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A DSC STUDY OF THE PHASE TRANSFORMATIONS OF AMMONIUM NITRATE

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ABSTRACT

A literature survey has been made of heat capacity and transition enthalpy values for ammonium nitrate. New DSC experiments lead to ΔH^0 values for the IV → III, III → II and II → I transitions in good agreement with older data, and to a new value for the enthalpy of fusion. The effect of thermal history and moisture content is discussed.

INTRODUCTION

The polymorphic transitions of ammonium nitrate (AN) have induced a voluminous literature since first discovered by Frankenheim [1] in 1854. The various crystalline modifications are usually denoted in the literature in the following way

Phase	Structure	Stability range
V	Tetragonal	below − 17°C
IV	Orthorhombic	− 17°C to 32.25°C
III	Orthorhombic	32.25°C to 84.2°C
II	Tetragonal	84.2°C to 125.5°C
I	Cubic	125.5°C to 169.6°C

(A high pressure modification, phase VI, and a questionable low temperature phase VII are not of interest here.)

Values of heat capacity and enthalpy are needed for AN process design purposes. We therefore compiled data available in the literature, as given in Tables 1 and 2. It can be seen that the enthalpy of melting is not known very precisely, and that the phenomena occurring during cooling of AN have not been studied by quantitative methods. Also, a precise interpretation of the behaviour of AN in the temperature range 32 to about 55°C is still lacking, but would be of great technical interest.

This paper reports the results of a DSC study on pure AN. DSC has been

TABLE 1

Transition temperatures and enthalpies of ammonium nitrate

Transition	Temp. (°C)	ΔH (J g^{-1})	Method	Ref.
V⇌IV	−18	6.8	Dil., cal.	2
	−16.6		Dil.	3
	−17.0±0.4	5.80	Cp	4
		5.91±0.08	Cp	5
	−17	6.2	Compilation	6
	−18	6.8	Compilation	7
	−17	6.2	Compilation	8
IV⇌III		21	Cal.	3
	32		Dil.	2
		19.5	dT/dP	3
	32.1		Dil.	9
	31–36		Compilation	9
	32.3	20.88	Dil., Cp	10
		21	?	3
	32.25	21.43±0.02	Cp	4
	32±10		X-ray	11
	55(dry)		DTA, X-ray	12
	35(0.1% H_2O)			12
		16.7	DSC	13
	31(heating)		DTA	14
	26(cooling)			14
		21.24±0.12	C_p	5
	32.22		Dil.	15
	43–51		DTA, X-ray	16
	33–50 (heating)		DTA	17
	32.1–32.4		Dil.	18
	40–50 (monocryst.)		Raman	19
	32 (polycryst.)		Raman	19
	32	20.9	Compilation	6
	32.1	19.86	Compilation	7
	32	20.9	Compilation	8
III⇌II		22.3	Cal.	3
	83		Dil.	2
		16.7	dT/dP	3
	84.2		Cooling curves	9
	81–87		Compilation	9
	84.2	16.2±0.3	"DTA"	20
		16.7	DSC	13
	84.0±0.1	16.87±0.19	Cp	5
	83	16.2	Compilation	6
	84.2	16.73	Compilation	7
		16.2	Compilation	8

TABLE 1 (continued)

Transition	Temp. (°C)	ΔH (J g^{-1})	Method	Ref.
II$\rightleftharpoons$I		49.6	Cal.	3
		54.2	dT/dP	3
	125.2		Cooling curves	9
	123.5–127		Compilation	9
	125.2	51.2	"DTA"	20
		51.9	DSC	13
	125	63	DTA	14
	125.8±0.05	55.41±0.38	Cp	5
		53.8	Compilation	6
	125.2	52.8	Compilation	7
		53.8	Compilation	8
I$\rightleftharpoons$liq		67.8	dT/dp	3
	169.6		Cooling curves	9
		72.6	Cal.	21
	169.3	80.0	Cryoscopy	22
		79.5	DSC	13
	169.5	70	Cryoscopy	23
	169.6	67.95	Compilation	7
		76.4	Compilation	8

