NATIONAL BUREAU OF STANDARDS REPORT

10503

THE CALCIUM SULFATE–WATER SYSTEM
1. DIFFERENTIAL THERMAL ANALYSIS AND PREPARATIVE STUDIES

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U.S. DEPARTMENT OF COMMERCE

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THE CALCIUM SULFATE-WATER SYSTEM
1. DIFFERENTIAL THERMAL ANALYSIS AND PREPARATIVE STUDIES

by

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ABSTRACT

This is the first in a series of reports on the properties of the products formed in the calcium sulfate-water system, which is part of our overall study of the properties of gypsum plaster.

Existence of two forms of calcium sulfate hemihydrate is suggested by differential thermal analysis studies. The α-form can be prepared by crystallization methods whereas the β-form is prepared by the dehydration of calcium sulfate, either in air or in vacuo. Some preparative methods resulted in impure products.

The peak temperatures of the endothermic curves of $CaSO_4 \cdot 2H_2O$, α-and β-$CaSO_4 \cdot 1/2H_2O$ and the exothermic curve of α-$CaSO_4 \cdot 1/2H_2O$ are pressure dependent, shifting to lower temperatures as the gaseous pressure within the DTA cell is decreased. This phenomenon can be explained on the basis of the van't Hoff equation.

1. INTRODUCTION

In the $CaSO_4 \cdot nH_2O$ system (designates number of H_2O molecules) three kinds of products are generally recognized with n = 2, 1/2 and 0. The existence of two forms of $CaSO_4 \cdot 1/2H_2O$, α and β, however, has not been firmly established. Apparent slight differences in densities [1] [1/], heat of formations [2] and differential thermal analysis curves [3] have been cited as evidence for the existence of two forms. Gay [4] reported that the similarity in the x-ray diffraction patterns of the two supposed forms, however, suggests the lack of polymorphism.

There are conflicting interpretations of the binding of water in the hemi-hydrate (n = 1/2). Some investigators believe that the water is zeolitic and, therefore, moves freely through the lattice (in which case n can have varying values), while others contend that the water occupies energetically favorable lattice sites [4].

[1/] Numbers in brackets refer to references given at the end of this report.

It is surprising that the properties of $CaSO_4 \cdot 1/2H_2O$ have not been better characterized, since the $CaSO_4 \cdot nH_2O$ system has been the subject of numerous studies. This can possibly be attributed to both the study of impure products, which will be explored in the present work, and the limited scope of previous studies.

The purpose of the present work is to characterize well some preparative methods and the properties of $CaSO_4 \cdot 1/2H_2O$, and to ascertain if two forms exist. If two forms are found to exist the preparation of two forms of gypsum (n = 2) will be undertaken by allowing α-and β-$CaSO_4 \cdot 1/2H_2O$ to hydrate under controlled conditions.

Results of preparative studies of the supposed α-and β- forms of $CaSO_4 \cdot 1/2H_2O$, along with the differential thermal analysis curves (hereafter termed DTA curves) of the products, are presented and interpreted in this report. Throughout this and future reports the unqualified use of the α and β terminology does not imply that the existence of two forms of $CaSO_4 \cdot 1/2H_2O$ has been proven.

2. EXPERIMENTAL

2.1 DTA Methods

The DTA curves were recorded using a DuPont Model 900 DTA instrument equipped with a micro-sample standard cell. The reference material was anhydrous Al_2O_3 (Baker and Adamson Reagent Grade) heated to 400°C for an hour and stored in a vacuum desiccator over phosphorus (v) oxide until used. Gaseous pressures within the DTA cell were measured with the gauge accompanying the instrument, and are not claimed to be highly accurate, possibly varying by ±8%. Temperature measurements were made using chromel alumel thermocouples, with a reference junction temperature of 0°C, and are accurate to ±5°C. The ultimate vacuum of the system was estimated to reduce the residual pressure in the DTA cell to about 1 Torr.

Evaluation of atmospheric conditions within the specimen compartment was complicated by the furnace and sample housing arrangement of the DTA cell. Samples were loaded into small Pyrex glass tubes, which were closed at one end and the thermocouple wires were inserted into the tubes above the sample, with the thermocouple joint being embedded in the sample. The thermocouple wires fitted tightly in the tube, thereby hindering the diffusion of water vapor from samples and increasing the partial pressure of water vapor in the specimen tube above that in the bulk atmosphere [2/]. Furthermore, allowing nitrogen gas to flow into the DTA cell probably did not produce dynamic conditions within the specimen tubes, as the nitrogen gas was prevented by the tight fit to be an effective purging agent. For the same reasons, in studies carried out with reduced pressures the water vapor pressures within sample tubes were probably much greater than the bulk residual pressures.

2.2 Materials

The $CaSO_4 \cdot 2H_2O$ (Baker and Adamson Reagent Grade) used in this study was found, by dehydration at 375°C, to contain the stoichiometric percentage of water (theoretical 20.9%, found 21.0%). All other chemicals used in this study were of reagent grade.

2.3 Preparation of $CaSO_4 \cdot 1/2H_2O$

2.3.1 β-$CaSO_4 \cdot 1/2H_2O$

β-$CaSO_4 \cdot 1/2H_2O$ was prepared from $CaSO_4 \cdot 2H_2O$ by two dehydration methods. In one method samples of $CaSO_4 \cdot 2H_2O$ were dehydrated in an air oven at 150 to 175°C for 3 to 12 hours. Then γ-$CaSO_4$ was allowed to equilibrate with 50% laboratory air at room temperature. This resulted in the uptake of water with the final product having slightly more than the stoichiometric amount of H_2O, as n ranged from 0.54 to 0.57. An alternate method was the removal of 1 1/2 molecules of H_2O from

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[2/] Bulk atmosphere denotes the average atmosphere within the DTA cell.

$CaSO_4 \cdot 2H_2O$ by vacuum line techniques, at 100°C. The product was then annealed for 60 hours by heating at 100°C in a closed system. This preparative method was also carried out at temperatures of 50, 75 and 100°C with the annealing process being eliminated.

2.3.2 α-$CaSO_4 \cdot 1/2H_2O$

α-$CaSO_4 \cdot 1/2H_2O$ was prepared by modifying the method of Weiser and Milligan [5]. Mixed together were 210 ml of 16.3 M HNO_3, 3 ml of 18 M H_2SO_4 and 60 ml of distilled H_2O. Added slowly to this mixture was a solution of 45.3 g of $Ca(NO_3)_2 \cdot 4H_2O$ dissolved in 100 ml of distilled H_2O. The final solution was transferred to a glass-stoppered glass-chemical-bottle and heated at 50°C in an air oven. A white precipitate formed after about three hours and was allowed to age for 14 days. Then, the precipitate was separated from the supernatant liquid by decanting the liquid. The solid product was washed four times with about 50 ml of absolute ethanol, pressed between filter paper, and finally air dried. The white product contained the stoichiometric amount of H_2O (theoretical 6.62%, found 6.68%) and gave the DTA curve ascribed to α-$CaSO_4 \cdot 1/2H_2O$ [3]. The effects of changing both the aging time and aging temperature were studied. In one run the aging temperature was increased to 70°C and the aging time was kept at 14 days. While in another study the product was separated from the supernatant liquid after an aging time of 4 hours at 50°C.

2.4 Dehydration Process of $CaSO_4 \cdot 2H_2O$ with External Water Vapor

Known amounts of $CaSO_4 \cdot 2H_2O$ (between 0.0419g, 0.243 millimoles, and 0.166g, 0.963 millimoles) were transferred to pyrex reaction tubes. The pyrex reaction tubes were sealed at one end and had a standard tapered joint at the opposite end for attachment to the vacuum line. Their volumes were about 100 cm^3. A quantity of distilled H_2O calculated to give a desired gaseous water pressure at 165°C was transferred to the reaction tubes containing $CaSO_4 \cdot 2H_2O$. The reaction tubes were connected, through a closed stopcock, to the vacuum line, the tubes were cooled with liquid nitrogen, and deaerated by opening the stopcock. While exposed to the vacuum system the reaction tubes were sealed using an oxygen torch. Sealed tubes were placed in an air oven, 165°C, for heating periods of either 66 hours or 19 days. After the tubes had cooled to room temperature, the uncombined water was separated from the product by condensing it in the opposite end of the tubes. The tubes were then opened and the white products were air-dried.

