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Heat Content and Specific Heat of Six Rock Types at Temperatures to 1,000° C

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By David P. Lindroth and Walter G. Krawza

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HEAT CONTENT AND SPECIFIC HEAT OF SIX ROCK TYPES AT TEMPERATURES TO 1,000° C

by

David P. Lindroth[1] and Walter G. Krawza[2]

ABSTRACT

The heat content above 25.0° C up to 1,000° C was measured for six rock types: St. Cloud Gray Granodiorite, Holston Limestone, Sioux Quartzite, Rockville Quartz Monzonite, Salem Limestone, and the basalt at Dresser, Wis. The calorimetric data were obtained with an isothermal jacket-copper block calorimeter. The experimental heat content data for each rock type are presented, along with specific heat data obtained from the temperature derivative of the heat content. For the six rock types the maximum deviations of the specific heats at a given temperature were within 10 percent below 575° C and within 34 percent above 575° C. The increase in the values of specific heat range from a minimum of 13 percent for the basalt at Dresser, Wis. (temperature range, 100° to 1,000° C) to a maximum of 46 percent for Holston Limestone (temperature range, 100° to 870° C).

INTRODUCTION

This investigation was designed to provide specific heat data at elevated temperatures on the rock types currently under investigation at the Bureau of Mines Twin Cities Mining Research Center and to determine the overall accuracy of the calorimeter system. Thermal fragmentation studies of rock being done at this Center require highly accurate data on the thermophysical properties of rock at elevated temperature. This report presents the heat content and specific heat data so important in the derivation of other thermodynamic properties, for example, thermal diffusivity, when the thermal conductivity and density are known.

Although the specific heat of most minerals and oxides has been well established (<u>1</u>, <u>10</u>),[3] the specific heat of rocks (mineral aggregates) at elevated temperatures has been studied less extensively (<u>15</u>, <u>20</u>). The

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

specific heat of rocks can be obtained by employing the Neumann-Kopp rule, in which the heat capacity of a gram atom of a solid phase may be considered to be the weighted sum of the heat capacities of the elements forming the phase (17). This method is claimed to produce specific heat values, over the temperature range from 0° to 800° C, to within ±10 percent for practically all rock systems (20). However, the accuracy of this method is dependent upon the precision and accuracy of the chemical and mineralogical analysis. Owing to the complexity of the rock structure and the wide variation in composition within a single rock type, the chemical and mineralogical analysis may not yield consistent data for the computation of specific heat. Therefore, an experimental determination of the specific heat of test rocks at elevated temperatures accurate to a few percent is attempted in this study.

This report presents the results of experimental determinations of the heat content of six rock types at temperatures between 100° and 1,000° C and gives the corresponding specific heat values. The rock types studied are listed in table 1. For the reader's convenience their commercial names will be used throughout the rest of the report.

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The authors thank R. L. Marovelli, research manager, rock disintegration technology (presently Acting Chief, Division of Health and Safety Research), and R. E. Griffin, electronic research engineer (instrumentation), of the Twin Cities Mining Research Center for the design and procurement of the test system for specific heat measurements and for the initial formulation of the experimental procedure for the study. The authors are also indebted to M. L. Boucher, geologist, for the petrographic analysis, and to R. H. Jefferson, chemist, for the chemical analysis.

EXPERIMENTAL PROCEDURE

Method

Heat content data were measured by the drop calorimetry method. In this method the sample is heated within a capsule of known heat content, in a furnace, to a measured temperature and dropped into a copper calorimeter whose heat capacity has been previously determined. The temperature rise of the calorimeter measures the difference in heat content of the sample at the initial furnace temperature and at the final calorimeter temperature. The design of the calorimeter system permits the capsule to be returned to the furnace for another determination without dismantling any portion of the apparatus.

Apparatus and Materials

Calorimeter

The calorimeter system used was a prototype of the commercial unit built by Dynatech Corp.[4] The specifications for construction of the calorimeter

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[4] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

prescribed by the Bureau of Mines conformed to those of the calorimeter used by Kelley and King (11). Figure 1 shows the experimental apparatus, which consisted of a gold-plated copper cylinder (approximately 41 kg and 152 mm diameter by 298 mm high), resting on three plastic cones in a gold-plated brass jacket. The jacket was immersed in a stirred water bath maintained at 25.00 ± 0.01° C. The jacket cover was a brass plate in the center of which was a 76-mm-diameter by 114-mm-long collar (through which the capsule passed on dropping) protruding above the level of the constant-temperature bath. The cover was sealed to the jacket by an elastomer O-ring and secured by a series of bolts located in the perimeter of the cover.

The copper cylinder was machined with a slightly tapered central well to accommodate a capsule approximately 25 mm in diameter. A hinged circular copper gate about 3.3 mm thick and part of the cylinder proper covered the well, except for the brief time required to drop the capsule. In the annulus of the cylinder four holes (9.5 mm in diameter by 158.8 mm deep) were drilled 90° apart to accommodate a 20-junction thermopile. Five copper-constantan junctions were placed in the bottom of each hole and were referenced in ice (0° C). The junctions were electrically insulated by a thin coating of silicone rubber sealant. Through the appropriate switching, the temperature of the calorimeter proper could be measured by 5, 10, 15, or 20 of the thermopile junctions. In the measurements reported here, all 20 junctions were used.

The heat capacity of the calorimeter was determined by electrical calibration. A lightweight electrical heater was inserted into the well. The heater was constructed of Chromel wire with a total resistance of 4.5 ohms. The wire was insulated with a thin layer of Fiberglas, wound in a spiral, and cemented to a thin disk of aluminum foil. The total weight of the heater was 0.426 gram. Copper wires supplied the heater with power from a compensating circuit that gave a constant wattage input and thus eliminated the errors caused by the change in heater resistance with temperature. During each calibration, approximately 50 watts were dissipated in the heater over a period of 10 minutes to achieve a temperature rise which could be measured accurately. The results of the calibration runs were within 0.12 percent of the value given by the manufacturer.

During operation of the calorimeter, a slow stream of nitrogen gas (9.4×10^{-8} m^3/sec) was kept flowing around the block and through the furnace to help prevent moisture condensation. The heat exchange rate for a temperature difference of 1° C between the block and the bath (bath at 25° C) was found to be approximately 0.0025° C per minute and was reproducible from run to run. The time required for the calorimeter to reach thermal equilibrium after the sample was dropped ranged from 45 to 60 minutes.

Furnace

The furnace (approximately 0.40 m in diameter by 0.80 m long) was positioned vertically about 0.22 m above the calorimeter on two support legs. Only one leg was fixed, to allow rotating the furnace out of the way when the calorimeter had to be inspected. The furnace was heated by a three-zone Kanthal heating element wound on a tube with an inside diameter of 0.07 m and

