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# THE HEAT CONTENT, HEAT CAPACITY AND ENTROPY OF

CeO2 BETWEEN 30° AND 900°C

A THESIS

# Presented to

the Faculty of the Graduate Division

by

Walter Madison Ligon

In Partial Fulfillment

of the Requirements for the Degree Master of Science in Chemical Engineering

Georgia Institute of Technology

November, 1957

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## ACKNOWLEDGMENTS

I would like to express my sincere appreciation to Dr. W. T. Ziegler not only for his original suggestion of this investigation, but also for his guidance and patience during the carrying out of this work; to the Engineering Experiment Station for placing its facilities at my disposal; to the Tennessee Eastman Corporation for the year 1954-55 and the Ethyl Corporation for the year 1955-56 for providing the fellowships that made my residence at Georgia Tech possible; and to the others who gave assistance during this time.

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#### SUMARY

The lanthanide series of chemical elements and their compounds are a group of substances for which relatively few thermodynamic data are available. The paucity of such information has been due in large measure to the difficulty involved in their separation and purification. This difficulty has recently been obviated through the application of ion-exchange techniques to this problem.

The purpose of the present investigation has been to determine the high-temperature heat content of  $CeO_2$  and to use these measurements to obtain other related thermodynamic quantities.

The heat content of  $\text{CeO}_2$  was determined in an apparatus previously described by Blomeke and Ziegler, J. Am. Chem. Soc. 73, 5099 (1951). The operating characteristics of this apparatus were checked by comparing the heat content of a sample of  $\propto -\text{Al}_2O_3$  (corundum) measured by this apparatus with the heat content reported for this substance by Ginnings and Furukawa, J. Am. Chem. Soc. 75, 522 (1953). This comparison gave a maximum deviation of 0.70 per cent with an average deviation of 0.29 per cent.

The heat content data of CeO2 were formulated into the equation

$$CeO_{2} (s): H_{T} - H_{303.2} = 18.64 T - 0.0000512 T^{2} + (1)$$

$$346.600/T - 6789.7$$

which is believed to represent the true heat content of  $CeO_2$  to within  $\pm$  0.7 per cent in the range 303.2 to 1172.6°K. In formulating this

equation, an accurate value of the heat capacity of CeO<sub>2</sub> at 303.2°K was used (unpublished data of E. F. Westrum, Jr. and D. H. Terwilliger, University of Michigan).

The equation for the heat content was used to obtain the following heat capacity equation,

$$CeO_2$$
 (s):  $C_p = 18.64 - 0.000102 T - 346,600/T^2$  (2)

and the entropy equation,

$$CeO_2$$
 (s):  $S_T - S_{303,2} = 42.93 \log T - 0.000102 T +(3) $173,300/T^2 - 108.4$$ 

The results are expressed in defined calories, degrees on the international Kelvin scale and gram-moles.

## CHAPTER I

#### INTRODUCTION

<u>The Purpose</u>.--This investigation was conducted to determine the hightemperature heat content of ceric oxide, CeO<sub>2</sub>. Other related thermodynamic data were derived from an algebraic expression which represented the measured heat content data.

The Data.--Thermodynamics is a very powerful and useful tool in the hands of the scientist or the engineer, for within its scope is included the important subjects of energy and its transformations, and tendency to change and equilibria. In dealing with these subjects, many useful results may be obtained from a meager amount of data by use of the principles of thermodynamics. The type and amount of data necessary, of course, depend upon the problem and the desired accuracy of results.

Most metallurgical processes involve reactions at elevated temperatures. For problems involving these elevated temperatures, experimentally determined heat content or heat capacity data are very helpful. By use of free-energy and heat capacity data, the position of the reaction equilibria under various conditions required by experimental or industrial practice may be calculated. This permits projected processes to be examined to determine whether or not a reaction will occur and, if it will, to what extent it will proceed under the conditions that may be imposed by practical considerations. Existing processes may be examined to determine whether increased efficiency or improvements in yield-ratio are thermodynamically possible. Heat capacity measurements also can serve as a tool in the study of the structure of solids, as they offer one of the surest means of disclosing transitions.

Since many thermodynamic processes are conducted at conditions which approximate those of the pressure of the atmosphere, that thermodynamic path was chosen for this investigation. These conditions are particularly likely to be encountered for the case of systems consisting entirely of solids or liquids, where there is usually little advantage to be gained from changing the pressure, unless really high pressures are to be considered.

<u>The Substance</u>.--Ceric oxide is the substance whose thermodynamic properties have been studied in this investigation. Cerium is a member of the first inner transition series of chemical elements which, classically, was known as the rare earth series. In modern terminology this series, to avoid implications of relative scarcity and to conform to the designation of the second inner transition series, is frequently referred to as the lanthanide series.

A characteristic of the lanthanons is that a large number of them invariably occur in nature together. Although the lanthanons are quite generally distributed throughout the Earth's crust, there exist only scattered deposits which are concentrated in quantities large enough to be important as ores. However, with the increasing search for mineral deposits of strategic importance, the scarcity of these ores have decreased until now many of the members of this group are sufficiently abundant to permit production in technical quantities should the demand

arise. Cerium is generally the lanthanon in greatest abundance in these deposits and is more abundant in the Earth's crust than many of the so-called "common" elements, such as tin, mercury, or tismuth (1).<sup>1</sup>

With increase of atomic number in the lanthanide series, there is a progressive filling of the 4f orbitals of the electronic configuration, leaving the two outermost shells of electrons essentially unaltered. Since the outermost shells of electrons determine to a large extent the chemical properties, there is a very marked similarity of chemical properties in this group of elements. The separation problem associated with these elements has long been recognized as one of the most challenging and difficult in the field of chemistry. Many workers have spent years using the classical fractional crystallization technique to obtain compounds of these elements of reasonably high purity. Much of the general lack of data on these elements and their compounds can be directly attributed to this cause.

The difficulty of separating the lanthanons has been obviated through the efforts of the Manhattan Project to apply the methods of ionexchange separations (2), (3). Today this technique has made it possible to obtain these substances in an exceedingly high degree of purity in a very much shorter period of time than was previously possible. Initial work was directed at preparation of tracer or milligram quantities, but further work has demonstrated that many of these elements can be separated in kilogram quantities in very high purity. This greater accessibility to pure cerium compounds will undoubtedly give impetus to further

Reference numbers refer to the "Literature Cited" section of the Bibliography.

scientific and technological investigations and development of uses for an already commercially important element and its compounds, for economic and competitive forces are inextricably a part of the development of any chemical.

The Literature.--In the literature thermodynamic data for the lanthanide series of elements is totally lacking or is of limited range and reliability. In 1931 Kelley (4) expressed doubts that thermodynamic data would become available within the next few years due to the rarity and high costs of these materials. These doubts seem to have been almost fully sustained, for there have been few thermodynamic data reported within recent years and the factors stated above have proven to influence the availability and applicability of such data.

A search of the literature revealed that only a limited amount of thermodynamic data were available for  $\text{CeO}_2$ . Milson and Petterson (5) have reported a single measurement of the mean heat capacity for the temperature range 0°C to 100°C. The sample was reported to be in the pure state; however, no quantitative statement was made regarding it. The formula weight was given as 171.5, which is in slight disagreement with the present accepted value of 172.13 (6).

A. S. Russell (7) reported a value for the mean heat capacity in the range 3.4 to 48.1°C which is about five per cent higher than that of Nilson and Petterson. Nothing is said concerning the purity of the sample except "very pure preparation." Russell expressed doubts that the actual temperature interval in his measurements was accurately reported.

By far the most extensive data found in the literature were those of A. J. Brons (8). This report gives mean specific heat data for a number of temperatures in the range 220°C to 770°C from a datum temperature near 21°C. However, nothing is said concerning the purity of the sample. His method of measurement was essentially the same as that employed in this investigation.

## CHAPTER II

#### APPARATUS AND INSTRUMENTATION

The Principle of Operation.--The method of mixtures was the principle of operation of the earliest calorimeter, which employed water as the calorimetric medium (9). High-temperature heat capacities of solids are most conveniently measured by use of this method. While water may be used as the calorimetric medium, there are certain restrictions in the range and certain errors resulting from the evaporation of water. In present practice water has commonly been replaced by a copper or aluminum block as the calorimetric medium.