3. RESULTS

3.1 DTA Curves of $CaSO_4 \cdot 2H_2O$

The differential thermograms of $CaSO_4 \cdot 2H_2O$, with several different bulk atmospheric conditions in the DTA cell, are reproduced in Figures 1 and 2. A decrease in the peak temperatures, T_{peaks}, of the two endothermic peaks was observed when the gaseous pressure in the cell was reduced and when the residual pressure approached 1 Torr the second endothermic peak had shifted sufficiently to merge with the first peak. Peak temperatures are listed in Table 1. Peak temperature is the temperature of the maximum point in an exothermic curve or the minimum point in an endothermic curve and is used in this report since the merging tendency of the two peaks makes the estimation of the incipient temperatures difficult. DTA curves obtained under static conditions of nitrogen flow were similar to those observed with supposed dynamic nitrogen flow.

3.2 DTA Curves of β-$CaSO_4 \cdot 1/2H_2O$

In Figures 3 and 4 are reproduced the DTA curves of β-$CaSO_4 \cdot 1/2H_2O$ recorded, respectively, with a dynamic N_2 atmosphere and a small residual pressure (ca. 1 Torr) in the DTA cell. The endothermic peak has the same temperature-pressure behavior (Table 2) as previously noted for the second endothermic curve of $CaSO_4 \cdot 2H_2O$. The position and shape of the small exothermic peak, T_{peak} = 375°C, was not affected by changes in the atmospheric conditions in the DTA cell.

3.3 DTA Curves of α-$CaSO_4 \cdot 1/2H_2O$

The DTA curve of α-$CaSO_4 \cdot 1/2H_2O$, with a N_2 atmosphere in the DTA cell is shown in Figure 5. Results of pressure dependence studies on the shape and position of the curves are reproduced in Figure 6 and T_{peak} are listed in Table 2. The position of the endothermic peak of α-$CaSO_4 \cdot 1/2H_2O$ shifts to lower temperatures with reductions in the gaseous pressure in the DTA cell. The small exothermic peak, also, has the same temperature-pressure behavior.

3.4 DTA Curve of Mixture of α- and β-$CaSO_4 \cdot 1/2H_2O$

The DTA curve of an equal molar mixture of α- and β-$CaSO_4 \cdot 1/2H_2O$ includes the small exothermic peak of the respective components (Fig. 7), which indicates that this method can be used to identify the two forms in the presence of each other.

3.5 Preparation of β-$CaSO_4 \cdot 1/2H_2O$

A simple and reproducible preparative method for β-$CaSO_4 \cdot 1/2H_2O$ was the complete dehydration of $CaSO_4 \cdot 2H_2O$, at 150° to 175°C, and the subsequent rehydration of γ-$CaSO_4$ to β-$CaSO_4 \cdot 1/2H_2O$ at room temperature at 50% R.H. This method resulted in a product containing slightly more than the stoichiometric amount of water with n ranging from 0.54 to 0.57. It was not practical to remove the stoichiometric amount of H_2O from $CaSO_4 \cdot 2H_2O$ to directly form β-$CaSO_4 \cdot 1/2H_2O$ by this method.

An alternate method was the removal, by vacuum line techniques, of the stoichiometric amount of H_2O from $CaSO_4 \cdot 2H_2O$ to directly form β-$CaSO_4 \cdot 1/2H_2O$. This method was studied using dehydration temperatures of 50, 75 and 100°C, with and without annealing the product. DTA curves of the products are represented in Figure 8. Products were found to be impure, containing $CaSO_4 \cdot 2H_2O$, γ-$CaSO_4$ as well as β-$CaSO_4 \cdot 1/2H_2O$. The DTA curve of the unannealed product formed by dehydration at 50°C has a strange endothermic peak with a T_{peak} of 120°C, the origin of which is unknown.

3.6 Preparation of α-$CaSO_4 \cdot 1/2H_2O$

Increasing the aging temperature had an inverse effect on the yield of α-$CaSO_4 \cdot 1/2H_2O$. The yield was estimated to be four-fold greater with an aging temperature of 50°C as compared with 70°C.

An aging time of 14 days at 50°C resulted in a pure product, according to the DTA analysis. Shortening the aging time to 4 hours at 50°C, did result in a product that was slightly impure as indicated by the indentation at about 155°C in the DTA curve, Figure 9. This impurity, possibly, could be occluded $CaSO_4 \cdot 2H_2O$.

3.7 Studies of the Dehydration of $CaSO_4 \cdot 2H_2O$ in Reaction Tubes

In a typical study, a reaction tube containing 0.243 millimoles of $CaSO_4 \cdot 2H_2O$ was heated at 165°C for 66 hours with an internal water vapor pressure of 730 Torr. Thermograms were recorded on the same day the sample was removed from the reaction tube and at 4, 5, 6 and 40 days. A wide endothermic curve with T_{peak} of 320°C was initially observed (Figure 10). During exposure to laboratory air at 50% R.H. the T_{peak} of the curve increased and its width decreased until after 40 days the curve had disappeared. TGA studies (to be discussed in a later report) indicated that the endothermic reaction was not accompanied by a weight loss and, therefore, must be associated with a phase transition. Other studies conducted with different gaseous water pressures, 375 to 1520 Torr, and heating times, 19 days, gave similar results.

4. DISCUSSION

4.1 DTA Curves of $CaSO_4 \cdot nH_2O$

4.1.1 Nitrogen Gas at 760 Torr in DTA Cell

The differential thermogram of $CaSO_4 \cdot 2H_2O$, recorded with a nitrogen atmosphere in the DTA cell (Figure 1) can be understood on the basis of three transformation steps with peak temperatures of 150, 197 and 380°C:

$$(1)\ CaSO_4 \cdot 2H_2O_{(s)} \xrightarrow{150°C} \beta\text{-}CaSO_4 \cdot 1/2H_2O_{(s)} + 3/2H_2O_{(v)}$$

$$(2)\ \beta\text{-}CaSO_4 \cdot 1/2H_2O_{(s)} \xrightarrow{197°C} \gamma\text{-}CaSO_{4(s)} + 1/2H_2O_{(v)}$$

$$(3)\ \gamma\text{-}CaSO_{4(s)} \xrightarrow{380°C} \beta\text{-}CaSO_{4(s)}.$$

Steps (1) and (2) are dehydration processes and, consequently, result in endothermic curves, while step (3) is exothermic and is attributed to a lattice modification. The above assignments infer that reaction (1) is completed before reaction (2) commences, however, some overlapping does take place. The extent of overlapping is smaller in the present study, probably because of using micro samples, than previously reported [6].

The solid product formed in reaction step (1) is presumed to be β-$CaSO_4 \cdot 1/2H_2O$ since the curves of steps (2) and (3) are identical to those observed in the differential thermogram of pure β-$CaSO_4 \cdot 1/2H_2O$ (Figure 3). Furthermore, pure β-$CaSO_4 \cdot 1/2H_2O$ can be prepared by removal of the stoichiometric amount of H_2O from $CaSO_4 \cdot 2H_2O$, if followed by an annealing treatment. The necessity of the annealing treatment does, however, suggest a more complicated reaction sequence could be taking place than the scheme outlined by steps (1) and (2).

The endothermic curve in the differential thermogram of α-$CaSO_4 \cdot 1/2H_2O$ (Figure 5) has the same shape and T_{peak} as the endothermic curve of β-$CaSO_4 \cdot 1/2H_2O$. The endothermic curve of α-$CaSO_4 \cdot 1/2H_2O$, however, is closely followed by an exothermic curve with T_{peak} of 217°C. Another difference is the lack of the exothermic curve of β-$CaSO_4 \cdot 1/2H_2O$ with $T_{peak} = 380°C$, in the thermogram of α-$CaSO_4 \cdot 1/2H_2O$. From the basis of DTA studies, however, no definite conclusions on structural differences between the two forms can be made.

4.1.2 Reduced Atmospheric Pressure in the DTA Cell

The effect of decreasing the bulk atmospheric pressure in the DTA cell on the differential thermograms of $CaSO_4 \cdot 2H_2O$, and α-and β-$CaSO_4 \cdot 1/2H_2O$ is discussed in this section. It is instructive to first examine the thermogram of $CaSO_4 \cdot 2H_2O$ and then compare the thermograms of α-and β-$CaSO_4 \cdot 1/2H_2O$.

Substantial decreases of the bulk atmospheric pressure within the DTA cell were found to significantly perturb the DTA curves of $CaSO_4 \cdot 2H_2O$. Results of this study are presented in Table 1 and Figure 2. T_{peak} of the first endothermic curve ($CaSO_4 \cdot 2H_2O_{(s)} \rightarrow \beta\text{-}CaSO_4 \cdot 1/2H_2O_{(s)} + H_2O_{(v)}$) was shifted from 150°C to 123°C when the bulk pressure was reduced from 760 Torr to near 1 Torr. T_{peak} of the second endothermic curve ($\beta\text{-}CaSO_4 \cdot 1/2H_2O_{(s)} \rightarrow \gamma\text{-}CaSO_{4(s)} + 1/2H_2O_{(v)}$) was shifted even more, being 197°C at 760 Torr and merging with the first endothermic curve when the bulk residual pressure approached 1 Torr. The position of the exothermic curve, attributed to the phase transformation of γ-$CaSO_4$ to β-$CaSO_4$, was not pressure dependent.

