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Note

STUDY OF THE INFLUENCE OF EXPERIMENTAL CONDITIONS ON THE COURSE OF THE DSC CURVE OF AMMONIUM NITRATE (20–140°C)

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In the range between laboratory temperature and the ammonium nitrate fusion temperature four phases are known, which on heating or cooling, respectively, of the substance undergo reversible phase transitions.

The phase transition of IV → III was observed over the temperature interval 32–51°C, for ammonium nitrate of a high degree of purity the range of 43–51°C is observed [1]. This phase transition is connected with drastic structure changes and is supposed to occur by recrystallization of ammonium nitrate after its dissolution in the humidity present [2].

In addition to phase III in the region of about 50–55°C, the formation of a metastable phase III was also observed [3,4]. According to ref. 5, the formation of this phase appears to depend to a certain extent on the circumstances, viz. whether at 86°C, an endothermic excursion on the DTA curves is observed, corresponding to the III → II phase transition, which is registered for these curves only irregularly. The phase transition of II → I takes place at 120–122°C [1].

The aim of the present work was to study the effect of the sample weight and of the heating rate on the temperatures of phase transitions and on the respective ΔH values.

EXPERIMENTAL

Chemicals

The measurements were performed using commercial ammonium nitrate, p.a., which by powder diffractograms was identified as phase IV. A weighed sample of 0.3 g was ground in an untempered ball mill for three minutes. Immediately after grinding, the substance was weighed into aluminium dishes which were closed. The samples were kept at laboratory temperature.

Equipment

A Perkin-Elmer calorimeter type DSC-2 was used. The integration of the excursion planes on the DSC curve were performed by the computer attached. An empty aluminium dish was used as a reference. The samples used were of 2, 5 and 8 mg. The heating rate was 2.5, 5, 10 and 20 K min^{-1}. The device was calibrated using the latent heat of fusion of indium. The measurements were performed in the range 20–140°C. The results presented here represent the average of five to ten measurements.

RESULTS AND DISCUSSION

The studied temperature range should cover three phase transitions of ammonium nitrate, which on heating appear to be endothermic. As the measurements of this study showed and as is also known from the literature [5], the phase transition of III → II was not observed regularly. The suggestion was also made, that when the III → II transition cannot be registered,

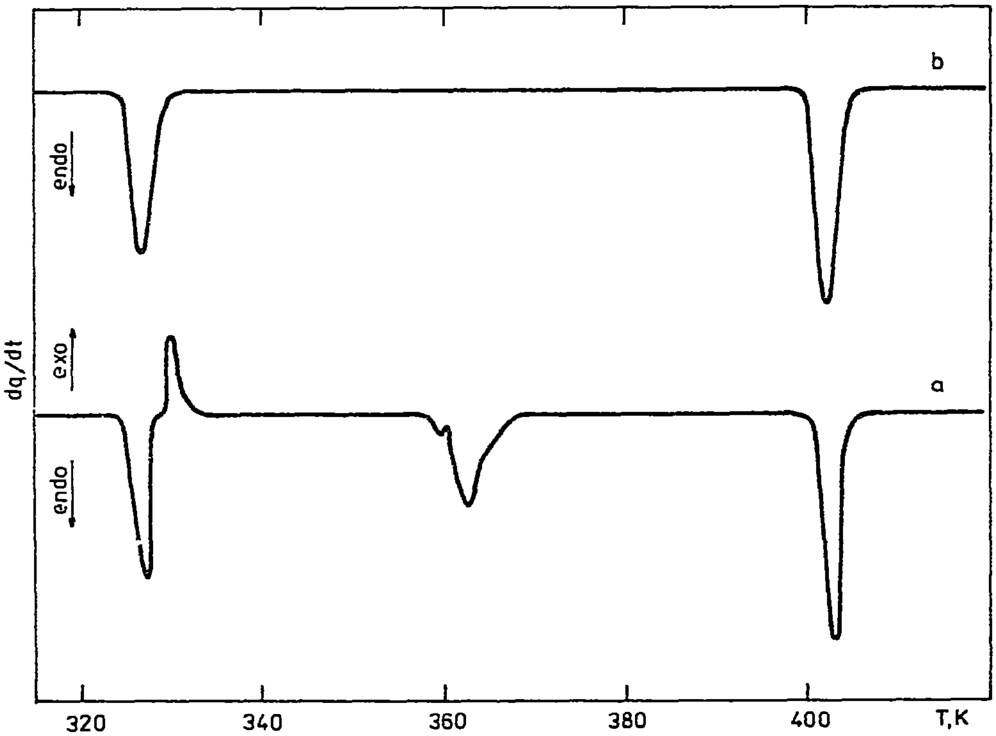

Fig 1. (a) Typical DSC curve for a sample with III → II phase transition and (b) the DSC curve of the same sample measured after 24 h.

the phase transition IV → II takes place instead of IV → III, owing to morphological and crystallographical inhomogeneities of the sample [5]. From the total number of about sixty measurements made in the present study, the endothermic excursion on the DSC curve corresponding to the phase transition of III → II was observed in ten cases. Each of these diagrams showed the excursion corresponding to the IV → III transition being accompanied by an exothermic excursion (Fig. 1a) with the temperature maximum at 56°C. It was concluded that the exothermic excursion indicates the formation of a metastable phase III, which is tetragonal like the stable phase above temperatures of 86°C, however, with a different symmetry space group [3,4]. Then, in agreement with ref. 5 one could suppose that the formation of this phase is the condition for registering an endothermic excursion, corresponding to the III → II phase transition. If the dish containing the sample in which the III → II transition was observed was left to cool and the measurement was repeated after 24 h, the DSC curve did not exhibit any exothermic process accompanying the IV → III transition, nor was, however, the transition of III → II registered (Fig. 1b). On this point the results of the present study differ from those in ref. 5. They are, however, in agreement with the thermodynamic conclusions on the irreversibility of processes that on heating are accompanied by the release of heat.

