initial sample temperature, M is the molecular weight of the sample, C_p is the heat capacity of the calorimeter in cal. per degree, ΔT is the change in temperature of the copper block and m is the mass of the dropped sample. The reference temperature is the temperature at which the copper block is calibrated and is usually 298.15 °K. Corrections for the heat leakage from the copper block to the surroundings are described below.

Temperature Rise Correction

Since an insulating gas void is located between the block and the constant temperature reservoir, convective heat transfer is virtually eliminated, leaving radiative and conductive transfer. One direct heat leak route is through the quartz probe lead. However, this leakage has been estimated at less than 0.0001 °C per 10 seconds and does not affect

the assumption of a linear total heat leak as examined by Stretz (1).

The rate of heat transfer is assumed to follow Newton's law of cooling and is given by

$$\frac{dH_e}{dt} = -k(T - T_j) \quad (4)$$

where dH_e/dt is the change in heat content of the block per unit time, k is a constant, T is the block temperature and T_j is the temperature of the constant temperature bath.

At the beginning of each experiment the copper block was at a lower temperature than the surroundings. The result of one run in the calorimeter yields three temperature-time profiles. These are the initial period when the block is increasing in temperature at a constant rate, the main period when the sample raises the block temperature, and the final period when the temperature of the block gradually increases nearing the temperature of the surroundings. For the initial and final periods the temperature time curve is nearly linear. Figure 1 shows these three periods which are typical of each run.

During the main period, the block increases in temperature because of the hot sample and the heat loss to the surroundings. This heat exchange is described by the relation

$$\Delta H_s + \Delta H_e = C_p(T_f - T_i) \quad (5)$$

where ΔH_s is the heat content change of the block due to the heat of the sample, ΔH_e is the heat content change of the block due to the heat exchange to the surroundings, C_p is the heat capacity of the block

Figure 1. Temperature versus time curve for the copper block calorimeter.

and T_i and T_f are the beginning and ending temperatures of the block relative to the main time period limits, t_i and t_f . By definition:

$$\Delta H_s = C_p \Delta T \quad (6)$$

and

$$\Delta H_e = C_p \Delta T_{\text{correction}} \quad (7)$$

where ΔT is the temperature rise due to the sample and $\Delta T_{\text{correction}}$ is the temperature change due to the surroundings. Rearranging and substituting gives

$$\Delta T = T_f - T_i - \Delta T_{\text{correction}}.$$

Applying Newton's law of cooling yields

$$\Delta T_{\text{correction}} = - \frac{k}{C_p} \int_{t_i}^{t_f} (T - T_j) dt. \quad (8)$$

The rate of change of temperature at time t_i is

$$\left. \frac{dT}{dt} \right|_{t_i} = - \frac{k}{C_p} (T_i - T_j) \quad (9)$$

and at time t_f is

$$\left. \frac{dT}{dt} \right|_{t_f} = - \frac{k}{C_p} (T_f - T_j). \quad (10)$$

Establishing a midtime, t_m , to Equation 8 yields

$$\Delta T_{\text{correction}} = - \frac{k}{C_p} \left[\int_{t_i}^{t_m} (T - T_j) dt + \int_{t_m}^{t_f} (T - T_j) dt \right]. \quad (11)$$

Introducing T_i and T_f by integral manipulation gives

$$\Delta T_{\text{correction}} = -\frac{k}{C_p} \left[\int_{t_i}^{t_m} (T_i - T_j) dt + \int_{t_i}^{t_m} (T - T_i) dt + \int_{t_m}^{t_f} (T_f - T_j) dt + \int_{t_m}^{t_f} (T - T_f) dt \right]. \quad (12)$$

The midtime is defined as

$$\int_{t_i}^{t_m} (T - T_i) dt = - \int_{t_m}^{t_f} (T - T_f) dt \quad (13)$$

and is represented in Figure 1. Applying this definition while T_i , T_f and T_j are constant and integrating equation 12 gives

$$\Delta T_{\text{correction}} = -\frac{k}{C_p} [(T_i - T_j)(t_m - t_i) + (T_f - T_j)(t_f - t_m)]. \quad (14)$$

Substituting equations 9 and 10 into this yields

$$\Delta T_{\text{correction}} = \left. \frac{dT}{dt} \right|_{t_i} (t_m - t_i) + \left. \frac{dT}{dt} \right|_{t_f} (t_f - t_m) \quad (15)$$

Final substitution yields

$$\Delta H = \frac{MC_p}{m} \left[T_f - T_i - \left. \frac{dT}{dt} \right|_{t_i} (t_m - t_i) - \left. \frac{dT}{dt} \right|_{t_f} (t_f - t_m) \right] \quad (16)$$

where the slopes $(dT/dt)_{t_i}$ and $(dT/dt)_{t_f}$ are measured from the temperature versus time curves for the initial and final periods and where T_j is the isothermal surrounding temperature.

To simplify the raw data reduction a numerical integration technique is applied to equation 8. The computer numerical technique and the expanded form above yield identical results.

Levitation Melting

Induction heating involves the placement of a sample in a non-uniform, alternating, electromagnetic field. The eddy currents established within the sample enable the sample to be supported without the aid of a container if the vertical component of the field is equal to or greater than the weight of the sample. As described by Jenkins et al. (17), the force on the sample depends on the field strength and gradient. Stabilization of the sample occurs by placement of a uniform opposing force against the sample. Figure 2 illustrates how a sample under these restraints will reside at the position of minimum field strength.

Various coil designs have been investigated by Jenkins et al. (17), Okress et al. (18) and Wroughton et al. (19). Levitated materials and their optimum coil designs have been discussed by Bonnell (2) and Stretz (1).

Sample temperature depends upon the position of the sample in the field, the rate of heat loss, the shape of the coil, the power to the coil and the weight of the sample. Identical sample temperatures can be maintained by different parameter adjustments. For example, if the weight of a sample is increased, the sample will sit lower in the field yielding a higher temperature, assuming all other variables are held constant. However, if samples of constant mass are considered, decreasing the power causes the sample to sit lower in the coil causing an increase in the temperature of the sample. In both instances, the sample is subjected to more electromagnetic field intensity.

Figure 2. Levitation field contours for a typical solenoid coil.

The rate of sample heat loss is regulated by the inert atmosphere composition. This argon-helium mixture can be easily regulated, usually giving lower temperatures for a pure helium atmosphere and higher temperatures for a pure argon atmosphere. Maximum temperature could be obtained if the operation was performed under vacuum, where heat losses would only be by radiation. Under vacuum, sample vaporization would add to temperature measurement problems, equipment assembly would be hampered and intense corona discharge would be evident from the levitation coil.

Bonnell (2) has discussed designs of levitation melting systems, including the matching of coil impedance to high-frequency generators. However making efficient coil designs appears to be an empirical problem, with experience being the best guide.

EQUIPMENT

The experimental equipment involved in levitation calorimetry may be divided into two major sections. These two sections and their components are listed as follows:

1. Calorimeter
 - a) Constant temperature bath
 - b) Calorimeter jacket and block
 - c) Temperature monitoring equipment
 - d) Miscellaneous support equipment
2. Levitation apparatus
 - a) High-frequency generator
 - b) Matching transformer
 - c) Current adjusting type (C.A.T.) generator controller
 - d) Modified sample drop controller
 - e) Levitation coils
 - f) Levitation chamber
 - g) Drop tube
 - h) Sample temperature measurement apparatus.

