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INFLUENCE OF FREQUENT RHOMBIC—MONOCLINIC CRYSTAL TRANSFORMATION AND OF MOISTURE CONTENT ON AMMONIUM NITRATE CRYSTAL TRANSFORMATION ENERGIES*

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The aim of this paper was to determine the influence of a great number of successive rhombic monoclinic crystal transformations on the ammonium nitrate crystal transformation energies. The energies of ammonium nitrate crystal transformations from rhombic into monoclinic, from monoclinic into trigonal and from trigonal into cubic were observed as functions of the number of previous crystal transformations and the moisture content.

The phase transformations of ammonium nitrate have been extensively investigated by DTA, DSC and dilatometry [1–15]. The structures of the phases have also been investigated [16–22]. Open questions remain as regards the behaviour of ammonium nitrate in the temperature range from 30° to about 60° and the influence of repetition of heating and cooling cycles through the NH_4NO_3(IV) $\rightleftharpoons NH_4NO_3$(III) phase transformation point [1, 17, 19, 21].

The purpose of the present work was to investigate the changes in temperature and energy of the rhombic into monoclinic (IV $\rightarrow$III), monoclinic into trigonal (III $\rightarrow$II) and trigonal into cubic (II $\rightarrow$I) crystal transformations for prilled ammonium nitrate samples after 5, 10, 15, 20, 35 and 50 rhombic–monoclinic crystal transformations. The ammonium nitrate samples contained from 0.01 to 1.21% (mass) of moisture, and the influence of the moisture content on the crystal transformation energies was also investigated.

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Experimental

All investigations were carried out on technical ammonium nitrate prilled from the melt. The investigated salt originally contained a minimum of 99.5% (mass) of ammonium nitrate and a maximum of 0.5% (mass) of water. The contents of impurities in the dried investigated ammonium nitrate are shown in Table 1.

Table 1 Contents of impurities in investigated ammonium nitrate

Impurities	Content, % (mass)	Impurities	Content, % (mass)
CaO	0.08	NaO	0.06
MgO	0.05	K_2O	0.05
Fe_2O_3	0.06	SO_4	0.02
BaO	0.06	Cl	0.01
NiO	0.04	NO_2	0.03
ZnO	0.06	SiO_2	0.04

Samples with the same chemical composition but with different moisture contents, 0.01, 0.03, 0.10 and 0.35% (mass), were selected. The sample with 0.35% (mass) of moisture was kept in air at 25° with a relative humidity of 75% in a climatic chamber, and samples with of moisture contents 0.61, 0.87, 1.13 and 1.21% (mass) were prepared from it. The moisture contents of the samples were determined by Karl Fisher titration.

The samples to be investigated in amounts of 10 g, were packed in double polyethylene bags to prevent moisture exchange with the environment. The bags were closed by sealing. Samples packed in this way were heated to 60° in 12–14 min, left in the dryer at 60° for 2 hours, then cooled to 5° in 18–22 min and left in the climatic chamber at 5° for 2 hours. Under such conditions, reversible crystal transformation of rhombic into monoclinic ammonium nitrate and back takes place. Such a period of heating and cooling, in the course of which the crystals are transformed from the rhombic into the monoclinic form and then back into the rhombic form, will be referred to as a thermalshock.

After 5, 10, 15, 20, 35 and 50 thermalshocks, the samples of prilled ammonium nitrate were broken up in a porcelain mortar, separately for each experiment, immediately before investigation. Differential thermal analysis was then carried out with a derivatograph, whereby the temperatures and energies of the ammonium nitrate crystal transformations from rhombic into monoclinic (IV $\rightarrow$III), monoclinic into trigonal (III $\rightarrow$II) and trigonal into cubic (II $\rightarrow$I) were determined. The derivatograph was calibrated by means of the potassium nitrate crystal transformation.

For the transformation of the trigonal into the cubic crystal form of ammonium nitrate, the same samples were investigated with a Perkin–Elmer DSC–1B differential scanning calorimeter.

