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HEATS OF MELTING OF SODIUM NITRATE AND INDIUM BY DIFFERENTIAL SCANNING CALORIMETRY: A SUGGESTION FOR A NEW CALIBRATION SUBSTANCE

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ABSTRACT

Measurements with a Perkin-Elmer DSC-2 differential scanning calorimeter that has been calibrated with indium, tin, and lead have yielded values for the heat of melting of sodium nitrate. Analysis of these results along with those from earlier investigations gives ΔH_m = 3615 cal mol^{-1} as a recommended "best" value for the heat of melting of $NaNO_3$. The consistency of our results over a period of three years in which many samples were investigated, in combination with results of earlier investigations, leads us to suggest that $NaNO_3$ is a useful substance for calibration of differential scanning calorimeters. Results of our measurements of the heat of melting of indium are presented and discussed in relation to earlier investigations.

INTRODUCTION

Although differential scanning calorimetry is now well known as a convenient technique for obtaining several kinds of useful information, "thermodynamicists" have been generally cautious or even reluctant about applying this technique to determination of thermodynamic properties. Because of the potential usefulness of differential scanning calorimetry for determining thermodynamic properties, we are undertaking several investigations intended to establish just how good (or bad) this method is for such work. In this paper, we report results of our measurements of the heat of melting of sodium nitrate and compare our results with those from several earlier investigations. Our results demonstrate that it is possible to obtain an accurate and reliable heat of melting of this substance by differential scanning calorimetry. On the basis of our results and those of earlier investigators, we suggest that sodium nitrate can be used as a calibration substance for differential scanning calorimetry. We also present some information on the heat of melting of indium.

Before proceeding with the description of our work on heats of melting, we note that Mills[1] has demonstrated recently that differential scanning calorimetry can lead to thermodynamically useful heat capacities of solids.

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. Measurements were made with several batches of aluminium sample pans supplied by Perkin-Elmer. We have made measurements with both sealed and unsealed (crimped) pans, with indistinguishable results. There was no evidence of reaction of pans with any of the substances we have investigated, except for some reaction of $NaNO_3$ with pans from just one of the batches supplied by Perkin-Elmer.

Pan and sample weighings were made with a Cahn Model 4700 automatic electrobalance using an empty pan as a tare. Sample sizes ranged from 4 to 7 mg, weighed with an uncertainty less than 0.1%.

Samples of lead, tin, and indium were supplied by Perkin-Elmer to be used for calibration of the DSC.

At various times (1975–1977) we have worked with five different lots of analytical reagent grade sodium nitrate from BDH. Several separate samples were prepared from this material by drying at 100°C and at 200°C for periods ranging from 10 to 90 days. Still other samples were prepared by recrystallizing portions of the original $NaNO_3$ from very dilute aqueous nitric acid and then drying over P_2O_5 for periods ranging from 10 to 30 days.

Measurements were made with heating rates ranging from 2.5 to 20 K min^{-1}. Range selections on the DSC varied from 2 to 10 mcal sec^{-1}. Recorder sensitivities were varied from 10 to 50 mV for full-scale deflection. Within all of these ranges, we observed no systematic variations in results of calibrations with metals or in results of measurements on $NaNO_3$.

Baselines were consistently linear and flat after "optimizing" the instrument as specified in the Perkin-Elmer operating manual. Areas under peaks on recorder traces were obtained with a Hruden planimeter as averages of 10 evaluations; standard deviations of such areas were typically about 0.1%. Areas under peaks from some runs were also obtained by square counts. Agreement of these areas with areas obtained with the planimeter was generally within 0.2%, with the worst disagreement amounting to 0.5%.

RESULTS

Calibration of our DSC by way of measurements on melting of indium, tin, and lead is based on selected values for the heats of melting of these substances as described below.

For tin (m.p. = 505 K) we have a heat of melting ΔH_m = 14.45 cal g^{-1} (= 1715 cal mol^{-1}) from Perkin-Elmer. Kelley[2] listed ΔH_m = 1720 cal mol^{-1} (= 14.49 cal g^{-1}) as his selected "best" value.

For lead (m.p. = 601 K) we have ΔH_m = 5.50 cal g^{-1} (= 1140 cal mol^{-1})

from Perkin-Elmer. Kelley[2] has also selected ΔH_m = 1140 cal mol^{-1}. We adopt this value, which is based on the apparently excellent work of Douglas and Dever[3]. We also note that Dosch and Wendlandt[4] have reported ΔH_m = 5.6 cal g^{-1} for lead.