A more detailed description of each component is given below. Figure 3 shows a schematic view of all the major components. Exact dimensions and individual illustrations are given by Stretz (1).

Figure 3. Levitation calorimetry apparatus.

Calorimeter

Constant temperature bath

The constant temperature bath was a large steel tank 18 inches in diameter by 20 inches in depth. The tank was contained in a wooden box with a minimum of three inches of vermiculite insulation around the circumference and the bottom.

The tank was filled with water to a depth just above the calorimeter assembly and was heated by a 500 watt Calrod heater. Bath cooling was provided by immersing a 10 foot, 1/4 inch diameter water cooled copper tube. The bath was agitated by an impeller type stirrer.

The power output for the Calrod heater was supplied by a Bayley Model #252 precision temperature controller with ± 0.0001 °C tolerance over a period of 8 hours. Due to generator interference, the control system was modified by the use of a Precision Scientific #62541 Microset Thermoregulator. The interference generated caused a power increase, raising the bath temperature. With the additional controller and a normally closed relay, the bath temperature could be maintained at ± 0.006 °C, while the generator was in operation.

The temperature of the bath was monitored by a quartz thermometer which is discussed in the monitoring equipment section.

Calorimeter jacket and block

The calorimeter jacket was made of 4 inch O.D. brass tubing with a 1/4 inch wall. The bottom was made from 1/4 inch brass plate. A gas inlet port was provided at the bottom of the jacket. The lid of the jacket was constructed from 1/4 inch brass plate with outlets for the

block cover gate lever and the thermometer lead. A one inch I.D. tube extended up from the center of the lid to a one inch sliding gate valve which served as a radiation gate. A one inch I.D. tube extended from the gate valve to a 4-7/8 inch flange. This flange provided the mounting for the drop tube. All metal portions were chrome plated to reduce radiative heat transfer. The total height from bottom to flange top is approximately 11-1/2 inches.

The calorimeter block was a copper cylinder 2-1/2 inches in diameter and 7-3/4 inches in height. A 3 inch deep, tapered recess, 1-1/4 inch diameter at the top, was used to accommodate the copper sample receiving well. This type system was used to simplify the taking of sample weights.

The temperature sensing probe for the quartz thermometer was inserted in a drilled hole near the bottom of the copper block. The position of the probe relative to the receiving well is not critical as long as the probe is not moved after electrical calibration. The position of the probe was chosen to avoid transient temperature responses.

The receiving well lid was 1/8 inch thick and made of copper. The operating mechanism from the lid to the outside of the jacket was made of nylon to minimize heat loss.

The outside surface of the calorimeter block was gold plated to reduce heat exchange between the block and jacket. All surfaces were kept well polished. A schematic drawing of the calorimeter assembly is given in Figure 4 as presented by Stretz (1).

Figure 4. Copper block calorimeter assembly.

Temperature monitoring equipment

The temperature of the calorimeter block and constant temperature bath was monitored with a Hewlett-Packard 2801-A Quartz Thermometer. Convenience and accuracy were the primary reasons for this type of operation. Direct readings were recorded on paper tape by a Hewlett-Packard 562-A Digital Recorder.

The basic principle of the quartz thermometer involves the cutting of a quartz crystal in such a way that its resonance frequency varies linearly with temperature. This frequency is electronically compared to a reference oscillation and gives temperature readings to 5 decimal accuracy in degrees Celsius. Calibration corrections for the matching of probes to a specific base unit are included with each probe.

The probe lead is a teflon coated coaxial cable. It exits the jacket at the top surface where it is sealed by a swagelock fitting using a teflon ferrule.

Miscellaneous support equipment

Because water at constant temperature was needed for the constant temperature bath, the in-house water supply was directed through two auxiliary constant temperature baths. The secondary baths were controlled to within ± 0.1 °C at approximately 24 °C. This system served to damp out the inconsistencies in the house water system temperature.

A system was designed to remove traces of oxygen from the helium-argon purge gas. This was accomplished by passing the gas through a titanium sponge at 600 °C. After being cooled to room temperature, the gas next passed through a bed of molecular sieves where any residual

moisture was removed. The gas stream was brought to the temperature of the main bath by passing it through a coil of 1/4 inch copper tube immersed in the bath. Finally, the gas was fed to the calorimeter assembly through 3 different ports to reduce gas currents inside the assembly.

Levitation Apparatus

High-frequency generator

The high-frequency generator used as the furnace for this study was a Lepel model #T-20-3-KC-F-S which operated at approximately 450 kh.

Matching transformer

A transformer between the generator and the small work coil was needed to match impedances. This transformer was wound at the Ames Laboratory and consisted of a 12 turn, 6-3/4 inch diameter primary coil made of 1/4 inch copper tubing and a 3-1/2 turn, 7-1/2 inch diameter secondary coil made of 1/2 inch copper tubing. Polyethylene was used between the coils for insulation. Glyptol insulating paint was used to cover the entire transformer surface to eliminate shorting. The water for the primary coil was supplied by the generator cooling system and for the secondary and levitation coils by the in-house water. A booster pump was used to increase the flow rate of water through the work coil, allowing the generator to be used at higher power levels.

Current adjusting type (C.A.T.) generator controller

The power to the levitation coil from the generator was regulated by a Leeds and Northrup M-Line C.A.T. (current adjusting type) Controller, Model C-1A. This controlling system was used in place of the generator power control.

Modified sample drop controller

Previous experiments involving sample drops from the levitation coil field were performed by shutting off the power to the levitation coil. This procedure was proven ineffective with many lost experiments due to erratic sample drop paths.

A sample that is dropped from levitation must fall approximately 30 cm. through a one inch opening into the calorimeter assembly. When the generator is shut off, residual magnetic fields due to the electronic structure of the generator sometimes altered the path of the sample as it leaves the levitation coil. In most instances, the sample falls on the flange area surrounding the entrance to the calorimeter jacket.

To eliminate this problem, a control was installed between the generator and the current adjusting type controller which in affect lowered the power quickly to zero. In this way, constant fields around the levitation coil diminished rapidly without any residual field surges. The control consists of a variable shunt between the two leads going from the C.A.T. controller to the generator. The shunt is controlled by a toggle switch and is variable from 0 to 10,000 ohms. In this

fashion the C.A.T. controller can be adjusted to a minimum power level when the shunt is activated.

Under levitation conditions the shunt was on an open circuit. At drop time, the shunt circuit was closed reducing the power directed to the levitation coil to a minimum value preset by the variable shunt resistance.

Reducing the power manually rather than using the shunt was ineffective. The time involved in turning the power control down to a level where the sample would fall, allowed the sample temperature to decrease, yielding incorrect results. As a result, increasing power levels gave increasing sample temperature errors. This addition to the equipment is shown in Figure 3.

Levitation coils

The levitation coils were wound from 1/8 inch diameter soft copper tubing. Work coil designs were made by trial and error, but were patterned after those used by Stretz (1) and Bonnell (2). Three basic forms were used for the levitation of cerium. These forms were solenoid, conical and reverse conical. Schematics of these basic shapes are given in Figure 5. The success and variations of these coils are discussed in the results section.