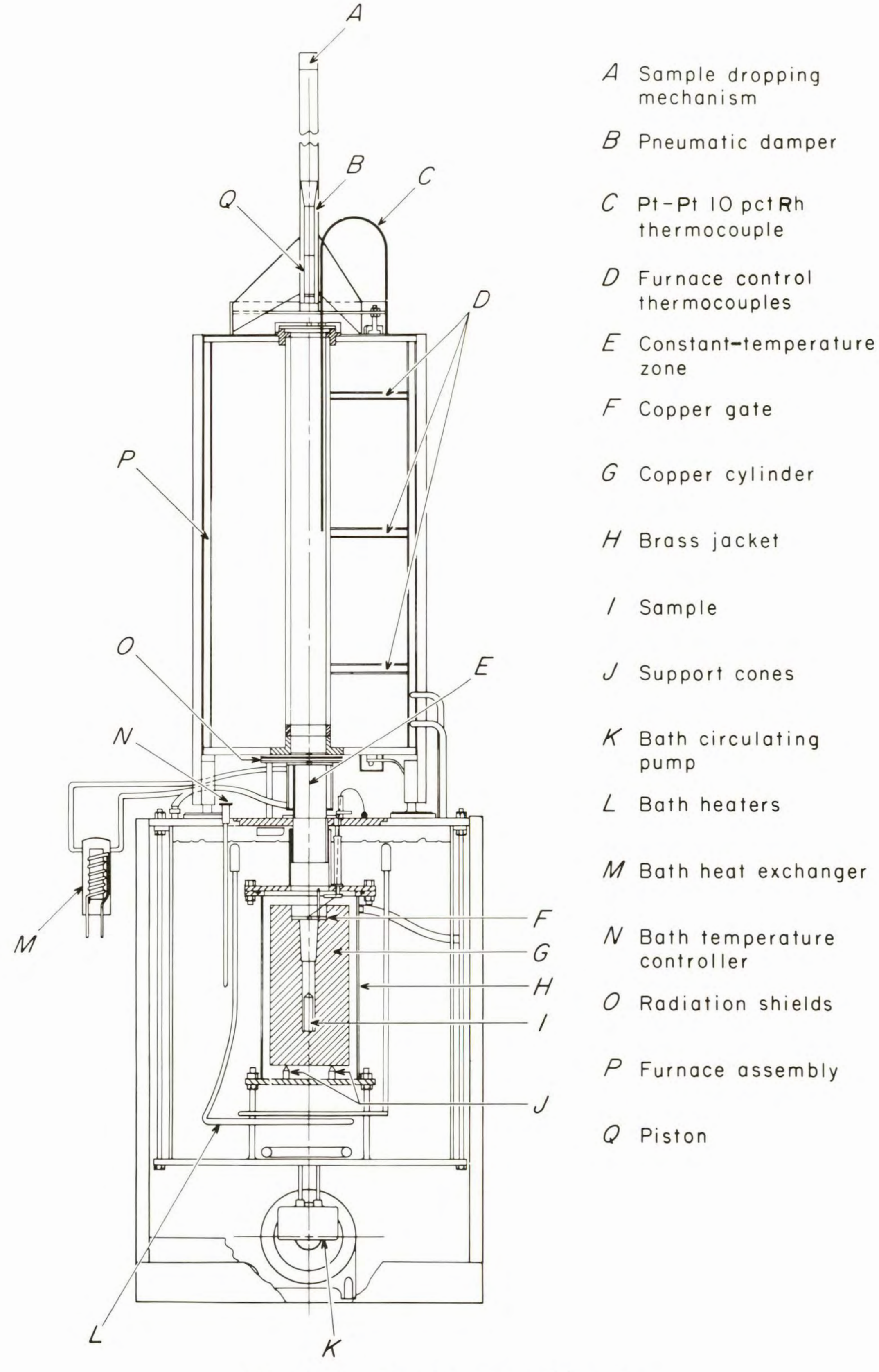

FIGURE 1. - Drop Calorimeter Schematic.

a length of 0.76 m (length to bore ratio approximately 11:1). The central portion and both of the end zones were individually controlled by proportional temperature controllers. The top and bottom zones of the heating element were controlled to the temperature of the central zone by a null-balance controller in conjunction with silicone control rectifiers. The heating element was surrounded by high-temperature insulation and enclosed in a water-cooled jacket. Investigation showed that at 1,000° C the furnace had a region 0.1 m in length which was isothermal to 1°. This space proved to be ample to contain the capsule and a single-junction thermocouple.

The sample-dropping mechanism was similar in design to the one used by J. C. Southard (16). The sample was suspended in the furnace by a 90 percent platinum-10 percent rhodium wire attached to a piston placed inside a slotted cylinder arrangement above the furnace. The sample release mechanism was synchronized with two slotted heat shields placed between the furnace and calorimeter. When the release mechanism was actuated, the sample fell freely until the piston reached the lower portion of the slotted cylinder. At this point the piston was pneumatically braked, and the capsule settled gently to the bottom of the calorimeter. The slotted heat shields were open only during the fall of the capsule and automatically closed after the capsule passed the lower shield. Correction was made for the heat radiated to the calorimeter during the few seconds these shields were open while the capsule was falling.

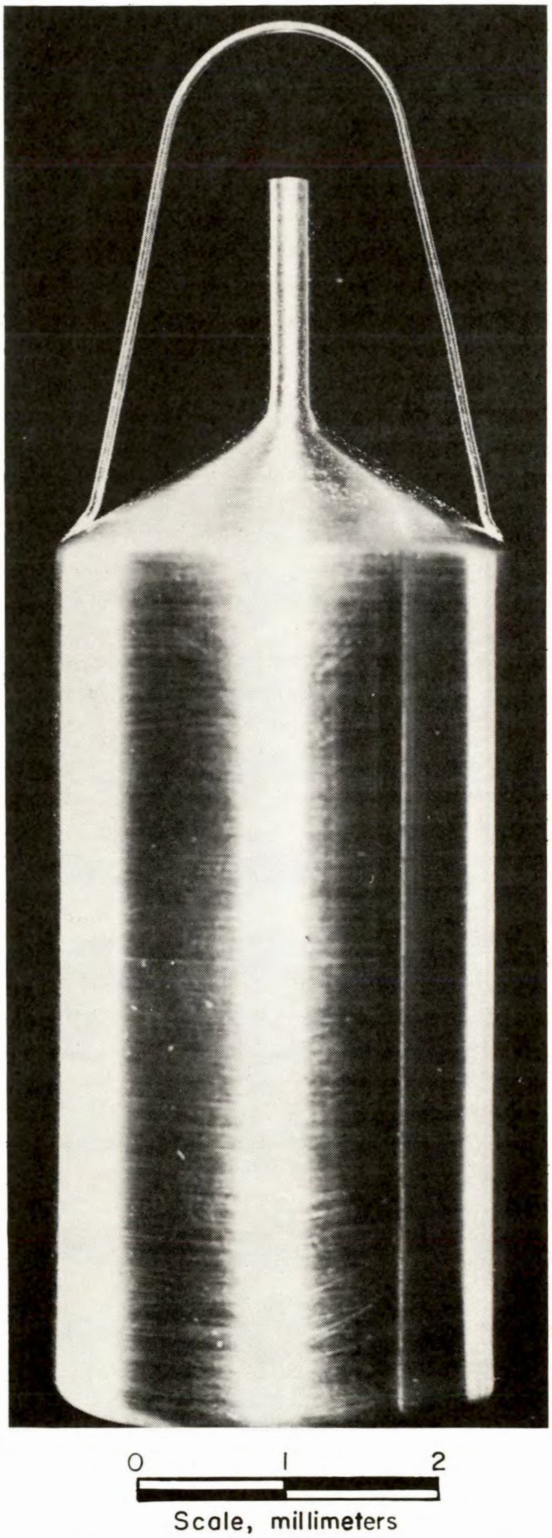

FIGURE 2. - 90 Pct Platinum-10 Pct Rhodium Sample Container.

Sample Containers

As recommended by E. G. King (11), the sample containers were constructed of 90 percent platinum-10 percent rhodium. The containers (fig. 2) were cylinders (30.5 mm in diameter by 55.9 mm high) with a tapered top (9.0 mm high) and a 3.0-mm-diameter, 15.0-mm-long chimney. A container was suspended in the furnace by a bail of No. 20 gage wire (90 percent platinum-10 percent rhodium) platinum-welded to the top of the container. The wall thickness was 0.22 mm, and all seams were platinum-welded gastight, to withstand 15 lb gage air pressure.