This principle of operation consists in having a calorimetric medium, whose heat capacity is known, and a means for bringing the test sample at some predetermined temperature into contact with the calorimetric medium. When thermal equilibrium is attained between the sample and the block, the change in temperature of the medium defines the quantity of heat exchanged. Certain corrections, which depend upon the technique, must be considered to obtain the total quantity of heat exchanged by the sample. From the change in temperature of the test specimen and the quantity of heat exchanged from it, the heat capacity can be established.

<u>General Description</u>.—The calorimeter employed in this investigation uses this method of mixtures and was patterned after one which has been previously described by Southard (10). This calorimeter was designed and constructed by Blomeke (11, 12), who made measurements, similar to those carried out in this study, on  $La_2O_3$ ,  $Pr_6O_{11}$ , and  $Nd_2O_3$ , as well as on a sample of  $\alpha - Al_2O_3$  (corundum).

This apparatus is a modification of the standard one in which a capsule containing the sample is heated in a furnace to a specified temperature and at a given moment dropped into a calorimeter of known heat capacity. The modifications in this apparatus were made to allow the capsule to be reintroduced into the furnace without the necessity of dismantling a considerable portion of the apparatus.

The calorimeter was designed to measure heat contents from room temperature to approximately 1,000°C using the "drop" technique. This involved heating the sample, in a capsule of known heat capacity, to a predetermined temperature in a furnace, then dropping it into a calibrated copper block. The resulting transfer of heat to the block causes a rise of temperature, which is measured by a change of resistance of a copper resistance thermometer wound around the copper block. From the resulting change of resistance, plus corrections, the heat content of the sample between the temperature of the furnace and 30°C can be calculated.

A complete description of the furnace, calorimeter and associated temperature measuring systems is given by Blomeke (13) in his thesis. A condensed description of the working parts taken from this source is given below. No significant changes were made in the equipment for use in the present investigation.

The Furnace, -- The purpose of the furnace is to raise the temperature of the sample to some predetermined level and hold it at this temperature

until the temperature is uniform throughout the sample. The furnace was constructed of a heating element of No. 19 B. & S. gage Nichrome V wire wound on an Alundum tube (l in. inside diameter by lk in. long). The furnace was insulated with a layer of Refrasil insulation and a layer of Armstrong insulating firebrick A-23. Except for the ends of the furnace tube, the furnace was completely enclosed by a water jacket to produce a more nearly constant environment.

The top of the furnace was closed with a refractory plug, through which a No. 32 B. & S. gage Nichrome wire passed to support the capsule in the furnace. The bottom end of the furnace tube was closed by a water-cooled gate, which rotated on a Bakelite shaft eccentric with the center line of the furnace. This gate was arranged so that it could be opened to permit passage of the capsule during a drop and, when closed, prevented heat from being exchanged between the furnace and the calorimeter.

The maximum temperature of the furnace was limited by the heating element to temperatures below about 1,000°C.

The temperature of the furnace was indicated by a single-junction platinum, platinum--10 per cent rhodium thermocouple, which was led into the top of the furnace through the refractory plug. The tip of the thermocouple was placed within 1 mm. of the top surface of the capsule.

The furnace temperature, as indicated by this thermocouple, is not the same as the sample temperature. Appendix A, Figure 3 gives the relationship between these two temperatures.

The thermocouple used in this work was a platinum, platinum--10 per cent rhodium thermocouple (L. & N. Catalogue No. Standard 780-B;

No. 24 B. & S. gage wire, 24 in. long) and was calibrated by the National Bureau of Standards according to Schedule 203.102a. Over the range 0° to 1,100°C, the calibration was certified to agree to 0.5°C with the International Temperature Scale of 1948 (14).

The cold junction of the thermocouple was maintained at 0°C in an ice bath of distilled water and ice made from city water from which no impurities were removed. Calculations revealed an insignificant deviation of the temperature of this bath from 0°C from impurities in the ice.

Roeser and Wensel (15) have shown that platinum, platinum--10 per cent rhodium thermocouples made of high quality materials can be relied upon to retain their calibrations to within 0.25 per cent for about a year when used in clean, oxidizing atmospheres below 1,000°C. The thermocouple and conditions of use in this work met those specifications.

The thermocouple was connected with No. 16 B. & S. gage Durex leads to a Leeds and Northrup type K-2 potentiometer (Serial No. 714,088), which was used in conjunction with a high-sensitivity galvanometer (Serial No. 1,064,440) for the potential measurements. This potentiometer was not calibrated in an absolute sense, but was guaranteed by the manufacturer to be accurate to 0.02 per cent. It was used with an Epply standard cell, which was compared at the beginning of each series of potential measurements with another standard cell calibrated by the National Bureau of Standards and used only for reference.

Power was supplied to the furnace windings through a 1 kva General Electric voltage stabilizer (Serial No. 9,638,844) in series with a variable voltage transformer (Powerstat).

<u>The Calorimeter</u>.—The calorimeter block was of copper (h in. diameter by 7-1/2 in. high) which was supported in a brass case by three Bakelite cones. The top of the brass case was connected to the furnace by a 1 inch brass tube through which the capsule passed as it dropped into the copper block. The top of the case was fastened to the lower portion by means of a flanged joint with a Neoprene gasket. The center of the block was bored to fit a receiving well which was a bored, cylindrical plug, tapered near its top so as to produce a snug fit in the block. The receiving well was wound with a 100-ohm heater for electrical calibration purposes.

A circular copper gate about 3/4 inch thick and recessed into the top of the block was provided to cover the receiving well except during the drop period of a measurement. This gate was operated on the same shaft as was the water-cooled gate.

The temperature of the copper block was indicated by a resistance thermometer consisting of 395 turns of No. 34 B. & S. gage single-cotton enameled copper wire. This thermometer was fitted with four leads of the same material. The thermometer was protected by a copper can which fitted around the bottom and side of the block. The finished thermometer had a resistance of 103.9 ohms at 25°C.

The resistance of this thermometer was measured by a Leeds and Northrup Model G-2 Mueller Bridge (Serial No. 740,545), which was used in conjunction with a high-sensitivity galvanometer (Serial No. 740,876). This bridge had been calibrated by the National Bureau of Standards and certified to be correct to 2 parts in 100,000 when used to measure resistances greater than one ohm.

The inside surfaces of the case, the top of the block and the outside of the can were gold plated and buffed to a bright finish to serve as a chemically inert surface and to reduce the radiative heat losses.

<u>The Bath</u>.--A water bath thermostated at  $30.00 \pm 0.02$ °C was used to provide a constant temperature environment for the calorimeter. The bath was provided with a stirrer, a 1,500-watt Lo-Lag Immersion heater and a Sargent mercurial thermoregulator. The thermoregulator used a "zero-current" relay circuit which turned the current to the heater on and off to regulate the temperature. The power was supplied to the heater through a Powerstat, an ammeter, and a switch set to turn the power off when the temperature reached 35°C. These were connected in series to serve to safeguard against the possibility of the water overheating if the regulating circuit failed and also to limit the power to the heater so that a more nearly uniform environment for the block could be attained.

<u>Other Equipment</u>.--Capsules of platinum--10 per cent rhodium were provided to contain the sample. These capsules were cylinders (3/4) in. diameter and 3/4 in. high) made with a neck and a cap to seal the end of the neck. The cap was provided with a loop to take the wire by which the capsule was suspended in the apparatus.

The wire which suspended the capsule was fastened to a loop in the bottom of the piston of the drop mechanism. The drop mechanism consisted of a vertical slotted tube in which the loosely fitting piston moved. The lower 6-1/2 inches of the tube were not slotted so that the capsule was

air-cushioned as it settled into the receiving well. This piston mechanism was attached by a piece of string to a counter-weight to keep the time of drop nearly uniform.

A  $CO_2$  cylinder was provided to maintain a slow stream of gas through the calorimeter. A  $CO_2$  flow rate of 50 cc. per minute was measured through a capillary tube connected across a manometer, which indicated this flow rate by two inches of Merian red oil. A silica gel trap was placed in the line after the capillary to trap any oil or water vapor present in the  $CO_2$ .

