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The Heat Content of $NaNO_2$ Between 450 and 800K

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Abstract

The heat content of $NaNO_2$ has been measured with a drop calorimeter. Relations of the heat content as a function of temperature were obtained for the solid and liquid states. The heat and entropy of fusion were found to be $\Delta H_f = 3570\ (\pm 200)$ cal/mole and $\Delta S_f = 6.41\ (\pm 0.36)$ eu at 557K.

Introduction

Measurements of properties of liquid $NaNO_3$ exhibit some scatter. It has been shown[12] that the different melting points reported for this salt can be explained by the partial decomposition that takes place in the solid phase. As a matter of fact the thermal decomposition of $NaNO_3$ proceeds by a mechanism[2] of simultaneous and successive reactions of which the first step is

$$NaNO_3 \rightleftharpoons NaNO_2 + \tfrac{1}{2} O_2 .$$

Thus the original $NaNO_3$ samples contain varying amounts of $NaNO_2$ in solution. It has been pointed out recently[11] that this contamination is

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one of the most serious drawbacks of the use of alkali metal nitrate melts as reaction media. When repetitive results are required, this contamination must be taken into account.

Since the literature search indicated that the heat content of $NaNO_2$ was not reported, we proceeded with the measurements.

The following data were found for $NaNO_3$: low temperature heat capacity[20] at 16-286K, and two sets of measurements of the high temperature heat capacity[19,13] at 313-660 and 333-624K, respectively. These three sets of data are in excellent agreement and also agree with the heat content measured at 483-747K[8].

For $NaNO_2$ there are no low temperature measurements and those at high temperature are not satisfactory. High temperature heat capacities have been measured by conduction calorimetry at 373-473K[14] and at 275-453K[16] and by adiabatic calorimetry at 373-473K[6]. However, all of these were concerned with the λ-anomaly caused by a transition from the ferroelectric to the paraelectric state of the crystal. Comparison is difficult because only one[16] gives tabular values; the other values are shown only by small scale graphs.

Other nitrate-nitrite results were compared in order to evaluate the above $NaNO_2$ results. Only values for $AgNO_3$[18] and $AgNO_2$[1] were found. Assuming Neumann-Kopp's rule and comparing with the $NaNO_3$[20] values they indicate the $NaNO_2$ data[16] are too small by about 14%. This difference is not too surprising since conduction calorimetry is not a precision method. This evaluation leads to $S_{298.15}$ = 24.67 eu for $NaNO_2$.

Experimental

Heat contents were determined using a diphenyl ether drop calorimeter which has been previously described[7]. The $NaNO_2$ sample was Baker's analytical reagent with maximum certified impurities of 0.033%. It was further purified by recrystallizing three times, from water solution, discarding about 30% each time. The crystals were filtered through sintered glass and dried under vacuum at 110°C for more than 72 hours. After crushing them under a nitrogen atmosphere in a glove box, they were placed in sample tubes sealed under vacuum for storage. The color of the samples was white with a slight yellow tinge.

For each series of runs, the salt was melted into pure silver or pure platinum capsules sealed in air or in vacuum. The calorimeter was calibrated and the heat loss during the drop determined, by using two samples of pure platinum, of 16 and 35g, respectively. The mass of $NaNO_2$ tested was from 4.5 to 5.5g.

Results

The silver capsules ruptured and failed at 623K and the platinum capsules at 786K. The failure presumably was due to creep resulting from internal pressure of gas evolution by the reaction[2]

$$2NaNO_2 \rightarrow Na_2O + 2NO + \tfrac{1}{2} O_2.$$

These fixed the maximum temperatures of the measurements.

The results (above the λ-anomaly) were fitted by least squares to the following expressions

solid: $H_T - H_{298.15} = 31.89\ T - 10150\ (\pm 110)$ cal/mole (452-557K)

liquid: $H_T - H_{298.15} = 23.85\ T - 2100\ (\pm 90)$ cal/mole (557-786K) whence ΔH_f = 3570 (±200) cal/mole and

ΔS_f = 6.41 (±0.36) eu .

The uncertainties are twice the standard deviations from the smoothed values. The standard deviations were calculated from grouped values.

The melting point was taken at 557K from this work and from phase diagram studies[10,17].

Original data are given in Table 1; the points in Fig. 1 correspond to this Table. Smoothed values are in Table 2; the two straight lines in Fig. 1 correspond to the two previously given expressions.

TABLE 1

Experimental Heat Contents of $NaNO_2$

T, K	H_T-$H_{298.15}$	T, K	H_T-$H_{298.15}$	T, K	H_T-$H_{298.15}$
452	4273	534	6925	587	11935
460	4568	535	6906	628	12825
461	4513	544	7248	632	13207
463	4584	568	11350	635	12890
474	5041	567	11434	694	14510
501	5778	576	11631	695	14402
503	5794	577	11697	695	14425
534	6789	582	11770		

TABLE 2

Smoothed Heat Content and Entropy Values for $NaNO_2$

T, K	H_T-$H_{298.15}$	S_T-$S_{298.15}$
450	4200	10.77
500	5795	14.13
557(s)	7614	17.57
557(ℓ)	11184	23.98
600	12210	25.75
700	14595	29.43
800	16980	32.61

In order to calculate the entropy $S_{450}-S_{298.15}$ (below the present measurements) the heat capacity from 298.15K to 450K was estimated by increasing 14% the values reported by Sakiyama et al.[16] as previously discussed. $S_{450}-S_{298.15}$ then was obtained by numerical integration of those heat capacity values.