The heat content of the 90 percent platinum-10 percent rhodium containers was predetermined by a series of separate drops. Only one container out of a set of eight was used for these determinations. A total of 45 data pairs (heat content and temperature) was obtained over a temperature range from 60° to 1,100° C. A least squares (8) program was used to fit the data to a polynomial, expressing the heat content as a function of temperature. The best fit was obtained with a cubic. These data are presented in appendix B.

Sample Temperature Measurement

The temperature of the sample in the furnace was measured with a single-junction platinum versus platinum-10 percent rhodium thermocouple referenced at 0° C. The thermocouple was positioned approximately 2 mm from the side of the sample container and was located vertically at the median of the container. Except for the junction, it was enclosed in a two-hole ceramic sheath (4.2-mm diameter), led into the top of the furnace through a small hole, and mounted in such a way that it could be moved vertically ±100 mm to check the isothermality of the sample. The thermocouple was made from selected annealed wire, samples of which were calibrated at the gold, silver, and zinc points by the National Bureau of Standards. The uncertainties in the interpolated values of temperature were not more than 0.75° C in the range of 0° to 1,100° C. The overall uncertainty of the sample temperature measurements is ±1 percent.

The thermocouple reference junctions were maintained in an ice bath fashioned after the one used by Caldwell (2). Twenty-six copper constantan junctions and two platinum versus platinum-10 percent rhodium junctions were maintained in a Dewar flask 152 mm in diameter by 279 mm deep. Each junction was inserted in an 8-mm glass tube 216 mm long which was filled with a special heat-stable silicone fluid (Dow Corning No. 55) to a depth of 25 mm. After the junction had been properly placed in the tube, the top of the tube was sealed with a white adhesive silicone rubber sealant. This practice insured that all junctions were immersed to the same depth throughout the series of observations. The cover of the Dewar flask, drilled to receive the glass tubes, was made of 25-mm-thick polystyrene foam cemented to a slightly larger 13-mm-thick disk of Plexiglas. Because of the difference in diameter of the two disks, the polystyrene foam fitted snugly into the Dewar and left the Plexiglas as the main vertical support. Crushed ice made from distilled water was used in a water-ice slush filling the Dewar flask at all times during observations.

During the heat content determinations, the platinum versus platinum-10 percent rhodium thermocouple was calibrated by comparison with a similar one reserved solely for calibration. Before and after each set of runs on a given rock type, these calibrations were made with the thermocouples placed in a small muffle furnace but connected through the same electrical circuit and referenced in the same ice bath as were used in the runs.

The electromotive force developed by the thermocouple was measured with a Leeds and Northrup guarded six-dial potentiometer (No. 7556) in conjunction with a Leeds and Northrup electronic null detector (No. 9834). At 1,000° C the furnace current was turned off and on to check for sudden changes in electromotive force of the thermocouple. None were observed, an indication that the thermocouple reading was not influenced by possible electrical leakage from the furnace heaters.

Rock Samples

The rocks selected for this study represent a small cross section of the three major geologic groups (igneous, metamorphic, and sedimentary) under study at this Center. The Rockville granite, Dresser basalt, and Charcoal Gray Granite are igneous. The Jasper quartzite is metamorphic, and the Bedford limestone and Tennessee marble are sedimentary. More specific descriptions of these rocks types are given in the literature (12, 14, 18-19, 21). Table 1 presents a summary description of the rocks tested.

The bulk densities listed in table 1 represent an average value for each rock. Approximately 10 cores were drilled from a master block (approximately 1 m^3) of each rock type. The density of each core was determined, and the values were then averaged to produce the value given in table 1.

Table 2 shows the chemical analysis for the particular rock samples whose heat content and specific heat are presented in this paper. The totals given at the bottom of the table are the sums of all the components except H_2O and CO_2.

Sample Preparation

Two cores (150 mm long by 19 mm in diameter), drilled perpendicular to the natural in situ bedding from each master block, were selected for the heat content measurements. From the two cores, a sample was randomly selected for chemical analysis and another for petrographic analysis. The remainder of the cores was used to fill the 90 percent platinum-10 percent rhodium sample container.

The material was powdered in a diamond mortar and screened to a minus 20-mesh size (less than or equal to 833 μm). The new container was cleaned, dried, and weighed to an accuracy of ±0.1 mg and a precision of ±0.05 mg. The powdered material was funneled into the container and lightly tamped until it filled the container to the base of the chimney. The filled container was then placed in a vacuum desiccator which was evacuated for 3 hr to approximately 1 mm Hg. At the end of 3 hr the vacuum pump was turned off and the full container was baked at 105° C for 21 hr. At the end of 21 hr the vacuum pump was again started and run until the pressure was less than 1 mm Hg. The pump was then shut off, and helium was forced into the desiccator through a petcock until a positive pressure was noted. The desiccator cover was quickly removed, and the chimney of the container was pinched about 4 mm from the top. The part of the chimney above the pinch was sealed by flame welding with an oxy-hydrogen torch. As a check for leaks, the container was then immersed in a Pyrex vacuum desiccator half filled with distilled water, and the vacuum pump was started up again. Any leaks would have been quickly shown by bubbles issuing from the container, but none were observed in any of the seven containers used for this series of tests. After being checked for leaks, the container was dried and again weighed.

TABLE 1. - Summary geologic description

Rock type		Source location	Bulk density, g/cm^3	Petrographic (modal) analysis		Grain size range, mm	Appearance[1]
Geologic name	Commercial name (reference)			Mineral constituents	Volume-percent		
Sioux Quartzite...	Jasper quartzite (19).	Jasper, Minn.	2.64	Quartz................ Magnetite, hematite, rutile, zircon, amphibole.	99+ <1	0.1-1.0	Pinkish pale red (5R6/2-7/4), fine grained.
Salem Limestone...	Bedford limestone (12).	Bedford, Ind.	2.32	Calcite............... Organic (?) materials, voids.	90+ 10	0.25-1.0	Light gray--very light gray (N7-N8).
Holston Limestone	Tennessee marble (14).	Knoxville, Tenn.	2.68	Calcite............... Magnetite or pyrite.	99 <1	0.2-1.5	Grayish orange pink (10R8/2), medium to coarse grained.
Rockville Quartz Monzonite.	Rockville granite (21).	Rockville, Minn.	2.66	Microcline (perthitic) Plagioclase (and sericite). Quartz................ Biotite............... Hornblende, apatite...	34 (range 30-60) 29 (range 20-30) 30 (range 5-30) 6 (range 5-15) <1	0.5-10.0	Grayish pale red (5R4/2-5R6/2), very coarse grained.
St. Cloud Gray Granodiorite.	Charcoal Gray Granite (21).	St. Cloud, Minn.	2.72	Microcline............ Plagioclase........... Quartz................ Biotite-chlorite...... Hornblende............ Magnetite............. Apatite...............	46 24 17 9 2 1 <1	0.1-3.0	Medium dark gray--dark gray (N3-N4), medium grained to coarse.
Basalt from Dresser, Wis.	Dresser basalt (18).	Dresser, Wis.	2.97	Plagioclase........... Pyroxene-amphibole and olivine. Magnetite.............	50 45 5	0.01-3.0	Olive black--greenish black (5Y2/1-5GY2/1), fine grained.

[1] Colors given conform to the rock color chart distributed by the Geological Society of America, New York, reprinted 1963.