The mergence of the two endothermic curves of $CaSO_4 \cdot 2H_2O$ at bulk residual pressures approaching 1 Torr, is an interesting phenomenon that may be accounted for by several proposed mechanisms. According to one mechanism, two separate dehydration reactions are taking place when appreciable water vapor is in contact with the sample. Dehydration in vacuo, however, leads directly to the formation of γ-$CaSO_4$ and β-$CaSO_4 \cdot 1/2H_2O$ is not an intermediate product [7,8]. However, this is inconsistent with the findings of the present investigation that removal of 3/2 molecules of water from $CaSO_4 \cdot 2H_2O$ in vacuo yields an impure product, which is largely β-$CaSO_4 \cdot 1/2H_2O$. Furthermore, for the reasons previously stated in the experimental section of this report, although the bulk residual pressure in the DTA cell may be near 1 Torr, the water vapor pressure in contact with the sample is probably much higher.

A more firm explanation for the merging of the two endothermic curves is based on the van't Hoff equation

$$\frac{d\ln P}{dt} = \frac{\Delta H}{RT^2} .$$

In this equation ΔH is the heat of reaction at temperature T, and therefore is not a constant. The standard heat of reaction, ΔHo, is introduced by using the Kirchoff equation

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta C_p ,$$

thus

$$\Delta H = \Delta Ho + \int_{T_1}^{T_2} \Delta C_p dt$$

and

$$\frac{d\ln P}{dt} = \frac{\Delta Ho}{RT^2} + \frac{1}{RT^2} \int_{T_1}^{T_2} \Delta C_p dt .$$

The change in ΔC_p with dT is small in the temperature interval encountered in the present case so the mean value, $\overline{\Delta C_p}$, is used. Then the integrated form of the above equation becomes

$$\ln \frac{P_2}{P_1} = - \frac{\Delta Ho}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) + \frac{\overline{\Delta Cp}}{R} \ln \frac{T_2}{T_1} .$$

The pressure decrease necessary to shift T_{peak} of the second endothermic curve in the thermogram of $CaSO_4 \cdot 2H_2O$ from 197°C to 123°C can now be estimated by setting $T = T_{peak}$ and using the values of ΔHo and ΔC_p reported by Kelley, Southard and Anderson [2] for the reaction

$$\beta\text{-}CaSO_4 \cdot 1/2H_2O_{(s)} \longrightarrow \gamma\text{-}CaSO_{4(s)} + 1/2H_2O_{(v)} .$$

The calculated value

$P_2/P_1 = 0.25$

means a four fold decrease in the partial pressure of water vapor within the specimen tube can account for the shift in T_{peak} observed when the bulk pressure is decreased from 760 Torr to about 1 Torr. This calculated value can be considered only as an approximation to the actual situation within the specimen tube because of the non-rigorous treatment.

According to the present interpretation, a two step dehydration process is still taking place in vacuo, but is obscured by the overlapping of the two endothermic curves of $CaSO_4 \cdot 2H_2O$. The previously cited findings that β-$CaSO_4 \cdot 1/2H_2O$ is formed (among other products) from the dehydration in vacuo of $CaSO_4 \cdot 2H_2O$, is in agreement with this interpretation.

The endothermic curves of both α- and β-$CaSO_4 \cdot 1/2H_2O$ have similar T_{peak} dependence on pressure (Table 2 and Figures 4 and 6) as the second endothermic curve of $CaSO_4 \cdot 2H_2O$. Values of T_{peak} for these curves obtained with the same pressure conditions vary, primarily, because of differences in packing characteristics.

It is surprising that the location of an exotherm attributed to a lattice change would be significantly perturbed by changes in the bulk pressure, as observed for the exothermic curve of α-$CaSO_4 \cdot 1/2H_2O$. Obviously, the location of this exotherm is not directly pressure dependent but apparently is determined by the degree of completion of the preceding dehydration process. When the dehydration reaction of α-$CaSO_4 \cdot 1/2H_2O$ has reached a certain stage a thermodynamic unstable lattice structure is possibly produced which rearranges to a more stable form, giving an exothermic DTA curve.

4.2 Formation of α- and β-$CaSO_4 \cdot 1/2H_2O$

The present study appears to confirm the mechanisms proposed by Kuntze [9] to account for the formation of α- and β-$CaSO_4 \cdot 1/2H_2O$. According to his proposals, α-$CaSO_4 \cdot 1/2H_2O$ is formed by methods involving crystallization such as precipitation from solution or autoclaving, while β-$CaSO_4 \cdot 1/2H_2O$ is formed by dehydrations methods independent of the ambient water vapor pressure.

McAdie [10] has suggested that the designations "α" and "β" represent the terminals of a $CaSO_4 \cdot 1/2H_2O$ series and a product would have properties of both proportional to the percentage of terminal present. By DTA techniques the presence of both forms can be identified in an artificial mixture as shown in Figure 7. It is interesting, therefore, that the DTA curves of products formed by the dehydration, in vacuo and at atmospheric pressure, of $CaSO_4 \cdot 2H_2O$ clearly indicates lack of α-$CaSO_4 \cdot 1/2H_2O$. Although the results of the present study are inconclusive with regards to this matter, they do point to the need for further study of the α- and β-terminal concept.

The preparation of β-$CaSO_4 \cdot 1/2H_2O$ carried out by dehydrating $CaSO_4 \cdot 2H_2O$ to anhydrous γ-$CaSO_4$ which was then allowed to rehydrate at room temperature in laboratory air resulted in a product containing slightly more than the stoichiometric amount of H_2O. Theoretically, n (where n is the number of H_2O molecules per molecule of $CaSO_4$) should be 0.50, but was found to range from 0.54 to 0.57. The extra quantity of H_2O, possibly, can have zeolitic character, while the larger portion is lattice water. This interpretation agrees with the finding of Saito [11] that NMR studies suggests two forms of H_2O exist in $CaSO_4 \cdot 1/2H_2O$, one which is zeolitic H_2O.

4.3 Dehydration of $CaSO_4 \cdot 2H_2O$ under Static Conditions

Exposure of $CaSO_4 \cdot 2H_2O$ to static conditions of temperature and water vapor pressure for extended periods resulted in complete dehydration (see Section 3.7 and Figure 10). The product can possibly be characterized as having a meta-stable lattice structure which slowly transforms into the γ-$CaSO_4$ lattice. The complete dehydration at 165°C is not surprising as a calculation of $\Delta F°$ at 165°C for the process $CaSO_4 \cdot 2H_2O_{(s)} \longrightarrow \gamma\text{-}CaSO_{4(s)} + 1/2H_2O_{(v)}$, using the relationship of $\Delta F°$ versus temperature derived by Kelley, Southard and Anderson [2], gives the value of 2.2 K cal/mole. At 165°C and at standard conditions, therefore, $CaSO_4 \cdot 2H_2O$ is thermodynamic unstable with respect to γ-$CaSO_4$.

5. SUMMARY AND CONCLUSIONS

The contention that two forms of $CaSO_4 \cdot 1/2H_2O$, α and β, exist is apparently supported by DTA Studies. However, no insight to structual differences in the two forms are obtainable by DTA studies.

The peak temperatures of the endothermic curves of $CaSO_4 \cdot 2H_2O$, α and β-$CaSO_4 \cdot 1/2H_2O$, and the exothermic curve of α-$CaSO_4 \cdot 1/2H_2O$ are pressure dependent, shifting to lower temperatures as the residual pressure within the DTA cell decreases. This phenomenon can be explained on the basis of the van't Hoff equation.

The α-form of $CaSO_4 \cdot 1/2H_2O$ can be prepared by methods involving crystallization such as precipitation from solution. While dehydration of $CaSO_4 \cdot 2H_2O$ in air, followed by rehydration, and partial dehydration in vacuo lead to the formation of β-$CaSO_4 \cdot 1/2H_2O$. The former method gives a product that contains slightly more than the theoretical amount of H_2O, for β-$CaSO_4 \cdot 1/2H_2O$, the excess possibly being zeolitic water.

The analysis of every preparation of either α- or β-$CaSO_4 \cdot 1/2H_2O$ is strongly urged as it is not a simple matter to obtain pure products containing the stoichiometric amount of H_2O.