The investigations were carried out with both techniques because of previously observed differences in the behaviour of the same sample of ammonium nitrate in investigations with the derivatograph and the DSC [12]. The derivatograph investigations were carried out with a ceramic crucible for all samples, in a static atmosphere of air, at a heating rate of 5 deg/min. The sample weight ranged from 800 to 850 mg and preheated aluminia was used as reference material.

The DSC investigations were carried out in a dynamic atmosphere of nitrogen, in aluminium vessels for volatile samples and at a heating rate of 8 deg/min. The sample weight ranged from 9 to 11 mg. The calorimeter was calibrated via the melting of indium.

Each calculated energy is the average of the results from at least three independent experiments on the derivatograph, or of at least five DSC results.

Results and discussion

Figure 1 presents DTA curves of samples of ammonium nitrate with different moisture contents before thermalshocking. All curves exhibit peaks for the transformations IV $\rightarrow$III, III $\rightarrow$II and II $\rightarrow$I, and the melting of ammonium nitrate.

The shapes of the DTA curves and the temperatures of the crystal transformations for ammonium nitrate generally agree well with the literature data [2, 4, 10, 12, 15], but in the case of [1] only for the samples with higher water contents. Brown and McLarsen [1] have suggested that the IV $\rightarrow$III phase transformation takes place only in the presence of moisture, via a dissolution and recrystallization mechanism involving drastic structural change. Asadov et al. [16] investigated the morphology of crystal growth in polymorphic transformations by means of optical microscopy and established the existence of a new phase between the well-known modifications IV and III. Our results did not indicate any difference between the DTA curves of samples containing 0.01 and 1.21% (mass) of moisture.

The DTA curves of all investigated samples show that the temperatures of all crystal transformations and of the melting of ammonium nitrate decline with increase of the moisture content from 0.01 to 0.20%. Further increase in moisture content, in the investigated interval, does not influence the temperatures observed. The temperatures determined with this technique under the given conditions agree with those in the literature [1–4, 16] (Fig. 2).

When the temperatures of ammonium nitrate crystal transformations were

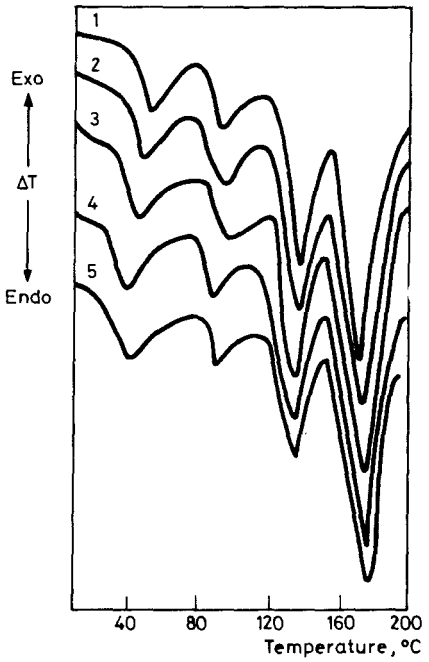

Fig. 1 DTA curves of ammonium nitrate samples with different moisture content before the thermoshocking. 1. 0.01%, 2. 0.03%, 3. 0.1%, 4. 0.87%, 5. 1.21%

studied as functions of the number of thermalshocks for samples with constant moisture contents clear-cut correlations were not established.

The crystal transformation energies from rhombic into monoclinic, monoclinic into trigonal and trigonal into cubic underwent expressed changes.

Figure 3 depicts the changes in energy of the ammonium nitrate crystal transformations as functions of the number of thermalshocks, determined with the derivatograph.

The determined energy of the rhombic into monoclinic crystal transformation is lower than that given in the literature. It decreases with increase of the number of crystal transformations, i.e. with increase of the number of thermalshocks, whereas the energies of the monoclinic into trigonal, and trigonal into cubic transformations increase with increase of the number of thermalshocks.