For indium (m.p. = 430 K) we have a heat of melting ΔH_m = 6.80 cal g^{-1} (= 781 cal mol^{-1}) from Perkin-Elmer. This value is in good agreement with ΔH_m = 780 cal mol^{-1} (= 6.79 cal g^{-1}) listed by Kelley[2] as his selected "best" value. More recently, Richardson and Savill[5] have cited nine investigations leading to heats of melting ranging from ΔH_m = 3.13 kJ mol^{-1} (= 6.52 cal g^{-1}) to ΔH_m = 3.37 kJ mol^{-1} (= 7.01 cal g^{-1}). Their own[5] careful DSC measurements, based on heat capacity calibrations, led them to report ΔH_m = 3.35 kJ mol^{-1} (= 801 cal mol^{-1} = 6.97 cal g^{-1}) for the heat of melting of indium. Because we have no immediate way of choosing a "best" value for the heat of melting of indium to be used in our calibrations, we shall begin by using two reasonable values, one from Kelley[2] (ΔH_m = 6.79 cal g^{-1}) and one from Richardson and Savill[5] (ΔH_m = 6.97 cal g^{-1}). Still another value for the heat of melting of indium can be obtained from the results of our own measurements as follows. During the course of our research directed toward determination of the heat of melting of sodium nitrate, we made many measurements that involved melting of tin, lead, and indium. Some of these measurements were made with the same instrument settings and in appropriate time sequences to permit use of the results for tin and lead for calibration of similar measurements on indium. Results of four such "pairs" of runs with indium and tin have led to an average ΔH_m = 6.82_2 cal g^{-1} for indium. Similarly, results of four such "pairs" of runs with indium and lead have led to an average ΔH_m = 6.85_2 cal g^{-1} for indium. The average of all eight such values is ΔH_m = 6.83_7 cal g^{-1}, with standard deviation 0.02_3 cal g^{-1}. Now, along with the two "reasonable" heats of melting of indium cited above, we include our own ΔH_m = 6.84 cal g^{-1}.

We have made 17 measurements of the heat of melting of $NaNO_3$ in paired experiments with indium as reference material for calibration of the calorimeter. These measurements involved four different samples of indium and three different samples of $NaNO_3$. Using ΔH_m = 6.79 cal g^{-1} for indium from Kelley[2] leads to ΔH_m = 3579 cal mol^{-1} for $NaNO_3$. Similarly, using our own ΔH_m = 6.84 cal g^{-1} for indium leads to ΔH_m = 3605 cal mol^{-1} for $NaNO_3$. Finally, we use ΔH_m = 6.97 cal g^{-1} for indium from Richardson and Savill[5] to obtain ΔH_m = 3674 cal mol^{-1} for $NaNO_3$. The standard deviation associated with all of these ΔH_m values for $NaNO_3$ is 55 cal mol^{-1}. We postpone assessment of these ΔH_m values for $NaNO_3$ until after presentation of our other results and consideration of related results from earlier investigations.

We have made 28 measurements of the heat of melting of $NaNO_3$ in paired experiments with tin as reference material for calibration of the calorimeter. These measurements involved seven different samples of tin and five different samples of $NaNO_3$. Using ΔH_m = 14.49 cal g^{-1} for tin as specified above, we have obtained ΔH_m = 3627 cal mol^{-1} for $NaNO_3$. Similarly, ΔH_m = 14.45 cal g^{-1} for tin leads to ΔH_m = 3617 cal mol^{-1} for $NaNO_3$. Standard deviations are 17 cal mol^{-1}.

TABLE 1

HEATS OF MELTING OF SODIUM NITRATE ($NaNO_3$)

Kind of measurement	ΔH_m *(cal mol^{-1})*	*Reference*
DSC based on ΔH_m = 6.79 cal g^{-1} for In from Kelley[2].	3579 (s.d. = 35)[a]	This work (1975)
DSC based on ΔH_m = 6.84 cal g^{-1} for In from our work.	3605 (s.d. = 55)[a]	This work (1975)
DSC based on ΔH_m = 6.97 cal g^{-1} for In from Richardson and Savill[5].	3674 (s.d. = 55)[a]	This work (1975)
DSC based on ΔH_m = 14.49 cal g^{-1} for Sn from Kelley[2].	3627 (s.d. = 17)[a]	This work (1976–1977)
DSC based on ΔH_m = 14.45 cal g^{-1} for Sn from Perkin-Elmer.	3617 (s.d. = 17)[a]	This work (1976–1977)
DSC based on ΔH_m = 5.50 cal g^{-1} for Pb.	3606 (s.d. = 23)[a]	This work (1976–1977)
Quantitative DTA	3564 ± 75[b]	6
F.P. depression	3600 ± 100[c]	7
High-temperature calorimetry	3570 ± 40[d]	8
High-temperature calorimetry	3695 ± 32[c]	9
High-temperature calorimetry	3690 ± 74[c]	cited in ref. 9
	3490 ± 244[c]	
	3596 ± 8[c]	