<u>Renovation of Apparatus</u>.--Blomeke's work had been completed for some time previous to the initiation of this investigation, therefore, it was necessary to check the calorimeter to ascertain its condition. The case surrounding the copper block and the can was taken apart in order to examine the gold-plated surfaces of the case, can and block, and to remove particles of Alundum which had fallen from the furnace lining. Oil was found in the bottom of the case around the CD<sub>2</sub> inlet. The previously mentioned trap was installed to prevent the reoccurrence of this oil in the calorimeter.

All of the electrical circuits were checked with an ohm-meter. The resistance of these circuits indicated that they were in approximately the same condition as they were when used by Blomeke. After reassembly of the apparatus it was further tested by redetermining its operating characteristics. This included a redetermination of the Kcurve and determination of the heat content of a standard substance. These checks are described in later sections of the thesis.

# CHAPTER III

#### EXPERIMENTAL PROCEDURE

<u>Materials</u>.--The sample of  $\propto -Al_2O_3$  (corundum) used in the present study was the same sample which had previously been used by Blomeke (ll) to establish the operating characteristics of the apparatus. This sample of  $\propto -Al_2O_3$  was obtained from the National Bureau of Standards, and was made available under a program set up to supply calorimetric standards to aid in the comparison of calorimeters (l6). The sample was in the form of particles, 2-4 mm. in diameter, and it is believed that this  $\propto -Al_2O_3$  contained less than 0.03 per cent impurities.

The ceric oxide was obtained from Research Chemicals Inc., Burbank, California. The sample of ceric oxide was in the form of a faintly yellowish-white powder, and was stated by the supplier to be 99.8 per cent CeO<sub>2</sub>.

Filling and Sealing the Capsule.--The capsule and cap were cleaned with dilute HCl prior to use. They were then washed with distilled water and put into a furnace at 850°C overnight. They were removed from the furnace, cooled in a desiccator, and weighed. The GeO<sub>2</sub> sample was then transferred to the capsule until the capsule was filled nearly to the neck, and then weighed. The capsule, cap and sample were fired overnight at 850°C, then removed to a desiccator, sealed with gold and reweighed to obtain the weight of CeO<sub>2</sub> in the capsule. The weight of the gold seal was obtained by weighing the wire before and after being used to seal the sample in the capsule.

<u>Mounting the Capsule in the Furnace</u>.--A No. 32 B. & 3. gage Nichrome wire was used to suspend the capsule in the furnace from the piston of the drop mechanism. The location of the capsule in the furnace was critical, so to minimize stretching, the wire was annealed electrically before it was used.

The annealing was accomplished as follows. About four or five feet of wire was suspended from a nail. Leads were connected to the wire at both ends, so that a current of two to three amperes could be passed through to heat the wire. The wire was kept at a low temperature at first, but the temperature was increased to a red heat at the end of one-half hour and remained there until the end of an hour when annealing was complete.

To mount the capsule in the furnace, the drop mechanism, refractory plug and thermocouple were removed from the top of the furnace. One end of the wire was attached to the loop in the piston and the other led through the hole in the refractory plug to attach the capsule by the loop in the cap. The capsule was positioned relative to the thermocouple by assembling the drop mechanism, refractory plug and thermocouple into the position that it would assume when in place on top of the furnace. The capsule was then fastened to the wire so that it was 1 mm. below the junction of the thermocouple when hanging under its own weight. This assembly was then carefully remounted into position on the furnace so as to avoid kinking the support wire.

<u>The K-Curve</u>.--In a heat content determination of a sample, the total quantity of heat transferred from the sample to the block must be established. A portion of this heat is measured in a temperature increase of the calibrated copper block above its initial condition when the block and the sample come to thermal equilibrium, and the remainder is determined as heat loss from the block to its surroundings. This presupposes that the temperature of the block is always higher than that of the surroundings, a condition met in all experiments described in this thesis.

Blomeke (17) discusses the determination of this loss, but since a part of this work involved the redetermination of the K-Curve, it will be discussed again.

When the hot capsule containing the sample is dropped from the furnace into the calorimeter block, heat flows into the block. This transfer of heat is rapid at first, but gradually decreases as the temperature of the capsule approaches the temperature of the block. As a consequence of this heat addition, the block temperature is displaced from equilibrium with its surroundings and it begins to transfer heat to the case and to the  $CO_2$  in the space between the case and the block. This heat loss from the block becomes more rapid as the temperature difference increases.

Under the effects of the accumulation of heat, the temperature of the block rises rapidly at first, goes through a maximum when the heat loss equals the heat gain, decreases while the loss exceeds the gain, and finally, decreases at a constant rate when the capsule and the block come to thermal equilibrium.

The heat loss from the block must be determined for the time interval beginning when the capsule is dropped into the tlock and extending until thermal equilibrium is established between them. This is accomplished by using Newton's law of cooling, which is commonly understood to imply that the rate of loss of heat of a hot body is proportional to the excess of its temperature above the temperature of its surroundings, or

$$dq/dt = K'(T_j - T) = K'\Theta$$
(1)

where

q = heat loss,

K' = thermal leakage modulus,

T = temperature of the block at time t,

 $T_j =$  temperature of the jacket (presumed to be the same as the thermostated bath), and

 $\Theta$  = temperature difference =  $T_i - T_i$ 

If the heat capacity of the body remains constant throughout the experiment, the heat loss is proportional to the fall in temperature and this proportionality constant may be incorporated into the thermal leakage modulus to give

$$dT/dt = K''(T_j - T) = K''\Theta$$
 (2)

Blomeke (18) found that the resistance of the block thermometer may be considered as varying linearly with temperature over the range  $30^{\circ}$  to  $40^{\circ}$ C within the limits of accuracy of the measurements. Under these circumstances T is a linear function of R, thus equation (2) becomes

$$dR/dt = K(R_{j} - R) = K\phi$$
(3)

where

R = resistance of the block thermometer at time t,

- R<sub>j</sub> = resistance of the block thermometer corresponding to the temperature of the jacket,
  - K = thermal leakage modulus, and
  - $\phi$  = thermal head = R<sub>1</sub> R.

K is determined experimentally by displacing the temperature of the block from its equilibrium position by a known amount. Then the change of resistance of the thermometer is observed as a function of time. Although in Newton's law of cooling, K is a function of  $\phi$ , it is found that for small temperature differences and moderate time intervals, the resistance of the block thermometer varies linearly with time within the limits of accuracy of the measurements. For such a case, if  $R_1$  and  $R_2$  be the resistance of the block thermometer at time  $t_1$  and  $t_2$ , respectively, the mean value of  $\phi$  would be

$$\vec{\phi} = R_j - 1/2(R_1 + R_2).$$
 (4)

Then, the equation for the resistance loss due to cooling becomes

$$K = (R_2 - R_1) / \bar{\phi} (t_2 - t_1).$$
 (5)

Heat Content Determinations.--Heat content determinations were made both on a standard sample of  $\propto -Al_2O_3$  and the CeO<sub>2</sub> sample. Procedure was identical for the determinations.

The samples were heated in the furnace whose temperature was controlled to the desired level by manipulation of the Powerstat. The sample was kept at this temperature for about 30 to 60 minutes so that thermal equilibrium was established with the temperature of the sample uniform throughout.

The resistance of the block thermometer was observed for a fore period of about ten minutes to determine the resistance of the thermometer at the time of drop of the sample. About two or three seconds before the sample was dropped, the gate was opened. The sample was then dropped and the gate closed immediately.

The resistance of the thermometer was measured periodically after the capsule was dropped until a period of constant cooling rate was reached. This steady cooling rate was reached 25 to 30 minutes after the drop of the sample.

After the resistance of the block thermometer indicated a steady cooling rate, the capsule was returned to the furance for the next determination.

CO2 was passed through the apparatus at about fifty cubic centimeters per minute during all the determinations.

#### CHAPTER IV

## DISCUSSION OF RESULTS

<u>The K-Curve</u>.--The relationship between K and  $\phi$ , the thermal head, was determined using the procedure outlined in Chapter III. Appendix B contains a sample calculation of a point on this curve, a summary of the points determined, and the relation of these points to the curve given by Blomeke (19) in Figure 5.