Levitation chamber

The levitation chamber was fashioned from a one liter round bottom flask, modified to provide several ports. One side of the flask was opened to a 71/60 ground glass inner taper. This connected to a 71/60 ground glass outer taper enclosed on one end by a rubber stopper. The

SOLENOID

CONICAL

REVERSE CONICAL

Figure 5. Three basic types of levitation coils.

coil leads and a purge gas inlet passed through this stopper. This format was used so that when the chamber was removed the seal on the rubber stopper would not have to be broken. The extra gas inlet allowed more efficient purging and more uniform gas flow around the levitation coil.

On the opposite side of the flask was a port terminating with a 65/40 ground glass ball joint. An extension from this supported a quartz pyrometer window and a gas inlet used to sweep fumes away from the window and to provide uniform gas flow around the levitation coil.

A third port was provided at the top of the flask for sample insertion, purge gas removal and drop path alignment. Offset slightly from this port, was a small tube which allowed the extension of a glass sample holder to pass through.

The bottom of the chamber opened to a 55/50 ground glass inner taper which connected to the drop tube. A schematic drawing of the chamber may be found in Figure 6.

Drop tube

The drop tube section consisted of a 2 inch O.D. pyrex column fitted with a 55/50 ground glass outer taper to be connected to the levitation chamber. The bottom of the column was clamped to the flange of the calorimeter jacket incorporating an "O-ring" seal. The total length of the drop tube assembly was approximately 6-1/2 inches.

Sample temperature measurement equipment

The temperature of the levitated sample was determined with a Leeds and Northrup 8641 Precision Automatic Optical Pyrometer with the output

Figure 6. Levitation chamber.

recorded on a L and N Speedomax W Adjustable Range (AZAR) single point recorder. The pyrometer determines the brightness temperature of the sample by automatically adjusting the current passing through an internal standard lamp to match the sample being observed. The standard lamp current is converted to a millivolt reading and passed to the recorder.

The pyrometer operates over four temperature ranges which are 775 °C to 1225 °C, 1075 °C to 1750 °C, 1500 °C to 2800 °C and 2000 °C to 5800 °C. The accuracy of the pyrometer is governed by the calibration and stability of the standard lamp. The limits of error for this pyrometer are the same as for manual pyrometers. These limits are ± 4 °C in the low range, ± 7 °C in the medium range and ± 16 °C in the high range. Uncertainty in N.B.S. calibration reports for L and N manually operated pyrometers are usually given as ± 4 °C at 800 °C, ± 3 °C at 1063 °C and ± 8 °C at 2800 °C.

The pyrometer resolution is given as 0.5 °C for a one second balance time at 1063 °C with a one second response time. The filters on the pyrometer have an approximate passband of 350 Å and an effective wavelength of approximately 0.645 μ .

Although calibration curves were furnished, several additional calibration checks were necessary. No recently acquired N.B.S. standard lamp was available, therefore a N.B.S. lamp acquired in 1963 was used. For comparative purposes, a manual pyrometer recently calibrated was used. The automatic and manual pyrometers were focused on the same location of the standard lamp filament. Temperature values were taken from 1050 °C to 1700 °C. Temperature values of the manual pyrometer were consistently 19 °C lower than the calibration temperature for the

lamp. These results were not surprising as a dark residue could be seen on the inside surface of the N.B.S. lamp bulb.

The automatic pyrometer readings were 13 °C less at 1050 °C and 52 °C less at 1700 °C than the manual pyrometer readings. The variation in the above range was linear with respect to temperature.

A second calibration check consisted of taking temperature readings from both pyrometers while observing a levitated sample of liquid cerium. In this case, the automatic pyrometer readings were 43 °C less at 1050 °C and 59 °C less at 1700 °C than the manual pyrometer readings. Again the variation was linear with respect to temperature.

A linear pyrometer correction factor was calculated from both sets of data giving

$$T'_{ac} = (1.0422)(T'_a) - 13.87 \quad (18)$$

where T'_a is the apparent sample brightness temperature and T'_{ac} is the corrected apparent sample brightness temperature. The correction with respect to the two different test methods should be reliable. The greatest deviation from the correction factor occurred at the lower temperature values.

The pyrometer window located in the optical path between the levitated sample and the pyrometer was a thin piece of polished quartz glass. This factor was corrected for by Stretz (1) by inserting the window in the optical path of a ribbon filament lamp at a known temperature.

EXPERIMENTAL PROCEDURE

The experimental procedure involved with levitation calorimetry may be divided into two sections. The initial setup involves the preparation of the system for runs and the actual runs. The major steps are listed below.

1. Construct a levitation coil which will levitate and melt a sample material. Individual coils were made from a 1/8 inch diameter soft copper tube 24 inches in length. The construction is aided with various shaped articles to give the desired contour. For example, solenoid type coils were shaped around metal shafts of various diameters. Conical sections were shaped around objects with a desired taper angle, such as a glass funnel. Care must be taken to avoid introducing unnecessary bends in the coil configuration. The open ends of the coil must be clean to allow maximum cooling water flow. Comparisons should be made between designed coils and coils which have been used successfully.

2. Install the coil and clamp the levitation chamber into place.

3. Test the new coil for sample levitation, melting and stability. Once the sample is levitated, stability is very important for uniform heating and accurate temperature values. Stability is accomplished by making a well-defined neutral zone between the upper and lower segments of the coil. Generally, the larger the sample the more the stability problem will be apparent. Several coils may be needed to take data on a wide temperature range.

4. Weigh the empty receiving well.

5. Line the empty receiving well with protective foil and reweigh to determine the liner weight. A copper lining was used for copper sample calibration experiments. A tantalum liner was used for the cerium runs to avoid the possibility of the cerium sample and the copper lining forming an alloy. Tantalum liners were found by Stretz (1) to be suitable when working with lanthanum, praseodymium, yttrium and neodymium.

After the above steps have been completed, the remainder of the procedure is associated with all actual runs.

1. Start the constant temperature bath and all the support equipment. The temperature of the bath must be stable before runs are made.

2. Weigh the receiving well, liner and old sample, if any. Determine the correction factor to be applied to the calorimeter constant.

3. Insert the well into the block and place the block cover gate over the well. After assembling the calorimeter, place it in the isothermal bath.

4. Raise the isothermal bath up to the levitation chamber and assemble the unit. Open the block cover gate and close the radiation gate.

5. Begin purging the system with inert gas at a helium-argon composition desired for the levitation run. Check the system for leaks.

6. After 1/2 hour, remove the sample to be levitated from vacuum storage. Place the sample on the glass manipulating rod positioned

inside the lower section of the levitation coil. Continue purging for approximately 2 hours.

7. Prepare levitation system for operation. (Warm up the generator and related equipment and turn on cooling water.)

8. Prealign the pyrometer so only minor adjustments will be necessary.

9. Turn quartz thermometer to monitor calorimeter temperature at 0.0001 °C resolution and switch on digital recorder. The time interval between readings will be approximately 10 seconds. An exact time interval of 10 seconds is not necessary. The time interval should, however, remain constant between calorimeter temperature readings for the duration of one run.

10. Eight minutes later, turn on the levitation power and maintain stable sample levitation by altering the power. Realign the pyrometer at this time.

11. When constant temperature is apparent, open the radiation gate and drop the sample by use of the sample drop mechanism.

12. Immediately close the block cover gate, then the radiation gate. Mark the digital temperature readout for the exact drop time.

13. Shut down the generator and pyrometer.

14. Take readings of the calorimeter temperature with respect to time until the dT/dt value has been constant for at least 5 minutes.

