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ABSTRACT

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Following earlier work, a high temperature differential thermal calorimeter was constructed, with a design based on heat transfer considerations. Heat content and heat capacity measurements by the instrument showed excellent agreement with accepted literature values, (±2%), in the case of quartz and alumina. Reasonable agreement was also obtained for the α-β quartz inversion enthalpy.

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I. INTRODUCTION

In the rapidly advancing field of ceramics, the need for fundamental knowledge of the basic properties of newly developed materials and of old long-established ones is imperative. The most important thermal properties to be considered in this connection are (a) heat contents and heat capacities, (b) heats of crystallographic transformation, and (c) heats of reaction.

The heat content of a substance is defined as

\[ H_T = H_{298} + \int_{298}^{T} C_P \, dT \]

Where \( H_T \) = Heat content at \( T \)°K
\( H_{298} \) = Heat content at 298°K
\( C_P \) = Heat capacity cals/mole/°K

Ceramic raw materials are difficult to analyze for thermodynamic properties, as powders place severe limitations on the use of orthodox calorimeters.

The ideal calorimeter for the accumulation of thermodynamic data for ceramics should:

(a) be operational up to high temperatures

(b) be capable of following continuously the slow evolution or adsorption of heat involved in both physical and chemical ceramic reactions, and

(c) be able to compile accurate data in a short time.

The basic principle of a differential thermal calorimeter is to supply or abstract heat to or from a reacting system so as to maintain
the temperature at some point in the system, the same as that of a similar point in a physically identical inert system. A small heater is used to supply the necessary heat and the power supplied to this heater is monitored. The technique is not new and was first used by Eyraud in 1954 and the following year by Charuel and Traynard and Clareborough, Hargrieves and West. Charuel and Traynard studied a solution reaction by supplying heat to an inert solution and thus keeping its temperature the same as that of an identical reacting solution. Clareborough, Hargrieves and West took two identical pieces of metal and cold worked one of them. They then heated both samples and estimated the release of energy accompanying the annealing of the worked sample. This they did by supplying a measured amount of heat to the inert sample to keep both sample temperatures identical. The heat of formation of solid alloys was estimated by Orani and Murphy utilizing the same principle. Kleppa investigated the heat of mixing in liquid sodium-potassium nitrates in a similar way.

The first attempt to apply the method to the thermodynamic investigation of ceramic systems was made by Barner. Barner's results contained large errors (±30%) when compared with accepted literature values.

**Description of Barner's Apparatus**

Barner used two identical cylindrical metal cells, each with a small cylindrical heater down its center. The apparatus used by Barner is shown diagrammatically in Figure 1.

The D.T.C. cells were hung on a platinum wire. By locating this wire in furnace top-and-bottom plugs, the cells were maintained in the center of the furnace. To eliminate environmental temperature gradients
in the furnace, a heavy nickel tube was placed inside it and this constituted the radiating area seen by the cells. This tube was grounded outside the furnace eliminating any induction effects due to the heating coil. To preclude axial heat losses from the furnace, the nickel tube was not carried to the ends of the furnace proper. The cells were spaced apart by porcelain insulation beads. Two nickel sheet baffles were placed half way down the bead-row, lying exactly between the cells and in the center of the furnace. These served to eliminate any convection currents between the cells and between their immediate environments.

The cell heaters were wound on boron nitride formers and platinum foil was used for the attachment of the thermocouples to the cell outer walls. The cell temperature was monitored on the outside wall by a standard Pt/Pt 10% Rh thermocouple with the bead recessed into the porcelain shieldings. This precaution was necessary to avoid electrical contact between the monitor and differential thermocouples. The sample and the inert substance were packed in their respective cells between the heater wall and the outer cell wall. End-caps were used to complete the containers. The two beads of a differential thermocouple were located at identical positions on the outer wall of each cell and the differential temperature of these two positions maintained at zero by supplying or abstracting power to (or from) the inert cell heater as required. The necessary power to maintain this equilibrium was plotted on a time base and a direct measure of any heat effects in the sample thus obtained.

Barner found that the sensitivity of the system was markedly increased if the control cell were left empty. In this case an incremental increase in the environmental furnace temperature will necessitate a
decrease in the power supplied to the control cell owing to the heat capacity of the sample. Such an incremental furnace temperature increase is shown diagrammatically in Fig. 2 together with the accompanying power-time curve. Also shown is the peak associated with an endothermic reaction in the sample. This peak will be superimposed on the heat capacity peak.

Considering the mechanism by which Barner's differential thermal calorimeter system gave results, a number of points can be drawn up essential for its functioning correctly:

(a) Each cell must be identical and be subject to identical environmental conditions.