[a] Uncertainties are discussed in the text.
[b] The spread of reported values is from 3545 to 3575 cal mol^{-1}; we have estimated the uncertainty.
[c] These ± values are from the cited source.
[d] Our present analysis leads to ± 40 cal mol^{-1} as the probable uncertainty in this ΔH_m.

We have also made 28 measurements of the heat of melting of $NaNO_3$ in paired experiments with lead as reference material for calibration of the calorimeter. These measurements involved seven different samples of lead and six different samples of $NaNO_3$. Using ΔH_m = 5.50 cal g^{-1} for lead as specified above, we have obtained ΔH_m = 3606 cal mol^{-1} for $NaNO_3$, with standard deviation 23 cal mol^{-1}.

All of the ΔH_m values from our work are summarized in Table 1, along with results of several earlier investigations.

It is immediately obvious from the first six entries in Table 1 that we obtain the best internal consistency for the heat of melting of $NaNO_3$ by using ΔH_m = 6.84 cal g^{-1} for indium based on our own work. Furthermore, we can find some evidence in support of our ΔH_m of indium from the earlier results cited by Richardson and Savill[5]. However, a few other results cited by Richardson and Savill[5] provide evidence for a smaller ΔH_m of indium, while a greater number of results point toward a larger ΔH_m of indium. As a result of all this, we tentatively suggest that the "best" ΔH_m for indium is larger than the ΔH_m = 6.79 cal g^{-1} that has often been used and is smaller than the recent ΔH_m = 6.97 cal g^{-1} from Richardson and Savill[5]. This

suggested "best" heat of melting of indium might be close to our $\Delta H_m = 6.84$ cal g^{-1}, which we also express as 785 cal mol^{-1}, 28.6_2 J g^{-1}, and 3.28_6 kJ mol^{-1}.

We now turn to selection of a "best" ΔH_m for $NaNO_3$, based on the following considerations.

We have not been able to obtain and read the paper by Sokolov and Schmidt cited by Kleppa and McCarty[9], who have quoted $\Delta H_m = 3596 \pm 8$ cal mol^{-1} for $NaNO_3$. However, on the basis of our own experience with various methods of obtaining heats of melting and uncertainties reported by other workers (see Table 1), we arbitrarily assign an uncertainty of ± 40 cal mol^{-1} to this value. Various weighted averages of the results summarized in Table 1 (both omitting and including our results based on calibration with indium) are consistent with $\Delta H_m = 3615$ cal mol^{-1} as the "best" heat of melting of $NaNO_3$. We note, however, that there is some reasonable evidence for both larger and smaller values. First, earlier calorimetric results from Hu et al.[6] and from Sokolov and Shmidt as cited by Kleppa and McCarty[9] provide evidence for a ΔH_m value about 30 cal mol^{-1} smaller than the $\Delta H_m = 3615$ cal mol^{-1} given above for $NaNO_3$. Second, the calorimetric measurements of Kleppa and McCarty[9] and our DSC results based on the heat of melting of indium from Richardson and Savill[5] provide some evidence for a ΔH_m value about 65 cal mol^{-1} larger than the $\Delta H_m = 3615$ cal mol^{-1} cited above for $NaNO_3$.

On the basis of the above suggested "best" value and the evidence for larger and smaller values, we now select $\Delta H_m = 3615 \pm 50$ cal mol^{-1} for the heat of melting of $NaNO_3$, where ± 50 is intended to indicate a reasonable upper limit to the uncertainty. We also express this heat of melting as 42.5 ± 0.6 cal g^{-1}, 15.12 ± 0.21 kJ mol^{-1}, and 180.0 ± 2.5 J g^{-1}.

Because sodium nitrate of adequate purity is inexpensive and easy to handle, it is a convenient substance to use in differential scanning calorimetry. Our assessment of ΔH_m values as summarized above indicates that the uncertainty in our "best" value is no worse than 1.4%. We therefore recommend that those who use differential scanning calorimeters consider $NaNO_3$ for calibration of their instruments.

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