

## DSC INVESTIGATION OF THE THERMAL BEHAVIOUR OF $(\text{NH}_4)_2\text{SO}_4$ , $\text{NH}_4\text{HSO}_4$ AND $\text{NH}_4\text{NH}_2\text{SO}_3$

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### ABSTRACT

Gaseous products evolved from  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{NH}_2\text{SO}_3$  during successive heating and cooling cycles were flushed with inert gas into analyzer Dräger tubes hooked tightly to the terminal port of the DSC cell base. This simple procedure allowed the starting temperature of the decomposition to be determined and the amount of the individual gases in the mixture to be identified and even estimated.  $\text{NH}_4\text{NH}_2\text{SO}_3$  at 523 K in humid air produced  $\text{HNH}_2\text{SO}_3$  initially and, on further cycling,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  also appeared. The  $\Delta H_f$  values for  $\text{NH}_4\text{HSO}_4$  were ( $\text{kJ mole}^{-1}$ ): in an airtight sample holder 12.67, in a dry argon atmosphere 11.93, and in a static air atmosphere 10.92. Endothermic peaks for  $(\text{NH}_4)_2\text{SO}_4$  at 498 and 411 K represented the incongruent melting point and the polymorphic transition of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{HSO}_4$ . After the first heating in air to 530 K,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  exhibited closely similar cyclic DSC curves. The endothermic peaks at about 393–420 K may be assigned to different combinations of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ .

### INTRODUCTION

Literature data for the products [1,2] and the temperature [3–5] of the thermal decomposition of  $(\text{NH}_4)_2\text{SO}_4$  and for the melting point of  $\text{NH}_4\text{NH}_2\text{SO}_3$  [4–7] are ambiguous and contradictory. The equation



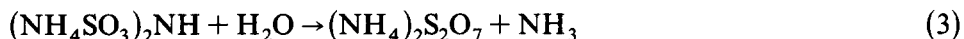
is well known for the first step of the thermal decomposition of  $(\text{NH}_4)_2\text{SO}_4$ . Little is known of the thermal behaviour of  $\text{NH}_4\text{HSO}_4$  [2–5].

This work was aimed at examining the thermal decomposition of  $(\text{NH}_4)_2\text{SO}_4$  and its main solid decomposition product,  $\text{NH}_4\text{HSO}_4$ . As  $\text{NH}_4\text{NH}_2\text{SO}_3$  can be deduced theoretically from  $(\text{NH}_4)_2\text{SO}_4$  with the loss of one molecule of  $\text{H}_2\text{O}$ , this compound was also examined.

During the successive thermal treatment above 450 K,  $\text{NH}_4\text{NH}_2\text{SO}_3$  is transformed into  $(\text{NH}_4\text{SO}_3)_2\text{NH}$  with  $\text{NH}_3$  loss [3–5].



If water is present, the reaction



may take place [5].

Considering these data, we were interested in the "fingerprint" of the products of  $\text{NH}_4\text{NH}_2\text{SO}_3$  decomposition during the thermal treatment.

## EXPERIMENTAL

Analytical grade reagents were used:  $(\text{NH}_4)_2\text{SO}_4$  from Reanal, Hungary;  $\text{NH}_4\text{HSO}_4$  prepared from  $(\text{NH}_4)_2\text{SO}_4$  with the calculated amount of  $\text{H}_2\text{SO}_4$ ; and  $\text{NH}_4\text{NH}_2\text{SO}_3$  (Fluka AG, Buchs SG, Switzerland). Samples of 2–10 mg were weighed for DSC, 100–1000 mg for derivatography and 10 mg for the Mettler thermoanalyzer.

Measurements were made with a DuPont 990 Thermal Analyzer supplied with DSC module in air and in inert atmosphere. The gaseous products which evolved during the thermal treatment of the sample were flushed into Dräger tubes hooked to the terminal port of the DSC cell base. The products were identified by colour reactions in the Dräger tubes supplied with special indicators (Drägerwerk AG, Lübeck).

Additional experiments were carried out by means of a Derivatograph (system F. Paulik, J. Paulik and L. Erdey) in air, and a Mettler-type thermoanalyzer in argon and under a hot stage microscope to follow the thermal processes visually.