On the basis of this behaviour, we assumed first that in the pretreatment of the sample the rhombic into monoclinic transformation occurs, and that in the cooling period, the monoclinic into rhombic transformation is not fully reversible and that part of the ammonium nitrate is always left in the monoclinic form. Such an

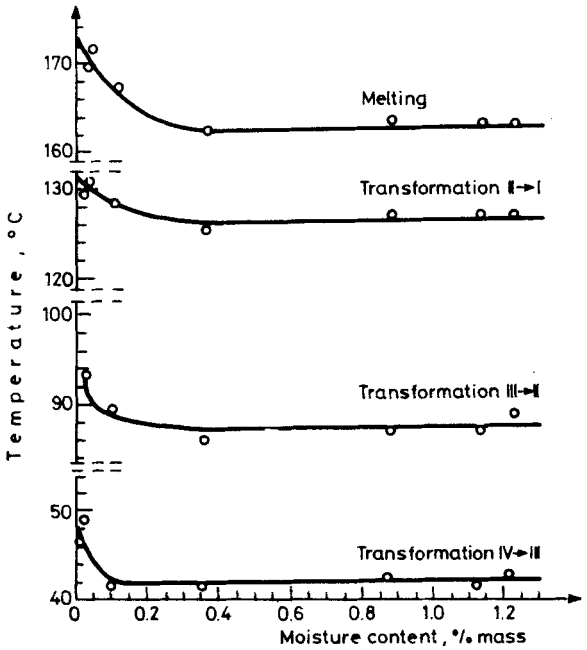

Fig. 2 The change in temperature of ammonium nitrate crystal transformations IV →III, III →II, II →I and in melting with the increase of moisture contents

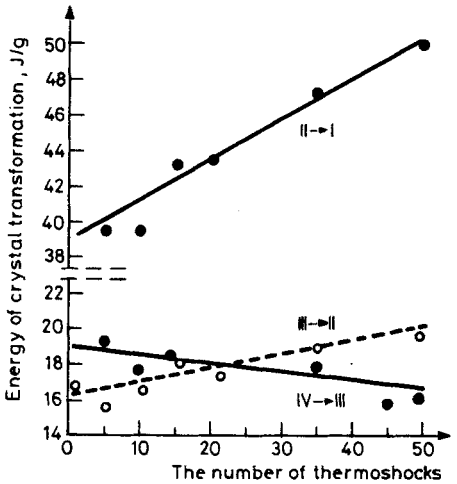

Fig. 3 The change in energy of crystal transformations from rhombic into monoclinic (IV →III), monoclinic into trigonal (III →II) and trigonal into cubic (II →I) form of ammonium nitrate for the sample with 0.35% of moisture

explanation appeared acceptable as concerns the definite energy values of this transformation.

The energy of the monoclinic into trigonal transformation tends to increase with increase of the number of thermalshocks; it exceeds the energy reported in the literature [3]. If a rhombic sample is transformed into the monoclinic form on differential thermal analysis, the resulting monoclinic form is subject to transformation into the trigonal form. If part of the sample is in the rhombic, and part in the monoclinic form, we record first the rhombic into monoclinic transformation, and then the overall transformation of the monoclinic form (produced during differential thermal analysis and thermalshocks) into the trigonal form. However, there is no reason for this energy to increase with increase of the number of thermalshocks.

A more acceptable explanation is as follows: According to the literature, both the rhombic into trigonal transformation and the reverse are known at temperatures above 50°; the trigonal into rhombic transformation is most frequently observed when samples with low moisture contents are cooled [1, 3, 21]. It could be assumed that, with increase of the number of thermalshocks, rhombic ammonium nitrate is transformed partially into the monoclinic, and partially into the trigonal form. The latter, the proportion of which appears to increase with increase of the number of thermalshocks, overlaps with the monoclinic into trigonal transformation and seemingly causes the increase in energy of this transformation.

The energy of the trigonal into cubic transformation also tends to increase with increase of the number of thermalshocks.