In studying the effect of the rate of temperature increase on ΔH values and on the temperature maxima of the endothermic excursions corresponding to the phase transitions of IV → III and II → I the sample weight was ≈ 5 mg and the heating rates were 2.5, 5, 10 and 20 K min^{-1}. The results obtained indicate (Table 1) that with increasing heating rate also the temperature maxima (T_m) of the excursions on the DSC curves slightly increases, and likewise also the ΔH values show a moderate increase. This is in

TABLE 1

The average values of temperature maxima for endothermic excursions, T_m, on the DSC curve and the ΔH value of IV → III and II → I phase transitions in dependence on the heating rate

Heating rate (K min^{-1})	T_m (K)	Standard deviation, σ	Transition heat ΔH (kJ mole^{-1})	Standard deviation, σ	Phase transition
2.5	325.446	0.2267	1.8196	0.0138	IV → III
5	326.764	0.3051	1.8204	0.0429	
10	328.946	0.3736	1.8065	0.0271	
20	332.395	0.6984	1.8553	0.0134	
2.5	401.110	0.2036	4.3833	0.0131	II → I
5	402.234	0.3732	4.3685	0.0832	
10	405.092	0.6532	4.4105	0.0181	
20	407.977	0.7925	4.4321	0.0296	

TABLE 2

The average values of the temperature maxima for endothermic excursions, T_m, on the DSC curve and the ΔH values of IV → III and II → I phase transitions in dependence on the sample weight

Sample weight (mg)	T_m (K)	Standard deviation, σ	Transition heat ΔH (kJ mole^{-1})	Standard deviation, σ	Phase transition
2	328.517	0.2166	1.8010	0.0093	IV → III
5	328.946	0.3736	1.8065	0.0271	
8	329.069	0.5040	1.8456	0.0110	
2	403.654	0.3652	4.3722	0.0237	II → I
5	405.092	0.6532	4.4105	0.0181	
8	405.028	0.5765	4.4174	0.0197	

agreement with the knowledge of the influence exerted by the heating rate on the quantitative characteristics of the transitions at which the sample weight does not undergo any change [6].

The influence of the sample weight on the characteristics of the phase transitions of ammonium nitrate was investigated at the heating rate of 10 K min^{-1}. The values obtained for the maxima of the endothermic excursions (T_m) and those of ΔH for IV → III and II → I phase transitions are shown in Table 2. With increasing sample weight the temperature of the excursion maxima and the respective ΔH values also slowly increase. As for changes in the heating rate similarily for changes of the sample weight, the differences between the T_m values and between the ΔH values are comparatively small. It seems, however, that the sample weight also influences the circumstances as to whether the III → II phase transition is registered on the DSC curve. For a 2 mg sample this transition was not registered in a single instance from ten measurements; for the sample weight of 5 and 8 mg this transition was registered in only once in six measurements.

The temperatures of ammonium nitrate phase transitions IV → III and III → II determined in this work are in agreement with the data found [1] for very pure NH_4NO_3. The enthalpy change for the IV → III phase transition measured at temperatures of 32.4°C and 32.1°C was 1.72 kJ mole^{-1} [7], and 1.59 kJ mole^{-1}, respectively [8]. The ΔH values determined in this study for different experimental conditions exhibit smaller differences than those cited above. The average value of ΔH for phase transition IV → III was 1.822 kJ mole^{-1} $\pm 1.6 \times 10^{-2}$, while that for phase transition II → I was found to be 4.399 kJ mole^{-1} $\pm 2.4 \times 10^{-2}$ a near value to 4.22 kJ mole^{-1} presented in ref. 8 for a temperature of 125.2°C.

REFERENCES

1 R.P. Sowell, M.M. Karnowski and L.C. Walters, J. Therm. Anal., 3 (1971) 119.
2 N.R. Brown and A.C. McLaren, Proc. R. Soc London Ser. A, 266 (1962) 428.
3 N.L. Bowen. J. Phys. Chem., 30 (1952) 721 (cited in A.J. Majumdar and R. Roy, J. Inorg. Nucl. Chem., 27 (1965) 1961).
4 J.L. Amoros, F. Arrese and M.L. Canut, Z. Kristallogr., 117 (1962) 92
5 I. Konkoly-Thege, J. Therm. Anal.. 12 (1977) 197.
6 A. Blažek, Termická Analýza (Thermal Analysis), Státní nakladatelství technické literatury, Praha, 1972, p. 95.
7 C.C. Stephenson, D.K. Betz and D.A. Stevenson, J. Am. Chem. Soc., 77 (1955) 2161.
8 Landolt-Bornstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Vol. II, Part 4, Springer Verlag, 1961, p. 208.