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Heat Capacities and Latent Heats of $LiNO_3$, $NaNO_3$, and KNO_3[1]

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Enthalpies of fusion and transition together with heat capacities in both solid and liquid phases have been measured on $LiNO_3$, $NaNO_3$, and KNO_3 with a high accuracy by differential scanning calorimetry (DSC). Polynomial expressions of heat capacities are given.

KEY WORDS: differential scanning calorimetry; enthalpy of fusion; enthalpy of transition; heat capacity; KNO_3; $LiNO_3$; $NaNO_3$.

1. INTRODUCTION

Heat capacity and latent heat of fusion are important thermophysical properties in consideration of thermal energy storage materials and heat transfer media. There is a variety of mixed salts of alkali–metal nitrates such as HTS (54 wt% KNO_2–7 % $NaNO_2$–40 % $NaNO_3$), draw salt (54 wt% KNO_3–46 % $NaNO_3$), and mixtures of NaOH and $NaNO_3$; some of them are already used and some are proposed for these purposes.

A considerable number of heat capacity data above room temperature have been reported on $LiNO_3$, $NaNO_3$, and KNO_3 [1–15]. Some of the data have been obtained by differential scanning calorimetry (DSC) [2, 3, 7] and some others have been determined from enthalpy data obtained by the conventional drop method [5, 6, 10–14]. The latter can sometimes provide only average values over a rather wide temperature range, although the enthalpy of fusion can be determined with high accuracy. Ichikawa and Matsumoto [1] measured the heat capacity of these nitrate salts by adiabatic calorimetry; however, heats of fusion are not

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reported. All these data are not always in agreement with each other. Furthermore, heat capacity data of KNO_3 below room temperature [16] are not connected smoothly to the high-temperature data reported in the literature.

The purpose of the present study is to determine enthalpies of fusion and transition together with heat capacities in both solid and liquid phases of $LiNO_3$, $NaNO_3$, and KNO_3 with a high accuracy by one measuring method: DSC.

2. EXPERIMENTAL

2.1. Samples

A chemical reagent of $LiNO_3$ with a 99.8% purity was purchased from Wako Pure Chemical Industries, Ltd.; $NaNO_3$ with a 99.99% purity and KNO_3 with a 99.99% purity were purchased from Showa Chemical Co., Ltd. They were used without further purification. Sapphire was used as a standard material for the measurements.

2.2. Apparatus

DSC measurements were made with a Perkin–Elmer DSC-2. Data acquisition, data processing, and control were done with a personal computer (HP-9816S) and a data acquisition/control unit (HP-3497A). Aluminum sample pans were used for the present molten salts, since they are not corrosive and do not creep up as hydroxides of alkali metals.

2.3. Measurements

Heat capacity measurements were made with a scanning method as described elsewhere [17]. Heat capacity data were obtained every 1 K except for regions of transition or fusion, where the interval of data acquisition was 0.25 K.

We evaluated the precision of our measurements by measuring heat capacities of sapphire over a temperature range between 334 and 733 K. Figure 1 shows the deviation of the data points from the smoothed values obtained by the method of least-squares. Literature values [18] are also plotted in Fig. 1. As can be seen, the scattering of most of the data is within ±0.5%: the standard deviation is 0.26% over the whole temperature range measured. The deviations from the literature values are within ±0.5%. From repeated measurements on sapphire and the nitrate salts, we consider that the reproducibility of the heat capacity measurements is within ±1.5% in the worst case.