(b) All the heat supplied to the sample must come from the cell heater, i.e. heat must always flow out of the cell.

(c) The response of the inert cell must be as rapid as possible so as to maintain adequate control of the system.

(d) The gradient across the sample must be as small and as constant as possible.

(e) All heat must flow radially from the cell, i.e., through the powder.

(f) The cells must be completely thermally isolated from each other.

Taking each point in turn, the symmetry of the system, consistent with constructional considerations, can be assured by proper design. With regard to point (b), it might be assumed that if the cell center is hotter than the cell wall, heat must be flowing from the cell at all times. However, there are circumstances when this is not true. The specimen powder is subject to two sources of heat, the cell heater and the main
furnace. It is essential for the differential operation that all heat from the cell heater flow outward through the sample to the differential thermocouple. Consider four hypothetical temperatures, $T_1$ to $T_4$, across a section of the furnace corresponding to the center of the filled cell (Fig. 3). For all the heat from the cell heater to flow outward through the sample,

$$T_1 > T_2 > T_3 > T_4$$

It might be assumed that for these conditions it is enough that $T_1 > T_3$. This is a fallacy. If $T_3 < T_4$ then even though $T_1 > T_3$, a gradient can develop such as $T_2 < T_3$ (see (b) in Fig. 3). Hence the temperature minimum will be within the sample instead of being at the cell wall or beyond. Such a situation would lead to erroneous results as heat to the sample is being supplied by both the internal and external source.

The response of the inert or active cell to any change in a sample cell must be immediate. The sensitivity of the response, therefore, depends entirely on the thermal conductivity of the inert species in the cell. This conductivity should be as high as possible and thus an empty cell is used.

The fourth point is concerned with an error due to the sample radius. The actual temperature of the sample is measured at the outside cell wall and this temperature, therefore, will be a little below the average sample temperature. However, as long as the gradient across the cell is small, this error is not too large. The larger this gradient, the larger the error and to minimize this, the powder thermal conductivity should be as large as possible.
Considering point (e), all the power applied to the heater must be transferred to the sample or erroneous values will result. For this reason, axial heat flow from the cells must be a minimum. In the same way, any thermal link between the sample and inert reference cell must be avoided since exchange of energy between the two will introduce errors. With these points in mind, heat transfer conditions in Barner's design were investigated.

II. HEAT TRANSFER INVESTIGATION OF THE BARNER DESIGN

A small hole was drilled in the cap of the top cell and a thermocouple introduced to measure the heater wall temperature. Two other thermocouples were set up, one on the outer wall of the cell and one 1/4 inch away in the gaseous environment. All three signals were printed out on a multipoint recorder. Hence, the four temperatures indicated in Fig. 3 were monitored.

The sample cell was filled with A-14 alumina powder. Helium was used as the inert gaseous phase. The furnace temperature was increased at the rate of 180°C/h for half an hour and then the system was allowed to equilibrate for the same period of time. After thermal stabilization the four temperatures, T₁, T₂, T₃, and T₄ were read. The temperature was then increased to 800°C following this one-hour cycle. Throughout the entire experiment, the power to the cells was adjusted when the gradient conditions required it. In this way the temperature sequence T₁ > T₂ > T₃ > T₄ was carefully maintained. Identical runs were performed in argon.

Plots were made of the temperature gradients across the system vs the furnace temperature and are shown in Figs. 4 and 5.
(1) Discussion of Results

If all the heat required by the sample is to be supplied by the cell heater, it is essential that $T_2 > T_3$. It is also desirable to maintain a steady gradient across the sample so that dynamic equilibrium conditions may apply. The sample gradient should also be as small as possible consistent with $T_2 > T_3$. Hence, an ideal $\Delta T$-vs-$T$ plot would be two horizontal parallel straight lines in the positive $\Delta T$-vs-$T$ quadrant.

Considering the two plots made, a helium atmosphere gives the lowest temperature gradient across the sample and the least change of this gradient with temperature; however, argon best maintains the $T_2 > T_3$ condition.

(2) "Double Cell" Design

The only way to achieve the temperature gradient sequent $T_2 > T_3$ during the heating cycle is to have an outer cell environment similar to that inside the cell. Thus powder was packed around the cells and the temperature gradient measurements repeated. The "double-cell" design is shown in Fig. 6.

A thin-walled nickel tube, larger in diameter than the cells, was cut into lengths such that the difference in length between it and a cell was twice the difference in their radii. Boron nitride pieces were cut which when assembled would fix the cell in the center of the nickel tube. In essence a cell-within-a-cell combination was made. The boron nitride pieces were carefully drilled to facilitate the passage of thermocouples and electrical leads to the inner cell. The two complex cells were assembled on the platinum support wire and the top one was completely filled with ball-milled A-14 alumina. The outer part of the
bottom cell was filled with alumina also. The assemblage was then lowered into the furnace with no extra insulation added.