The points determined in this investigation show an agreement to within one per cent maximum deviation, except at four points, when compared with the curve determined by Blomeke. These deviations are within the limits of accuracy imposed by this procedure, and the points are randomly distributed about this curve. In consequence of these considerations, the curve is assumed to be correct and the calorimeter to be operating in this respect, essentially the same as when used by Blomeke to make his measurements.

Deviations from the curve are greatest in the lower portion of the curve where thermal heads are small, but this is where corrections to the heat content amount to the smallest percentage of the total heat transferred from a sample, hence, in this region, K need not be known with greater accuracy.

All of the heat content determinations were begun with the block nearly in thermal equilibrium with the jacket. This made corrections to the total heat of less than four per cent, and since the K-curve is known to one per cent, this would result in an uncertainty of 0.04 per cent in the final results.

The Heat Content of  $\propto -Al_2O_3$ .—The heat content of  $\propto -Al_2O_3$  was determined to serve as a check on the operating characteristics of the calorimeter and to compare the performance of the calorimeter with other calorimeters. The heat content determinations were conducted according to the procedure outlined in Chapter III. The data obtained by this procedure were treated by the method outlined in Appendix C to yield the heat contents, which are contained in Appendix D. These determinations cover the range 219.5°C to 875.0°C, which is roughly the range of the CeO<sub>2</sub> heat content determinations.

Several investigators (21), (22), (23) have reported the heat content of  $\alpha - Al_2O_3$  in the range of this investigation. All of these agree to within about one per cent maximum deviation from each other. The results of Ginnings and Furukawa (22) have been taken to be the most reliable of these measurements.

Selected values from the data of Ginnings and Furukawa are contained in Table 11 of Appendix D. The heat contents at the temperatures of the heat content determinations of this investigation were calculated from the more complete data reported by these investigators, and are contained in Table 1.

The energy unit used throughout this investigation was the defined thermochemical calorie. The temperature scale used was the International Temperature Scale of 1946 (14) and the Kelvin scale was obtained from the centigrade scale, taking the ice point to be 273.16°%. The formula weights

Table 1. Comparison of the Heat Content of  $\simeq -Al_2O_3$  above 303.2°K with other Investigations. (The heat content is in defined thermo-chemical calories per gram mole.)

_		(∆H) <sup>1</sup> 3	303.2,	Deviation from Data of G. & F.		
Temp., t°C.	This Research	Bloneke <sup>l</sup>	G. & F. <sup>2</sup>	This Research	Blomeke	
219.5 417.0 417.2 422.9 718.5 875.0	4367 9578 9597 9723 18216 22973	4313 9542 9547 9704 18193 22911	4336 9570 9576 9735 18303 23007	0.70 0.08 0.22 - 0.13 - 0.147 - 0.15	- 0.51 - 0.29 - 0.30 - 0.30 - 0.60 - 0.42	
875.0	22973	22911 	23007	- 0.15	- 0.	

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<sup>2</sup>D. C. Ginnings and G. T. Furukawa, (22).

were calculated from atomic weights, which are in agreement with the values accepted by the Council of the Internation Union of Chemistry, which met July, 1953, as recommended by the International Commission on Atomic Weights (20).

This table has the deviations which were calculated from this data. There is an average deviation of 0.29 per cent with a maximum deviation of 0.70 per cent at 219.5°C, where the greatest deviation is expected. There is an inexplicable tendency for the heat content as measured in this investigation to be higher at low temperatures and lower at higher temperatures than would be predicted from the data of Ginnings and Furukawa. When Blomeke (21) compared his results with those of Ginnings and Corruccini (23), he discovered the same peculiarity.

A comparison of the results with those of Blomeke revealed that the heat content of  $\propto -Al_{23}^{0}$  measured by this investigation is greater at all points. The maximum deviation of 1.24 per cent occurs at 219.5°C, and the average deviation is 0.46 per cent. These deviations cannot be accounted for by any known differences in experimental procedure.

These comparisons suggest that the calorimeter is operating essentially the same as when used by Blomeke, but that results should be slightly high at temperatures below 420°C and slightly low at higher temperatures. These deviations should be about two per cent high at 100°C to zero at 420°C to one-half of one per cent low at 900°C. This is shown graphically in Figure 1, where the mean heat capacity above 303.2°K is plotted against the temperature in degrees Kelvin.

The Heat Content of CeO2.---The determinations of the heat content of



Figure 1. Mean Heat Capacity of X-Al203 from 303.2° to T°K vs. T°K.

 $CeO_2$  were conducted on a sample obtained from Research Chemicals, Inc. and was stated by them to be 99.8 per cent  $CeO_2$ . These determinations were made according to the procedure outlined in Chapter III to cover the temperature range 109.0 to 899.4°C.

A summary of the data of these determinations is contained in Table 12 of Appendix E, and the heat contents calculated from these data are in Table 2.

The greatest error in the heat content determined for  $CeO_2$  resulted from uncertainty in the temperature of the sample in the furnace. This uncertainty came from the difference in temperature between the sample and the thermocouple<sup>1</sup>, minor fluctuations of the temperature of the furnace, and other causes. This uncertainty probably amounts to one degree, or slightly more than one per cent of the temperature difference at 110°C to about one-tenth of one per cent at 900°C (24).

Smaller inaccuracies were expected from such sources as variation of the length of time for the capsule to drop from the furnace into the block, variation of the length of time the gates were open during the drop, inaccuracies in reading the resistance of the copper thermometer, and inaccuracies in reading the thermocouple E. m. f. These deviations were less than one-twentieth of one per cent of the total measured heat content in any measurement. Thus, the results were expected to be accurate to within about one per cent with the error decreasing to 0.3 per cent at the highest temperatures. However, as discussed above about the heat content of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the results were expected to be about two

<sup>1</sup>See Figure 3, Appendix A.

Temperature		$(\Delta H)_{303,2}^{T}$	$(\Delta H)_{303,2}^{T}$	Deviation from		
t °C	т °К	Obs.	Calc'd Eq'n (13)	Eq'n (13), Per Cent		
30.0	303.2	0	0	0		
109.0	382.2	1253.4	1233.4	1.59		
211.0	484.2	2971.3	2939.1	1.08		
286.3	559.5	4292.6	4242.2	1.17		
427.6	700.8	6780.6	6741.8	0.57		
591.8	865.0	9689.2	9695.4	- 0.06		
717.8	991.0	11978	11981	- 0.03		
725.1	998.3	12096	12114	- 0.15		
810.3	1083.5	13647	13666	- 0.13		
899.4	1172.6	15326	15292	0.22		

Table 2.	The	Heat	Content	of	CeO,	above	303.2	°K	in	Defined	Calories
	per	Gram	Mole.	For	mula <sup>-</sup> i	Neight:	: 172	.1	3.		

per cent high at the lowest temperature and at the highest a deviation of 0.5 per cent low was expected. There has been no satisfactory explanation of this behavior.

For representation of heat content data above the base temperature, 298.16°K, Kelley (25) has adopted an algebraic equation,

$$^{H}T = ^{H}298.16 = aT + bT^{2} + cT^{-1} + d,$$
 (6)

which was recommended by Maier and Kelley (26). In this equation,  $H_T = H_{298.16}$  is the heat content in calories per mole above 298.16°K; a, b, c, and d are constants to be determined from experimental data; and T is the temperature in degrees Kelvin. This equation was adopted because it gives adequate fit without introducing too much complexity.

The heat contents measured in this investigation used the base temperature of 30.0°C, or 303.2°K, therefore, this equation became

$$H_{\rm T} - H_{303.2} = aT + bT^2 + cT^{-1} + d.$$
 (7)

Constants for such an equation were first calculated using the method of selected points, in which the heat contents from Runs Ce2, Ce5, and Ce8, and the heat content at  $303.2^{\circ}$ K ( $\Delta$  H = 0) were used. The resulting equation is

$$CeO_2$$
 (s):  $H_T = H_{303.2} = 17.90 T + 0.0002464 T^2 + 246,000/T$   
= 6.260 (8)

When the heat content is evaluated from this equation and compared with the experimentally determined values, there is a maximum deviation of  $\pm 0.53$  per cent. These deviations are in the lower range of the measurements (382.2°K and 559.5°K); above 700.8°K to 1172.6°K the average deviation is only 0.10 per cent.