The dependence of the energy changes of the ammonium nitrate crystal transformations on the number of thermalshocks, for samples with different moisture contents, can be expressed as follows:

Table 2

Moisture content, % mass	Transformation IV →III	Transformation III →II	Transformation II →I
0.01	$y = 13.8391 - 0.0387x$	$y = 14.7365 + 0.0048x$	$y = 44.5623 - 0.0404x$
0.03	$y = 13.9027 - 0.0248x$	$y = 13.9099 + 0.0110x$	$y = 37.8505 - 0.0305x$
0.10	$y = 15.9260 - 0.0243x$	$y = 14.8822 + 0.0693x$	$y = 38.3480 + 0.2334x$
0.35	$y = 17.4553 - 0.0312x$	$y = 16.0355 + 0.0730x$	$y = 38.9093 + 0.2566x$
0.61	$y = 16.8878 - 0.0768x$	$y = 17.8511 + 0.1031x$	$y = 45.9083 + 0.4538x$
0.87	$y = 19.6153 - 0.1116x$	$y = 16.1174 + 0.0966x$	$y = 44.8339 + 0.2656x$
1.13	$y = 18.5812 - 0.0751x$	$y = 15.5109 + 0.0547x$	$y = 43.0936 + 0.2521x$
1.21	$y = 20.6502 - 0.1101x$	$y = 12.1270 + 0.0996x$	$y = 33.5664 + 0.2728x$

In these equations y is the energy of transformation in J/g and x is the number of thermalshocks. For $x=0$, y is the energy of crystal transformation of the hypothetical sample without a previous history of thermalshocks. The equations show that the energies of ammonium nitrate crystal transformations in the hypothetical samples (without thermalshocks) vary with increase of the moisture content of the sample.

The energy for the rhombic into monoclinic transformation tends to increase in the investigated interval of moisture contents from 0.01 to 1.21% (Fig. 4). Bearing in mind the tendency of the energy of this transformation to vary with increase of the number of thermalshocks, it could be assumed that, with increase of the moisture content of the sample, the rhombic into monoclinic transformation becomes predominant in relation to the assumed rhombic into trigonal transformation.

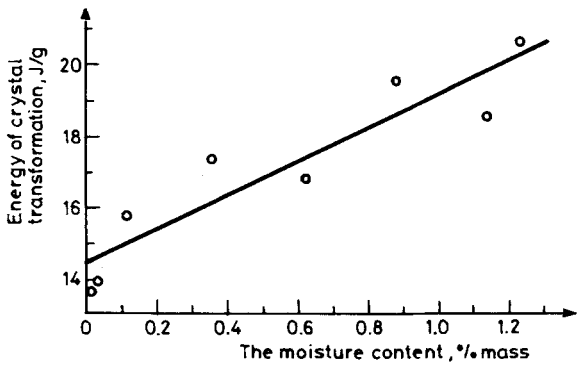

Fig. 4 The change in energy of the transformation from rhombic into monoclinic (IV →III) form of ammonium nitrate in function of moisture contents for the hypothetical sample without a previous thermal treatment

The energies of the monoclinic into trigonal and trigonal into cubic transformation of the hypothetical samples of ammonium nitrate tend to increase up to moisture contents of about 0.60%, and to decrease with further moisture content increase.

Figure 5 presents the DSC curves of the same samples of ammonium nitrate, with different moisture contents, before thermalshocking. All DSC curves show the peak of the trigonal into cubic crystal transformation at 123°, and only one peak at 67°, which grew with increase of the moisture content of the sample. The temperature at which this peak appears does not correspond to the temperature of the rhombic into monoclinic or monoclinic into trigonal transformation.