6. Acknowledgement

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Table 1. Peak Temperatures of Endothermic DTA Curves of $CaSO_4 \cdot 2H_2O$

Bulk Pressure (Torr)	Peak Temperature (°C)	
	1	2
760	150	197
590	147	179
380	144	162
1	123	123-126 [a]

[a] Exact location difficult to estimate as curves 1 and 2 overlap

Table 2. Peak Temperature of DTA Curves of α- and β-$CaSO_4 \cdot 1/2H_2O$

Bulk Pressure (Torr)	Peak Temperature (°C) Endotherm	Peak Temperature (°C) Exotherm
	α-$CaSO_4 \cdot 1/2H_2O$	
760	198	217
380	182	200
1	132	163
	β-$CaSO_4 \cdot 1/2H_2O$	
760	195	375
1	132	375

CAPTIONS FOR FIGURES

Figure 1. DTA curve of $CaSO_4 \cdot 2H_2O$ with $N_{2(g)}$ at atmospheric pressure in the DTA Cell.

Figure 2. Differential thermograms of $CaSO_4 \cdot 2H_2O$ with reduce pressures in the DTA cell. The pressures with runs A, B, and C were 590, 380 and about 1 Torr, respectively.

Figure 3. DTA curve of β-$CaSO_4 \cdot 1/2H_2O$ with $N_{2(g)}$ at atmospheric pressure in the DTA cell.

Figure 4. DTA curve of β-$CaSO_4 \cdot 1/2H_2O$ with a pressure near 1 Torr in the DTA cell.

Figure 5. DTA curve of α-$CaSO_4 \cdot 1/2H_2O$ with $N_{2(g)}$ at atmospheric pressure in the DTA cell.

Figure 6. Differential thermograms of α-$CaSO_4 \cdot 1/2H_2O$ with reduced pressures in the DTA cell. Pressures were 380 and about 1 Torr, respectively, with runs A and B.

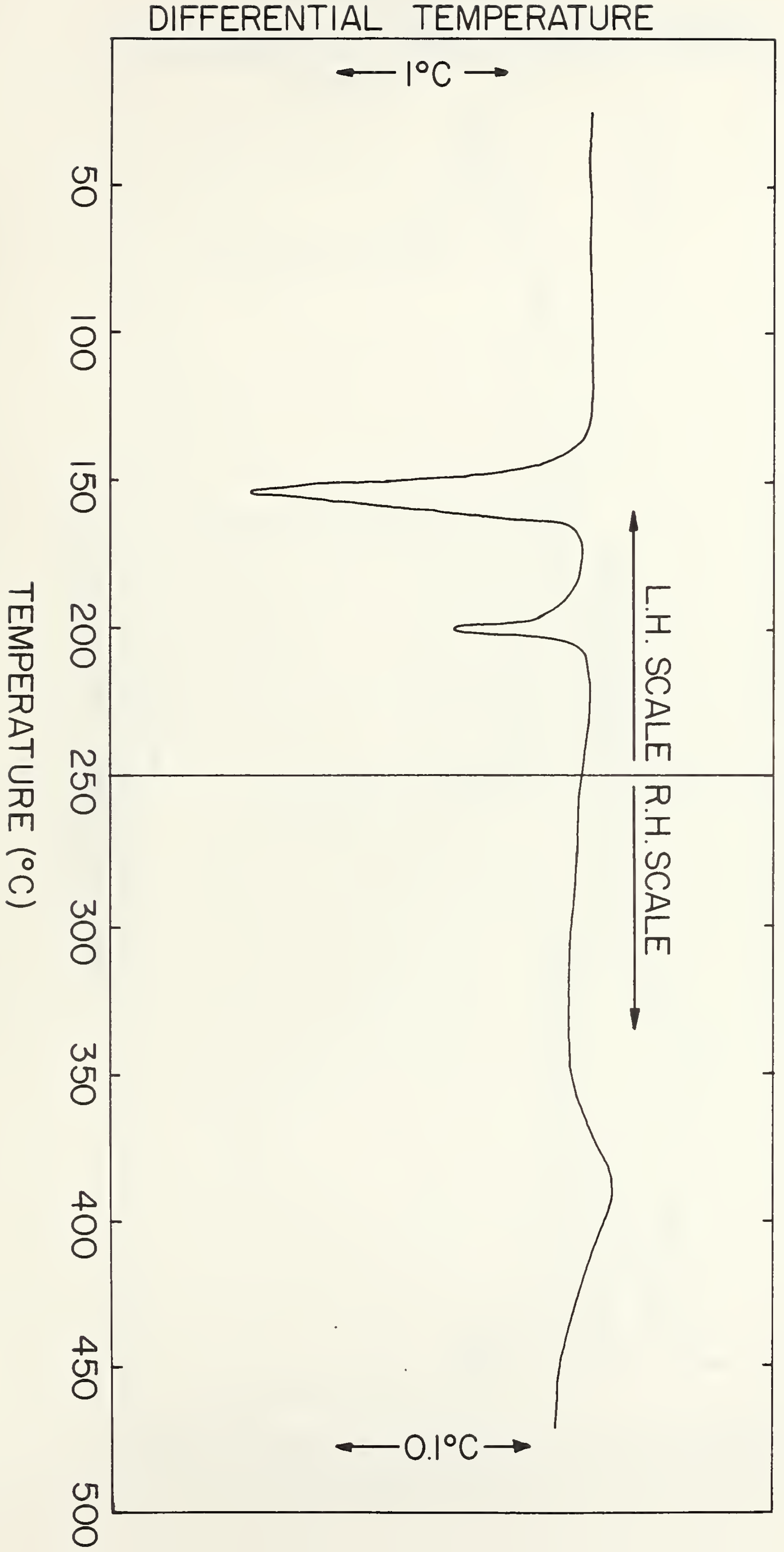
Figure 7. DTA curve of an equal molar mixture of α- and β-$CaSO_4 \cdot 1/2H_2O$.

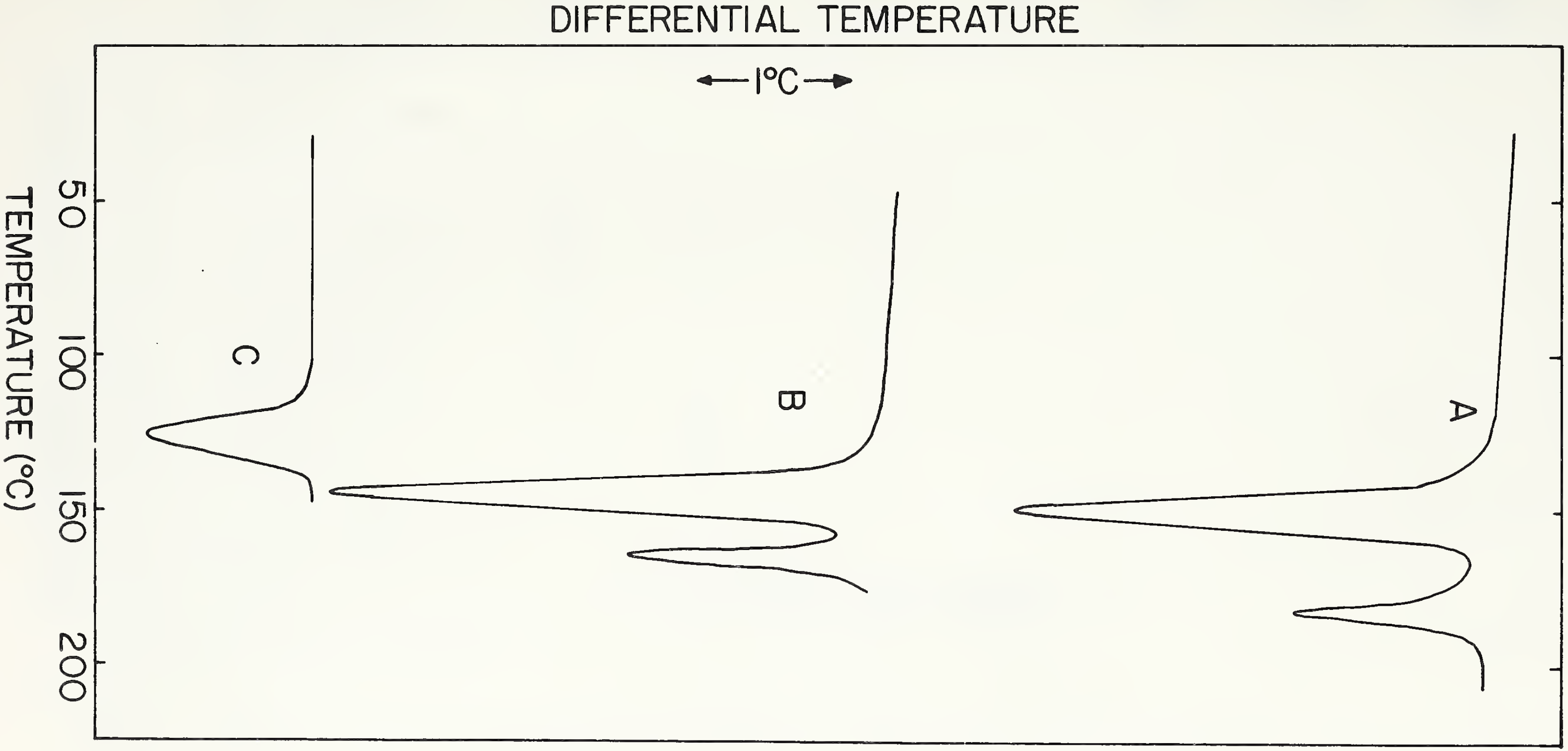
Figure 8. DTA curves of products resulting from removal, in vacuo, of stoichiometric amount of H_2O from $CaSO_4 \cdot 2H_2O$ to form β-$CaSO_4 \cdot 1/2H_2O$. Dehydration temperatures and annealing conditions were as follows:

