Thermochimica Acta, 137 (1989) 365–371
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC HEAT OF TRANSITION ASSIGNMENTS BY MICROCOMPUTER-BASED DIFFERENTIAL THERMAL ANALYSIS. PART II. THE γ–β (ORTHORHOMBIC TO HEXAGONAL) TRANSITION OF BARIUM CARBONATE

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(Received 22 March 1988)

ABSTRACT

The enthalpy change (ΔH) associated with the $\gamma-\beta$ (orthorhombic to hexagonal) crystalline transition for a specimen of barium carbonate standard (NBS-SRM 760) which is sold for temperature calibration of differential thermal analyzers was studied. The mean value obtained by numerous operators of the same model of a commercially available computerized differential thermal analysis system is reported. These data were collected at three different heating rates and a variety of sample sizes. The mean value reported in this study (98.2 J g^{-1}) was compared with that obtained by earlier workers. An average molar entropy of transition was calculated to be +17.9 J K^{-1} mol^{-1}.

INTRODUCTION

Barium carbonate ($BaCO_3$) is one of the most important compounds of barium. It has a wide range of industrial applications. It is used in brick, glass, oil-drilling muds, ceramic materials, in manufacturing photographic paper, and in the electronics and chemical manufacturing industries. Barium carbonate occurs in nature as the mineral witherite which is mined in both England and California. Precipitated barium carbonate is the most widely used barium chemical second only to natural barite ($BaSO_4$). The precipitated barium carbonate used in ceramics is obtained from barite mineral which is reduced to barium sulfide ("black ash") and then converted to the carbonate by precipitation with soda ash [1].

The many industrial applications of barium carbonate depend on its chemical reactions or one of its physical properties. Like most alkali metal salts, barium carbonate is ionic and exhibits greater thermal stability than calcium, magnesium, and strontium carbonates. At room temperature barium carbonate exists in an orthorhombic (γ) form which undergoes a transition to a hexagonal (β) phase near 810 °C when heated at atmospheric pressure. On further heating, the hexagonal (β) form transforms to a face-centered

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cubic (α) form near 976 °C. On continued heating, barium carbonate decomposes to barium oxide at temperatures depending upon the heating rate and atmosphere [2,3].

In the previous study [4] with bismuth oxide, a value for the transition was determined using the differential scanning calorimetry (DSC) mode of a computerized commercial differential thermal analysis (DTA) instrument. Owing to the dispersion of the previously published values for the heat of transition in bismuth oxide, the reader may find it difficult to judge the accuracy of the value assigned for the transition in this work. It is also true that student operators would feel more confident of the DSC mode of this instrument if a material were selected which exhibits a heat of transition which is better established.

For these reasons, barium carbonate ($BaCO_3$) was chosen for use in the quantitative training exercise for students. As has been stated previously, at atmospheric pressure barium carbonate exhibits two polymorphic transitions on heating prior to its eventual decomposition to barium oxide. In the work which follows both crystalline transitions were observed by computerized DTA. The endothermic heat associated with the orthorhombic (γ) to hexagonal (β) form at 810 °C was quantified and compared with previously published values for the transition.

EXPERIMENTAL

All DTA thermal curves were obtained using a Perkin–Elmer DTA 1700 high temperature DTA system. A Perkin–Elmer model 3700 computer used in conjunction with a Perkin–Elmer graphics plotter 2, and DTA standard software package was employed as the data-handling device. When used with thermal analysis systems, this data-handling device is referred to by the vendor as the Thermal Analysis Data Station (TADS). For all studies, the DTA 1700 was used in the DSC mode of operation. The DTA instrument was temperature calibrated using high purity (99.999%) aluminum shot (lot #070880) which was obtained from Alfa Products, Thiokol/Ventron division (Danvers, MA)

The DSC ordinate heat flow axis of the DTA 1700 was also calibrated using the same aluminum standard from Alfa Products. This calibration is achieved by entering a factor into the thermal analysis software (DTA standard). This factor is determined experimentally by ratioing the known heat of fusion of aluminum to that which is experimentally observed using the DTA 1700. In the work which follows, an average value of 1.27 was used for the DCS ordinate calibration factor.

A NBS-ICTA standard reference material 760 barium carbonate specimen was purchased from the National Bureau of Standards (Washington, DC).