When this equation is differentiated and the heat capacity evaluated at 303.2°K a value of 15.37 cal. per mole deg. is obtained which does not agree with 14.838 obtained from a short extrapolation of the unpublished data of Westrum and Terwilliger<sup>1</sup> (27). (Westrum and Terwilliger used a precision adiabatic calorimeter for their measurements) Since the heat contents obtained in the present investigation were expected to be least accurate in the lowest temperature range, it was felt that the thermodynamic properties could best be represented by an equation which would give a heat capacity of 14.84 calories per mole per degree centigrade at 303.2°K and which would fit the heat content data at higher temperatures. The equation which best fits these criteria was calculated by substituting the following conditions into the equation:

$$H_{303,2} - H_{303,2} = 0$$
 (9)

<sup>1</sup>E. F. Westrum and D. H. Terwilliger, Private Communication to Dr. W. T. Ziegler (June 17, 1957) give the following data, where  $\overline{T}$  is in degrees Kelvin and  $C_{D}$  is in defined thermochemical calories per mole per degree Kelvin (ice point 273.16°K):

at T = 256.58	$C_{-} = 13.772$
265 .54	P 14.003
274.58	14.226
283.63	14.423
292.64	14.628
301.69	14.796

The writer wishes to express his appreciation to Drs. mestrum and Terwilliger for making these data available prior to publication.
$$c_{p_{303,2}} = 14.84$$
 (10)

$$H_{1100.0} - H_{303.2} = 13966$$
 (11)

$$c_{p_{1100.0}} = 18.24$$
 (12)

The last two conditions were derived from Equation (8). The heat content as calculated at 1100.0°K was raised slightly to obtain a better fit of the data, and the heat capacity was used as calculated.

The resulting equation is

$$CeO_{2} (s): H_{T} - H_{303.2} = 18.64 T - 0.0000512 T^{2} + 346,600/T$$

$$- 6789.7 (303.2 - 1172.6^{\circ}K)$$
(13)

which fits the experimental data to within 1.59 per cent maximum deviation with an average deviation of 0.56 per cent. The deviations are such as would have been expected from the  $\simeq -Al_2O_3$  heat content comparisons. The experimental results are compared with the results from this equation in Table 2.

The molal heat capacity, obtained by differentiation of Equation (13), is represented by

$$CeO_2$$
 (s):  $C_p = 18.64 - 0.000102 T - 346,600/T^2$  (14)

The entropy above 303.2°K, obtained from Equation (14), is

$$CeO_2$$
 (s):  $S_T - S_{303.2} = 42.93 \log T - 0.000102 T + (15) 173.300/ $T^2 - 108.h$$ 

The heat content as determined by this investigation is plotted in Figure 2.

The experimental heat capacity derived from Equation (lh) has been compared with those of Nilson and Pettersson (5), who gave the mean heat capacity for the range 0° to 100°C to be 15.04 calories per mole per °C. In the present investigation, the heat capacity at 50°C was found to be 15.29, which is 1.7 per cent higher than that of Nilson and Pettersson.

Russell (7) has reported the mean heat capacity for the range 48.3 to 3.5°C to be 15.79 calories per mole- °C. In the present investigation, the heat capacity at 30°C was found to be 14.84, which is 6.0 per cent lower.

Comparison of the mean heat capacities reported by Brons (8) revealed that the present investigation was about 3.5 per cent higher at 500°K with the difference decreasing to zero at 1050°K. These results are presented graphically in Figure 10 of Appendix E. The discrepancies between these two investigations have not been accounted for.



Figure 2. The Heat Content of CeO<sub>2</sub>, H<sub>T</sub> - H<sub>303.2</sub>, vs. Temperature, T<sup>\*</sup>K.

APPENDIX A

OPERATING CHARACTERISTICS OF FURNACE

### OPERATING CHARACTERISTICS OF THE FURMACE

Blomeke (13) gives a detailed discussion of the operating characteristics of the furnace. His Figure 2, which gives the relationship between the temperature of the sample and the temperature of the furnace as a function of the temperature indicated by the thermocouple, when this reference junction is 7-1/2 in. below the top of the furnace and the capsule is in place 1 mm. below it, is reproduced in Figure 3 to illustrate the corrections necessary to the determination of the temperature of the sample. This relationship was established by Blomeke to allow for the capsule and the thermocouple not being located in the isothermal zone of the furnace at all of the temperatures used in the heat content determinations. This relationship was determined by comparison of the temperature indicated by the reference junction with the temperature indicated by a thermocouple identical with the reference thermocouple and located inside the capsule, when they were in the position employed in the heat content determinations.



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APPENDIX B

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THE K-CURVE AND A SAMPLE CALCULATION OF K

### A SAMPLE CALCULATION OF K AND THE K-CURVE

Determination 9 (see Table 5) was chosen to demonstrate the calculation of a point on the K-curve. The procedure outlined in Chapter III<sup>1</sup> for the determination of a point on this curve was followed and the data obtained is given in Table 5.

K was defined in Chapter III to be

$$K = (R_2 - R_1) / \hat{\phi} (t_2 - t_1)$$
 (5)

where

$$\vec{\phi} = R_{j} - 1/2(R_{1} + R_{2})$$
 (4)

The resistance of the thermometer at any time is the average of the readings obtained with the commutator of the Mueller Bridge in the N position and the R position. Simultaneous reading of the two is not possible, hence interpolation is necessary. The present readings were observed to vary linearly with time, therefore, the N readings were interpolated linearly to obtain the readings at a common time with the R readings. The resistance of the thermometer was then the average of these two readings. The resulting resistance of the thermometer, given in Table 4, was plotted in Figure 4 and the smoothed values

$$R_1 = 108.1564 \pm 0.0002$$
 ohms, at  $t_1 = 1.42200$ , and  
 $R_2 = 108.1066 \pm 0.0002$  ohms, at  $t_2 = 1.52200$ 

<sup>1</sup>Supra, p. 16.

of Kueller Bridge in:	
Time t N Position R .	Position
1:41:00 108.2106	
1:42:00 10	8.1066
1:43:00 108.2008	8 0070
1:544:00 108.1931	0.0910
1:45:00	8.0869
1:47:00 108.1814	
1:48:00 10	8.0766
1:49:00 108.1713	0 0//п
1:50:00 10: 1:50:00 10:	σ•000γ
1:52:00 100,1014	8.0566
1:53:00 108.1516	
1:51:00	8.0466

Table 3. Data for Determination 9 of  $\boldsymbol{K}$ 

Time t	R. of Block RTh, Abs. Ohns	
1:12:00	108.1552	
1:46:00	108.1366	
1:48:00 1:50:00	108.1255 108.1156	
1:52:00	108.1056	

Table 4. Resistance of Block Thermometer for Determination 9 of K



Figure b. Resistance of Block Thermometer vs. Time for Determination 9 of K.

was gotten. The resistance,  $R_j$ , of the block thermometer corresponding to the jacket temperature (presumed to be the same as the bath temperature, which may vary as much as  $\pm 0.02^{\circ}$ C or  $\pm 0.0080$  ohms), was 105.9082  $\pm$ 0.0080 ohms. Therefore, with a bridge correction of -0.0018 ohms to add to  $R_1$  and  $R_2$ 

Hence

$$K = (R_2 - R_1) / \overline{\phi} (t_2 - t_1)$$
 (5)

$$= \frac{0.0498 \pm 0.0004}{(-2.2215 \pm 0.0082) (10)} = 0.002240 \pm 0.000023 \text{ min.}^{-1}$$

A series of points on the curve were determined using different thermal heads to cover the range 0 abs. ohms  $\langle \vec{\phi} \leq 1$  abs. ohms. The curve in Figure 5 was taken from Blomeke (19), and the points in the figure are from Table 5 as determined in this investigation. Comparison of the data from this investigation showed deviations within the accuracy of the measurements. These deviations are given in Table 5.