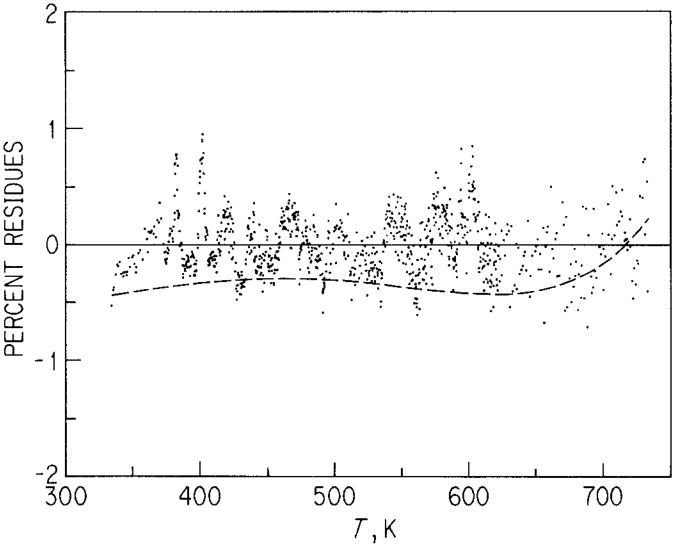

Fig. 1. Deviation plot of experimental heat capacities of sapphire. Dots are the data points and the ordinate shows the deviations from the smoothed curve obtained by the least-squares method. The dashed line shows the literature values [18].

In order to determine the latent heat, the usual DSC method of heat capacity determination was applied to the temperature range of phase change. Although dynamic methods such as DSC provide only apparent heat capacities near the phase change regions, precise values for latent heat can be obtained from the integration of the apparent heat capacities [19]. The apparent heat capacities measured were integrated to obtain the enthalpy increase. Latent heat was estimated from the difference between the linear enthalpy increase in the lower temperature range and that in the higher temperature range at the extrapolated onset temperature. This method needs only one standard material (sapphire) with highly accurate heat capacity data, so that the accuracy can be remarkably improved with less effort. Furthermore, it can eliminate ambiguity of the conventional method when baselines above and below the peak are determined.

3. RESULTS AND DISCUSSION

3.1. Heat Capacity

Specific heat capacities of $LiNO_3$, $NaNO_3$, and KNO_3 measured in this study are listed in Tables I–III at 5 K intervals. The experimental

Table I. Measured Specific Heat Capacities of $LiNO_3$

T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)
335	1.33	415	1.48	495	1.65	575	2.06
340	1.34	420	1.50	500	1.67	580	2.05
345	1.36	425	1.52	505	1.69	585	2.05
350	1.37	430	1.53	510	1.71	590	2.06
355	1.38	435	1.54	515	1.78	595	2.05
360	1.39	440	1.57			600	2.08
365	1.40	445	1.56	($T_m = 525.9$ K)		605	2.06
370	1.41	450	1.59			610	2.06
375	1.40	455	1.58	535	2.03	615	2.05
380	1.41	460	1.59	540	2.04	620	2.07
385	1.42	465	1.59	545	2.02	625	2.12
390	1.42	470	1.61	550	2.04	630	2.11
395	1.43	475	1.60	555	2.02	635	2.10
400	1.45	480	1.63	560	2.03	640	2.10
405	1.44	485	1.64	565	2.04	645	2.10
410	1.46	490	1.67	570	2.06	650	2.09

Table II. Measured Specific Heat Capacities of $NaNO_3$

T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)
335	1.16	415	1.35	495	1.73	($T_m = 577.5$ K)	
340	1.17	420	1.37	500	1.78		
345	1.18	425	1.36	505	1.83	585	1.67
350	1.20	430	1.38	510	1.89	590	1.66
355	1.21	435	1.40	515	1.96	595	1.67
360	1.22	440	1.42	520	2.05	600	1.68
365	1.23	445	1.43	525	2.14	605	1.67
370	1.24	450	1.46	530	2.28	610	1.67
375	1.24	455	1.48	535	2.45	615	1.66
380	1.27	460	1.51	540	2.81	620	1.68
385	1.27	465	1.53	545	3.35	625	1.68
390	1.28	470	1.56	550	1.93	630	1.67
395	1.30	475	1.58	555	1.71	635	1.66
400	1.31	480	1.62	560	1.66	640	1.66
405	1.32	485	1.66	565	1.64	645	1.67
410	1.34	490	1.71	570	1.78	650	1.67

