Thermochimica Acta, 59 (1982) 251-252
Elsevier Scientific Publishing Company, Amsterdam - Printed in The Netherlands

Note

MOLAR ENTHALPY OF THE SOLID-SOLID TRANSITION IN $NaNO_3$

EDNA A. DANCY

Institut de Recherche d'Hydro-Québec, Varennes, Québec JOL 2PO (Canada)

(Received 13 May 1982)

Published values for the enthalpy of the solid-solid transition in sodium nitrate vary between 174 and 1056 cal mole^{-1} [1-5]. Some of the measurements have been by drop calorimetry, others by differential scanning calorimetry. The value obtained previously in this laboratory (by drop calorimetry) lies between the two extremes at 380 cal mole^{-1} [3]. More recently, a brief investigation was made using a Perkin-Elmer DSC-2 differential scanning calorimeter. Our observations during these measurements prompted the present remarks.

Milligram quantities of dried (at ~ 380 K) reagent grade $NaNO_3$ in an aluminum pan were scanned over a temperature range between ambient and ~ 620 K at various heating rates. Two separate peaks were obtained at all but the highest scanning rates, a sharp peak at the fusion temperature (578 K) and a smaller, broader peak with its maximum at 545 K. These findings are in agreement with Zeeb et al. [5]. After calibration with indium, measurement by planimeter of the area of the fusion peak gave a heat of fusion, ΔH_F, of 3540 cal mole^{-1}, which is in agreement with literature values and our own previously obtained 3500 cal mole^{-1}.

In the case of the solid-solid transition, however, it was found difficult to decide at what temperature the transition begins, and hence, what enthalpy change should be assigned to it rather than to a gradually increasing heat capacity. Is it reasonable to assume that the transition begins at ~ 450 K, at which temperature the heat capacity is of a magnitude that is consistent with the heat capacity after the transition? If so, the heat of transition, ΔH_{tr}, is large, ~ 880 cal mole^{-1}. If, on the other hand, a rather higher temperature is taken as the beginning of the transition, a very much lower ΔH_{tr} is obtained. For example, a slightly accelerating upward trend can be detected beginning at ~ 510 K. If this is taken as the beginning of the transition, values of between about 350 and 600 cal mole^{-1} are obtained depending on the method chosen for defining the area of the peak in the case of different heat capacities before and after a transition. Thus it appears that the source of the discrepancies in the values obtained from DSC measurements lies in the difficulty in identifying the beginning of the transition.

The drop calorimetry measurements of Janz et al. [1] and that of Nguyên-

0040-6031/82/0000-0000/$02.75

Duy and Dancy [3] lend support to the lower values, yielding 174 and 380 cal mole^{-1}, respectively. The reason for this is obvious. In each case, only a relatively small temperature range was covered below the transition, and this range began at ~480 and ~450 K, respectively. Thus the linear approximation for the enthalpy as a function of temperature covered only the range where it is unclear whether the transition has begun or not and where the DSC trace has a distinct upward curve. At the same time, the break at the transition temperature included only the change in enthalpy occurring over a few degrees. This, in the DSC trace, constitutes a slice of the broad peak in the region of the apex.

Thus the discrepancies in the published values can be explained, but, until the nature of the transition is better understood, none of the values can be regarded as "best". Most are probably good, provided they are accompanied by a definition of the temperature range included in the transition and a description of how the data were obtained.

It is outside the scope of this note to discuss the nature of the transition. In the course of the present work, however, we obtained some results of interest in this respect. In two runs, the DSC heating scan was interrupted at 530 K. In one case, the sample was held isothermally for half an hour, in the other, overnight. In each case, on resuming the scan, the trace followed its usual path, with the peak developing normally. In other words, the extent to which the transition has proceeded at 530 K (if, indeed, the transition has begun) is a function only of temperature and not of length of time at temperature.

REFERENCES

1 G.J. Janz, F.J. Kelly and J.L. Pérano, J. Chem. Eng. Data, 9 (1964) 133.

2 C.N.R. Rao, B. Prakash and M. Natarajan, Crystal Structure Transformations in Inorganic Nitrites, Nitrates and Carbonates, Natl. Bur. Stand., NSRDS-NBS 53, U.S. Department of Commerce, Washington, DC, 1975.

3 P. Nguyên-Duy and E.A. Dancy, Thermochim. Acta, 39 (1980) 95.

4 R.W. Carling, Proc. 3rd Int. Symp. Molten Salts, The Electrochemical Society. Inc., Pennington, NJ, 1981, p. 485.

5 K.G. Zeeb, M.G. Lowings, K.G. McCurdy and L.G. Hepler, Thermochim. Acta, 40 (1980) 245.