Determination	Thermal Head, -Ø Abs. Ohms	Kx10 <sup>3</sup> Obs. min. <sup>-1</sup>	Kxl0 <sup>3</sup> Blonekel min1	Per cent Deviation
1	0.210	1.440	1.422	1.2
2	0.690	J.•770	1,767	0.2
3	1,022	1.875	1.398	1.2
Ī,	1,163	1,929	1.735	1.3
5	1.385	2.016	2.031	0.7
6	1.600	2.088	2.098	0,5
7	1.981	2.183	2.194	0.5
8	2.140	2.230	2.233	0.1
9 <sup>*</sup>	2.222	2.240	2.249	0.4
10	2.395	2.288	2.286	0.1
11	2.195	2.330	2.310	0.9
12	2.585	2.341	2.326	0.6
13	2.945	2.406	2.398	0.3
īĹ	3.016	2.115	2.109	0.2
15	3.011	2.441	2.420	0.9
16	3.295	2.435	2.461	1.1
17	3.355	2.467	2.474	0.3
18	3.415	2.486	2.494	0.3
19	3.599	2.499	2.517	0.7
20	3.975	2.580	2.585	0.2

Table 5. Summary of K-Curve Data

1<sub>Blomeke</sub> (19).

\*Used in Sample Calculation.



Figure 5. Relationship between K and Thermal Head

APPENDIX C

CALCULATION OF A HEAT CONTENT DETERMINATION

#### CALCULATION OF A HEAT CONTENT DETERMINATION

In order to demonstrate the calculations involved in the determination of the heat content, the Run Cell of the determination of the heat content of  $CeO_2$  at  $\pm 27.6^{\circ}C$  will be considered in detail.

The Corrected Weight of Sample and Capsule .---

Wt. capsule and CeO <sub>2</sub> Mt. empty capsule	= $23.0358$ g. = $12.1027$ g.
Wt. CeO2	= 10.9331 g.
Wt. Au wire before sealing Wt. Au wire after sealing	= 2.6415 g. = 2.4994 g.
Wt. Au seal	= 0.1421 g.
Wt. empty capsule Wt. Au seal	= $12.1027$ g. = 0.1 $h21$ g.
Wt. empty capsule and Au seal	= 12.2448 g.
Buoyancy corrections were applie	ed using the following constants:
Density of CeO2	= $7.3 \text{ g./ml.}^1$
Density of Pt	= 21.5 g./ml. <sup>2</sup>
Density of brass weights	$= 8.4 \text{ g./ml.}^3$

1<sub>N. A.</sub> Lange, <u>Handbook of Chemistry</u>, Handbook Publishers, Inc., (1956), p. 237.

= 0.0012 g./ml.4

<sup>2</sup><u>Ibid</u>., p. 287. <sup>3</sup><u>Ibid</u>., p. 1848. <sup>4</sup><u>Ibid</u>., p. 1411.

Density of air

.

For CeO,,

Wt. air displaced by  $CeO_2 = \frac{(10.9)(0.0012)}{(7.3)} = 0.0018$  g. Wt. air displaced by weights  $= \frac{(10.9)(0.0012)}{(8.4)} = 0.0016$  g. Net buoyancy effect = 0.0018 - 0.0016 = 0.0002 g. Corrected weight of  $CeO_2 = 10.9331 + 0.0002 = 10.9333$  g.

For the capsule,

Wt. air displaced by capsule =  $\frac{(12.2)(0.0012)}{(21.5)} = 0.0007$  g. Wt. air displaced by weights =  $\frac{(12.2)(0.0012)}{(8.4)} = 0.0017$  g. Net buoyancy effect = 0.0007 - 0.0017 = -0.0010 g. Corrected weight of capsule = 12.2448 - 0.0010 = 12.2438 g.

True Thermometer Rise,  $(\Delta R)_s$ .--The true thermometer rise,  $(\Delta R)_s$ , or the rise in resistance of the block resistance thermometer corresponding to the total measured quantity of heat transferred in a heat content determination, is equal to the sum of the observed thermometer rise,  $(\Delta R)_o$  and the calculated rise in resistance,  $(\Delta R)_{bl}$ , due to the loss of heat from the block through convection, conduction, and radiation.

Table 6 gives the block resistance thermometer readings for Run Cell as a function of the time. The observed resistance of the block thermometer at the end of the fore period,  $R_1$ , was obtained from Figure 6 for  $t_1 = 4:01:00$ , and was found to be 105.96278 abs. ohms. From the reaction period curve of Figure 8, it was estimated that constant cooling began at  $t_2 = 4:30:00$ , and the resistance,  $R_2$ , of the block resistance

	Observed Resistance, in Abs. Ohms, with Co	R', of Block Thermometer mutator of Bridge in:	
Time, t	N Position	R Position	
	Fore Period		
3:50:00		105,91675	
3:51:00	106.01000		
3:55:00		105.91650	
3:56:00	106.00965		
3:59:00		105,91630	
4:00:00	106.00940		
4:01:00	Capsule Dropped - Re	action Period Begins	
L:02:00	106.0500		
Li:03:00	-	106.0200	
4:04:00	106,1540		
4:05:00		106.0860	
4:06:00	106.1950		
L:07:00		106.1117	
4:08:00	106.2109		
4:09:00		106,1218	
4:10:00	106.2170		
4:11:00		106.12520	
4:12:00	106.21965		
4:13:00		106.12660	
4:14:00	106.22000		
4:15:00		106.12660	
4:16:00	106.21985		
4:17:00		106.12625	
4:18:00	106.21950		
4:19:00		106.12575	
4:20:00	106.21880	4 4	
4:21:00		106.12510	
4:22:00	106.21805		
4:23:00		106,12420	
4:24:00	106.21750	206 2026	
4:25:00	106 01690	100.12305	
4:20:00	100.21000	106 10200	
4-21-00	106 21500	100.15200	
4+20+00	100.21370	104 10060	
4+22+00	106 21500	100 • 15 500	
4.30.00	100.51300		

## Table 6. Block Resistance Thermometer Measurements for Run Cela



Figure 6. Resistance of Block Thermometer for Fore Period of Heat Content, Run Celu



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Figure 7. Resistance of Block Thermometer for After Period of Heat Content, Run Celu.

Time, t	R, Abs. Ohms = R' - 0.0018	$-\phi$ , Abs. Ohms = R - R <sub>j</sub>	K x 10 <sup>3</sup> min. <sup>-1</sup>	$-K\phi \times 10^3$ Ohms/min.
4:01:00	105.9628	0.0648	1.140	0.0739
4:04:00	106.1080	0,2100	1.385	0 <b>.29</b> 09
4:06:00	106.1460	0.2480	1.430	0.3546
4:08:00	106.1625	0.2645	1.445	0,3822
4:10:00	106.1689	0.2709	1.453	0.3936
4:12:00	106.1711	0.2731	1.456	0.3976
կ։1կ։00	106.1715	0.2735	1.457	0.3985
4:16:00	106.1714	0.2734	1.457	0.3983
h:18:00	106.1710	0.2730	1.456	0.3975
4 <b>:20:</b> 00	106.1703	0.2723	1.455	0.3962
4:22:00	106.1697	0.2717	1.454	0.3951
4:24:00	106.1691	0.2711	1.453	0.3939
4:26:00	106.1683	0+2703	1.452	0.3925
4:28:00	106.1675	0,2695	1.451	0.3910
4:30:00	106.1668	0.2688	1.450	0.3898

Table 7. Summary of Run Celi



thermometer read from Figure 7 at this time was 106.16846 abs. ohms. The dial corrections for the Mueller Bridge were - 0.00176 abs. ohms and - 0.00177 abs. ohms, respectively; therefore,

$$R_2 = R_2' - 0.00177 = 106.16669 \text{ abs. ohns}$$
  
 $R_1 = R_1' - 0.00176 = 105.96102 \text{ abs. ohns}$ 

The observed thermometer rise, ( $\Delta R$ )<sub>o</sub> = 0.20567 abs. ohms

Table 7 was constructed from the reaction period data using a constant dial correction of - 0.0018 abs. ohms and  $R_j = 105.8980$  abs. ohms, which corresponded to a bath temperature of 30.03°C. Values of K were read from Figure 5. The temperature rise correction,  $(\Delta R)_{cl}$ , was calculated using the equation

$$dR = K \phi dt$$
(16)

where

R = resistance of block thermometer at time t,

K = thermal leakage modulus, and

 $\oint = \text{thermal head} = R - R_{+}$ .