Table III. Measured Specific Heat Capacities of KNO_3

T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)	T (K)	c_p ($J \cdot g^{-1} \cdot K^{-1}$)
335	0.97	435	1.22	535	1.30	635	1.38
340	0.98	440	1.23	540	1.30	640	1.38
345	0.99	445	1.22	545	1.31	645	1.39
350	1.00	450	1.23	550	1.32	650	1.39
355	1.01	455	1.22	555	1.33	655	1.39
360	1.01	460	1.23	560	1.33	660	1.39
365	1.03	465	1.24	565	1.35	665	1.38
370	1.04	470	1.24	570	1.35	670	1.39
375	1.03	475	1.24	575	1.36	675	1.38
380	1.04	480	1.24	580	1.37	680	1.38
385	1.06	485	1.25	585	1.39	685	1.39
390	1.07	490	1.25	590	1.40	690	1.38
395	1.08	495	1.26	595	1.41	695	1.38
400	1.10	500	1.26	600	1.43	700	1.38
($T_{tr} = 402.9$ K)		505	1.27	($T_m = 607.4$ K)		705	1.38
410	1.24	510	1.27			710	1.39
415	1.23	515	1.27	615	1.40	715	1.39
420	1.23	520	1.28	620	1.40	720	1.39
425	1.22	525	1.29	625	1.39	725	1.39
430	1.22	530	1.29	630	1.39	730	1.39

molar heat capacities are also plotted in Figs. 2–4 together with literature values.

The present values for $LiNO_3$ are in fairly good agreement with the values obtained by Ichikawa and Matsumoto [1] with adiabatic calorimetry. All the other data are measured by drop calorimetry. The data of Kamimoto [12] and those of Tye et al. [13] are average values, and they are also in good agreement with the present results. On the other hand, the data of Goodwin and Kalmus [6] and those of Douglas [14] are lower than the present values. It should be noted that the present experimental heat capacities near the melting temperature are apparent values, although the enthalpy of fusion can be calculated using these apparent values of heat capacities [19].

Heat capacities of $NaNO_3$ measured in this study are in fairly good agreement with those of Ichikawa and Matsumoto [1], of Carling [3], and of Rogers and Janz [2] (DSC). These data are connected smoothly to the low-temperature data of Southard and Nelson [16]. It should be noted that the present scanning method can determine the heat capacities with smaller temperature intervals in the temperature range of the transition.

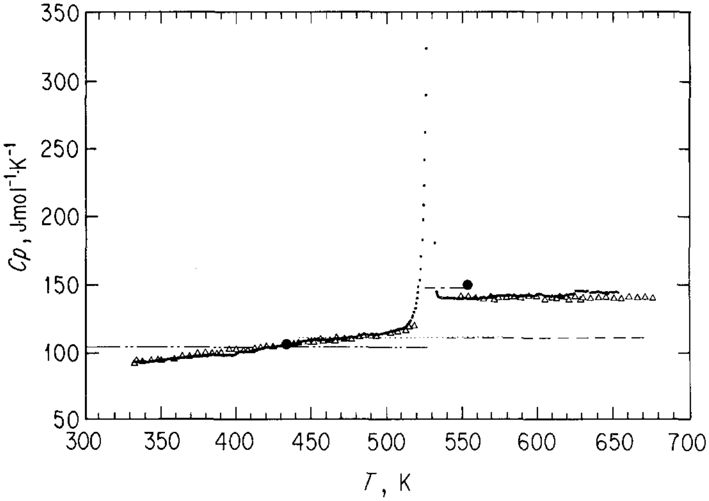

Fig. 2. Heat capacity of $LiNO_3$. (·······) This work; (△) Ichikawa and Matsumoto [1]; (◇) Tye et al. [13]; (—··—) Kamimoto [12]; (—·—) Goodwin and Kalmus [6]; (––––) Douglas [14].

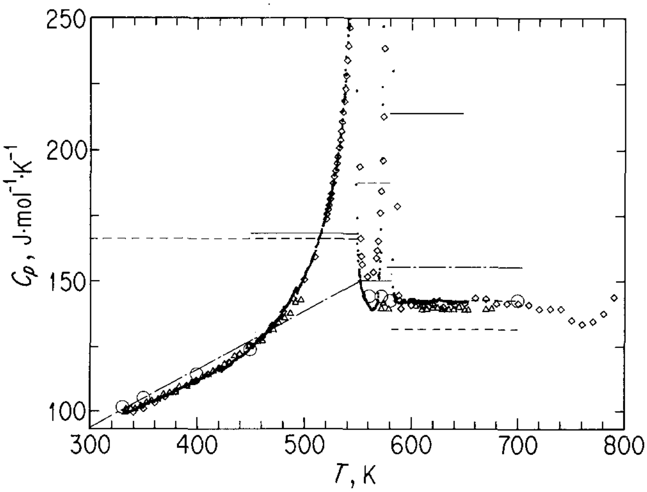

Fig. 3. Heat capacity of $NaNO_3$. (·······) This work; (△) Ichikawa and Matsumoto [1]; (◇) Carling [3]; (○) Rogers and Janz [2]; (——) Nguyen-Duy and Dancy [10]; (––––) Janz et al. [11]; (—·—) Blander [15].