## RESULTS AND DISCUSSION

### *Hot stage microscopy*

On heating at 402 K, hot stage microscopy revealed that the previously regular colourless, orthorhombic structure of  $\text{NH}_4\text{NH}_2\text{SO}_3$  suddenly disappeared. Then in the range of 410–448 K the melting material became confluent showing a sharp and broad boundary with an apparently empty inside. At 456 K it seemed to constrict.

$\text{NH}_4\text{HSO}_4$  at room temperature consisted of long rhombic prisms. It began to melt partly at 417 K and at 420 K it suddenly became a liquid. On cooling, it solidified at about 383 K; the crystals were noticeably smaller than at the start.

At room temperature,  $(\text{NH}_4)_2\text{SO}_4$  appeared as rhombic crystal heaps in layers. Up to 483 K it remained practically unchanged, then it became more transparent and remained so to 530 K.

### *Ammonium sulfamate*

DSC experiments carried out in air and in argon showed that the average value of the melting point of  $\text{NH}_4\text{NH}_2\text{SO}_3$  was 407.1 K with the corresponding melting enthalpy  $\Delta H_f = 15.23 \text{ kJ mole}^{-1}$  (indium was used as standard). The solidification of the fused salt had two exothermic peaks. On repeated heating, the profile of the melting was not so sharp as at the first heating [see Fig. 1(a) and (b)], presumably partly because the crystals became smaller due to the sudden crystallization and partly because of the slight decomposition of the salt. On fast cooling, the phenomenon of supercooling appeared [Fig. 1(a) and (c)]. When the fused salt was cooled very quickly with liquid air to below 300 K, only an exothermic heat effect appeared at about 320 K, but the melt did not solidify. This finding was confirmed at the next heating, while on the thermogram only the  $C_p$  changes were recorded [Fig. 1(c)].

Decomposition of  $\text{NH}_4\text{NH}_2\text{SO}_3$  started at about 390 K as indicated by the Dräger tube method; at this temperature, no weight change due to  $\text{NH}_3$  loss was detectable by the derivatograph or by the Mettler instrument. A measurable degree of decomposition took place at about 470 K (Figs. 2. and 3). The resulting exothermic enthalpy changes indicated that formation of a new compound began. A definite endothermic period was observed above 540 K both in air and in an argon atmosphere. At 483 K, there was a sharp

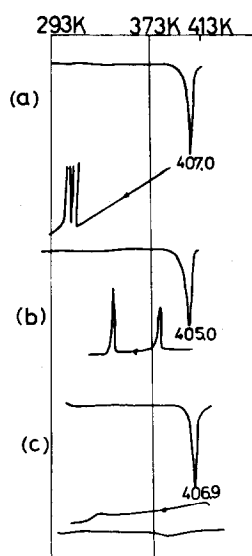


Fig. 1. Cyclic DSC thermograms showing the melting and crystallization behaviour of  $\text{NH}_4\text{NH}_2\text{SO}_3$ . (a)  $m = 5.01 \text{ mg}$   $\text{NH}_4\text{NH}_2\text{SO}_3$ ;  $v = 5 \text{ K min}^{-1}$ ; sensitivity =  $4.2 \text{ mJ sec}^{-1} \text{ in}^{-1}$ , in air. Fast cooling (with ice) after heating. (b) The same sample on repeated heating. Slow cooling (self-cooling) after heating. (c)  $m = 4.89 \text{ mg}$   $\text{NH}_4\text{NH}_2\text{SO}_3$ ;  $v = 10 \text{ K min}^{-1}$ ; sensitivity =  $8.4 \text{ mJ sec}^{-1} \text{ in}^{-1}$ , in air. Very fast cooling (with liquid air) after heating.

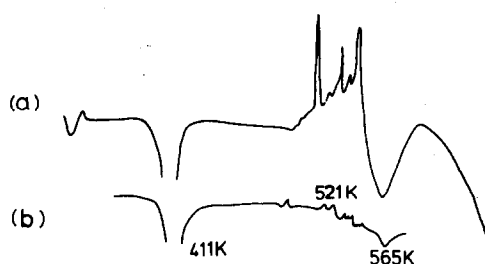


Fig. 2. Characteristic thermograms of  $\text{NH}_4\text{NH}_2\text{SO}_3$ , using (a) DuPont DSC thermal analyzer heating up to 623 K,  $m = 7.38$  mg  $\text{NH}_4\text{NH}_2\text{SO}_3$ ,  $v = 10$  K  $\text{min}^{-1}$ , in argon; and (b) Mettler thermal analyzer heating up to 573 K  $m = 8.54$  mg  $\text{NH}_4\text{NH}_2\text{SO}_3$ ,  $v = 4$  K  $\text{min}^{-1}$ , in argon.