TABLE 2. - Chemical analysis, percent

	Charcoal Gray Granite	Rockville granite	Dresser basalt	Jasper quartzite	Bedford limestone	Tennessee marble
SiO_2	63.48	66.26	48.42	97.84	0.34	0.06
FeO	2.70	2.58	6.70	.25	.03	.03
Fe_2O_3	1.85	1.04	6.60	.27	.11	.11
Al_2O_3	15.62	15.62	15.23	.87	<.06	<.06
CaO	4.15	2.65	8.35	.81	55.02	55.86
MgO	2.23	.70	6.14	.05	.56	.28
MnO	.05	.06	.18	<.05	<.05	<.05
P_2O_5	.21	.13	.17	.009	.004	.057
S	.071	.016	.033	.011	.062	.016
TiO_2	.56	.46	1.90	.02	.01	.01
CO_2	-	-	-	-	42.75	43.48
Na_2O	3.59	3.51	2.30	.02	.03	.02
K_2O	3.58	4.85	.58	.03	.02	.01
H_2O	.11	.10	.14	.08	.01	.04
LOI	.59	.47	2.26	.32	43.53	43.80
Total	98.68	98.35	98.86	100.55	99.83	100.37

Note: H_2O at 105° C; (LOI) loss on ignition at 1,000° C.

Experimental Measurement

The isoperibol procedure (4, 13) was used for the heat content determinations. In this procedure the copper cylinder was cooled to a desired temperature below that of the temperature-controlled water bath while the container and contents were coming to thermal equilibrium in the furnace. The cylinder was cooled by water, Dry Ice, or liquid nitrogen, depending on the cooling rate desired. The desired temperature was determined by experiment such that the final temperature of the copper cylinder after the drop was 25°±1° C.

Once the container and contents were at thermal equilibrium with the furnace, the platinum versus platinum-10 percent rhodium thermocouple was moved vertically up and down over the length of the capsule to check for isothermality. If the region was not isothermal, the proportional controllers were adjusted until the isothermal zone observed over the full length of the capsule was within 1° C. The temperature of the calorimeter and furnace was measured with the Leeds and Northrup guarded six-dial potentiometer.

During the last 15 minutes preceding the drop, the temperature of the calorimeter and furnace was recorded at 3-minute intervals. At the end of the 15 minutes, a trigger release was depressed which simultaneously dropped the capsule and opened the radiation gates. During this operation the radiation gate open time was 2 to 3 seconds. Runs were made to determine the amount of heat received by the calorimeter from the furnace during this operation. The heat received at 950° C was approximately 8.5 calories. Below 700° C the effect was found to be negligible. As the calorimeter heated, its temperature was recorded at 30-second intervals for 10 minutes. After the equilibrium point had been reached, readings were taken at 5-minute intervals for 30 to

50 minutes until a constant heat exchange rate was observed. The corrected temperature rise was computed by the analytical method Dickinson (3) and Jessup (9) describe. The data were corrected to a base of 25° C, and corrections were made for the radiation contribution from the furnace, as well as for thermometric lags in the temperature rise of the block.

RESULTS

The experimental heat content values above 25° C (298.15° K) for the six rock types are listed in table 3. The columns labeled "t, ° C" give the temperature of the sample before it was dropped into the calorimeter. The temperature values are accurate to ±1.0 percent over the entire range and have been rounded to the nearest whole number.

The columns marked "$H_t - H_{25}$" list the heat liberated per gram for that rock type as it cooled from t° to 25° C. The heat content values are estimated to be accurate to within ±1.2 percent. This estimate is substantiated by the data obtained on the NBS Calorimetry Conference standard synthetic sapphire (Al_2O_3). These data are listed in appendix A and show a maximum difference of +1.22 percent at 954.5° C (1,227.7° K). The mean difference shown is ±0.72 percent.

The heat content data were curve fitted by a least squares (8) computer program, which generated polynomials up through the fourth order for each rock type. The program also performed a regression analysis on the data, and the method of stepwise regression (7) was employed to determine the order of polynomial best fitting the data. The equations of best fit found for the rock types with high SiO_2 content were those in which two regions were considered separately. Consequently, the four rocks of high SiO_2 content have two heat content equations: one valid for the temperature range 100° to 575° C (region I), and the other for the temperature range 575° to 1,000° C (region II).

The regression analysis on the NBS synthetic sapphire data showed a definite trend in the percent difference as a function of temperature (appendix A) and that the percent error in the measurement is negative for temperatures below 575° C (region I) and positive for temperatures above 575° C (region II). The equations of best fit were obtained individually for these two regions. The influence of the alpha to beta inversion of quartz in the experimental data of the test rocks is not determined.

TABLE 3. - Experimental heat content data for the six rock types

(1 cal = 4.184 abs joules)

Charcoal Gray Granite		Dresser basalt		Jasper quartzite		Rockville granite		Bedford limestone		Tennessee marble	
t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g
97	12.7	99	13.8	97	13.4	100	13.9	100	15.7	100	14.8
100	14.3	103	14.7	98	13.2	100	14.0	100	15.2	100	15.3
200	36.4	201	37.5	200	36.9	200	36.5	201	39.3	200	39.2
200	36.2	203	38.2	200	36.8	201	37.0	201	39.4	200	38.8
309	63.1	310	65.0	310	64.0	311	63.9	310	67.9	309	67.0
310	63.5	311	65.0	310	64.0	312	63.9	311	68.1	310	67.4
423	93	423	95	425	95	425	93	425	99	425	99
425	94	425	95	427	96	425	93	425	99	425	99
536	124	535	126	540	129	540	125	540	132	540	133
536	124	536	126	540	129	540	125	540	132	540	133
565	132	565	134	565	137	565	131	565	139	565	140
565	132	569	135	566	137	565	131	565	139	565	140
650	155	650	159	649	163	650	156	649	164	650	165
650	155	652	159	651	163	650	156	650	165	650	165
759	186	757	184	760	194	760	185	760	197	760	200
761	186	758	186	761	194	760	185	760	199	761	201
868	215	869	214	869	225	871	216	870	236	870	238
870	216	871	215	870	225	871	216	870	236	871	239
1,000	253	1,000	249	1,000	262	1,000	254				
1,001	254	1,000	249	1,000	262	1,000	254				

Heat content data for rocks of the high calcite content (Bedford limestone and Tennessee marble) were obtained only up to 870° C because the thermochemical reaction ($CaCO_3 + \text{heat} \rightarrow CaO + CO_2$) at 898.6° C released so much CO_2 as to rupture the container in the furnace. The heat content equations of best fit found for Bedford limestone and Tennessee marble are quadratics covering the temperature range from 100° to 870° C.

The heat content equations representing the experimental data in table 3 are listed below, where H is in calories per gram, referred to 25° C, and t is in ° C. The standard deviation of the heat content equation from the experimental data, the number of data points, n, used in fitting the equation, and the number of constants fitted, K, are given below each equation. The corresponding specific heat equations, obtained by differentiating the heat content equations, are also given, where C_p is the specific heat at constant pressure in calories per gram--° C.