The right side of this equation was integrated graphically by measuring the area under the curve of Figure 8 between the time limits  $t_1 = 4:01:00$ and  $t_2 = 4:30:00$ . This area corresponded to a correction of 0.01051 abs. ohms. The true thermometer rise was, therefore,

 $(\Delta R)_{s=} (\Delta R)_{o} + (\Delta R)_{c1} = 0.20567 + 0.01051 = 0.21618$  abs. ohms.

The Corrected True Thermometer Resistance Rise. -- The true thermometer rise was corrected for the difference between the temperature of the block at

the end of the reaction period and  $30^{\circ}$ C by applying two corrections. The first of these corrects for the capsule and the other for the CeO<sub>2</sub>.

The thermometer resistance rise for the empty capsule heat content determination from 110.5°C to 30.0°C was reported by Blomeke (28) to be 0.01177 abs. ohms, when the weight of the capsule was 11.8996 grams. (See Table 8) The weight of the capsule when used in the  $CeO_2$  measurements was 12.2438 grams, the increase in weight being due to the accumulation of gold used for sealing the cap in place. Calculations have shown that there is negligible error introduced when the heat capacity of gold is assumed to be the same as for the Pt-10 per cent Rh of the capsule provided a correction for the gain of weight is applied. The true resistance rise due to the capsule in the  $CeO_2$  heat content determination was

$$(\Delta R)_{e'} = \frac{(\Delta R)_{c}(wt. capsule)}{11.8996} . \qquad (17)$$

At 110.5°C, therefore,

$$(\Delta R)_{e^{1}} = \frac{(0.01177)(12.2438)}{11.8996} = 0.01213 \text{ abs}. \text{ ohms.}$$

The mean heat capacity of the empty capsule between 110.5°C and 30.0°C was assumed to be represented by

$$\overline{C}_{p} = \frac{0.01213}{110.5 - 30.0} = 0.000146$$
 abs. ohms per degree.

The sensitivity of the block resistance thermometer was reported by Blomeke (18) to be 0.4026 abs. ohms per degree. The capsule correction factor was

Temp., *C	True Rise, (AR) <sub>t</sub> , Ohms	
110.5	0.01177	<u> </u>
200.7	0.02516	
300.9	0.04056	
426.7	0.05992	
579.0	0.08368	
723.8	0.10663	
829.4	0.12311	
898.7	0.13464	
l <sub>Blomeke</sub> , (28).		

# Table 8. Heat Content for Empty Capsule<sup>1</sup>. Weight Capsule: 11.8996 g.

$$\frac{0.000146}{0.403} = 0.000362 \frac{\text{abs. ohms}}{\text{ohms rise of RTh above } 30.0^{\circ}\text{C}}$$

A correction was made for the same reason to account for the final temperature of the sample not being at  $30.0^{\circ}$ C. The resistance rise of the CeO<sub>2</sub> drop made from 109.0°C was found to be 0.00062 abs. ohms. When it was corrected with the capsule correction factor, it became 0.00064abs. ohms. The resistance rise due to the capsule was calculated assuming that the heat capacity of the capsule at  $110.0^{\circ}$ C was the same as the mean heat capacity of the capsule between  $110.5^{\circ}$ C and  $30.0^{\circ}$ C. The resistance rise due to the capsule then becomes

$$(\Delta R)_{e} = (\Delta R)_{e'} \frac{109.0 - 30.0}{110.5 - 30.0}$$
 (18)

therefore,

$$(\Delta R)_{e} = (0.01213) \frac{109.0 - 30.0}{110.5 - 30.0} = 0.01190$$
 abs. ohms.

The portion of the total rise due to the  $CeO_2$  is 0.04064 - 0.01190 = 0.02874 abs. ohms.

The mean heat capacity of the sample between 109.0°C and 30.0°C was represented by

$$\overline{C}_{p} = \frac{0.02874}{109.0 - 30.0} = 0.000364$$
 abs. ohms per degree.

Accordingly, the sample correction factor was

When this factor was used to correct the resistance rise, a new rise due to the CeO<sub>2</sub> of 0.02878 abs. ohms was obtained. The mean heat capacity was unchanged when this value was used in recalculating the sample correction factor.

To correct the true thermometer rise of  $CeO_2$  at  $427.6^{\circ}C$ , the two above factors were employed. The value of  $R_2$  for Run Ce4 was 106.16669 which corresponded to a rise in the resistance thermometer above 30.0°C of 106.16669 - 105.8864 = 0.28029 abs. ohms. Therefore,

True thermometer rise,  $(\Delta R)_s$  = 0.21618 abs. ohms Capsule correction = (0.28029)(0.000362) = 0.00010 Sample correction = (0.28029)(0.000903) = <u>0.00025</u> Corrected true rise of sample plus capsule,

 $(\Delta R)_{+}$  = 0.21653 abs. ohms

Since the furnace temperature was  $h27.6^{\circ}$ C and the nearest temperature of the empty capsule heat content determination reported by Blomeke (28) and given in Table 8, was  $h26.7^{\circ}$ C, the resistance rise due to the empty capsule was corrected to this drop temperature. This was done by first correcting the resistance rise due to the capsule with the weight correction as applied to find the capsule correction factor. The heat capacity was calculated to be  $1.59 \times 10^{-h}$  abs. ohms per degree for the temperature range  $h26.7^{\circ}$ C to  $h27.6^{\circ}$ C. The resistance rise due to the capsule was then,

True rise at  $426.7^{\circ}$ C,  $(\Delta R)_{e}^{i} = 0.06166$  abs. ohms Corr'n to  $427.6^{\circ}$ C,  $(427.6 - 426.7)(1.59 \times 10^{-4}) = 0.00014$  True rise at 427.6°C,  $(\Delta R)_e$  = 0.06180 abs. ohns The net rise due to the CeO<sub>2</sub>,  $(\Delta R)_n$ , was

 $(\Delta R)_n = (\Delta R)_t - (\Delta R)_e = 0.21653 - 0.06180 = 0.15473$  abs. ohms (19)

Using the following data,

Block calibration factor <sup>1</sup>	= 2783.6 def. cal. per abs. ohm
Wt. CeO <sub>2</sub> ( <u>in vacuo</u> )	= 10.9333 g.
Mol. wt. Ce02 <sup>2</sup>	= 1"2.13 g. per g. mol.

the heat content of  $CeO_2$  between  $427.6^{\circ}C$  and  $30.0^{\circ}C$  was

$$(A H)_{30.0}^{427.6} = \frac{(2783.6)(172.13)(0.15473)}{10.9333} = 6780.6 \text{ def. cal. per g. mol.}$$

<sup>1</sup>Blomeke, (29). 1 det. calorie = 4.1840 abs. j. = 4.1833 int. j. <sup>2</sup>N. A. Lange, op. <u>cit</u>., p. 236. APPENDIX D

THE HEAT CONTENT OF  $\propto -\text{Al}_2\text{O}_3$ 

THE HEAT CONTENT OF  $\propto -Al_2O_3$ 

A summary of the heat content determinations run on an  $\propto -Al_2O_3$ (corundum) sample is given in Table 9. This is the same sample and capsule that was used by Blomeke (11), who obtained it from the National Bureau of Standards.<sup>1</sup> These heat content determinations covered the range 219.5°C to 875.0°C, which is roughly the range for the CeO<sub>2</sub> determinations. Table 10 contains the heat content calculated from these measurements for the  $\propto -Al_2O_3$  sample above 30.0°C.

These heat content data are presented graphically for comparison with data from other investigations in Figure 9.

<sup>1</sup>Cf. <u>Supra</u>, p. 6.