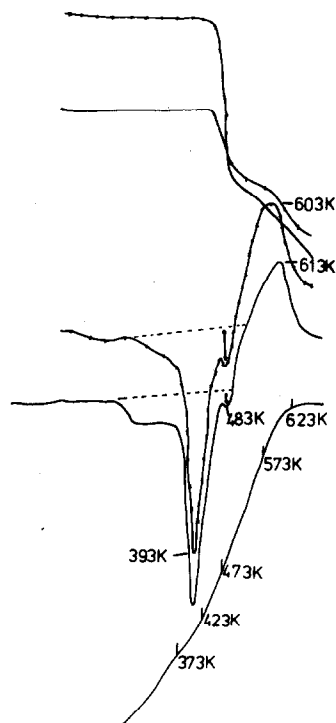


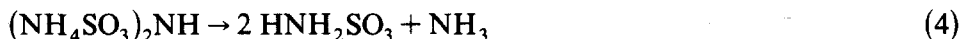
Fig. 3. Thermal behaviour of  $\text{NH}_4\text{NH}_2\text{SO}_3$  using a MOM Derivatograph. —, 571.6 mg in static air;  $\times - \times - \times$ , 595.0 mg with continuous air flushing.  $v = 10$  K  $\text{min}^{-1}$ ;  $T = 500$  K, TG = 200 mg, DTG = 1/3, DTA = 1/3.

break in the TG curves (see Fig. 3) and, at the same time, an endothermic heat effect on the DTA curve. With continuous air flushing, the weight loss and endothermic peak area increased. On DSC and Mettler thermograms (with smaller amount of  $\text{NH}_4\text{NH}_2\text{SO}_3$ ), this endothermic peak appeared only during the second heating and mostly in an inert dynamic atmosphere. In the presence of air, it rapidly disappeared.

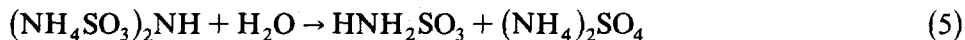
The  $\text{NH}_3$  evolution stopped at 513 K and the reaction according to eqn. (2) probably ended.

When the upper limit of the cyclic DSC thermal treatment was 523 K (Fig. 4) and the sample was exposed to air, the subsequent heating curve showed at least two endothermic peaks in the ranges 389–391 and 408–410 K, which were never observed in an inert atmosphere. On the 4th and subsequent heating and cooling cycles, the peak height at 408–410 K increased, whilst that at 389–391 K decreased (Fig. 4).

The suggested equations are as follows.



(The pure  $\text{HNH}_2\text{SO}_3$  melts with decomposition at 478 K.) In an atmosphere of moist air



According to the literature data,  $(\text{NH}_4\text{SO}_3)_2\text{NH}$  in the presence of  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  below 373 K gives  $\text{NH}_4\text{NH}_2\text{SO}_3$ .



On the basis of the above equations, the melting point of  $\text{HNH}_2\text{SO}_3$  presumably appeared on the derivatogram at about 483 K, but in the DSC and Mettler experiments, the smaller sample mass and the dynamic atmosphere were disadvantageous to the development or to the prolonged persistence of  $\text{HNH}_2\text{SO}_3$ . The effect of moisture may result in lower melting

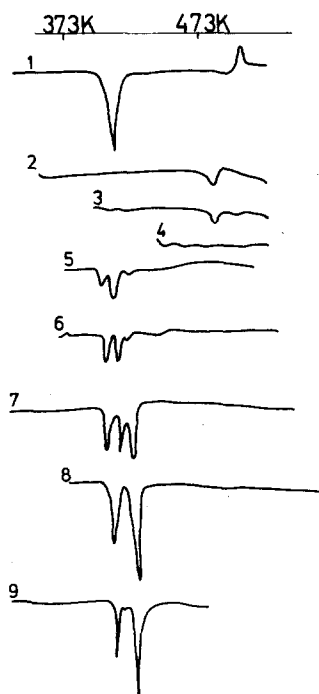


Fig. 4. The influence of air on the thermal behaviour of  $\text{NH}_4\text{NH}_2\text{SO}_3$ . Cyclic DSC curves.  $m = 7.30 \text{ mg NH}_4\text{NH}_2\text{SO}_3$ ;  $v = 10 \text{ K min}^{-1}$ ; sensitivity  $= 8.4 \text{ mJ sec}^{-1} \text{ in}^{-1}$ . in argon (1-4) and in air (5-9) after standing overnight.