15. Shut off purge gas flow and cooling water supplies. Break down the system removing the calorimeter for final weighings and inspection.

16. Dry and disassemble the calorimeter.

17. Inspect the calorimeter for sample contact and splash.

18. Weigh the well to determine the weight of the dropped sample.

This is determined after the drop since some of the sample will vaporize during levitation.

To make further runs reassemble the calorimeter with the well that has been previously weighed. At this time the block should be cooled with liquid nitrogen to approximately 18 °C. This will allow the temperature of the block to rise to the desired level after the 2-1/2 hours of purge time if the bath is maintained at approximately 25 °C. At this point, procedure 2 of the actual run sequence has begun.

The remainder of the procedure involves the computer data reduction routines TEMC, CAL, and COR2 as used by Stretz (1). The operation of these routines is explained in the calculation section of this thesis.

CALCULATIONS

The following section will be devoted to explaining the raw data reduction routines from a series of experimental trials on any given levitated sample. These calculations follow the procedures set forth by Bonnell (2) as presented by Stretz (1). The only deviation from that presented by Stretz (1) will be the added pyrometer correction factor explained in the equipment section of this thesis.

The primary raw data from the levitation operation consisted of the apparent brightness temperature, T'_a , of the levitated sample and the temperature versus time data for the calorimeter block. The heat content, heat capacity, entropy, enthalpy function and free energy function were calculated according to the raw data reduction routines with the aid of supplementary data. These reduction routines include the conversion of the apparent brightness temperature to a true sample temperature, the correction of the calorimeter constant, the evaluation of the corrected temperature rise of the block, and the correction to the experimental heat content for the energy lost by radiation and convection during the sample drop. Finally the heat capacity is calculated from the heat content values and the thermodynamic functions are calculated accordingly. Details are given in the following sections.

True Sample Temperature

The brightness temperature is defined as the temperature at which a perfect radiator would radiate energy with the same intensity as the sample. In order to obtain a true temperature from the brightness

temperature, a correction for nonblackbody behavior has to be made.

The correction was made using the following equation.

$$T = \frac{1}{\frac{\lambda}{C_2} \ln \epsilon_{N\lambda} + \frac{1}{T_a}} \quad (19)$$

In this equation T is the true temperature, T_a is the brightness temperature, λ is the wavelength of the pyrometer, C_2 is Plank's second radiation constant and $\epsilon_{N\lambda}$ is the normal spectral emittance of the sample material. Emittance by definition is the ratio of the emitted radiant flux per unit area by a body to that of a blackbody radiator at the same conditions. In comparison, the emissivity ratio is the same as for emittance except that the body in question is opaque and has a smooth, polished surface. Emittance is then an extensive property while emissivity is an intensive property. Theory and derivation of equation 19 is cited in Stretz (1, 20) and in Stretz and Bautista (21).

The brightness temperature, T_a , was obtained from the corrected apparent brightness temperature, T'_{ca} . The corrected apparent brightness temperature was found according to the correction as discussed in the equipment section. This correction is

$$T'_{ca} = (1.0422)(T'_a) - 13.87 \quad (18)$$

where T'_a is the apparent brightness temperature. The brightness temperature was then obtained by correcting for the absorbance of the optical system between the sample and the pyrometer. The main source of this absorbance was the quartz window located on the levitation chamber. The absorbance effects were determined from

$$T_a = \frac{1}{K_{abs} + \frac{1}{T'_{ca}}} \quad (20)$$

where K_{abs} is the absorbance constant. The constant was determined as described in the equipment section.

The error in determining the apparent brightness temperature is dependent on the accuracy of the pyrometer readings. The true sample temperature is relatively insensitive to spectral emittance or absorbance constant errors. At 2000 °K errors of about $\pm 5\%$ in spectral emittance or absorbance constant result in errors of less than $\pm 0.5\%$ in true sample temperature.

Corrected Block Temperature Rise

The apparent block temperature rise is the difference in the temperature of the calorimeter block before and after the main period of temperature change. This apparent temperature rise must be corrected for energy losses to the surrounding purge gas. The evaluation of this heat loss was performed according to the method presented in the theory section.

The thermal leakage constant, k , from equation 8 was evaluated by correlating the initial and final period values of temperature versus time relations with the associated value of dT/dt at the midtime. The corrected equation was then numerically integrated by the trapezoidal rule. The estimated truncation error for this type of integration was significantly less than the accuracy by which the quartz thermometer

could measure the temperature rise. Specific details of this correction are given by Stretz (1).

Calorimeter Constant

An actual calorimeter constant was not determined in this work. This calibration was not necessary due to the results of the copper calibration experiments and the calibration previously performed by Stretz (1). The electrical calibration resulted in a block constant of 472.122 cal. per degree. This value was corrected according to the following equation

$$C_p = 472.122 + (mC^*)_{p \text{ well}} + (mC^*)_{p \text{ liner}} + (mC^*)_{p \text{ old sample}} \quad (21)$$

In this form C_p is the corrected block constant in cal per degree, m is mass in grams and C^* is heat capacity in cal per degree per gram.

Experimental Heat Capacity Calculation

The experimental heat content of a specific sample is given as follows in cal per mole

$$H_T - H_{298.15}(\text{exp}) = \frac{MC_p \Delta T}{m} \quad (22)$$

In this form M is the molecular weight of cerium, C_p is the calorimeter constant, ΔT is the corrected temperature rise of the calorimeter block and m is the mass of the cerium sample.

A correction is applied to this heat content in the form of radiative and convective energy losses, while the sample fell from the coil to the block.

The convective heat loss was treated as a stationary sphere in a flowing inert gas stream. The composition of the purge gas is an important part of this calculation. Pure helium removes heat from the sample at a much quicker rate than pure argon. This is illustrated by Stretz (1) for the heat loss from yttrium samples.

The equation used for this heat transfer was

$$\Delta H_c^* = \int_0^{t_d} h_m A \Delta T dt \quad (23)$$

where ΔH_c^* is the convective heat loss in calories, h_m is the mean heat transfer coefficient, A is the surface area of the sample, ΔT is the temperature difference between the sample and the bulk purge gas and t_d is the time involved in the actual drop.

The radiative heat loss was treated in much the same fashion, using the Stefan-Boltzman law.

$$dH_r^* = \epsilon_{HT} A_s \sigma T^4 dt \quad (24)$$

In this form, dH_r^* is the differential radiative heat loss, ϵ_{HT} is the hemispherical total emittance of the sample, A_s is the surface area of the sample, σ is the Stefan-Boltzman constant, T is the sample temperature and dt is the differential time or drop time.

The application of the radiative heat loss required the use of the sample heat capacity. To combine the radiative and convective heat loss required an iteration procedure involving the experimental heat

content values. This procedure included the fitting of a straight line to the final heat content values. The slope represented the heat capacity of the material. Specific details of the iteration process are given by Stretz (1).

The value of the hemispherical total emittance, ϵ_{HT} , for cerium is the only primary source of error in this calculation. This value is not available for cerium. The value of the normal spectral emittance had been found by Moscowitz et al. (22) to be 0.309 ± 0.02 . This value was measured under vacuum conditions for the temperature range 1100 °C to 1500 °C. The accuracy of this value is verified by more recent work involving the determination of normal spectral emittance values for cerium up to 1800 °C using an inert atmosphere. The value was found to be 0.320. (T. King, D. N. Baria and R. G. Bautista, Iowa State University, Ames, Iowa, unpublished data, 1973.)

