HEATS OF TRANSITION AND MELTING OF SODIUM NITRATE BY DIFFERENTIAL SCANNING CALORIMETRY: USE OF INDIUM AND SODIUM NITRATE AS CALIBRATION SUBSTANCES

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ABSTRACT

Information about the heat of melting of indium is summarized and a best value of the ΔH_m is selected for use in calibrating differential scanning calorimeters. We have reviewed earlier determinations of the heat of melting of sodium nitrate and have made new measurements with a Perkin-Elmer DSC-2, all leading to a selected ΔH_m that can also be used for subsequent calibration. Further DSC measurements have led to a ΔH_{tr} for the solid—solid transition that occurs 31° below the melting point. Finally, we have established that "ordinary" care with sample handling is sufficient to avoid problems due to water pick-up by sodium nitrate.

INTRODUCTION

Several investigations have shown in recent years that thermodynamically useful results can be obtained by way of differential scanning calorimetry. For example, Mills and Richardson [1] have used this method to obtain useful heat capacities of solids. Also, we have used differential scanning calorimetry to obtain [2] heats of melting of indium and of sodium nitrate. The apparent high accuracy of these results led us to suggest [2] that the commonly used heat of melting of indium should be revised and that sodium nitrate might be a useful calibration substance in differential scanning calorimetry.

In this paper we report the results of some further measurements on sodium nitrate and also call attention to other recent results that bear on the selection of the best heat of melting of indium.

EXPERIMENTAL

All of our calorimetric measurements have been made with a Perkin-Elmer DSC-2 differential scanning calorimeter with output recorded on a Perkin-Elmer single channel multi-range thermal analysis recorder. Aluminum

pans supplied by Perkin-Elmer were used. There was no evidence of reaction of pans with either sodium nitrate or indium.

The scanning calorimeter was operated with heating rates from +1.25 to +160°C min^{-1} and with cooling rates from −1.25 to −40°C min^{-1}. Range selections varied from 1 to 10 mcal sec^{-1}. Recorder sensitivity was 10 mV for full-scale deflection.

Areas under peaks on recorder traces were obtained with a Hruden planimeter and also by square counts. Pan and sample weighings were made with a Cahn Model 4700 automatic electrobalance, using an empty pan as a tare. Sample sizes ranged from 3 to 9 mg.

Samples of indium were supplied by Perkin-Elmer for use as a calibration substance. Samples of sodium nitrate were prepared as described previously [2] and also more simply by heating for 2 h at 120°C and then storing in a desiccator. "Wet" samples of sodium nitrate were also prepared as follows. Previously dried sodium nitrate was placed in the bottom of a beaker, which was then covered with a watch glass and allowed to stand open to the atmosphere at room temperature (relative humidity typically ranges from a low of 10% in winter up to about 45% in summer) for 3 weeks. The uncovered beaker was then stored in a desiccator containing water in the bottom for 100 min.

RESULTS

We have calibrated our DSC by way of the heat of melting of indium, which requires a selection of the best available value for this quantity. As part of our earlier work [2] on the heat of melting of indium, we called attention to previously reported values for this heat of melting ranging from ΔH_m = 6.52 to 7.01 cal g^{-1}. More recently, Grønvold [3] has cited values ranging from ΔH_m = 6.52 to 7.93 cal g^{-1}. In spite of the wide range of these earlier results, it is now possible to select a best value with considerable confidence on the basis of the following.

First, our earlier DSC measurements [2] led to ΔH_m = 6.83$_7$ cal g^{-1} for indium. Next, Richardson has informed us that improved analysis of the DSC results reported previously [4] leads to a new ΔH_m = 6.85 cal g^{-1} instead of their originally reported ΔH_m = 6.97 cal g^{-1}. By way of Dr. Richardson, Dr. J.F. Martin (National Physical Laboratory, Gt. Britain) has informed us that his recent measurements with an adiabatic calorimeter have led to ΔH_m = 6.84 cal g^{-1} for indium. Finally, Grønvold [3] has also made measurements with an adiabatic calorimeter and has reported ΔH_m = 3283 ± 7 J mole^{-1}, which corresponds to ΔH_m = 6.834 ± 0.015 cal g^{-1}. It is now clear that the results of all four of these recent investigations are in excellent agreement. Because of our considerable respect for both the reliability and the accuracy of Grønvold's work, we choose his [3] ΔH_m = 3283 J mole^{-1} = 28.59 J g^{-1} = 784.7 cal mole^{-1} = 6.834 cal g^{-1} as the basis for our calibration.