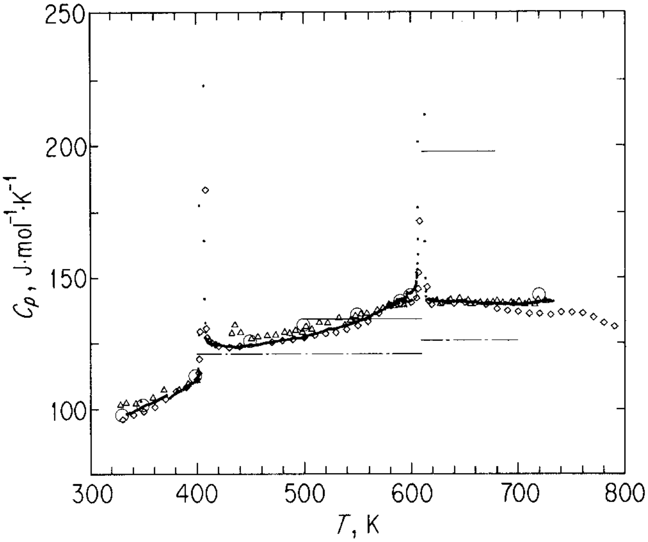

Fig. 4. Heat capacity of KNO_3 above room temperature. (·······) This work; (△) Ichikawa and Matsumoto [1]; (○) Rogers and Janz [2]; (◇) Carling [3]; (——) Nguyen-Duy and Dancy [10]; (—·—) Blander [15].

The old data of Janz et al. [11] by drop calorimetry are a little lower in the liquid state and quite high in the solid state; there is the possibility that the heat capacities in the solid state include the enthalpy of transition. The results of Nguyen-Duy and Dancy [10] obtained by drop calorimetry seem too high.

For KNO_3, the present data agree well with the data of Rogers and Janz [2] and those of Ichikawa and Matsumoto [1]. These data are, however, not connected smoothly to the low-temperature data of Southard and Nelson [16] as shown in Fig. 5. The data of Nguyen-Duy and Dancy [10] are much higher than the other data in the liquid state and the data selected by Blander [15] are a little lower in the whole temperature range measured. It is well known that the transition of KNO_3 splits into two transitions during a cooling mode. DSC unfortunately cannot measure heat capacity on cooling.

According to Carling [3], heat capacities of $NaNO_3$ and KNO_3 have a significantly negative temperature dependence above the melting temperature. The present results show that the heat capacity in the liquid state is almost constant for all the salts measured. The specific heat capacities (in $J \cdot g^{-1} \cdot K^{-1}$) fitted to a polynomial equation in temperature (in K), except for a transition region, are as follows:

$LiNO_3$,

$$c_p = 0.585 + 2.182 \times 10^{-3}T, \qquad 334\text{–}493\ \text{K (solid)}$$

(SD of percentage residue = 0.8%)

$$c_p = 2.06, \qquad 540\text{–}653\ \text{K (liquid)}$$

(SD of percentage residue = 0.6%)

$NaNO_3$,

$$c_p = 3.15 - 1.186 \times 10^{-2}T + 1.807 \times 10^{-5}T^2, \qquad 334\text{–}493\ \text{K (solid)}$$

(SD of percentage residue = 1.0%)

$$c_p = 1.67, \qquad 586\text{–}653\ \text{K (liquid)}$$

(SD of percentage residue = 0.4%)

KNO_3,

$$c_p = 0.326 + 1.91 \times 10^{-3}T, \qquad 334\text{–}400\ \text{K (solid)}$$

(SD of percentage residue = 0.6%)

$$c_p = 2.442 - 5.682 \times 10^{-3}T + 6.628 \times 10^{-6}T^2, \qquad 423\text{–}600\ \text{K (solid)}$$