According to the procedure outlined by Baria and Bautista (23), the value of the **hemispherical spectral emittance**, $\epsilon_{H\lambda}$, may be approximated by

$$\epsilon_{H\lambda} = (1.07)(\epsilon_{N\lambda}) \quad (25)$$

and the hemispherical total emittance, ϵ_{HT} , may be approximated by

$$\epsilon_{HT} = (1.25)(\epsilon_{H\lambda}) \quad (26)$$

Errors in the estimate of the hemispherical total emittance values are discussed by Stretz (1) relative to his work with yttrium. Possible errors concerning these values relative to cerium are discussed in the results section.

Thermodynamic Functions

The corrected values of the heat content and heat capacity are relative to the standard reference state of 298.15 °K and 1 atm pressure.

The entropy is found from the following integral where $S_o^o = 0$.

$$S_T^o - S_o^o = \int_0^T \frac{C_p}{T} dT. \quad (27)$$

This integral was split into 5 sections giving

$$S_T^o - S_o^o = \int_0^{T_t} \frac{C_p}{T} dT + \Delta S_t + \int_{T_t}^{T_m} \frac{C_p}{T} dT + \Delta S_f + \int_{T_m}^T \frac{C_p}{T} dT, \quad (28)$$

where T_t is the $\alpha - \beta$ transition temperature of solid cerium, ΔS_t is the entropy of transition, T_m is the melting temperature and ΔS_f is the entropy of fusion for cerium. The first 4 values were taken from McKeown (3). The value of the third integral is taken from this experimental evaluation as presented in the results section of this thesis.

The enthalpy function, $(H_T^o - H_{298.15}^o)/T$, was found according to the following relation

$$\frac{(H_T^o - H_{298.15}^o)}{T} = \frac{1}{T} \left[\int_{298.15}^{T_t} C_p dT + \Delta H_t + \int_{T_t}^{T_m} C_p dT + \Delta H_f + \int_{T_m}^T C_p dT \right] \quad (29)$$

where ΔH_t is the heat of transition and ΔH_f is the heat of fusion. The temperatures are the same as those in the entropy equation. The first four parts of this equation were taken from McKeown (3) and the third integral was evaluated as presented in the results section of this thesis.

The free energy function, $-(F_T^{\circ} - H_{298.15}^{\circ})/T$, was found as follows.

$$-\frac{(F_T^{\circ} - H_{298.15}^{\circ})}{T} = S_T^{\circ} - S_o^{\circ} - \frac{(H_T^{\circ} - H_{298.15}^{\circ})}{T} \quad (30)$$

This is derived by adding the enthalpy function, $(H_T^{\circ} - H_{298.15}^{\circ})/T$, to both sides of the free energy function as shown below.

$$\frac{F_T^{\circ} - H_T^{\circ}}{T} + \frac{H_T^{\circ} - H_{298.15}^{\circ}}{T} = -S_T^{\circ} + \frac{H_T^{\circ} - H_{298.15}^{\circ}}{T} \quad (30a)$$

Simplifying yields the following equation which is equivalent to equation 30.

$$\frac{F_T^{\circ} - H_{298.15}^{\circ}}{T} = -S_T^{\circ} + \frac{H_T^{\circ} - H_{298.15}^{\circ}}{T} \quad (30b)$$

All thermodynamic functions are in units of cal per mole per degree Kelvin.

RESULTS AND DISCUSSION

High purity samples of cerium were prepared (24) within the Ames Laboratory of the U.S. Atomic Energy Commission. These samples were swaged from cerium stock into 1/4 inch diameter cylinders, 1/4 inch and 3/8 inch in length. The samples were stored under vacuum until needed, at which time they were recut to obtain specific sample weights, electropolished and again stored under vacuum. This procedure was necessary to avoid rapid oxidation. Electropolished samples could be kept 2-4 days under vacuum without the oxide forming. The cerium used was approximately 99.98% pure. A complete analysis of impurities before levitation is given in Table 1.

Prior to beginning the work on cerium, the heat content of liquid copper was measured in order to check the previous calibration made by Stretz (1). Copper is used as the calibration standard since it is easy to levitate, resists oxidation and the heat content of the liquid phase been determined to 700 °K above the melting point (1358 °K), by several investigators at different laboratories. Furthermore, a wide range of temperatures may easily be obtained, as the levitation of copper only requires one basic coil design up to an estimated temperature of 2200 °K.

Calibration Evaluation

Seven runs on samples of 99.999% pure copper were made over a temperature range from 1700 °K to 2000 °K. Data from these runs was treated as described in the calculation section. The value of the

Table 1. Impurities of cerium metal samples before levitation in ppm atomic

Be < 0.003	B < 0.01	Na = 0.04	Mg < 0.01	Al = 0.02
Si = 0.079	P = 0.02	S < 1	Cl = 0.7	K = 0.03
Ca = 0.2	Ti = 0.21	V = 0.014	Cr = 3.4	Mn = 0.75
Fe = 13	Co = 0.04	Ni = 3	Cu = 2	Zn = 0.08
Ga < 0.02	Ge < 0.1	As = 0.02	Se < 0.1	Kr < 0.5
Rb < 0.8	Sr < 0.4	Zr < 0.2	Nb < 20	Mo < 0.2
Ru < 0.09	Rh < 0.02	Pd < 0.05	Ag < 0.009	Cd < 0.02
In < 0.009	Sn < 0.003	Sb < 0.01	Te < 0.02	I < 0.01
Cs < 0.001	Ba < 0.3	Hf < 0.3	Ta = 7.0	W < 0.4
Re < 0.1	Os < 0.2	Ir < 0.08	Pt = 4.0	Au < 0.02
Hg < 0.02	Tl < 0.02	Pb < 0.05	Bi < 0.01	Th < 0.2
U = 0.3	Sc = 0.3	Y = 10	La = 9	Pr < 1
Nd = 4	Sm < 0.4	Eu < 0.05	Gd = 6	Tb < 1
Dy = 1	Ho < 1	Er = 5	Tm < 0.06	Yb < 0.3
Lu = 9	O ^a = 44	N ^a = 12	H ^a = 2	C ^a = 4
	O ^b = 120	N ^b = 39	H ^b = 10	

^aValues for this impurity in ppm by weight.

^bValues for this impurity in ppm by weight after levitation.

hemispherical total emittance, ϵ_{HT} , was 0.1 and the liquid density was taken to be 8.03 gram per cm³. The average percent deviation of the experimental values from the linear fit was 0.27%. The equation obtained from the linear fit for the heat content of liquid copper as a function of temperature was

$$H_T - H_{298.15} = 8.137(T - 1358) + 10130 \text{ cal/mole} \quad (31)$$

for 1700 °K < T < 2000 °K

where 8.137 is the experimental heat capacity in cal per mole per degree. A comparison of these results with the data presented by Kelley (8), Bonnell (2), Stretz (1) and Stephens (25) are given in Table 2 and Figure 7. The agreement with the literature values is excellent and verifies the previous calibration.

Cerium Evaluation

Cerium levitation coils

Runs on cerium samples were made with three different coil designs including several variations from the standard designs. These different designs are illustrated in Figure 8.