All DSC thermal curves of this work were obtained using 60 mm^3 ceramic

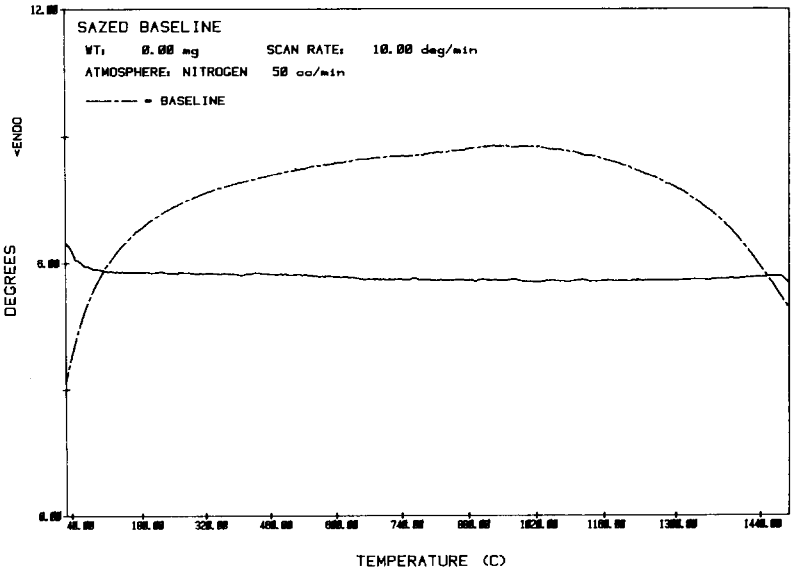

Fig. 1. Uncorrected (upper) and corrected ("SAZED") instrumental baseline for the microcomputer-based DTA system used in this study.

liners in the DTA sample holder cups. Flowing nitrogen was used as the dynamic purge atmosphere in the analyzer cell. Heating rates of 10, 20 and 30 °C min^{-1} were used in the quantitative heat of transition assignments of this study. Fresh, unused liners were employed for the sample cup for each heating run in the DTA. After each sample specimen had been placed into the ceramic liner, a small amount of calcined alumina was placed over the sample material. The reference cup of the DTA cell was filled with calcined alumina powder and was used in all studies as the reference material. All samples for analysis were weighed (by difference) using a Perkin–Elmer AD-2Z or AD-6 autobalance.

Prior to performing DTA of the aluminum standard or the barium carbonate specimen, a raw instrumental baseline was established and stored in the memory of the System 7/4 controller of the DTA 1700 DTA system. This is done by executing a coded Scanning Autozero function on the system 7/4 keyboard. The baseline was obtained using calcined alumina in both the sample cup and the reference cup of the DTA cell. After the instrumental baseline is stored, a mirror image signal is generated which offsets or nulls the characteristic instrumental baseline and results in a corrected instrumental baseline response in all subsequent runs with DTA 1700. Figure 1 shows an instrumental baseline for the DTA 1700 before (upper baseline) and after (lower straight baseline) executing the Scanning Autozero (SAZ) function of the DTA 1700 instrument.

Once an instrumental baseline is stored into the memory of the controller it remains there and will apply to all subsequent runs made with the instrument. A blinking light informs the operator that a SAZ baseline correction is in effect. The stored baseline may be removed by coded commands via the system 7/4 keyboard.

RESULTS AND DISCUSSION

A typical DTA thermal curve for barium carbonate obtained in a flowing nitrogen atmosphere at a heating rate of 20 °C min^{-1} is given in Fig. 2. The strong (lower temperature) endothermic event with peak minimum near 820 °C is due to the orthorhombic (γ) to hexagonal (β) crystal phase transition in the barium carbonate ionic lattice. The less intense endothermic event with a peak minimum near 980 °C corresponds to the conversion of the hexagonal (β) crystal phase to a face-centered cubic (α) form of the crystal lattice. Although only the γ–β transition will be quantified calorimetrically in this work, the β–α transition appears to be only about one seventh as energetic as the lower temperature endotherm.

Ten sets of data were accumulated in a fashion very similar to that obtained in the bismuth oxide study done earlier [4]. In all cases the students were required to determine the ordinate calorimetric factor for the instrument using the high purity aluminum standard. This experimentally determined calorimetric response factor for the DTA 1700 was then entered into the TADS software for the DSC mode of operation of the instrument. After obtaining the DTA thermal curve for the barium carbonate, the heat

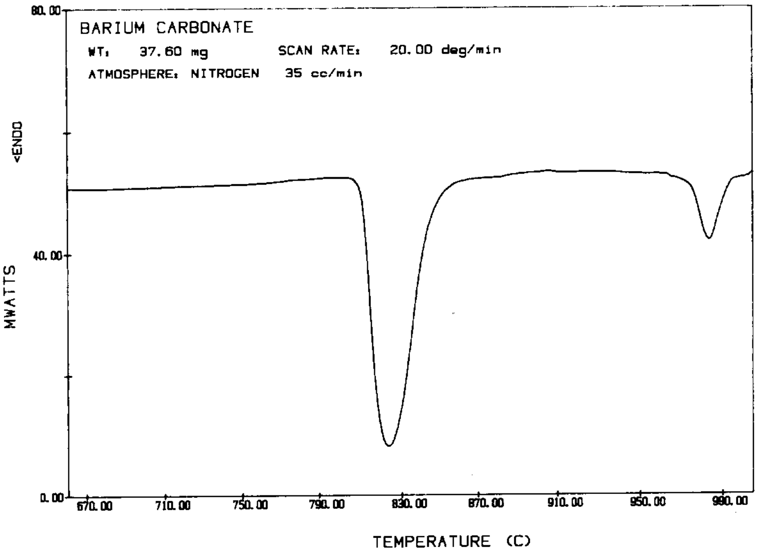

Fig. 2. DTA thermal curve for barium carbonate specimen using the "DSC Mode" of operation of the computerized DTA system.