TABLE 2

Heat capacity of ammonium nitrate. The bar denotes that the corresponding Cp value is an average value in the barred temperature range

Temp. (°C)	Phase	Cp (J $g^{-1}deg^{-1}$)	Ref.
−258–+137	V–I	See text	5
−258–+42	V, IV	See text	4
−262–+8	V, IV	See text	24
$\overline{0-+31}$	IV	1.70	3
$\overline{31-83.5}$	III	1.49	3
$\overline{82.5-124}$	II	1.78	3
$-\overline{15-+15}$	IV	1.65	2
$-\overline{79--20}$	V	1.47	2
$-\overline{190-+20}$	?	1.28	2
$\overline{0.5-20.1}$	IV	1.66	3
$-\overline{76.1-0}$	?	1.58	3
−20	V	2.00	25
$\overline{125-170}$	I	2.38	21
$\overline{170-270}$	liq	2.01	21
40	III	1.50	26
65	III	1.59	26
114	II	1.88	26
189	liq	1.96	26

used earlier as a quick method to establish transition temperatures [27], but the quantitative capabilities of such an instrument have only been used to a minor extent in connection with AN [13].

The references in Tables 1 and 2 are cited because of their pertinence to this particular study. A more comprehensive survey of the literature up to June 1973 has been made by Rao et al. [28].

EXPERIMENTAL

Ammonium nitrate p.a. from Merck was used. Moisture content was determined by Karl Fischer titration. When taken from the manufacturers bottle, the moisture content was 0.1–0.2%. Samples with higher moisture content were prepared by keeping AN over water in a desiccator for various lengths of time. Values of moisture content are believed to be fairly accurate per se, but changes during grinding, weighing and in the DSC during scans could not be measured. Different batches of AN were used. One of these was more than 5 years old, and the others (at least) a few months old.

An attempt to prepare pure phase IV followed the directions given by Vanderzee [29]. Most samples have been ground in an agate mortar before the run; in some cases the coarse crystals were used as such.

A Perkin-Elmer DSC 1B was used. The low temperature cover was cooled by means of a cooling thermostat, enabling operation from +15°C. The heating scan rate was usually +4°C min^{-1}, the cooling rate was −2°C min^{-1} above 50°C and −1°C min^{-1} below.

The sample cups used were mostly aluminium but gold cups were used in some experiments where the melting point was exceeded.

The DSC was calibrated against indium (enthalpy of melting 6.79 cal g^{-1}) [30] and potassium nitrate (enthalpy of melting 53.4 J g^{-1}) [31]. These chemicals were from Fluka AG (99.995%) and the National Bureau of Standards Reference Material No. 193, respectively. Sample weights were generally 10–14 mg, weighed on a Cahn electrobalance.

Peak areas were calculated by approximating the area under the peak with simple geometric figures. This procedure had a repeatability of ±1% on regularly shaped peaks, but is more uncertain on some of the irregularly shaped peaks obtained with AN.

No special precautions were taken during sample preparation. The relative humidity is rather high in the Landskrona laboratory, being 50–70%.

RESULTS

Transition enthalpies and temperatures

Runs on AN with moisture contents from 0.11 to 1.6% all showed a first peak at 50–55°C (average 53°C). The heating scan rate was varied from 2 to

8°C min^{-1}, with no change in the result. In two experiments, the scan was stopped at 50°C for 1/2 and 3 h, respectively. The scan was then continued. This did not affect the transition temperature. The next peak appears at 85–88°C (average 86°C). The size of this peak varies considerably. The II → I transition is well reproducible both as to size and temperature (126–127°C). The "thermal history" of these AN samples is that they had been kept at room temperature (~25°C) for several months. They should then consist of pure phase IV ammonium nitrate.