These results differ from the DSC results of Dellien [9], the DTA results of

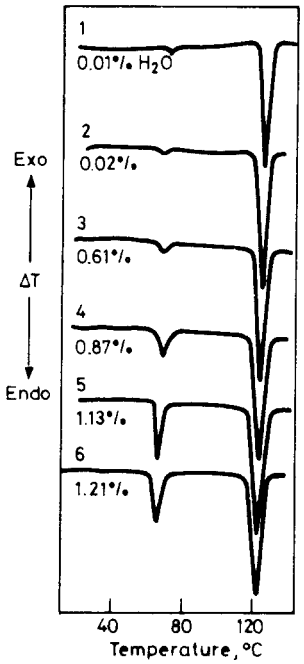

Fig. 5 DSC curves of ammonium nitrate samples with different moisture content before the thermoshocking

Langfelderova [11] and our own previous DSC results with ammonium nitrate p.a. [6].

The change in energy of the trigonal into cubic transformation as a function of the number of thermalshocks, determined by DSC, can be expressed as follows:

Table 3

Moisture content, % mass	Transformation II → I
0.01	$y = 51.6560 + 0.0072x$
0.03	$y = 51.9005 + 0.0048x$
0.35	$y = 50.9046 + 0.0095x$
0.61	$y = 50.4271 + 0.0401x$
0.87	$y = 50.2810 + 0.0292x$
1.13	$y = 50.1913 + 0.0169x$
1.21	$y = 50.0435 + 0.0128x$

These equations show a slight tendency of the energy of the trigonal into cubic transformation of hypothetical samples of ammonium nitrate to decrease in the whole interval of moisture contents examined.

With increase of the moisture content of ammonium nitrate, the DSC curves show the appearance of a distinct peak in the temperature interval from 60° to 72°. With increase of the moisture content, the peak increases, and the energy determined from the peak area does not depend on the number of thermalshocks, but only on the moisture content:

Table 4

Moisture content, % mass	Energy of transformation observed at 60–72°, J/g
0.01	2.62
0.35	7.74
0.61	5.20
0.87	14.44
1.13	15.80
1.21	16.09

From the temperature interval in which it appears, with a definite energy, this is possibly the transformation of monoclinic into trigonal ammonium nitrate.

This voluminous experimental work has established a series of phenomena connected with the changes in temperature and energy of the crystal transformations of ammonium nitrate as functions of previous thermal treatment and moisture content.

Conclusions

Investigations of the influence of thermalshocks on the temperatures and energies of the crystal transformations in prilled technical ammonium nitrate, the moisture content of which ranged from 0.01 to 1.21%, led to the following findings:

1. The temperatures of the rhombic into monoclinic (IV →III), monoclinic into trigonal (III →II) and trigonal into cubic (II →I) crystal transformations of ammonium nitrate decrease with increase of the moisture content from 0.01 to 0.20% and 0.35% respectively, further increase of the moisture contents in the investigated interval not causing any additional change.

2. A distinct influence of the number of thermalshocks on the temperatures of the investigated crystal transformations of ammonium nitrate was not established.

3. The energy of the rhombic into monoclinic crystal transformation decrease with increase of the number of thermalshocks, and increases with increase of the moisture content for the hypothetical samples.

4. The energies of the monoclinic into trigonal and trigonal into cubic transformations increase with increase of the number of thermalshocks.

5. The change in energy points to the possibility of the rhombic into trigonal crystal transformation of ammonium nitrate in the process of heating, due to the thermalshock effect.

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Zusammenfassung — Ziel dieser Arbeit war die Bestimmung des Einflusses einer grossen Anzahl von allmählichen rhombisch-monoklinen Kristallumwandlungen auf die Kristallumwandlungsenergie von Ammoniumnitrat. Es wurde festgestellt, dass die Energie der Umwandlungen von Ammoniumnitrat von der rhombischen in die monokline, von der monoklinen in die trigonale und von der trigonalen in die kubische Form eine Funktion der Anzahl der vorangegangenen Umwandlungen sowie des Feuchtigkeitsgehaltes ist.

Резюме — Определено влияние большого числа последовательных кристаллических ромбических-моноклинных переходов на кристаллические энергии превращения нитрата аммония. Найдено, что энергии кристаллических превращений нитрата аммония от ромбической до моноклинной, от моноклинной до тригональной и от тригональной до кубической зависят от числа таких кристаллических превращений и содержания влаги.