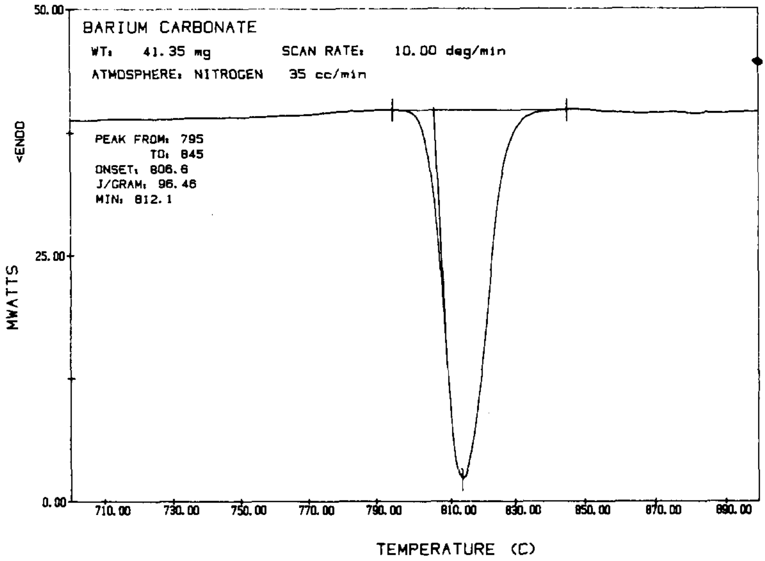

Fig. 3. Rescaled DTA thermal curve for barium carbonate showing heat of transition assignment for the $\gamma-\beta$ transition.

of transition was then assigned for the transition using the calorimetric factor with the DTA standard software.

Figure 3 shows a rescaled DTA thermal curve with peak analysis for a 41.35 mg specimen of barium carbonate obtained at a heating rate of 10 °C min^{-1} in a dynamic nitrogen atmosphere. This thermal curve was obtained by the author using the DSC mode of the instrument using metric units. This is one of ten such thermal curves with peak analysis which were generated for the $\gamma-\beta$ transition of barium carbonate. These thermal curves were obtained using sample sizes ranging from as small as 27.0 mg to as large as 57.0 mg. Heating rates of 10, 20 and 30 °C min^{-1} were employed for the analysis.

Table 1 gives the average of the ten values obtained over the past 2 years. This represents the values taken from at least four different DTA 1700 instruments and eight different operators. As can be seen in Table 1, the

TABLE 1

Published values for the endothermic $\gamma-\beta$ transition in barium carbonate

	ΔH (J g^{-1})
NBS Circ. 500 (Ref. 5)	95.3
MacKenzie and Ritchie (Ref. 6)	89.9
Gray (Ref. 7)	94.9
Mills and Coyle (Ref. 8)	99
Earnest (this work)	98.2

arithmetic mean for the data set is 98.2 J g^{-1} with an average deviation of ±3.4 J g^{-1}. This value is in excellent agreement (within 1%) with that reported recently by Mills and Coyle [8] who report the energy of transition to only two significant figures. The average value reported differs from that given in the NBS Circular 500 [6] by 2.9 J g^{-1} or 3.0%. The mean value of 98.2 J g^{-1} differs from that reported by Gray [7] by 3.3 J g^{-1} or 3.5%. Thus, our average value of 98.2 J g^{-1} compares favorably with values reported previously for the transition of barium carbonate.

As was pointed out in the previous bismuth oxide study [4], the precision of this data set, which was generated over a 2 year period with numerous student workers, is affected by the weighing procedure which immediately precedes the actual thermal analysis. Since the numbers within the data set were generated by different workers at different times on four different instruments, agreement within the set is more a measure of reproducibility than simple "repeatability".

Another measure of the reproducibility of the value for the heat of transition obtained here is obtained by comparing our value of 98.2 J g^{-1} with that reported by Mills and Coyle [8]. These workers used the same make and model of DTA instrument as that employed here (Perkin–Elmer DTA 1700). Although they employed the larger (100 mm) ceramic liners in the DTA cell and a different value for the calorimetric factor in the DTA standard software, close agreement (within 1%) with the heat of transition reported here is observed.

Since the γ–β transition for crystalline barium carbonate is thermodynamically reversible, the entropy of transition may be calculated by

$$\Delta S = \frac{q_{\mathrm{rev}}}{T}$$

where q_{rev} is the reversible heat associated with the process. For the reversible phase change observed here at atmospheric pressure, q_{rev} is equal to ΔH for the γ–β transition (98.2 J g^{-1} or 19.4 kJ mol^{-1}). T (K) in the above expression is the absolute temperature of the transition. Thus one obtains an average molar entropy of transition of +17.9 J K^{-1} mol^{-1}.

CONCLUSION

The average heat of transition obtained by the students with the "DSC Mode" of this computerized DTA system for the crystalline transition of barium carbonate is in good agreement with the reasonably well-established value for the energy of this transition. It is therefore concluded that the average heat of transition (71.2 J g^{-1}) obtained in the previous study [4] for the transition in bismuth oxide is also an accurate assignment.

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