Solenoid coil design A consisted of 2 turns in the upper section wound on a 3/4 inch form and 3 turns in the lower section wound on a 3/8 inch form. The neutral zone gap was approximately 3/8 inch wide. This coil worked particularly well in establishing the heat content of cerium between 1550 °K and 2000 °K. The results of these evaluations were consistent and provided a basis for the high and low temperature experiments.

Table 2. Liquid copper evaluations and comparative literature values

T °K	This work ΔH cal/mole	Stretz ^a ΔH cal/mole	Dev. %	Bonnell ^b ΔH cal/mole	Dev. %	Stephens ^c ΔH cal/mole	Dev. %	Kelley ^d ΔH cal/mole	Dev. %
1700	12913	12878	- 0.27	13134	1.7	13116	1.6	(12730)	- 1.4
1800	13727	13654	- 0.53	13961	1.7	13916	1.4	(13480)	- 1.8
1900	14540	14429	- 0.76	(14788)	1.7	14716	1.2	(14230)	- 2.1
2000	15354	15204	- 0.98	(15615)	1.7	15516	1.1	(14980)	- 2.4

Heat capacity = 8.137 ($\pm$ 0.20) cal/mole degree (this work)

= 7.75 ($\pm$ 0.18) cal/mole degree (Stretz^a)

= 8.27 ($\pm$ 0.38) cal/mole degree (Bonnell^b)

= 8.00 ($\pm$ 0.70) cal/mole degree (Stephens^c)

= 7.50 cal/mole degree (Kelley^d)

^aReference (1).

^bReference (2), values in parentheses extrapolated.

^cReference (25).

^dReference (8), values in parentheses extrapolated.

Figure 7. Experimental liquid copper heat content values and comparative literature values.

SOLENOID

CONICAL

REVERSE CONICAL

Figure 8. Levitation coils used for liquid cerium analysis.

In an effort to obtain lower temperature heat content values, the reverse conical coil was used. It consisted of 2 turns in the upper section wound on a 3/8 inch form and 3 turns in the lower section wound on a 30° taper. The gap between the upper and lower sections was adjusted from 1/4 to 3/8 inch depending on the weight of the sample. This coil yielded poor results. This can be attributed to poor mixing within the sample and severe interference directed into the temperature measuring equipment. The results for this coil indicated that the temperature values were approximately 150° lower than what the previous results indicated. This coil was considered ineffective and abandoned.

Solenoid coil design B was used in place of the reverse conical design in order to maintain maximum lift while reducing the power applied to the induction heating. This particular design has 2 upper section turns wound on a 3/4 inch form with 5 lower section turns wound on a 3/8 inch form. The neutral zone was adjusted from 1/4 to 3/8 inch depending on sample size. The structure of the solenoid coil C is very similar in that only one turn exists in the upper section. Solenoid coils B and C appeared to have nearly the same characteristics except that the stability of samples appeared to be the best in coil B.

Solenoid coil B was used successfully in conjunction with solenoid coil A. The first extended the temperature range to a value of 1400 °K while overlapping the midrange temperature values to 1600 °K. Heat content values obtained from the use of solenoid coil A below 1550 °K appear to verify results obtained by solenoid levitation coil B.

The results obtained for each coil are indicated in Figures 9 and 10. Heat content values labeled with a circle, "O", were taken from

Figure 9. Experimental heat content values of liquid cerium from the melting point (1077 °K) to 2500 °K.

Figure 10. Experimental heat content values of liquid cerium between 1077 °K and 1700 °K.

experiments using solenoid coil type A. Experiments with solenoid coil type B are labeled with a square, '□'.

The combined heat content values of solenoid coils A and B show a curving trend to the data below 1700 °K. These points are evaluated separately because of the indicated curvature. Experiments above 1700 °K are linear with temperature as shown in Figure 9.

Heat content values below 1400 °K were not experimentally determined due to the inability to levitate a sample while keeping the induction to a minimum. Lower temperatures may be reached but the samples must be decreased in size to less than 0.5 grams. The possibility for errors with the small samples became apparent by inconsistent heat content values, while sample temperatures were not lowered enough to merit further work. Figures 9 and 10 indicate the scattering of data below 1700 °K.

Conical coils A and B are very similar in that the lower section consists of 3 turns wound on a 30° taper. Coil A has 2 turns in the upper section wound on a 3/8 inch form while coil B has 2 turns wound on a 3/4 inch form. No detectable difference existed between the two concerning levitation melting qualities. Coil A was used to obtain high temperature heat content values from 2150 °K to 2500 °K using samples varying in size from 1.0 to 1.8 grams. Experiments involving conical coil type A are shown in Figure 9 as inverted triangles, '▽'. The results of runs with this coil were verified by making a run below 2200 °K. In this way experimentally determined heat content values could be compared to results obtained with an alternate coil design. No unusual conditions existed at 2500 °K except for the intense white light

and a considerable temperature rise in the purge gas outlet. No experimental runs were attempted above this temperature due to the increased vapor pressure of the sample.

From these results, a portion of the guesswork in coil designs has been eliminated. The purge gas composition, sample weight, coil neutral zone width and shape of the lower coil sections seemed to generate the variables associated with obtaining different temperatures. Consequently the power to the coil is not critical except during the initial levitation process. The power to the coil is most critical at this time to obtain levitation before melting, due to the low melting temperature of cerium. Once levitated, the sample weight and neutral zone width governed the position of the sample yielding a specific temperature for those conditions. This combined with the heat removed from the sample by the purge gas and the structure of the lower coil section dictated the ability to obtain a wide range of sample temperatures.

Cerium results

Results of the work with cerium are tabulated in Table 3. The linear fit to the corrected heat contents gave

$$H_T - H_{298.15} = [7.42 \pm 0.14] (T - 1077 \text{ } ^\circ\text{K}) + [9482.80 \pm 133.58]$$

for $1700 \text{ } ^\circ\text{K} < T < 2500 \text{ } ^\circ\text{K}$, (32)

with units in cal per mole. As shown in Table 3, the deviations from this linear fit were random and within expected variations. Equation 32 indicates a heat capacity of $7.42 (\pm 0.14)$ calories per mole per degree for the temperature range between $1700 \text{ } ^\circ\text{K}$ and $2500 \text{ } ^\circ\text{K}$. The extrapolated

Table 3. Results for liquid cerium between 1700 °K and 2500 °K using solenoid levitation coil type A and 66% helium atmosphere

Run No.	Apparent temperature °K	True temperature °K	Convection losses cal/mole	% of total heat content	Radiation losses cal/mole	% of total heat content	Heat content cal/mole	Smoothed heat content cal/mole	Dev. %
5	1553	1699	235	1.67	259	1.84	14046	14101	- 0.39
6	1571	1721	238	1.64	271	1.86	14545	14264	1.93
7	1593	1748	261	1.82	298	2.08	14339	14460	- 0.84
4	1603	1759	229	1.60	283	1.98	14298	14544	- 1.72
9	1631	1793	225	1.52	298	2.01	14798	14796	0.01
11	1656	1823	224	1.49	312	2.07	15054	15020	0.22
8	1668	1838	221	1.46	318	2.11	15090	15129	- 0.26
14	1685	1858	215	1.41	324	2.12	15262	15280	- 0.12
1	1715	1896	206	1.33	336	2.16	15528	15558	- 0.19
13	1745	1931	225	1.42	373	2.35	15862	15823	0.24
40 ^a	1762	1953	222	1.37	384	2.37	16196	15983	1.31
10	1775	1968	206	1.28	377	2.35	16062	16097	- 0.22
15	1810	2012	213	1.29	410	2.48	16551	16425	0.76

^aValues taken with conical levitation coil type A.