(3) Discussion of Results

Plots were made of $\Delta T_1$ and $\Delta T_2$ vs furnace temperature for both helium and argon atmospheres. The curves obtained are shown in Figs. 7 and 8. In both gases the gradient across the cell and across the immediate cell environment remained relatively constant with increasing temperature. The size of the sample gradient necessary to maintain correct heat flow conditions was significantly lowered in both cases. With this cell design control of temperature sequence, $T_1 > T_2 > T_3 > T_4$ and especially $T_2 > T_3$, should be possible with no difficulty.

III. DESIGN OF A D.T.C. CAPABLE OF PRODUCING ACCURATE RESULTS

Isothermal conditions for both cells can be achieved by surrounding both "double-cell" with a material of high thermal conductivity. Such a material would have to be a metal. One design that would fulfill all the stipulations is a metal block with two large circular holes drilled side by side in it to accommodate the calorimeter cells. The cavities should be much deeper and wider than the cells so that powder can be packed around the cells. Such a design would isolate the cells from each other.

If the cells are to be in the same isothermal environment, the isotherms in the surrounding metal must be circular about each cell. The closest practical approach to this is shown in Fig. 9. The cells are centered at the centers of the two end semicircles of a large metal block with such dimensions that each cell has an equal circle of metal around it. The advantage of this design is that the heating coil can be wound
directly on the nickel block periphery, eliminating the problem of erratic heat transfer to the block and hence to the cells. A detailed drawing of the cell assembly is shown in Fig. 10. The thickness of powder above and below the cells is four times that around them. In this way axial heat losses are kept to a minimum. The whole differential thermal calorimeter system is shown in Fig. 11.

IV. DIFFERENTIAL THERMAL CALORIMETRIC MEASUREMENT OF HEAT CONTENT AND SPECIFIC HEAT DATA FOR SiO₂ AND Al₂O₃

(1) Introduction

Having fabricated the modified calorimeter, it was calibrated by comparing data from it with accepted literature data. The materials chosen for the calibration runs were silica and alumina. The silica used was ground alpha-quarts from Brazil. The alumina was grade A-14 alpha-alumina. This material was milled for two hours before use in order to break up any agglomerates. Screen and chemical analysis of both materials is shown in Table I.

(2) Procedure

The sample powder was packed into the sample cell and its weight ascertained by difference. The apparatus was evacuated and then flushed with argon. Power was introduced to both cells and all the power circuits allowed to equilibrate for one hour. The main furnace was then turned on and programed to rise for 100 minutes at 1°C/min. The temperature was increased in steps of 100°C with isothermal periods of one hour between each step. This procedure was continued until the furnace temperature reached 1000°C. Continuous monitoring of the temperature across the system ensured the maintenance of correct heat transfer
conditions during the whole run. Each power-peak area, corresponding to
the retardation of the empty-cell-power due to the sample heat capacity
was then measured with a planimeter. Accepting the literature heat con-
tent values at room temperature, the measured increase in heat content/100°C was consecutively added and a heat content-temperature curve
plotted. Three estimations of total heat content were made on the quartz
and two on the α-alumina.

(3) Results

The results were compared with the data of Kelley in the case of
quartz and that of Furukawa, Douglas, McCostrey and Ginnings for the
alumina. The comparison is shown in Figs. 12 and 13. The data obtained
agreed with the literature values within ±2%.

Three estimations of the α→β quartz inversion enthalpy were made.
The values obtained were 305, 250, and 280 cals/mole SiO₂. These values
compare favorably with the 290 cals/mole SiO₂ of Kelley.

(4) Conclusions

In summary, therefore, the D.T.C. runs undertaken on quartz and
alumina demonstrate the instrument to be reasonably accurate means of
compiling thermodynamic data on ceramic powders in a short time.

ACKNOWLEDGMENTS

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encouragement in developing this device.