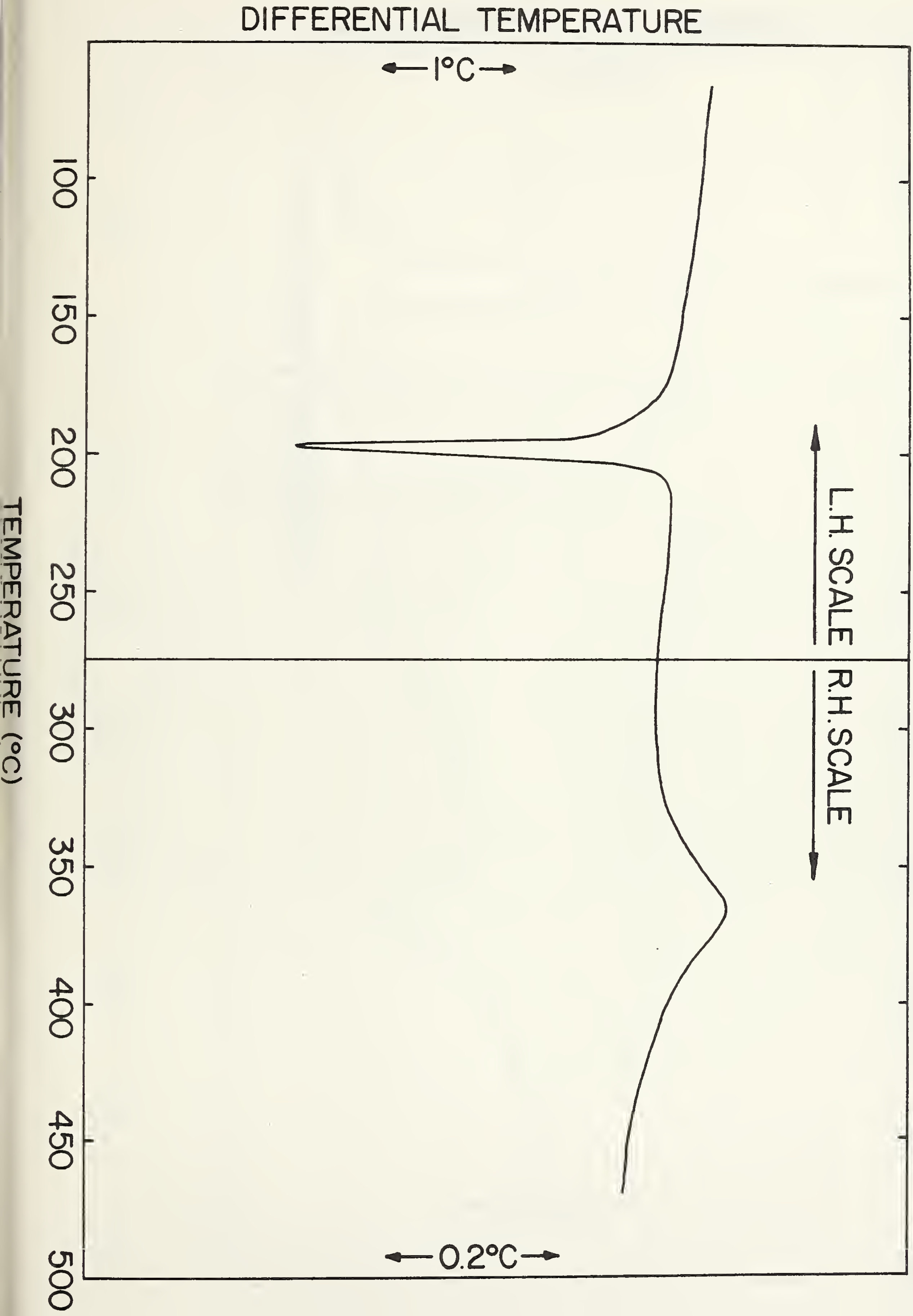
A. 100°C, annealed for 60 hours;
B. 100°C, no annealing;
C. 75°C, no annealing;
D. 50°C, no annealing.

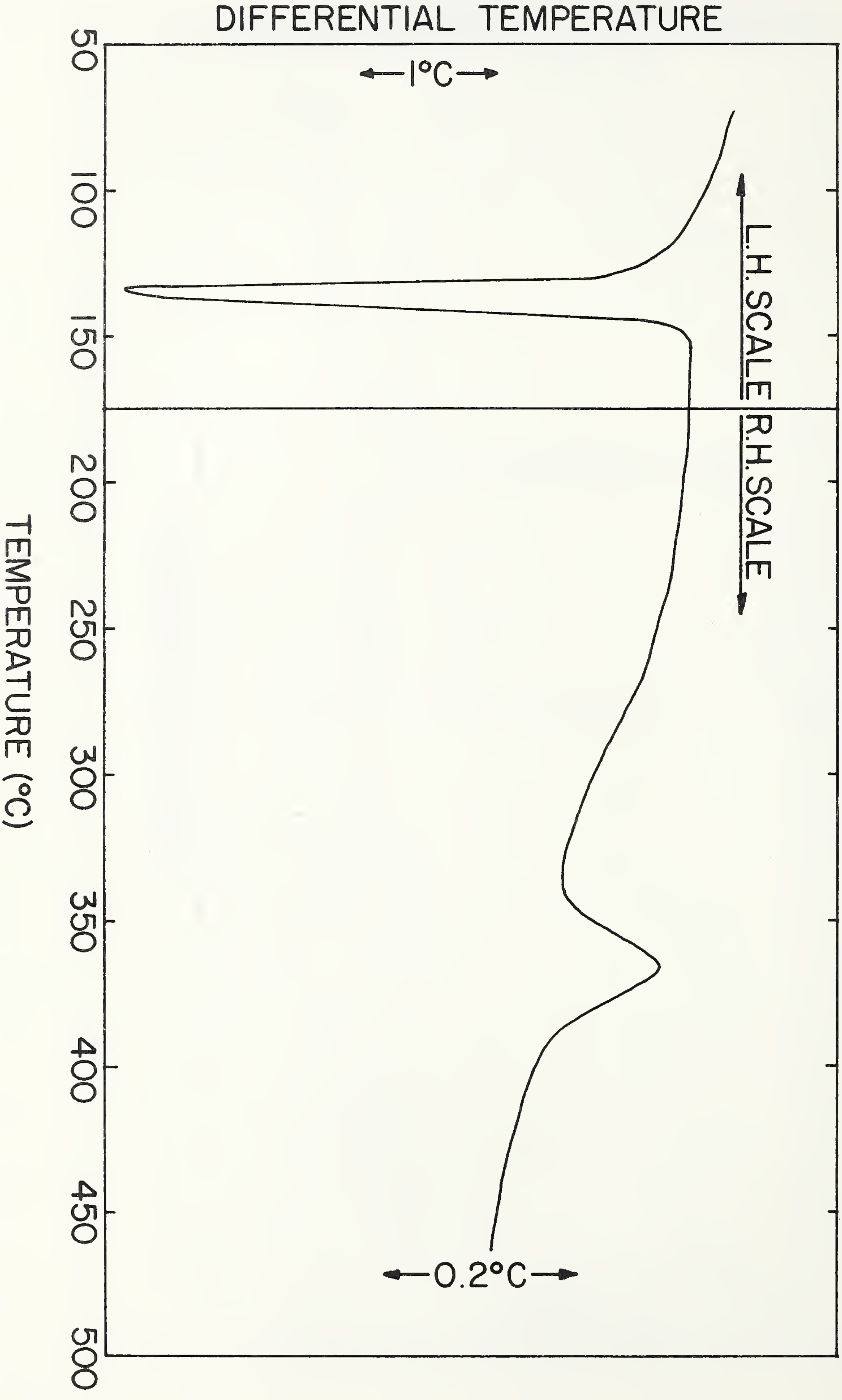
Figure 9. Differential thermogram of a precipitate of α-$CaSO_4 \cdot 1/2H_2O$ aged for 4 hours at 50°C.