Run No.	Temp., t°C.	Obs'd Rise, $(\Delta R)_{o}$ , Ohms	Block Loss, $(\Delta R)$ , Ohms	Block Temp. Corr'n Ohms	True Rise, $(\Delta R)_t$ , Ohms
	219.5	0.23110	0.00778	0.00069	0.23957
C2	422.9	0.50517	0.02427	0.00110	0.53054
C3	718.5	0.92948	0.05695	0.00239	0.98882
CL	417.0	0.49745	0.02390	0.00126	0.52261
C5	875.0	1.15705	0.08446	0.00297	1.24448
C6	L17.2	0.49805	0.02422	0.00129	0.52356

Table 9.	Summary of	Heat Content Determinations	for
	~ -A1203.	Weight Sample: 13.821 g. <sup>1</sup>	

<sup>1</sup>This is the same sample and capsule that Blomeke used in his investigation.

Temperature		True Rise,	Rise of Cap.	Rise of Sample,	(Дн) <sup>т</sup> 303.2
t°C	T°K	$(\Delta R)$ t'	(AR) Ohms	$(\Delta R)_n$ , Ohms	cal./mol.
219.5	492.7	0.23957	0.02689	0.21268	4366.6
417.0	690.2	0,52261	0.05610	0.46651	9578.0
417.2	690.4	0.52356	0.05613	0.46743	9596.8
422.9	696.1	0.53054	0.05698	0.47356	9722.7
718.5	991.7	0.98882	0.10159	0.88723	18216
875.0	11)48.2	1.24448	0.12554	1.11894	22973

Table 10. Heat Content of < -Al\_0<sub>3</sub> above 303.2°K. Formula Weight: 101.94



Figure 9. The Heat Content of  $\alpha$ -Al<sub>2</sub>0<sub>3</sub> between 303.2° and T<sup>\*</sup>K vs. T<sup>\*</sup>K.

Temp	Heat Content, H <sub>T</sub> - H <sub>303.2</sub>	Mean Heat Capacity, $\overline{C}_{p}$ ,
T•K.	cal./mol.	cal./mol./*K
303.2	0	
350	955	20.4
100	2073	21.4
L50	3268	22.26
500	4521	22.97
550	5832	23.63
600	7161	24.13
650	8534	24.61
700	9933	25.04
800	12798	25.76
900	15132	26.36
1000	18718	27.01
1100	21746	27.29
1180	24192	27.59

Table 11. The Heat Content and Mean Heat Capacity of  $\propto -A1_20_3$ between 303.2° and T°K from Data of Ginnings and Furukawa (22).

### APPENDIX E

THE HEAT CONTENT OF CeO 2

## THE HEAT CONTENT OF CeO2

A summary of the heat content determinations run on  $CeO_2$  is given in Table 12.

Table 13 contains the mean specific heat of  $GeO_2$  between T°K and 293.2°K calculated from Equation (13) in order to compare the results of the present investigation with that of Brons (8), who reported the mean specific heat of  $GeO_2$  above this base temperature for the temperature range 220 to 800°C and is given in Table 14. These results are compared graphically in Figure 10.

Table 12. Summary of Heat Content Determinations for CeO<sub>2</sub>. Weight Sample: 10.9333 g. Formula Wt.: 172.13<sup>2</sup>

03.2 01.	5000	
(∆H) 3 cal./m	1253. 2971. 2971. 1292. 6780. 9689. 12096 13647 15326	
Rise of Sample, (AR)n, Ohums	0.02878 0.06780 0.09795 0.15473 0.15473 0.22109 0.21140 0.31972 0.31972	
Rise of Cap. (∆R) Ohums e,	0.01190 0.02791 0.03971 0.06180 0.08776 0.10849 0.10849 0.10849 0.12292 0.13810	
True Rise (∆R) <sub>t</sub> ,	0.04068 0.09571 0.13766 0.38181 0.43132 0.43132 0.43782 0.48782	
Block Temp. Corr'n, Ohms	0.000017 0.00017 0.00017 0.00017 0.00017 0.00018 0.00018 0.00050 0.00051 0.00051	
Block Loss, (∆ <sup>R</sup> ) <sub>b1</sub> ,	0.00072 0.00282 0.00504 0.011051 0.01103 0.01139 0.01139 0.01581 0.01819	
Obs'd Rise (∆R) <sub>o</sub> , Ohms	0.03990 0.09275 0.13245 0.13245 0.13245 0.13245 0.29700 0.37345 0.37345 0.11800 0.37345 0.146905 0.466905	
rature, T'K	382.2 1481.2 559.5 700.8 865.0 991.0 998.3 1172.6 1172.6 1172.6 1172.6 1172.6	
Tempe t•C	109.0 211.0 211.0 2286.3 127.6 717.8 717.9 717.9 717.9 717.9 717.8 717.9	
Date	* 6/201 6/21 6/21 6/22 8/2 8/	
Run No.		
Temp., T°K.	$(\Delta H)_{293.2}^{T}$ def. cal./g. mol.	Mean Specific Heat, Cp def. cal./g/°C.
----------------	---	--
100	1674.1	0.0909
500	3360.2	0.0943
600	5102.9	0,0966
700	6877.6	0.0982
800	8671.9	0.0994
900	10479	0.1003
1000	12295	0.1010
1100	14122	0.1017
1200	15954	0,1022

Table 13.	The Heat Content and Mean Specific Heat of CeO, b	etween
	T°K and 293.2°K from Equation (13)	

Run No.	Temp., t°C.	Final Temp., t'°C.	Heat Content between t and 20°C, cal./g.	Mean Specific Heat between t and t <sup>1</sup> , $\overline{C}_{p}$ , cal./g/°C.
 hh	219.99	21.16	18.116	0.0907
113	220.02	21.03	18.197	0.0910
ñ	220.03	21.05	18.134	0.0907
34	220.20	20.76	18.153	0.0907
<u>16</u>	220.34	21.10	18.212	0.0909
35	230.09	20.73	19.161	0.0912
31	235.38	20,96	19.654	0.0913
16 16	239.58	20,90	20.088	0.0915
24	240.02	20.82	20,163	0.0916
15	240.30	20.86	20,190	0.0916
29	240.44	20.70	20.032	0.0909
28	249.93	20,90	20.992	0.0913
36	250.09	20.66	20.954	0.0911
Ž3	250.30	21,19	20,943	0.0909
37	253.37	20.72	21.340	0.0914
26	259.80	20.97	21,929	0.0914
20	260.00	20.94	22,178	0.0924
22	260.00	20.81	22.102	0.0921
17	260.09	21.10	22.141	0.0922
21	260.10	21.13	22,128	0.0922
19	260.15	21.24	22,112	0.0921
27	260.25	20.68	21.990	0.0915
33	269.89	21.08	22.891	0.0916
38	270.40	20.79	23.117	0.0923
15	280,04	20.22	23.963	0.0921
30	280.08	20.76	24.141	0.0928
39	289.84	21.06	25.051	0.0928
10	290.40	21.19	24.882	0.0920
32	300.32	20.81	25.995	0.0927
<u>4</u> 0	319.93	20.93	28.115	0.0937
12	320.17	21.35	28.113	0.0937
13	339.55	21.32	30.123	0.0943
41	350.13	21.26	31.243	0.0946
14	359.80	21.01	32.221	0.0948
18	379.79	21.07	34.121	0.0948
42	380.41	21.11	34.338	0.0955
9	389.16	21,96	35.340	0.0957
8	419 <b>.9</b> 0	21.70	38.455	0.0962

Table 14. The Mean Specific Heat of CeO<sub>2</sub> between 220° and 800°C from A. J. Brons, <sup>2</sup>(8).

(continued)

а.,

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Run No.	Temp., t°C.	Final Temp., t'°C.	Heat Content between t and 20°C, cal./g.	Mean Specific Heat between t and t', $\overline{C}$ , cal./g/°C.
6	470.21	21.61	43.663	0.0970
5	520.14	21.98	48.937	0.0978
<u>L</u>	570.00	21.46	54.211	0.0986
7	620.11	22.27	59.459	0.0991
3	670.05	22.02	64.715	0.0996
i	720.33	22.48	70.357	0.1005
2	769.96	22.17	75.930	0.1012
25	800,12	21.56	79.608	0.1020

## Table 14. The Mean Specific Heat of CeO<sub>2</sub> between 220° and 800°C from A. J. Brons, <sup>2</sup>(8). (continued)



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