The transition enthalpies found are collected in Table 3. The four experi-

TABLE 3

Transition enthalpies (J g^{-1})

Run	% H_2O	Transition temperature		
		53°C	86°C	126°C
Measured during heating				
1	0.11	24.6	2.3	58.6
2	0.11	24.6	0	57.2
3	0.11	23.3	0	59.8
4	0.11	23.4	4.8	56.9
5	0.11	23.4	0	58.4
6	0.11	11.5	12.0	56.5 [a]
7	0.11	13.4	9.5	[b]
8	0.15	22.4	2.2	53.1
9	0.15	21.3	1.8	53.1
10	0.15	18.5	6.0	56.1
11	0.15	24.0	0	61.1
12	0.15	22.3	0	55.2
13	0.40	25.0	0	61.1
14	0.40	22.8	0	59.0
15	1.58	23.5	0	56.9
16	1.58	22.0	1.2	60.7
17	0.12	22.2	0	56.1 [c]
18	0.12	23.4	2.2	56.1 [c]
19	?		16.8	
20	?		16.3	
21	?		16.9	
22	?		17.4	
Measured during cooling				
23		22.8 (48°C) [d]		
24		21.9 (48°C) [e]		

[a] Kept at 50°C for 0.5 h.

[b] Kept at 50°C for 3 h.

[c] Prepared according to Vanderzee [29] to be phase IV.

[d] Cooled from 130°C.

[e] Cooled from 103°C.

ments (Nos. 19–22) marked with ?% moisture were performed differently. In three cases the scan was stopped at 65°C, and some water (2 μl) was added. When the sample looked dry, the scan was resumed, giving the transition enthalpies listed. (The fourth will be described below.)

Upon cooling, generally only one transition is observed, at ~48°C. Two dry samples (moisture 0.12%) were heated to 130 and 103°C, respectively. Both showed exothermic transitions on cooling, at 48°C, $\Delta H^0 = (-22.3 \pm 0.5)$ J g^{-1}. In three experiments, the cooling scans were interrupted at ~65°C, and a little water was added and allowed to evaporate. When the cooling scan continued, the samples behaved differently: one behaved as the dry ones, but the other two had exothermic transitions at 50°C, followed by an endothermic peak at 49–46°C. The areas under these peaks were difficult to evaluate, but approximate values are $\Delta H(50°\text{C}) = -16$ J g^{-1}, $\Delta H(\sim 47°\text{C}) = 8$ J g^{-1}.

In one experiment, enough water was added to dissolve all AN, and then evaporated (65°C). This sample showed no transitions upon cooling to 17°C, and on renewed heating first transformed at 86°C (No. 22 in Table 3).

The enthalpy of melting was measured 13 times, using both aluminium and gold sample holders. The average values were the same with either type, and the baseline was stable after melting. Thus, there is no indication that the measured enthalpies are invalid because of decomposition. The result was ΔH^0 (melting) $= (77.4 \pm 2.5)$ J g^{-1} (mean value ±95% confidence interval of the mean, 13 values).

Influence of "thermal history"

Most of the samples in Table 3 have the "same" thermal history. (Stored for a "long" time at room temperature.) For these, some events are reproducible: all peak temperatures, and the peak size of the 126°C transition. The 86°C peak is small, sometimes zero. Repeated experiments using AN from the same bottle gave this lack of reproducibility.

Addition of water at 65°C affects the behaviour, both on subsequent heating and cooling, vide supra.

When the samples that had shown endothermic peaks upon cooling were reheated, the first peak appeared as low as at 37–40°C, and the 87°C peak is of considerable size ($\Delta H^0 = 17$–19 J g^{-1}).

Several samples from the same AN batch have been recycled up to 8 times in the temperature range 15–105°C. Although the results differ in details from sample to sample, the general pattern is the same. The events during the first scan are described above. Upon cooling, there is usually only one transition, at ~48°C. Sometimes, with moistened samples, there is an endothermic peak at a slightly lower temperature, or exothermic peaks already at 60–70°C. When the sample had experienced one single exothermic transition upon cooling, reheating gave the same general pattern as on the first heating. The second cooling pattern leads to another behaviour upon reheating: the temperature of the first peak is lowered, and the 86°C peak is big. When a sample is repeatedly recycled, it will sooner or later change to this latter pattern.