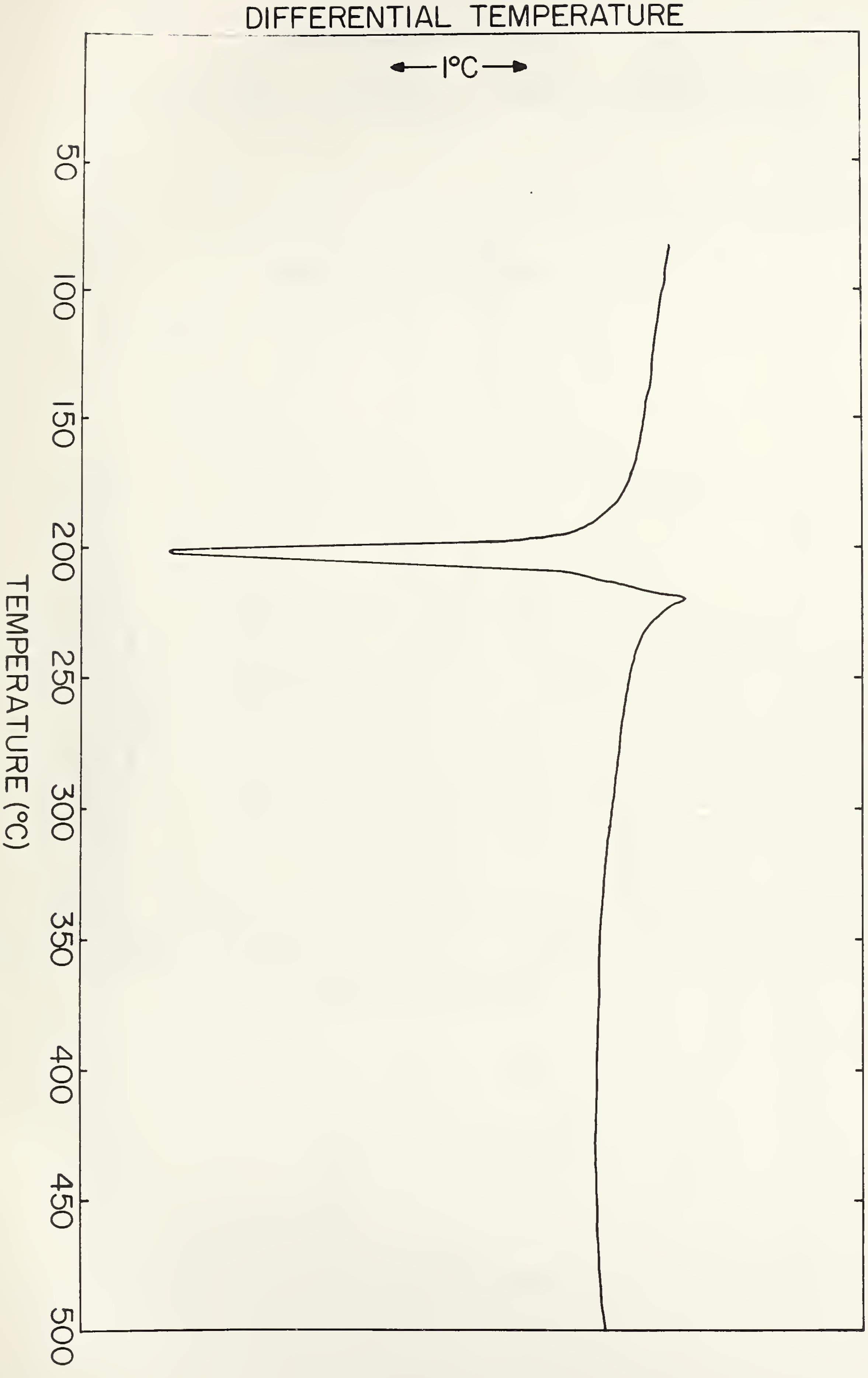
Figure 10. DTA curves of the product resulting from heating together 0.243 millimoles of $CaSO_4 \cdot 2H_2O$ and 730 Torr of $H_2O_{(v)}$ at 165°C for 66 hours, recorded immediately after products had cooled to room temperature (A), and at four (B), five (C), six (D), and forty days (E) later.

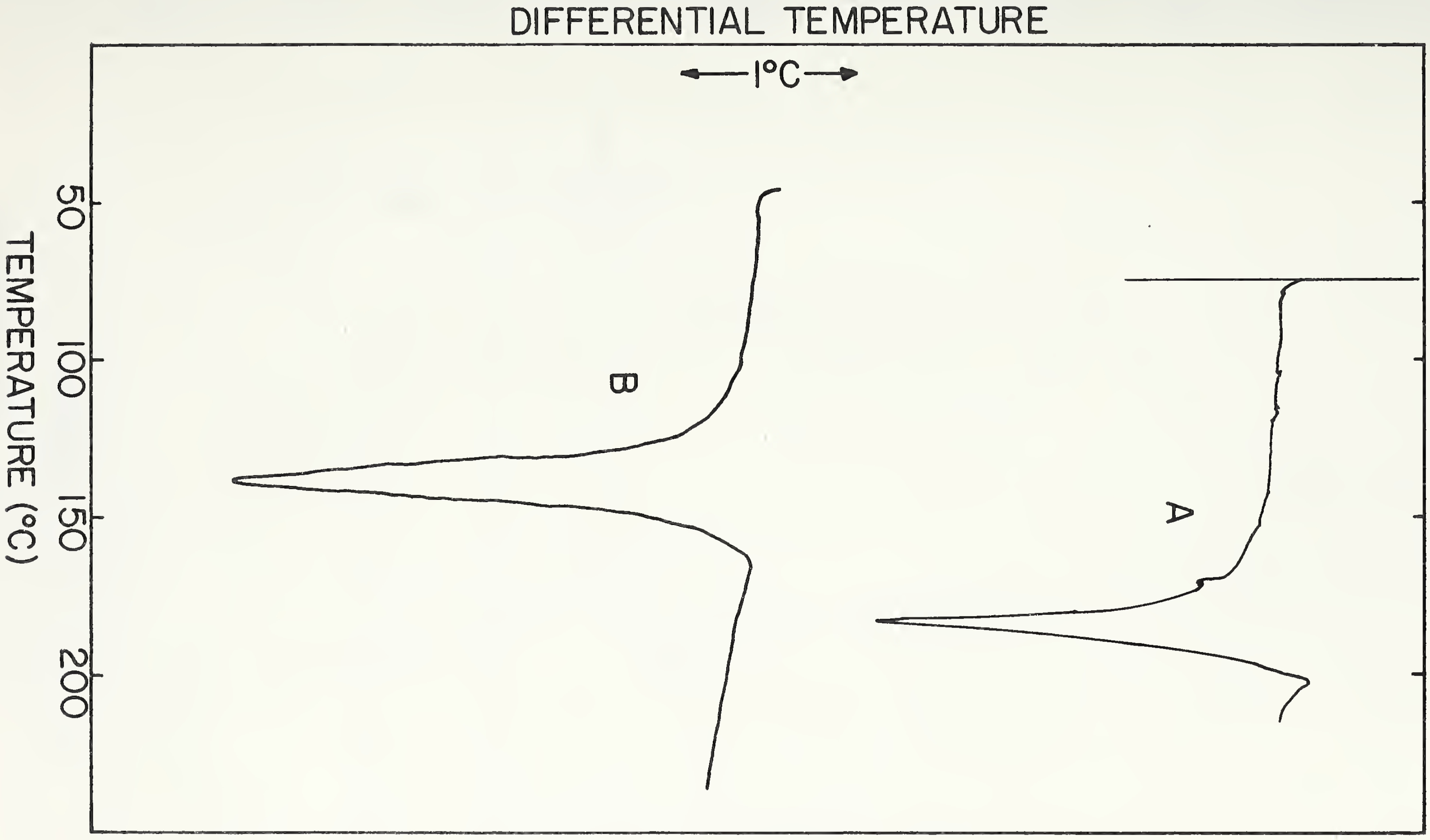

DIFFERENTIAL TEMPERATURE
1°C
0.1°C
L.H. SCALE
R.H. SCALE
50
100
150
200
250
300
350
400
450
500
TEMPERATURE (°C)