Discussion

From Fig. 1 it is readily seen that the results agree with those obtained from the heat capacity data of Sakiyama et al.[16], once the adjustment mentioned above is applied.

From the given relations one obtains the mean heat capacities for solid and liquid $NaNO_2$ as 31.89 and 23.85 cal/deg.mole, respectively. This rather unusual phenomenon, in which the heat capacity of the liquid is much lower than that of the solid, is exhibited also by some other ionic melts. For instance Janz et al.[8] find 39.63 and 31.22 cal/deg. mole for solid and liquid $NaNO_3$ by drop calorimetry. Sokolov and Shmidt[19] by adiabatic calorimetry give some heat capacity values of solid $NaNO_3$ near the melting point which are greater than for the liquid; their data indicate a constant heat capacity for the liquid. Also the same behavior occurs in Na_2SiO_3, Na_2SO_4, Na_2TiO_3, $NaClO_3$, and notably in NH_4NO_3, as cited by Kelley[9]. Of these seven salts only Na_2SiO_3 and and $NaClO_3$ do not exhibit a phase transformation of higher order in the solid phase. Another remarkable fact is the abnormal low heat of fusion of $NaNO_3$[8, 9] also found in this work for $NaNO_2$.

It has been suggested that the λ-transformations introduce so much disorder in the solid before fusion that melting produces less than normal disorder because of clusters or complex formation in the liquid. Sakiyama et al.[16] give a total λ-transition entropy of 1.26 eu which is so near $R\ell n2 = 1.337$ eu that they suggest the orientation order of NO_2^- ions is destroyed completely in the paraelectric phase. Evidence of association in liquid $NaNO_3$ near the melting point has been given by Ubbelohde et al.[15,21] X-ray evidence of association both in liquid $NaNO_3$ and $NaNO_2$ is given by Furukawa[3,4].

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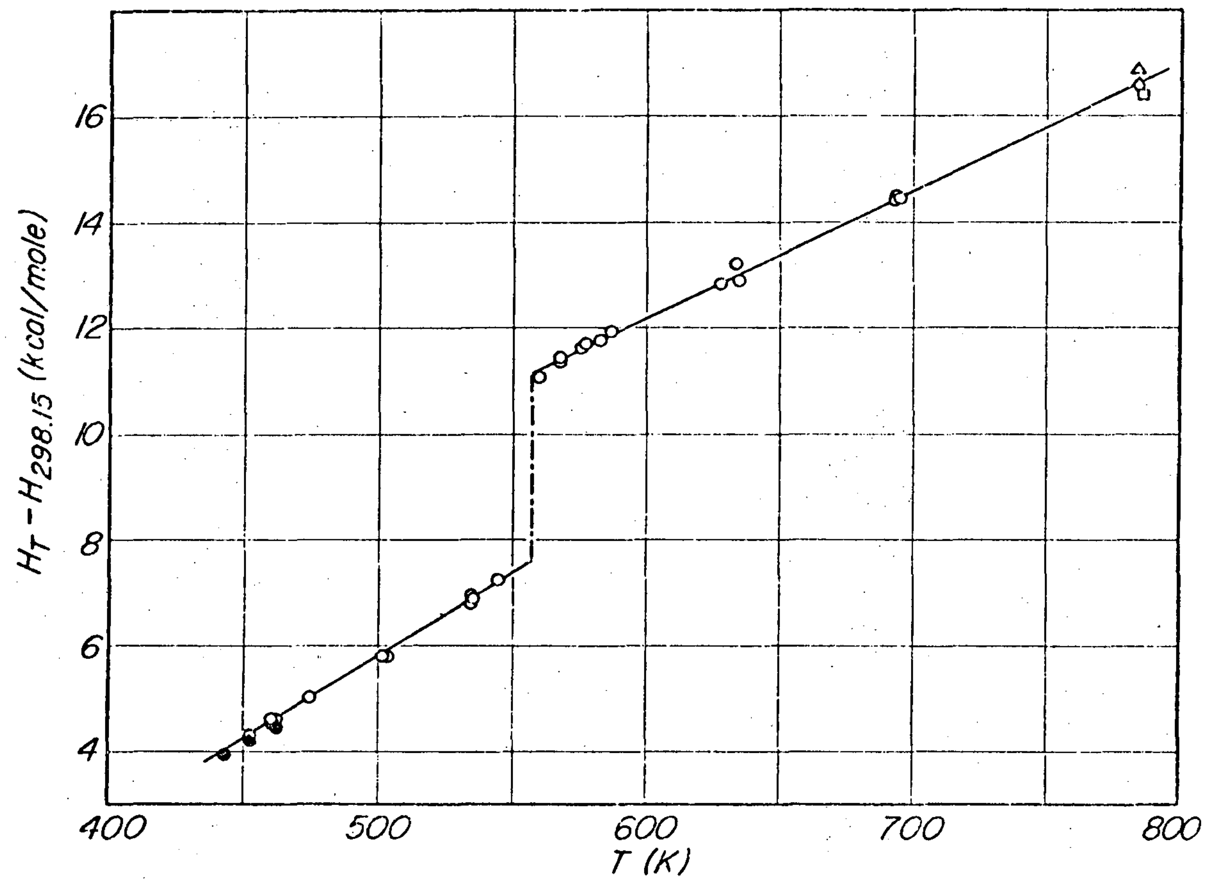

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Figure 1. Heat content of $NaNO_2$ as a function of temperature.
● corrected data from Sakiyama et al.[16]
⊙ this work
⊡ ◇ △ different experiments where the platinum capsule failed, corrected for weight loss.

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