Another way to affect the DSC spectrum is to heat the sample above 126°C. Such samples invariably (based on six experiments) have one transition at 48°C when cooled, and upon reheating the 53°C peak, and no or at most a very small 86°C peak. The temperature for the second peak increases upon recycling and occurs at 92–93°C after more than 5–6 cycles.

DISCUSSION

1. Literature data on transition enthalpies

As the interpretation of the results reported above will be based on values for transition enthalpies, some of the earlier investigations listed in Tables 1 and 2 will be commented upon. The results of Stephenson et al. [4] and Nagatani et al. [5] are in good agreement with each other, both as to transition enthalpies and heat capacity. Their data have been obtained with an adequate experimental technique. Nagatani et al. [5] also has a discussion of earlier results, notably the discordant findings of Eichenauer and Liebscher [24]. Data from Nagatani et al. will be quoted in connection with the DSC results, and Table 1 shows that the enthalpies of the IV → III and III → II transformations seem to be known within ± 0.2 J g^{-1}.

2. Effects of moisture and thermal history

Several investigations starting with Behn [2] in 1908 have found that the moisture content affects the IV → III transition upon heating. Brown and McLaren [11] state that IV → III does not occur in the dry state, and that thermal cycling raises the IV → III transition temperature from 37°C initially to about 50°C. (It is not evident whether this is considered to be a continuous process with both IV → III and IV → II occurring concurrently, or a sudden and complete change in transformation behaviour.) Michaelis et al. [32] found that the IV → III transformation is very slow in perfectly dry samples, requiring months at 33°C and 0.5 h at 40°C. However, opinions differ on the critical moisture content. Griffith [12] states that a dry sample reacts at 55°C (mainly IV → III), but with more than about 0.1% moisture present a constant transition temperature of 35°C is obtained. Sjölins comprehensive study comes to similar results [33]. These findings are difficult to reconcile with those of Cohen and Helderman [10], who found incomplete conversion from III to IV at 18°C with the solid sample in contact with the saturated aqueous solution for several days. Juopperi [17,34] clearly states that a IV → II transition never takes place, and that the IV → III temperature varies with the thermal history of the sample, but not with the moisture content. The experimental background for these statements is not clear for the present author.

Also, Sowell et al. [16] assert that IV → III occurs between 43 and 51°C, and then III → II at about 86°C. Contrary to this, Hendricks et al. [35] could confirm an older report [36] of a complete IV → II in some samples. Shinnaka [37] concludes that the water content of the specimen and the time and temperature of previous heat treatment are the factors that determine whether the IV → II ($\sim$50°C) or the stable IV → III transition will occur. Alekseenko and Boldyrev [38] find that the 32°C peak is more distinct in humid samples, and that repeated cycling (20–80°C) intensifies the 32°C peak and weakens the 50°C peak. In a paper of which only an abstract is available [39], drying is considered to first change the temperature of IV → III from 32 to 51°C, and then to replace the IV → III with a IV → II transition at 51°C.

It is also noted [39] that the III → II transition is not affected by the presence of water: in a subsequent communication [40] this transition temperature is reported to rise from 84.5 to 89°C on drying. Brown and McLaren [11] observed a higher III → II transition temperature after recycling. Such a dry sample (0.04% H_2O) also exhibits a II → IV transition (47°C). A short note [41] dealing with the II → IV transition at 50°C is difficult to evaluate because of the lack of experimental information.

To sum up, the moisture content either affects or does not affect the IV → III transition, the thermal history is of importance, and the reaction at 50°C during heating is either a IV → III, IV → II, or a mixed IV → III + II transition. In this study, only a 53°C peak but no 85°C peak has been observed on nine occasions (Table 3), with ΔH^0 (transition) $= (23.6 \pm 1.0)$ J g^{-1} (mean value ±one standard deviation). Using from Nagatani et al. ΔH^0 (IV → III, 32°C) $= 21.2$ J g^{-1}, ΔH^0 (III → II, 85°C) $= 16.9$ J g^{-1} and appropriate C_p values, ΔH^0 (IV → II, 53°C) $= 22.9$ J g^{-1} is calculated. It is also noted that ΔH^0 (125°C) does not depend on the previous events. The only explanation for these findings is that a complete IV → II transition has occurred at $\sim$53°C in these samples.