Table 3. Continued

Run No.	Apparent temperature °K	True temperature °K	Convection losses cal/mole	% of total heat content	Radiation losses cal/mole	% of total heat content	Heat content cal/mole	Smoothed heat content cal/mole	Dev. %
41 ^a	1873	2089	242	1.43	493	2.91	16931	16997	- 0.39
45 ^a	1927	2158	229	1.32	528	3.04	17379	17509	- 0.75
43 ^a	1933	2164	220	1.23	521	2.92	17814	17553	1.47
46 ^a	1975	2218	260	1.47	614	3.47	17717	17952	- 1.32
39 ^{a,b}	2020	2275	90	0.49	661	3.57	18497	18373	0.67
38 ^{a,b}	2055	2320	80	0.43	658	3.55	18544	18705	- 0.87
42 ^{a,b}	2121	2403	82	0.42	744	3.85	19322	19325	- 0.02
44 ^{a,b}	2193	2496	93	0.46	890	4.43	20075	20013	<u>0.30</u>
Average percent deviation									0.67
Experimental $C_p = 7.42 (\pm 0.14)$ cal per mole per degree						$\rho = 6.47$ grams per cm ³			
Experimental $\Delta H_f = 2686$ cal per mole						$m = 140.12$ grams per mole			
$\epsilon_{N\lambda} = 0.309$						$x = 36$ cm (drop distance)			
$\epsilon_{HT} = 0.414$						$Q \approx 0.6$ ft ³ per min (rate of purge gas flow)			

^bValues taken with 100% argon atmosphere.

heat of fusion from these results is 2686 cal per mole. The magnitude of this value tends to further indicate the possibility that the heat content function is nonlinear with respect to temperature below 1700 °K. Experimental results of heat content values below 1700 °K are given in Table 4. Included is coil types and calculated radiative and convective heat losses.

Figure 11 illustrates the heat content of cerium from 298.15 to 2500 °K using the combined data of McKeown (3) for the solid and liquid regions and the results of this work. The uncertainty region concerning the possible curving of the heat capacity function is from slightly above the melting point to 1700 °K. Figures 9 and 10 illustrate heat content values in the liquid phase determined in this work as compared to those of McKeown (3). Possible curvature below 1700 °K is indicated in Figures 9 and 10 by the dashed line. Since the work of Chiotti et al. (4) verifies the work of McKeown (3) concerning the heat of fusion value for cerium, the possibility of this curvature existing becomes more probable.

Estimated thermodynamic function values between 1077 °K and 1700 °K are given in 100 degree intervals in Table 5. The estimated heat capacity values in Table 5 have been derived from a polynomial curve which best fits the heat content data below 1700 °K, including the heat content value found by McKeown (3) at 1077 °K. This value was chosen because of the heat of fusion verification obtained by Chiotti et al. (4). The resulting estimated heat content function in the temperature range 1077 °K to 1700 °K is given as

Table 4. Results for liquid cerium between 1400 °K and 1700 °K using solenoid levitation coil type A and 100% helium atmosphere

Run No.	Apparent temperature °K	True temperature °K	Convection losses cal/mole	% of total heat content	Radiation losses cal/mole	% of total heat content	Heat content cal/mole
32	1298	1399	395	3.49	145	1.28	11314
50 ^a	1301	1403	435	3.75	154	1.33	11611
31	1302	1403	363	3.17	139	1.21	11455
48 ^a	1334	1441	406	3.43	161	1.36	11850
51 ^a	1343	1451	403	3.40	164	1.38	11853
30 ^b	1348	1457	259	2.10	172	1.39	12333
34	1363	1474	396	3.19	170	1.37	12423
33	1376	1489	426	3.36	183	1.44	12694
49 ^a	1386	1501	434	3.56	189	1.55	12189
29 ^b	1404	1522	292	2.23	210	1.61	13075
47 ^a	1419	1540	377	2.91	189	1.46	12963
21 ^b	1433	1556	274	2.09	217	1.66	13083

^aValues taken with solenoid levitation coil type B.

^bValues taken with 66% helium atmosphere.

Table 4. Continued

Run No.	Apparent temperature °K	True temperature °K	Convection losses cal/mole	% of total heat content	Radiation losses cal/mole	% of total heat content	Heat content cal/mole
28 ^b	1478	1610	278	2.06	240	1.78	13486
2 ^b	1510	1649	232	1.70	234	1.71	13659
3 ^b	1522	1662	246	1.81	248	1.82	13593
$\epsilon_{N\lambda} = 0.309$ $\epsilon_{HT} = 0.414$ $\rho = 6.47 \text{ grams per cm}^3$							
$m = 140.12 \text{ grams per mole}$ $x = 36 \text{ cm (drop distance)}$ $Q \approx 0.6 \text{ ft}^3 \text{ per min (rate of purge gas flow)}$

Figure 11. Heat content of liquid cerium from 298.15 $^\circ\text{K}$ to 2500 $^\circ\text{K}$.

Table 5. Estimated thermodynamic functions of liquid cerium between 1077 °K and 1700 °K (cal per mole per degree)

T °K	C _p	S _T ^o - S _o ^o	$\frac{H_T^o - H_{298.15}^o}{T}$	$-\frac{(F_T^o - H_{298.15}^o)}{T}$
1077 ^a	11.743	28.220	7.457	20.763
1100	11.609	28.467	7.554	20.913
1200	11.028	29.452	7.868	21.584
1300	10.447	30.312	8.089	22.223
1400	9.866	31.065	8.236	22.829
1500	9.285	31.726	8.326	23.400
1600	8.704	32.306	8.367	23.939
1700	8.123	32.816	8.370	24.446

^aValues at 1077 °K from McKeown (3).

$$H_T - H_{298.15} = -0.0029T^2 + 18T - 7975.3 \quad (33)$$

in cal per mole where T is in degrees Kelvin. Figure 10 represents the estimated heat content function between 1077 °K and 1700 °K. The estimated heat capacity in this range is given as

$$C_p = -0.00581T + 18 \quad (34)$$

in cal per mole per degree. The correlation coefficient for the curve fitting was 0.81.

Thermodynamic function values between 1700 °K and 2500 °K are given in Table 6. In this case the heat capacity is the slope of the experimental linear heat content data and is given as

$$C_p = 7.422 \text{ cal per mole} \quad (35)$$

Table 6. Thermodynamic function of liquid cerium between 1800 °K and 2500 °K (cal per mole per degree)

T °K	C _p	(S _T ^o - S _o ^o) ^a	$\left(\frac{H_T^o - H_{298.15}^o}{T}\right)^a$	$\left(-\frac{(F_T^o - H_{298.15}^o)}{T}\right)^a$
1800	7.422	33.240	8.249	24.991
1900	7.422	33.642	8.206	25.436
2000	7.422	34.022	8.167	25.855
2100	7.422	34.384	8.131	26.253
2200	7.422	34.730	8.099	26.631
2300	7.422	35.060	8.070	26.990
2400	7.422	35.375	8.043	27.332
2500	7.422	35.678	8.018	27.660

^aValues of entropy, heat content function and free energy function are based on the estimated values below 1700 °K.