points of about 407 and 419 K for  $\text{NH}_4\text{NH}_2\text{SO}_3$  and  $\text{NH}_4\text{HSO}_4$ , respectively.

### *Ammonium hydrogen sulfate*

The melting point of the  $\text{NH}_4\text{HSO}_4$  employed was 419.0 K (DSC) and was well reproducible in an airtight sample holder. In an open one with cyclic registration, a shoulder appeared on the melting profile, both in argon and in air, below the melting point. This endothermic peak was less sharp and its temperature decreased. These phenomena can be explained by the different crystallinity of the salt before and after melting. Melting enthalpies for  $\text{NH}_4\text{HSO}_4$  in different atmospheres varied characteristically because of the hygroscopic nature of the salt.

The measured  $\Delta H$  values were  $12.67 \text{ kJ mole}^{-1}$  in an airtight sample holder,  $11.93 \text{ kJ mole}^{-1}$  in a dynamic argon atmosphere, and  $10.92 \text{ kJ mole}^{-1}$  in a static air atmosphere.

During the thermal treatment of  $\text{NH}_4\text{HSO}_4$  in the DSC instrument, the  $\text{NH}_3$  evolution was demonstrated by the Dräger tube method above 523 K, but only to a very low degree. At 573 K, the amount of measured  $\text{NH}_3$  corresponded to only 0.05% of theoretically possible total  $\text{NH}_3$  loss. The weight loss at 543 K was 6.0% and at 573 K, 11.0%.

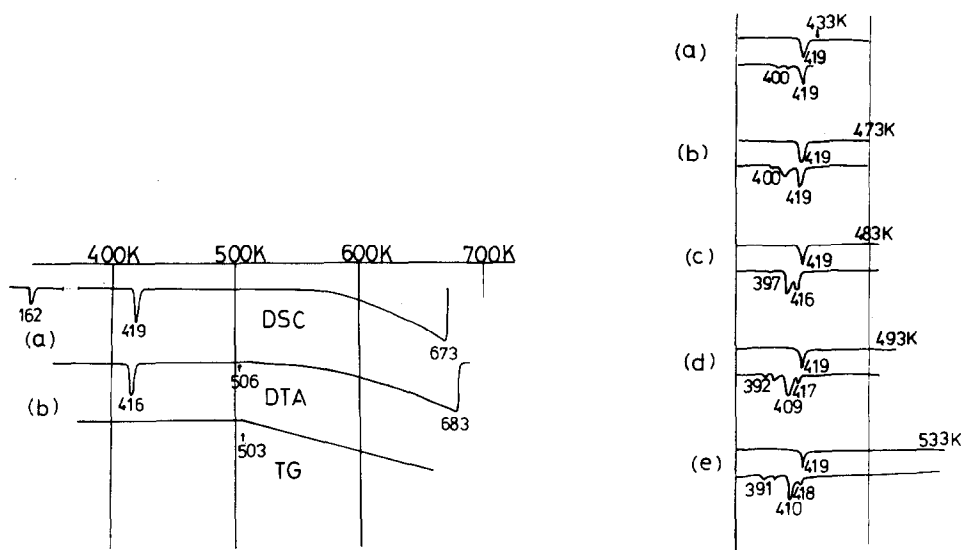


Fig. 5. Characteristic thermograms of  $\text{NH}_4\text{HSO}_4$  in air using (a) DuPont DSC thermal analyzer and (b) MOM Derivatograph.

Fig. 6. Characteristic cyclic DSC thermograms of  $\text{NH}_4\text{HSO}_4$  in air to illustrate the result of gradually increased heating.

By derivatography, using about a hundred-times larger amount of  $\text{NH}_4\text{HSO}_4$  with similar heating rate, the curves were very similar in character (Fig. 5). Above 506 K, both instrumental methods revealed the start of a weak decomposition, resulting in a large endothermic heat effect at about 680 K.