(SD of percentage residue = 0.3%)

$$c_p = 1.39, \qquad 620\text{–}733\ \text{K (liquid)}$$

(SD of percentage residue = 0.4%)

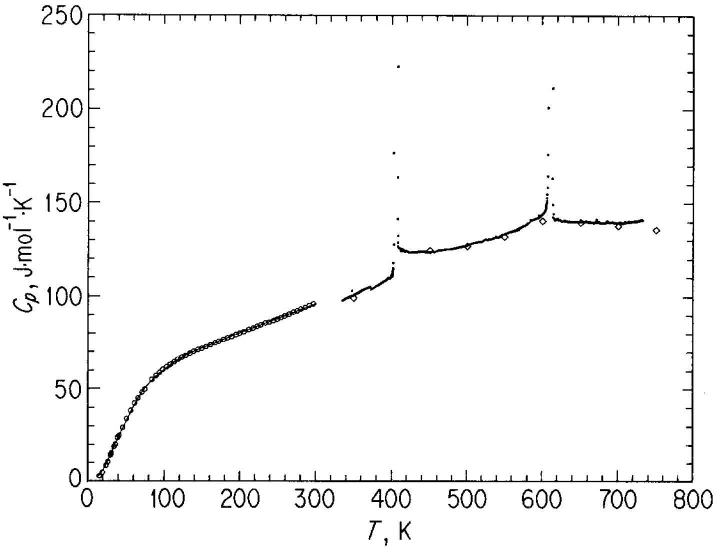

Fig. 5. Heat capacity of KNO_3 from 15 up to 800 K. (·······) This work; (◇) Carling [3]; (○) Southard and Nelson [16].

Table IV. Heats of Transition (Δh_{tr}) and Fusion (Δh_m) of $LiNO_3$, $NaNO_3$, and KNO_3

Material	T_{tr} (K)	T_m (K)	Δh_{tr} $(J \cdot g^{-1})$	Δh_m $(J \cdot g^{-1})$	Ref. No.
$LiNO_3$		525.9		363	This work
				357	3
				370	6
$NaNO_3$	548.5	577.5	45	173	This work
			—	172	10
			40.1	178	20
KNO_3	402.9	607.4	50.6	96.6	This work
			—	91	10
			—	98.9	5
			49.5	98.3	20

For the lambda transition region of $NaNO_3$, the smoothed specific heat capacities are obtained graphically from the experimental data in Table II. The specific heat capacity of solid at the melting temperature is obtained from extrapolation of the above equation up to the melting temperature. However, the precision of such an extrapolation is not clear.

3.2. Enthalpies of Fusion and Transition

Enthalpies of fusion and transition for the nitrate salts measured are listed in Table IV together with literature values. All the data for the heat of fusion are in reasonably good agreement with each other. On the other hand, the enthalpy of transition of $NaNO_3$ shows a discrepancy between the present value and that of Zeeb et al. [20]. It might be due to the difference of estimation of the baseline of a normal part of the heat capacity. From Table IV, the sum of the entropy of transition and the entropy of fusion was calculated: 47.6, 32.4, and 28.8 $J \cdot mol^{-1} \cdot K^{-1}$ for $LiNO_3$, $NaNO_3$, and KNO_3, respectively. It should be pointed out that $LiNO_3$ has a larger value compared with other nitrate salts of Na, K, Rb, Cs, Tl, and Ag, which have values between 25 and 33 $J \cdot mol^{-1} \cdot K^{-1}$. It has already been pointed out in the literature [12]; however, the reason has not been made clear.

4. CONCLUSION

Enthalpies of fusion and transition together with heat capacities in both solid and liquid phases have been measured for $LiNO_3$, $NaNO_3$, and

KNO_3 with a high accuracy by differential scanning calorimetry (DSC). Polynomial expressions of heat capacities have been obtained. For KNO_3, the low-temperature data of Southard and Nelson [16] do not connect smoothly to the data above room temperature, which are in fairly good agreement with each other. Heat capacity measurements are thus needed from low temperatures through room temperature, especially for KNO_3.

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