In four cases, there are indications that the sample was pure phase III during heating to above 86°C, and the $\Delta H^0 = 16.8$ J g^{-1} obtained is in experimental agreement with the value cited above. The two values given in Table 3 for the 48°C transition upon cooling are consistent with a II → IV reaction. The endothermic reaction at a lower temperature than the preceding exothermic encountered twice with moistened samples must be interpreted as the reaction IV → III, for thermodynamic reasons. The exothermic peaks that occur around 65°C should be II → III transitions.

In most cases, reactions occur both at 53 and 86°C, and the unambiguous interpretation is that a mixed IV → II + III transition has occurred

$$1\,\mathrm{AN(IV)} \rightarrow x\,\mathrm{AN(III)} + (1-x)\,\mathrm{AN(II)}$$

Samples free from phase III (that is the samples used here when first heated) react at 53°C with $x \approx 0$, independent of the moisture content (at least below 1.6% H_2O). Samples where phase III has been present "recently" or is present transform at a lower temperature with $x \approx 1$.

Samples that have been heated above 126°C invariably transform II → IV upon cooling and consequently react with $x \approx 0$ upon reheating. During recycling (15–105°C) sooner or later either a II → III (60–70°C) or a IV → III reaction (47°C) develops, and reactions during reheating have $x \approx 1$. Such a sample must change during storage and revert to the first reaction pattern, but the factors that influence this change have not been studied here.

It should be noted that the moisture values given are correct when the sample is heated for the first time, but the moisture content will diminish during the measurements. It is evident from the results discussed here that the presence of water facilitates the occurrence of phase III. However, the DSC is no suitable instrument to study the quantitative aspects of this problem. The two earlier reports [11,40] of the temperature rise for the III → II transition after cycling are confirmed here.

3. *Heat content of AN*

The difference between the DSC value ΔH^0 (II → I) $= (57.4 \pm 1.3)$ J g^{-1} (average ±95% confidence interval of the mean, 17 values) and the $\Delta H = (55.41 \pm 0.38)$ J g^{-1} from ref. 5 is hardly significant bearing in mind that there might be an additional $\leqslant 1\%$ systematic calibration error in the DSC data and that the precise meaning of "± 0.38 J g^{-1}" is not defined [5].

The literature values for the enthalpy of melting scatter considerably. The most recent cryoscopic investigation [23] was evaluated by the present author to lead to $\Delta H^0 \approx 65$ J g^{-1}. An earlier investigation [42] of the same kind leads to $\Delta H^0 = 75$ J g^{-1}. It is believed that the present $\Delta H^0 = 77.4$ J g^{-1} with its maximum uncertainty of ± 3.3 J g^{-1} is the best available estimate of the enthalpy of fusion. This conclusion is corroborated by "practical" experiences from Supra's AN-plant, which indicate that the true value of the enthalpy of melting is in the range of 75 to 80 J g^{-1}.

The heat content function for AN up to 170°C can now easily be constructed from the heat capacity and transition enthalpies from Nagatani et al. [5] and from this investigation. This is possible both for stable (with IV → III at 32°C) and metastable conditions (with IV → II at 53°C).

The two determinations of C_p° (AN, liq) with the average $C_p^\circ = 1.98$ J g^{-1} deg^{-1} indicate that ΔC_p° is negative for the fusion process, which is unusual.

4. *The IV → III transition temperature*

It might be noted that several dilatometric determinations of this temperature have all given results very close to 32.2°C. On the other hand, thermal

(DTA, DSC), X-ray, and optical experiments have resulted in values that range from 32 to 55°C. Although partial answers to this disparity are given above, the complete description of the phenomenon is still lacking.

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