Charcoal Gray Granite
(Region I)

$H_t - H_{25} = -8.022 + 0.20968t + 0.681303 \times 10^{-4}t^2$
Std. dev. = ±0.3755 (100°-575° C)
$n = 12$
$K = 3$

$C_p = 0.20968 + 0.136261 \times 10^{-3}t$

(Region II)

$H_t - H_{25} = -27.2216 + 0.280191t$
Std. dev. = ±0.6000 (575°-1,000° C)
$n = 8$
$K = 2$

$C_p = 0.280191$

Dresser basalt
(Region I)

$H_t - H_{25} = -8.4577 + 0.217579t + 0.617103 \times 10^{-4}t^2$
Std. dev. = ±0.2588 (100°-575° C)
$n = 12$
$K = 3$

$C_p = 0.217579 + 0.123421 \times 10^{-3}t$

(Region II)

$H_t - H_{25} = -10.0034 + 0.258507t$
Std. dev. = $\pm$ 0.9066 (575°-1,000° C)
n = 8
K = 2

$C_p = 0.258507$

Jasper quartzite

(Region I)

$H_t - H_{25} = -6.8797 + 0.197982t + 0.995707 \times 10^{-4} t^2$
Std. dev. = $\pm$ 0.1897 (100°-575° C)
n = 12
K = 3

$C_p = 0.197982 + 0.199141 \times 10^{-3} t$

(Region II)

$H_t - H_{25} = -21.0705 + 0.283013t$
Std. dev. = $\pm$ 0.2324 (575°-1,000° C)
n = 8
K = 2

$C_p = 0.283013$

Rockville granite

(Region I)

$H_t - H_{25} = -7.7156 + 0.209334t + 0.655168 \times 10^{-4} t^2$
Std. dev. = $\pm$ 0.3715 (100°-575° C)
n = 12
K = 3

$C_p = 0.209334 + 0.131034 \times 10^{-3} t$

(Region II)

$H_t - H_{25} = 17.4584 + 0.169624t + 0.66925 \times 10^{-4} t^2$
Std. dev. = $\pm$ 0.0316 (575°-1,000° C)
n = 8
K = 3

$C_p = 0.169624 + 0.13385 \times 10^{-3} t$

Bedford limestone

$H_t - H_{25} = -7.5889 + 0.222696t + 0.649667 \times 10^{-4} t^2$
Std. dev. $= \pm 0.6819$ (100°-870° C)
$n = 18$
$K = 3$

$C_p = 0.222696 + 0.129933 \times 10^{-3} t$

Tennessee marble

$H_t - H_{25} = - 7.9535 + 0.221873t + 0.69752 \times 10^{-4} t^2$
Std. dev. $= \pm 0.5559$ (100°-870° C)
$n = 18$
$K = 3$

$C_p = 0.221873 + 0.139504 \times 10^{-3} t$

The specific heat values as a function of temperature obtained from the least squares equations for the rocks of high SiO_2 content are shown in figure 3. Figure 3 also includes the predicted specific heat values of quartz for comparison. The heat content values of quartz were taken from Kelley (10), converted to calories per gram, and curve-fitted by the method of least squares mentioned above. The heat content equation was then differentiated to produce the specific heat equation for calculating the specific heat values for quartz.

Figure 4 shows the specific heat values for Bedford limestone and Tennessee marble. The specific heat of calcite obtained by the same method from Kelley's data (10) is also presented as a baseline comparison for those rocks of high calcite content. The specific heats for the six rock types tested are compared in figure 5.

DISCUSSION

The experimental values given for heat content and specific heat are valid only for the rock samples tested, whose modal and chemical analyses appear in tables 1 and 2. The heat content and specific heat are strongly dependent on the chemical composition of rocks. In general, the experimental measurements of heat content and specific heat of a highly monomineralic rock (for example, Jasper quartzite) vary less than the same properties of a multimineralic rock (for example, Rockville granite). The experimental data presented in the study show the relative variation of specific heat among the rock types tested.

The maximum difference of the specific heats for the six rocks at a given temperature is within 10 percent below 575° C and within 34 percent above 575° C. The increase in the values of specific heat range from a minimum of 13 percent for Dresser basalt over the temperature range 100° to 1,000° C to a maximum of 46 percent for Tennessee marble over the temperature range 100° to 870° C.

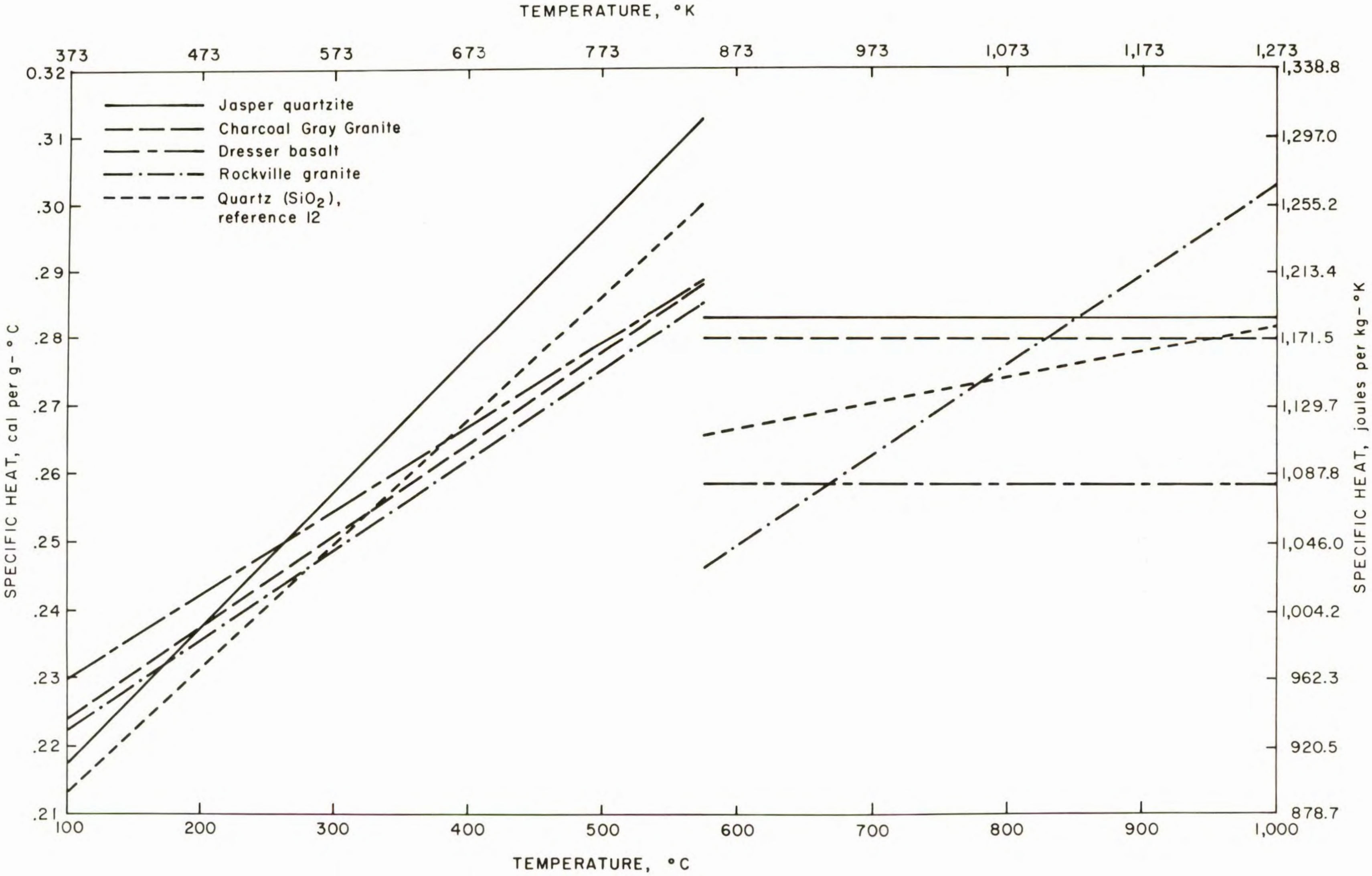

FIGURE 3. - Specific Heat Values of the High-SiO_2 Rock Types.