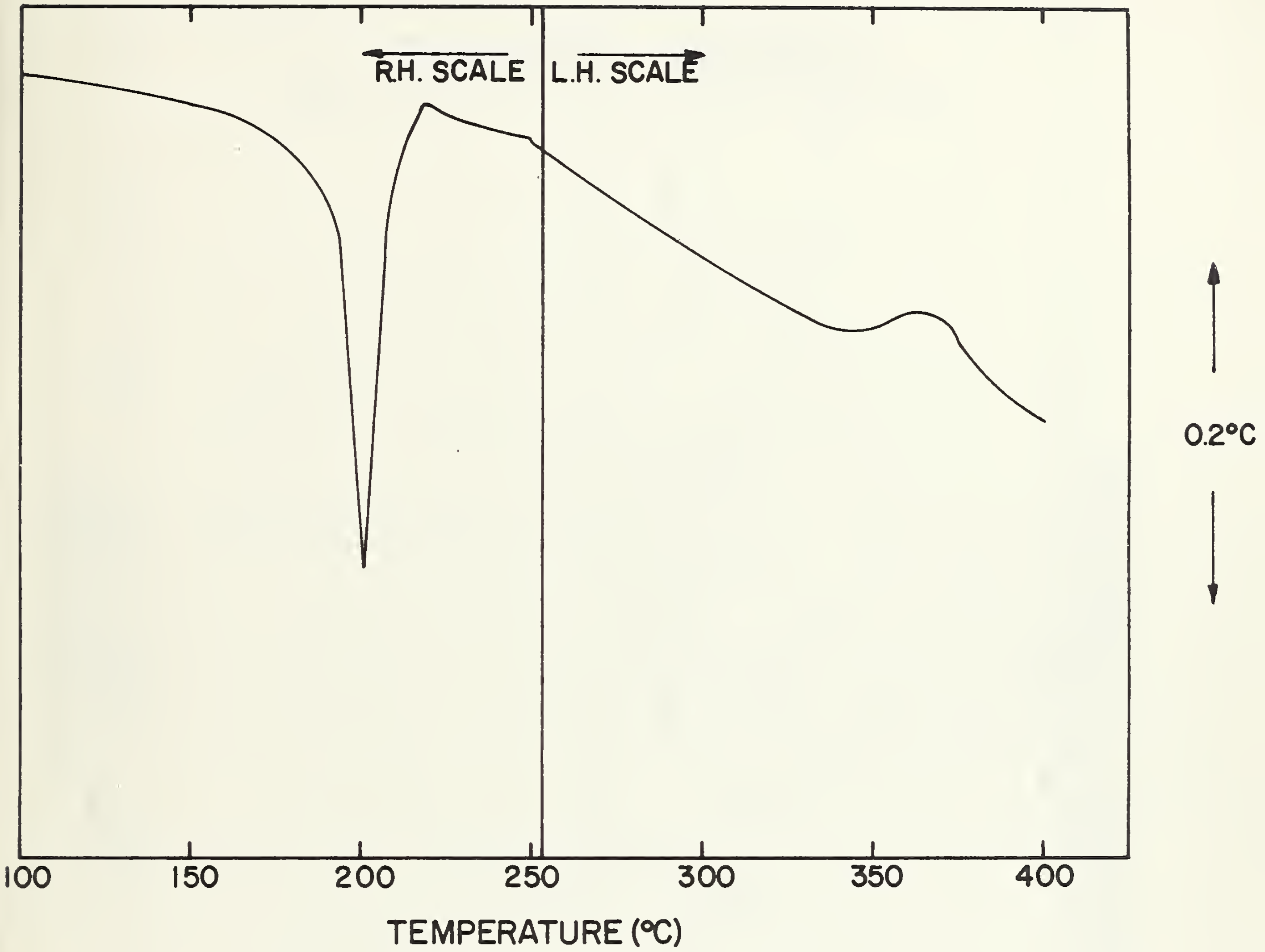

DIFFERENTIAL TEMPERATURE
1°C
TEMPERATURE (°C)
50
100
150
200
A
B
C

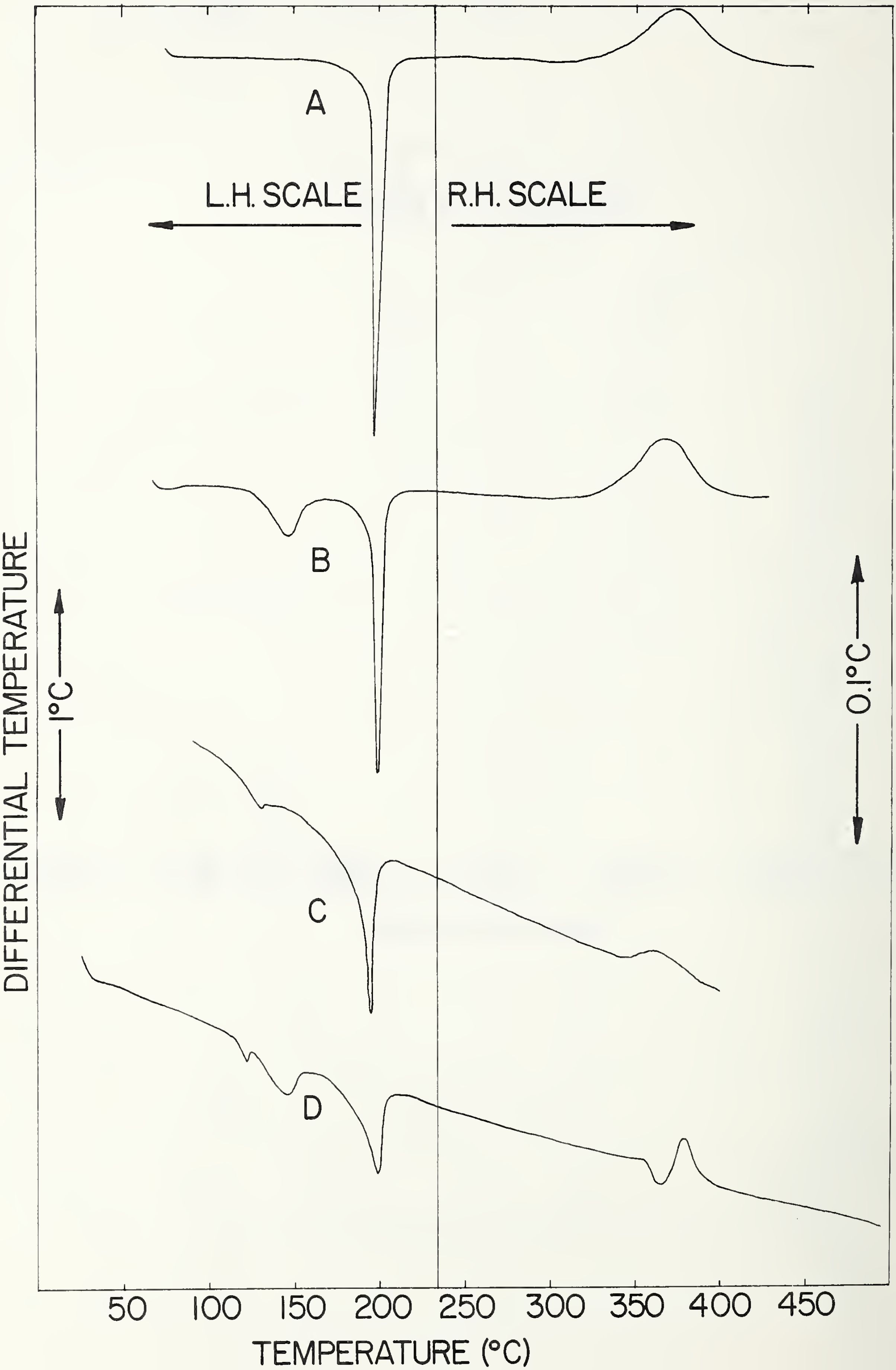

DIFFERENTIAL TEMPERATURE
←1°C→
L.H. SCALE
R.H. SCALE
←0.2°C→
100
150
200
250
300
350
400
450
500
TEMPERATURE (°C)