We now turn to consideration of the heat of melting of sodium nitrate. A summary of a considerable number of previous results is given in Table 1,

TABLE 1

Heats of melting of sodium nitrate ($NaNO_3$)

ΔH_m (cal mole^{-1})	Ref.
3690	5
3596	6
3780	7
3490	8
3696	9
3600	10
3730	11
3564	12
3520	13
3570	14
3614	2
3586 ± 42 [a]	This work

[a] Standard deviation, based on nine runs. The uncertainty in our present value is larger than for our earlier [2] value, primarily because of differences in DSC heads used in the different series of measurements.

which also includes the result of our most recent investigation. We previously [2] selected ΔH_m = 3615 ± 50 cal mole^{-1} as the best available value for the heat of melting of sodium nitrate. Neither our present results nor the additional results cited in Table 1 that were not considered before justify any substantial change in the previously [2] selected ΔH_m = 3615 cal mole^{-1} for indium. This value is also usefully expressed as ΔH_m = 42.53 cal g^{-1} = 15125 J mole^{-1} = 177.95 J g^{-1}.

It has been suggested [15] that sodium nitrate might not be a satisfactory calibration substance because it is "somewhat hygroscopic" and because of the solid—solid phase change that occurs 31° below the melting point. We now turn to consideration of both of these points, as follows.

First, in our previous experiments [2] and also in those being reported here, we had no difficulty with slow mass increases during weighing due to capture of water by sodium nitrate. Because the relative humidity in our laboratory (typically 10—45%) is lower than in some other laboratories, we also exposed samples of previously dried sodium nitrate for long times to atmospheric moisture and for shorter times to saturated or nearly saturated air, as described in the experimental section. The largest mass increase that we observed amounted to only 0.6% h^{-1}. This observation along with our previous experiences [2,10,14,16] with sodium nitrate strongly suggest that "ordinary" care in handling this substance is sufficient.

In our earlier experiments [2] we made no effort to measure the heat of the phase transition that occurs 31° below the melting point. Some of our measurements were made with samples that were heated fairly rapidly to about 280°C (above the temperature of the solid—solid transition), held at this temperature for several minutes, and then scanned through the melting point. It is unlikely that the results of these measurements were influenced

by the solid—solid transition. Other measurements were made by cooling already melted sodium nitrate to about 280°C (above the solid—solid transition point) and then scanning through the melting point. It is important to note that results for the heat of melting obtained in this way, which certainly avoids any problems with the solid—solid transition, were in excellent agreement with results obtained as described above. It is also worth pointing out that we have scanned from temperatures above the melting point to temperatures below the melting point to obtain heats of freezing (larger scatter than for heats of melting obtained by way of increasing temperature scans) that agree well with all of our other values. For all of these reasons we have been quite confident that our previous results were not "contaminated" with the heat of transition. The excellent agreement of our results [2] with several other heats of melting cited in Table 1 provides further support for our confidence in the "non-contamination" and also the general reliability of our previous results. Our present results (Table 1), which we will discuss later in connection with the heat of transition, are also in good agreement with our earlier results [2].

Partly because of the question that has been raised [15] about the possible influence of the solid—solid transition on the reported heat of melting, we have carried out new measurements intended to yield a value for this heat of transition. Another reason for undertaking these measurements is that results of previous investigations are in very poor agreement.

Previously reported enthalpies of the solid—solid transition in sodium nitrate at 276°C are the following, in chronological order. The first measurements that we know of are those of Miekk-oja [17]; Janz et al. [13] have cited an entropy of transition from Miekk-oja [17] that corresponds to $\Delta H_{tr} = 879$ cal mole^{-1}. Subsequent measurements by Mustajoki [8] led to $\Delta H_{tr} = 944$ cal mole^{-1}. Next, Janz et al. [13] found $\Delta H_{tr} = 174$ cal mole^{-1}. Finally, we have $\Delta H_{tr} = 920$ cal mole^{-1} from Riccardi and Sinistri [18].

Our measurements (23 runs) on sodium nitrate lead to $\Delta H_{tr} = 815$ cal mole^{-1}, with standard deviation 185 cal mole^{-1}. This result is a poor agreement with that of Janz et al. [13], but in fair agreement with the results of the other investigators [8,17,18] cited above.

We now consider the question of "overlap" of the solid—solid transition with melting, as investigated by making scanning runs at different heating rates. First, we always found two distinct peaks, one corresponding to the solid—solid transition and one due to melting, at all scan rates up to and including +160°C min^{-1}. However, it was found with the highest scan rates that there was overlap of the tail of the first peak with the beginning of the second so that evaluation of two separate heats was quite inaccurate. Adequate separation of the two peaks for separate evaluation of the two heats was achieved at scan rates less than about 40°C min^{-1}. Measurements leading to our ΔH_m (Table 1) were at scan rates from +1.25 to +20°C min^{-1}.

Finally, it may be of interest to point out that it is possible to obtain the heat of transition by way of measurements on samples of unknown mass, using the DSC without separate calibration. We have done this by using the ΔH_m of $NaNO_3$ as an "internal" calibration standard for each run, in which case the mass of $NaNO_3$ cancels out of the following calculation of the

desired ΔH_{tr}. The ΔH_{tr} obtained in this way by analyzing the 23 runs cited in Table 1 is in accord with our ΔH_{tr} reported earlier in this paper.

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