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Note

HEAT CAPACITIES OF ANHYDROUS AMMONIUM OXALATE AND OXALIC ACID AND THEIR CRYSTALLOHYDRATES

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The literature does not provide any data on the temperature dependencies of the heat capacities of compounds described in this paper. Reference 1 gives data on the heat capacities of anhydrous ammonium oxalate and other ammonium salts (nitrate and sulphate) within the range 183–293 K. A comparison of data [1] for ammonium nitrate and ammonium sulphate with those taken from the latest reference books proves that the results of ref. 1 are overestimated by more than 25%.

EXPERIMENTAL

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) crystallohydrates were of reagent grade and were recrystallized from distilled water. Anhydrous samples were prepared by drying the crystallohydrates in a thin layer at the dehydration temperature. These substances were pressed into pellets of 11 mm diameter and 15–18 mm height. The sample mass used was 1.5–1.8 g.

Heat capacity was measured within the range 150–440 K at a heating rate of 2 K min^{-1} by means of a dynamic calorimeter of triple heat bridge type [2]. The measurement error did not exceed 2%, which was evaluated by the determination of heat capacities of standard substances (copper and benzoic acid) using both adiabatic and triple-heat-bridge calorimeters.

RESULTS AND DISCUSSION

The experimental results were mathematically treated by means of a least-squares method and presented as $C_p = a + bT + cT^2 + dT^3$. Deviations of the experimental heat capacity data (J mol^{-1} K^{-1}) from those calculated using the above equation did not exceed 0.5%. The coefficients of the equation are presented in Table 1.

Table 2 gives values of the heat capacity of anhydrous ammonium oxalate which were measured in the present work and in ref. 1. As is seen from Table

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TABLE 1

Coefficients of the equation $C_p = a + bT + cT^2 + dT^3$ (J mol^{-1} K^{-1}) for the substances studied

Sample	Temp. range (K)	a	$b \times 10^1$	$c \times 10^4$	$d \times 10^7$
$H_2C_2O_4 \cdot 2H_2O$	170–300	−22.5	12.9	−34.2	47.9
$H_2C_2O_4$	150–360	23.4	3.29	−2.28	1.36
$(NH_4)_2C_2O_4 \cdot H_2O$	170–305	26.1	9.09	−13.7	15.4
$(NH_4)_2C_2O_4$	170–320	34.4	6.51	−6.92	7.93
$(NH_4)_2C_2O_4$	375–440	−1815	136	−306	237.6

2, our results differ from those in ref. 1 by more than 25%. Such a difference can most likely be attributed to the imperfection of the apparatus (the calorimeter design, thermometer and heater position, etc.) used in ref. 1. This is also confirmed by the fact that the data of ref. 1 for other substances (ammonium nitrate and ammonium sulphate) also differ from those known from reference books by approximately 25–30%. The average heat capacity value within the range 273–372.6 K for anhydrous ammonium oxalate in ref. 3 (211.7 J mol^{-1} K^{-1}) is in good agreement with the value (206 ± 4 J mol^{-1} K^{-1}) we obtained for the same temperature range.

The anhydrous ammonium oxalate shows a reversible phase transition within the range 320–375 K. The transition peak on heating appeared at 334 ± 2 K. The phase transition enthalpy was +380 ± 25 J mol^{-1}. It was also found that this transition is characterized by a hysteresis, i.e., the transition peak on cooling is at 309 ± 2 K. Table 3 gives values of ammonium oxalate heat capacity in the region of its phase transition obtained on heating and cooling. It also provides dilatometric measurement data which confirm the existence of a phase transition in the sample.

By means of a high-temperature X-ray method it was elucidated that the ammonium oxalate phase transition is not related to a rearrangement of its crystal lattice. On the basis of high-temperature IR spectrum data we found a relationship between the intensity of the 1700 and 1440 cm^{-1} bands and the anomalous part of the sample's heat capacity. These bands are assigned to NH_4^+ ion vibrations [4]. When the anhydrous ammonium oxalate is heated above its phase transition temperature, the 1700 cm^{-1} band practi-

TABLE 2

Heat capacity of anhydrous ammonium oxalate (J mol^{-1} K^{-1}) within the range 193–283 K

Temp. (K)	193	213	233	253	273	283
C_p (present work)	140	149	159	168	177	181
C_p [1]	144.6	158.8	171.3	191.3	214.0	227.3

TABLE 3

Heat capacity and relative linear expansion of anhydrous ammonium oxalate in the region of its phase transition

T (K)	C_p (J mol^{-1} K^{-1})		$\frac{\Delta l}{l_0} \times 10^4$	T (K)	C_p (J mol^{-1} K^{-1})		$\frac{\Delta l}{l_0} \times 10^4$
	Heating	Cooling			Heating	Cooling	
250	166	171		324	201	214	6.3
255	169	174		326	203	215	8.4
260	171	177		328	211	216	11.5
265	173	179		330	227	217	13.9
270	175	182		332	234	218	16.3
275	178	186		334	236	219	18.7
280	180	190		336	235	220	19.8
285	182	194		338	234	221	20.7
290	184	198		340	233	222	21.7
293	186	203		342	232	224	22.7
296	187	208		344	231	225	23.7
299	188	213	0.8	346	230	226	24.5
302	190	218	1.1	348	229	227	25.3
304	191	222	1.5	350	228	228	26.1
306	192	226	1.9	352	227	229	26.9
308	192	228	2.3	354	226		27.6
310	193	227	2.8	356	227		28.3
312	194	224	3.3	360	228		29.0
314	195	219	3.7	365	229		29.8
316	196	217	4.5	370	231		30.5
320	198	213	5.3	375	235		31.3

cally completely disappears. As it was noted in ref. 5 the disappearance of this band is due to the fact that NH_4^+ ions lose their orientation and begin to rotate freely. This phenomenon is also the reason for the 1400–1460 cm^{-1} band behaviour [5,6]. Until the phase transition, this band is split into three bands (1400, 1440 and 1460 cm^{-1}). After the phase transition only the 1400 cm^{-1} band remains. Thus, the observed phase transition should be assigned to transitions of order–disorder type, which are characteristic of ammonium salts.

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