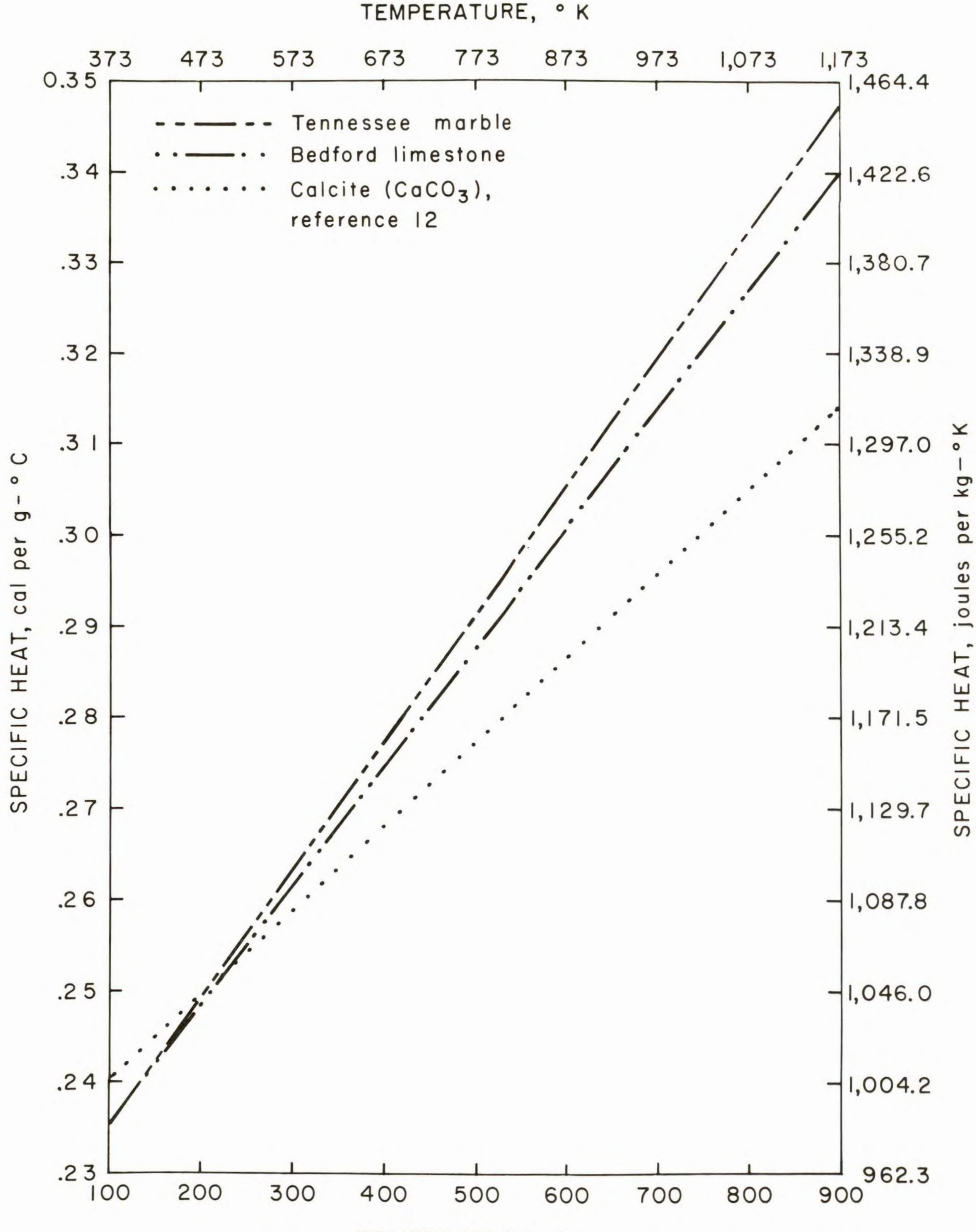

FIGURE 4. - Specific Heat Values for Bedford Limestone, Tennessee Marble, and $CaCO_3$.

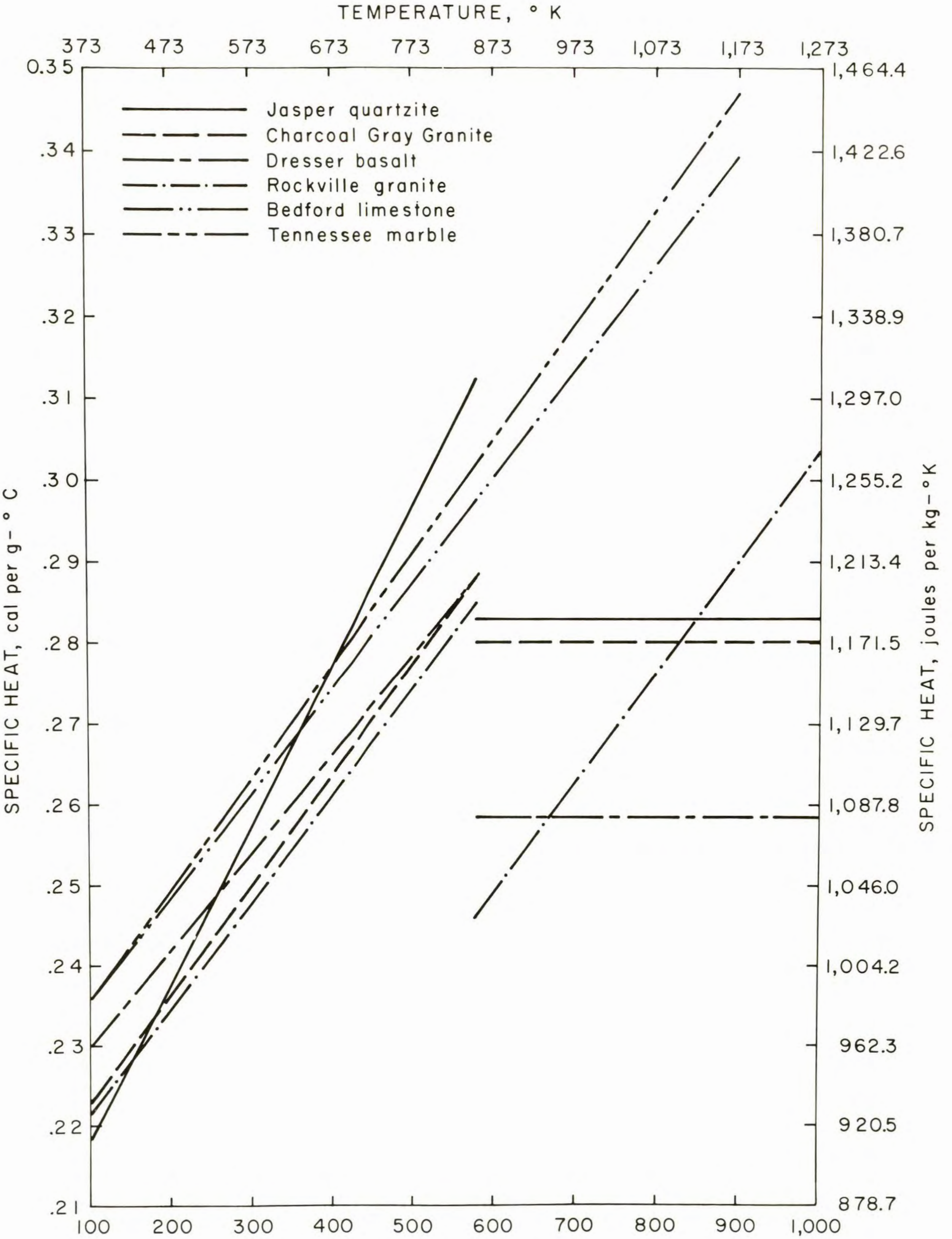

FIGURE 5. - Comparison of the Specific Heats for the Six Rock Types.