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Energy Commission.
REFERENCES


2. Ibid., 239, 423 (1955).


TABLE I

<table>
<thead>
<tr>
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<th>Screen Analysis</th>
<th>Chemical Analysis</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>-100 + 200</td>
<td>99.85% SiO₂</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-100 + 200</td>
<td>99.72% Al₂O₃</td>
</tr>
</tbody>
</table>

Screen and chemical analyses of SiO₂ and Al₂O₃
FIGURE CAPTIONS

Figure 1. Barner's design
Figure 2. Furnace temperature and corresponding differential power curves
Figure 3. Diagrammatical representation of a differential calorimeter cell and its environment
Figure 4. Plot of temperature gradient vs environmental furnace temperature, helium atmosphere
Figure 5. Plot of temperature gradient vs environmental furnace temperature, argon atmosphere
Figure 6. Diagram of double-cell
Figure 7. Plot of temperature gradient vs environmental furnace temperature, helium atmosphere
Figure 8. Plot of temperature gradient vs environmental furnace temperature, argon atmosphere
Figure 9. Design of nickel block for circular isotherms
Figure 10. New calorimeter design
(Key to differential thermal calorimeter)
Figure 11. D.T.C. system
Figure 12. Total heat content of SiO$_2$ vs temperature
Figure 13. Total heat content of Al$_2$O$_3$ vs temperature
A: Sample cell
B: Boron Nitride ends
C: Resistance heater of Pt wire wound on Boron Nitride
D: Sample powder
E: Pt foil to be wrapped around thermocouple beads
F: Pt support wire. Also acts as a common leg to both heaters through ① and ②
G: Other leg of heater
H: Differential thermocouple
I: Monitor thermocouple
J: Nickel baffles
K: Empty cell
L: Grounded Nickel tube
M: Insulating end plugs
N: Kanthal furnace coil on Al₂O₃ former

FIG. 1 Barner's Design
FIG. 2  FURNACE TEMPERATURE AND CORRESPONDING DIFFERENTIAL POWER CURVES.
FIG. 3 DIAGRAMMATICAL REPRESENTATION OF A DIFFERENTIAL CALORIMETER CELL AND ITS ENVIRONMENT

$T_1 =$ temperature of cell heater wall

$T_2 =$ temperature at some point inside sample

$T_3 =$ outside wall of cell temperature

$T_4 =$ environmental temperature

$T_5 =$ furnace wall temperature
$A = \Delta T_1 =$ Gradient across sample inside cell

$B = \Delta T_2 =$ Gradient between outer wall of cell and a point in the immediate environment

FIG. 4 PLOT OF TEMPERATURE GRADIENT vs. ENVIRONMENTAL FURNACE TEMPERATURE HELIUM ATMOSPHERE.
A = \triangle T_1 = \text{Gradient across sample inside cell}

B = \triangle T_2 = \text{Gradient between outer wall of cell and a point in the immediate environment}

Fig. 5 Plot of temperature gradient vs. environmental furnace temperature: argon atmosphere.
**T₁, T₃, T₄** Thermocouple positions

**T₃** Thermocouple position in Nickel furnace tube

**A** Powder sample in Platinum cell

**B** Cell heater

**C** Boron Nitride cap and spacer

**D** Insulating Al₂O₃ powder

**E** Boron Nitride top cap

**F, G** Heater leads

**H** Heater lead wrapped about common support wire G

**FIG. 6 DIAGRAM OF DOUBLE-CELL**
$A = \Delta T_1 =$ Gradient across sample inside cell

$B = \Delta T_2 =$ Gradient between outer wall of cell and a point in the immediate environment

FIG. 7 PLOT OF TEMPERATURE GRADIENT vs. ENVIRONMENTAL FURNACE TEMPERATURE: HELIUM ATMOSPHERE
A = \Delta T_1 = \text{Gradient across sample inside cell}

B = \Delta T_2 = \text{Gradient between outer wall of cell and a point in the immediate environment}

**FIG. 8** PLOT OF TEMPERATURE GRADIENT vs. ENVIRONMENTAL FURNACE TEMPERATURE: ARGON ATMOSPHERE
A. Cell
B. Insulating powder
C. Metal

Figure 9: Design of nickel block for circular isotherms.
Key to Differential Thermal Calorimeter

A. Sample in sample-cell.
B. Zirconia powder around each cell.
C. Chromel-alumel thermocouple measuring the nickel block temp.
D. C-A thermocouple differentially linked with C; comparing the temperature of the outer wall of the sample cell with that of the nickel block.
E. C-A thermocouple linked differentially with C; comparing the temperatures of the sample-cell heater wall and that of the nickel block.
F. Sample-cell-heater leads.
G. Platinum-platinum/10% rhodium differential thermocouple used to control the power input to the control-cell J.
H. C-A thermocouple controlling the main furnace N.
J. Boron nitride control-cell heater.
K. Temperature gradient thermocouples for the control-cell.
L. Nickel top.
M. Nickel bottom.
N. Main-furnace winding.
O. Boron nitride inserts.
FIG. II  D·T·C· system
FIG. 12 Total heat content of SiO₂ vs temperature
FIG. 13  Total heat content of $\text{Al}_2\text{O}_3$ vs. temperature.
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