Heat capacity values between 298 °K and 2500 °K are given in Figure 12 according to McKeown's (3) work between 298 °K and 1375 °K and this work from 1400 °K to 2500 °K according to equations 34 and 35.

The thermodynamic functions of Table 6 are based on the estimated values obtained in Table 5. The accuracy of these calculations are, therefore, limited to only approximations showing value trends and magnitudes. The thermodynamic functions were calculated according to the equations presented in the calculations section of this thesis.

The results of this work merited a review of experimental techniques and possible calculation errors. This analysis should help support the results obtained.

Figure 12. Heat capacity values of cerium from 298 $^{\circ}\text{K}$ to 2500 $^{\circ}\text{K}$.

Experimental Evaluation

The results obtained from the copper calibration runs were in excellent agreement with the cited literature values including the recent work of Stephens (25). These results tend to eliminate the possibility of error in technique. This includes calibration, evaluation of the new sample dropping technique and the accuracy of sample temperature measurements.

The most probable source of error seems to be in establishing the true sample temperature. Therefore extended work was performed with the measured cerium temperature and its emittance values.

A test was made with a levitated sample of cerium to see if an apparent temperature change was indicated by the introduction of 5 c.c. air into the levitation chamber under normal conditions with the purge gas at a normal flow rate and the power at a constant value. No apparent temperature increase was recorded by the pyrometer.

Vacuum fusion analysis before and after actual levitation runs indicated a 7.6×10^{-5} grams increase in oxygen content of a 1 gram sample. The introduction of 5 c.c. of air into the system would be an approximate addition of 1×10^{-3} grams of oxygen. This however does not discount the possibility of a surface film existing on a levitated sample.

If such a film existed the emittance of a levitated sample could be altered. The effects of this film on the temperature are shown in Figure 13. Errors of $\pm 50\%$ were introduced into the normal spectral emittance value of 0.309. This extreme variation was used to illustrate

Figure 13. Analysis of $\pm 50\%$ deviation in the normal spectral emittance of cerium.

the effect on the measured heat content. As Figure 13 illustrates neither deviation approaches the extended values of McKeown's (3) work. This indicates that the possibility of the normal spectral emittance being in error is very unlikely.

The possibility of hemispherical total emittance calculation errors are illustrated in Figure 14. Here the calculated hemispherical total emittance was varied by $\pm 20\%$. Since this value is used only in the correction of heat content for radiative heat loss, only a slight variation is indicated.

Both of these considerations show that errors of less than $\pm 20\%$ in either the normal spectral emittance and/or the calculation of the hemispherical total emittance would not alter the experimental results to values favorable to that of McKeown (3).

The possibility of error in the liquid phase experimental work by McKeown cannot be discounted. As previously discussed the purity of the water and mercury as well as the ability to maintain a constant volume calorimetric system govern the accuracy of this type of system. These possibilities plus inaccuracies in the heat loss correction could give unfavorable experimental results. Heat loss errors could be substantial in the liquid temperature region. Additional factors could be the dissolution of tantalum into the liquid cerium upon heating and the presence of thermal gradients through the sample and its tantalum crucible and platinum outer covering.

Although McKeown (3) has been proven successful for other materials, a question still exists as to its validity in cerium evaluation. Sample temperature measurement techniques, heat losses,

Figure 14. Analysis of $\pm 20\%$ deviation in the hemispherical total emittance of cerium.

and sample contamination seems to be an evident problem of previous work. This shows that the levitation calorimetry technique has advantages in regards to minimizing these possible errors. Reliable thermal emittance values and high sample purity will maintain accurate sample temperature readings. The corrections for radiative and convective heat losses including the calorimeter heat leakage is necessary for accurate results as shown in previous levitation calorimetry work. Tables 3 and 4 show the magnitude of radiative and convective heat losses for cerium runs. The accurate evaluation of these losses is critical in establishing accurate heat capacity data.

Sample contamination is minimized since no container is involved. The container consists of the generated electromagnetic field and the purified inert gas system. The advantages of levitation calorimetry appear to warrant its future application in this type of thermodynamic research.

SUMMARY AND CONCLUSIONS

Levitation calorimetry has been used to experimentally determine the heat content function of liquid cerium between 1400 °K and 2500 °K. Previous experimental work (3) was limited to several experimental values 300° above the melting point, 1077 °K.

The heat content function between 1700 °K and 2500 °K was found to be linear with respect to temperature. The heat content function in cal per mole is given as

$$H_T - H_{298.15} = [7.42 \pm 0.14](T - 1077 \text{ °K}) + [9482.80 \pm 133.58]$$

$$1700 \text{ °K} < T < 2500 \text{ °K.} \quad (32)$$

The heat capacity for this temperature range is 7.42 cal per mole per degree.

The heat content function between 1400 °K and 1700 °K was found to be nonlinear. The estimated heat content function for this temperature range in cal per mole is given as

$$H_T - H_{298.15} = -0.002905T^2 + 18T - 7976.3 \quad (33)$$

$$1400 \text{ °K} < T < 1700 \text{ °K.}$$

The estimated heat capacity in cal per mole per degree is given as

$$C_p = -0.00581T + 18 \quad (34)$$

$$1400 \text{ °K} < T < 1700 \text{ °K.}$$

The experimental heat capacity above 1700 °K does approach the rule of thumb values of between 7 and 8 cal per mole per degree. However the heat content function below 1700 °K does not agree with the experimental work performed by McKeown.

Alternate liquid state structures of cerium could be present up to a specific temperature in the liquid phase. These structures were previously mentioned as clustering. The history of clustering has been discussed in detail by Stretz (1). Clustering is mentioned as the near-solid association of large groups of atoms within the liquid phase. This possibility is of short range duration as opposed to long range.

The presence of short range clusters tend to yield higher heat capacity values than a homogeneous liquid phase. The results of this work between 1400 °K and 1700 °K indicate a possible estimated heat capacity of 11.75 cal per mole per degree at 1077 °K. This value would decrease to 7.42 cal per mole per degree at 1800 °K and remain constant up to 2500 °K.

Although other experimental work with the lanthanide metals does not show this clustering effect, cerium could behave this way because it has two 4f electrons which could be quite unstable under these conditions. Secondly the electromagnetic stirring of the liquid sample could be of such magnitude with the other metals in the lanthanide series that the clustering is immediately dispersed. This immediate dispersion could be attributed to the additional 4f electrons in the other rare earth metals. The dispersion would tend to artificially flatten the heat content curve.

McKeown's (3) work between 1077 °K and 1375 °K cannot discount this possibility due to possible errors as previously discussed. More experimental data in the temperature range 1077 °K to 1400 °K is needed to verify this possibility. The definite existence of clustering between 1077 °K and 1700 °K could only be proven conclusively

with further experimental work besides levitation calorimetry, such as high temperature x-ray work.

Possible sources of error in levitation calorimetry work include errors in calorimeter calibration, errors in sample temperature determinations, errors in measurements of the calorimeter block temperature and errors introduced by approximations and estimates in the calculations. The largest source of error is in the measurement of the sample temperature. The maximum estimated error calculated by Stretz (1) for the levitation calorimetry work is $\pm 2.5\%$.

The results of this work and other levitation calorimetry work have proven the need for extending liquid metals research by this technique. The void in high temperature liquid metal thermodynamic data will be filled as levitation calorimetry is applied to other systems of interest.

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