The heat content data have an accuracy of ±1.2 percent over the temperature range 100° to 1,000° C. The heat content values are low at temperatures below 575° C and high at temperatures above 575° C by the above uncertainty because of the error in the sample temperature measurement using the thermocouple. Douglas and King (4) point out that the experimental accuracy of the specific heat values is difficult to estimate. Since the specific heat is changing fairly rapidly in the temperature range 100° to 575° C, the percentage uncertainty, characteristic of the heat content (±1.2 percent) as determined by the differentiation process, may have to be multiplied by a factor of two or more. The estimated specific heat values therefore have corresponding errors.

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APPENDIX A.--HEAT CONTENT OF THE NBS CALORIMETRY CONFERENCE STANDARD SYNTHETIC SAPPHIRE

A sample of the NBS Calorimetry Conference (5) synthetic sapphire (70.3632 g) was obtained from the National Bureau of Standards for the purpose of determining the overall system accuracy of the drop calorimeter. The synthetic sapphire (original preparation described in reference (5))[1] was crushed and placed in a 90 percent platinum-10 percent rhodium container. The heat content-temperature function of the container was then established by a series of separate drops as described on page 6.

The heat content of the synthetic sapphire was determined at 16 temperatures between 400° and 1,300° K by the isoperibol method. No values were discarded. Corrections were made for the radiation contribution from the furnace and for the fact that the final calorimeter temperatures were above 298.15° K (25° C). The quantities ($H_T - H_{298.15}$) obtained are shown in table A-1, column 2.

TABLE A-1. - Heat content of the NBS Calorimetry Conference standard[1] synthetic sapphire

Temperature, ° K	$H_T - H_{298.15}$, cal/mole	Obs.--NBS equation 1, cal/mole	Percent difference[2]	Obs.--NBS equation 2, cal/mole	Percent difference[3]
406.4	2,299.7	-2.1	-0.09	-1.2	-0.05
653.8	8,604.1	-57.4	-.66	-57.1	-.66
721.1	10,448.2	-86.8	-.82	-84.9	-.81
778.6	12,086.3	-81.3	-.67	-77.5	-.64
843.1	14,001.1	-24.0	-.17	-17.7	-.13
978.6	18,073.1	+64.4	+.36	+78.1	+.43
1,058.5	20,500.6	+104.8	+.51	+124.3	+.61
1,058.6	20,580.9	+179.6	+.88	+199.1	+.98
1,058.9	20,495.0	+85.1	+.42	+104.6	+.51
1,108.5	22,045.3	+140.7	+.64	+164.3	+.75
1,107.4	22,097.5	+228.9	+1.05	+252.4	+1.16
1,168.6	23,900.0	+175.9	+.74	+205.0	+.87
1,168.5	23,949.2	+227.8	+.96	+256.8	+1.08
1,227.7	25,800.5	+276.8	+1.08	+311.8	+1.22
1,227.7	25,729.4	+207.1	+.81	+242.1	+.95

[1] Molecular weight = 101.96; 1 cal = 4.184 absolute joules.
[2] Average percent difference for column = ±0.66 percent.
[3] Average percent difference for column = ±0.72 percent.

Columns 3 and 4 of table A-1 show the difference between the present values and those calculated from the equation (5, 13).

$$(H_T - H_{298.15}) = 35.5092T - 4.0884 \times 10^{-4}\ T^2 - 11{,}232.04 \log T + 17{,}242.22, \qquad (1)$$

---

[1] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

representing the NBS 1956 smoothed data (5). The results of a similar comparison using Ginnings' "corrected" equation (6)

$$(H_T - H_{298.15}) = 35.3658t - 4.9711 \times 10^{-4}\ t^2$$

$$- 11{,}279.05 \log (T/273.15) - 454.88, \qquad (2)$$

where t is in ° C, are given in the last two columns. The maximum difference noted is +1.22 percent. The mean differences are less than 1.0 percent, but a definite positive trend occurs in both sets of data at the higher temperatures. This trend is shown by figures A-1 and A-2 in which the percent difference is plotted as a function of temperature. A least squares linear regression was performed on the data, and the solid line drawn through the points represents the regression equation. The dashed lines represent one standard deviation from the regression line. The errors in our data come primarily from the measurement of the sample temperature in the furnace, because the thermocouple junction was not in intimate contact with the container and also because of heat being conducted away from the thermocouple junction. Our temperature readings of the sample in the furnace are approximately 1 percent higher than actual at the lower temperatures and 1 percent

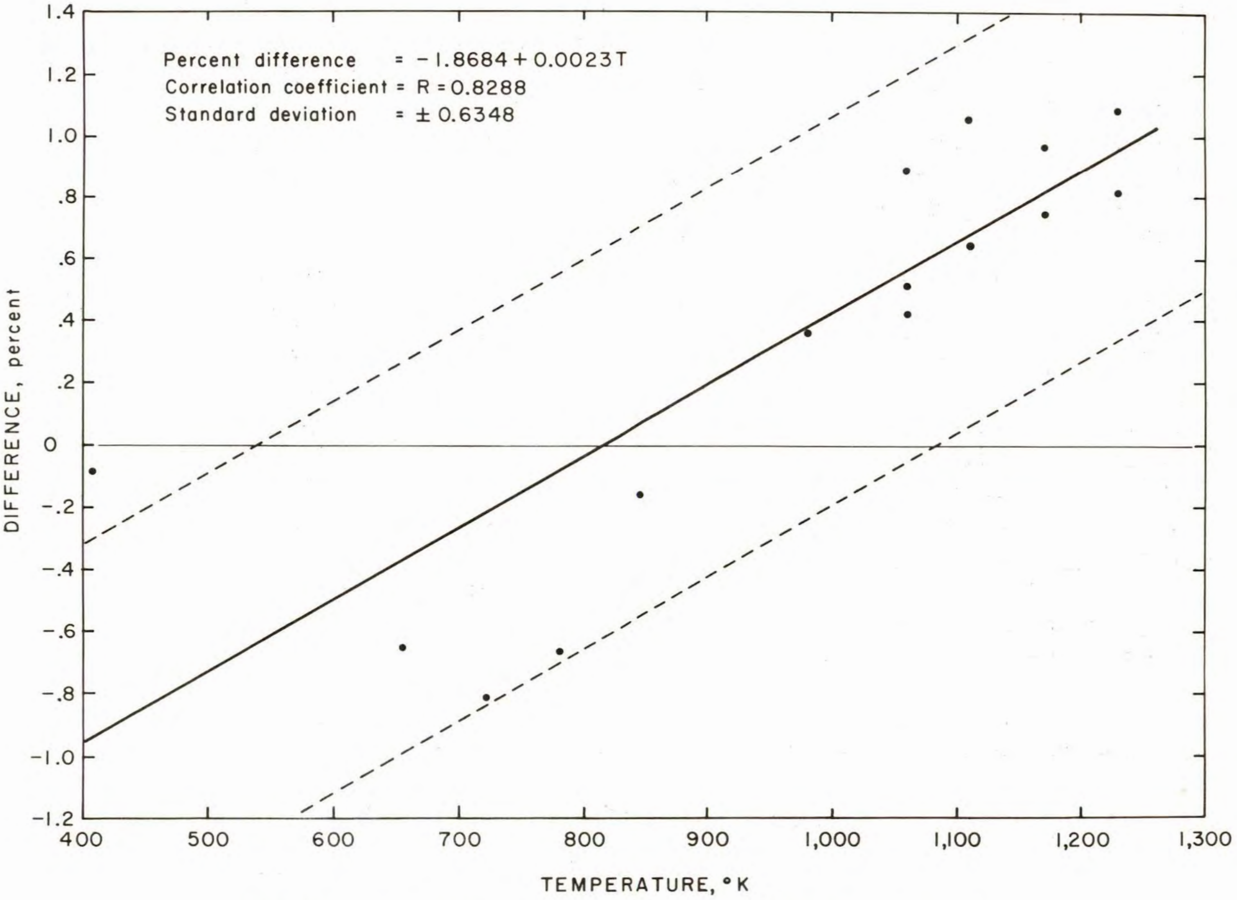

FIGURE A-1. - Percent Difference From NBS Equation 1.