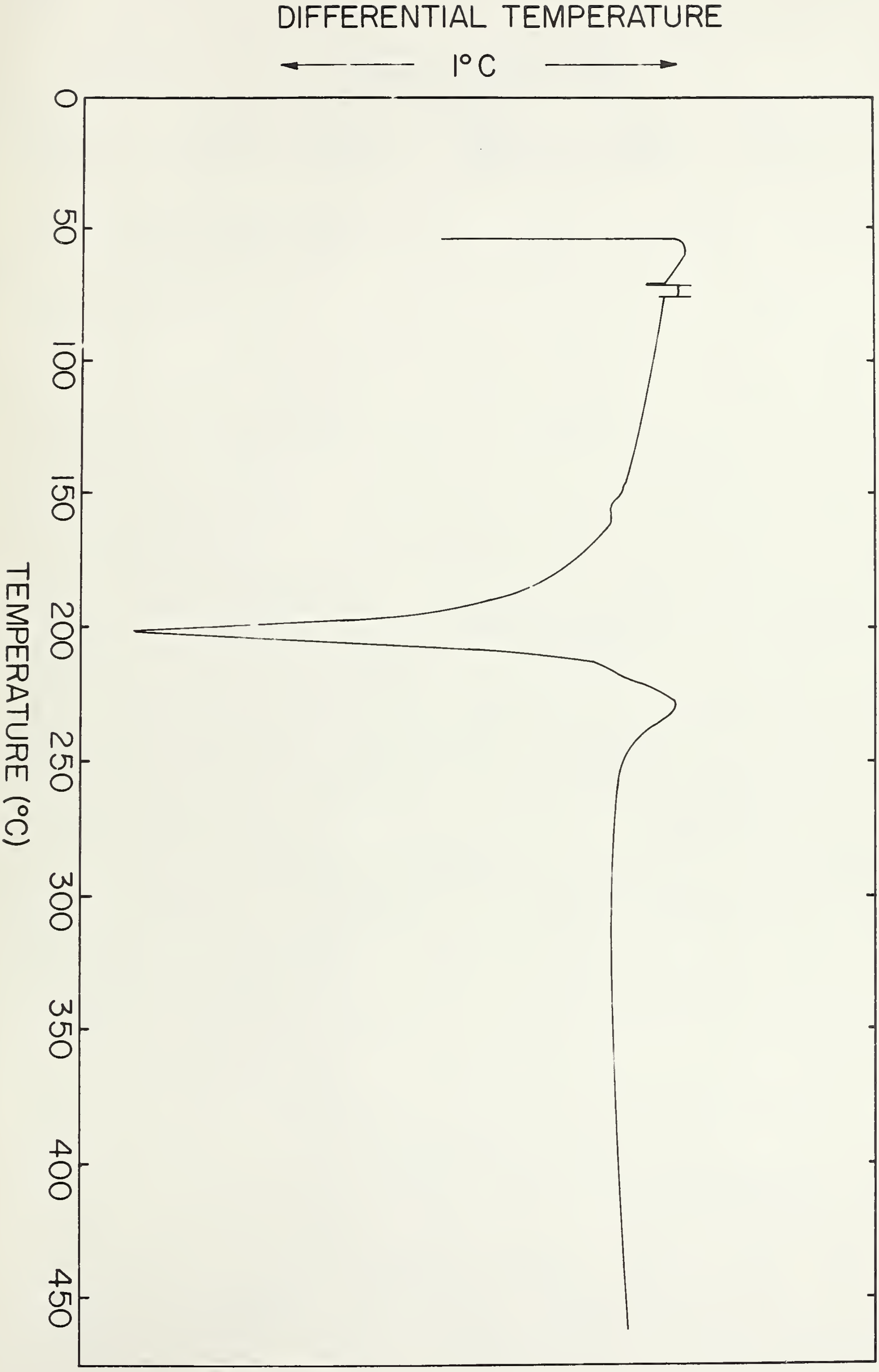

DIFFERENTIAL TEMPERATURE
←1°C→
L.H. SCALE
R.H. SCALE
←0.2°C→
TEMPERATURE (°C)
50
100
150
200
250
300
350
400
450
500

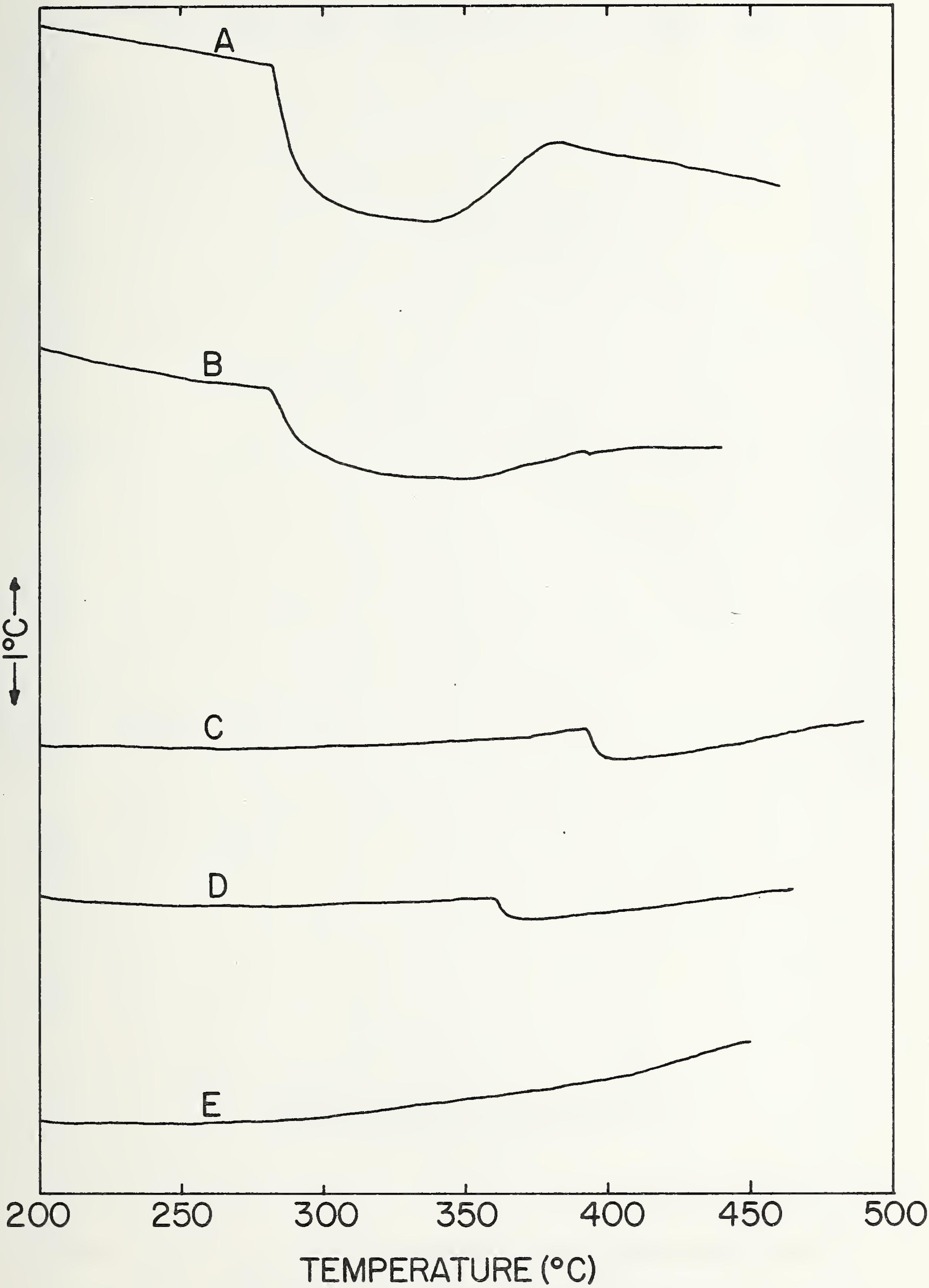

DIFFERENTIAL TEMPERATURE
←1°C→
50
100
150
200
250
300
350
400
450
500
TEMPERATURE (°C)

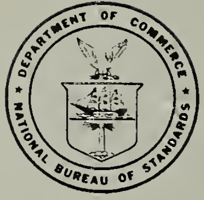

DIFFERENTIAL TEMPERATURE
←1°C→
TEMPERATURE (°C)
50
100
150
200
B
A


R.H. SCALE
L.H. SCALE
0.2°C
100
150
200
250
300
350
400
TEMPERATURE (°C)


A
L.H. SCALE
R.H. SCALE
B
C
D
DIFFERENTIAL TEMPERATURE
1°C
0.1°C
50
100
150
200
250
300
350
400
450
TEMPERATURE (°C)


DIFFERENTIAL TEMPERATURE
1°C
0
50
100
150
200
250
300
350
400
450
TEMPERATURE (°C)


A
B
C
D
E
1°C
200
250
300
350
400
450
500
TEMPERATURE (°C)



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