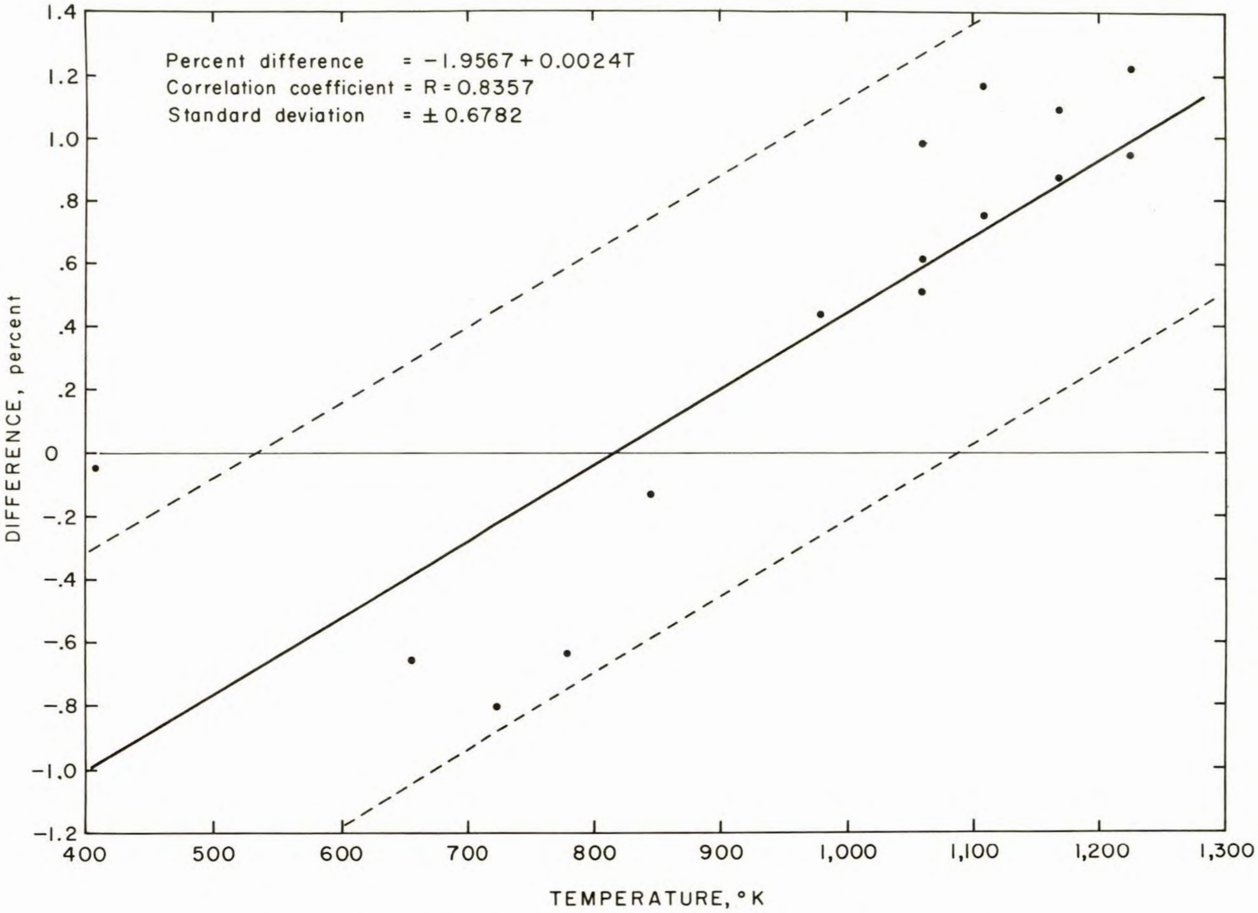

FIGURE A-2. - Percent Difference From NBS Equation 2.

lower than actual at the higher temperatures. MacLeod (13) noted some evidence, however, that the NBS 1956 data are a little low at temperatures approaching 1,200° K. Ginnings (6) and MacLeod (13) note that the positive trend in the deviations appears between 873° and 973° K and that this is the temperature region where a transition occurs in the Nichrome V-capsule used in the NBS experiments. In summary, we believe that the heat content values obtained with the above-mentioned system carry an uncertainty of not more than ±1.2 percent of the true heat content at a given temperature over the range 373° to 1,273° K.

APPENDIX B.--EXPERIMENTAL HEAT CONTENT OF 90 PCT PLATINUM-10 PCT RHODIUM SAMPLE CONTAINER

The heat content data for the sample container were obtained by the same apparatus, method, and experimental procedure as have been described and are given in table B-1. Since the heat loss is very nearly canceled out by running the sample in a container, and by running the empty container and then obtaining the difference, the heat content data presented here are somewhat less accurate than the ±1.2 percent accuracy claimed for the synthetic sapphire (Al_2O_3). The temperature values, however, are accurate to the same value as given in the text.

The heat content-temperature function derived by the method of least squares is given below, where H is in calories per gram and t is in ° C. The standard deviation from the mean, the number of data points, n, used, and the number of constants fitted, K, are given below the function.

$$H_t - H_{25} = -0.788945 + 0.032748t + 8.79611 \times 10^{-6}\ t^2 - 3.73927 \times 10^{-9}\ t^3$$

Std. dev. = ±0.2005

n = 45

K = 4

TABLE B-1. - Heat content of 90 pct platinum-10 pct rhodium sample container

90 pct platinum-10 pct rhodium		90 pct platinum-10 pct rhodium	
t, ° C	$H_t - H_{25}$, cal/g	t, ° C	$H_t - H_{25}$, cal/g
61.7	1.2	480.6	16.5
69.5	1.5	481.3	16.6
80.9	1.9	510.2	17.7
91.9	2.4	538.4	18.7
120.5	3.4	539.3	18.7
149.0	4.3	539.7	18.8
176.4	5.3	567.1	19.9
196.8	6.1	592.0	21.0
206.0	5.7	595.7	20.8
232.2	7.4	640.7	23.1
259.1	8.2	648.0	23.5
260.4	8.3	651.3	23.1
288.9	9.4	708.6	25.3
309.0	10.1	759.7	27.6
315.5	10.3	763.1	27.4
344.2	11.4	818.4	29.6
370.4	12.3	869.1	32.5
371.6	12.4	873.6	32.2
398.6	13.6	875.0	31.9
426.6	14.6	929.7	34.4
427.8	14.6	985.7	36.1
428.0	14.5	1,094.5	40.7
453.3	15.5		

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