Raising the upper limit of the temperature scan in the DSC instrument (473, 483, and 533 K, using a 5–10 times larger amount of  $\text{NH}_4\text{HSO}_4$  than usual), the thermograms were different in shape (Fig. 6), especially in the number, the temperatures and the area of the endothermic peaks. With the final temperature at 473 K, three endothermic peaks had already appeared at 400, 409 and 419 K. Raising the temperature gradually, the endothermic peaks at 416–418 K decreased and, at the same time, with successive heating, the peak at 410 K increased. When the sample was heated to 503–533 K, at the subsequent heating a new endothermic peak appeared at about 393 K.

With more cycling, when the sample was heated up to 503 K, similarly to the former results, only two endothermic peaks remained at 409 and 419 K. After several cycles, the thermal behaviour of the sample did not change. Using about a hundred-times greater amount of  $\text{NH}_4\text{HSO}_4$ , repeated heating up to 503 K gave similar successive derivatograms.

### *Ammonium sulfate*

In an airtight sample holder of the DSC instrument,  $(\text{NH}_4)_2\text{SO}_4$  failed to decompose below 523 K. Working in an open sample holder, a low degree of  $(\text{NH}_4)_2\text{SO}_4$  decomposition began at 463 K, as indicated by the  $\text{NH}_3$ -sensitive Dräger tube connected to the DSC instrument. Above 493 K, a small

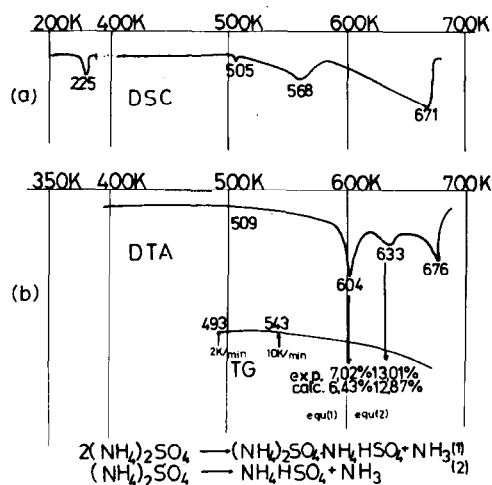


Fig. 7. Characteristic thermograms of  $(\text{NH}_4)_2\text{SO}_4$  in air using (a) DuPont DSC thermal analyzer and (b) MOM Derivatograph.

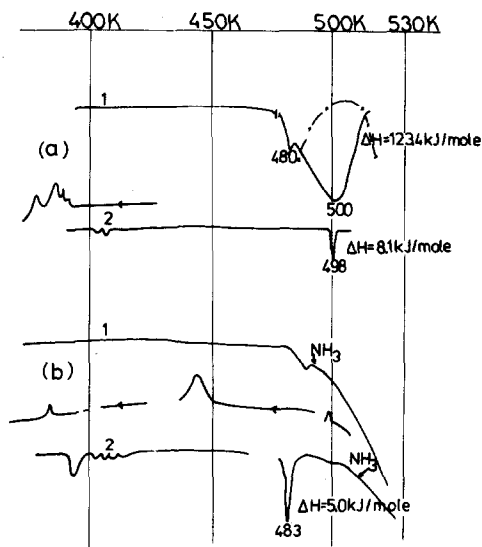


Fig. 8. Cyclic DSC thermograms of  $(\text{NH}_4)_2\text{SO}_4$ . (a)  $m = 4.38$  mg  $(\text{NH}_4)_2\text{SO}_4$ ;  $v = 0.5$  K  $\text{min}^{-1}$ ; sensitivity  $= 0.84$  mJ  $\text{sec}^{-1}$   $\text{in}^{-1}$ , in argon. Intensity of the  $\text{NH}_3$  evolution, indicated by the Dräger tube method (broken line). (b)  $m = 4.32$  mg  $(\text{NH}_4)_2\text{SO}_4$ ;  $v = 5$  K  $\text{min}^{-1}$ ; sensitivity  $= 2.1$  mJ  $\text{sec}^{-1}$   $\text{in}^{-1}$ , in argon.

loss of water was indicated. On continuous heating of a comparatively greater amount of the sample in the DSC cell, a small endothermic heat effect was recorded at about 505 K and two large ones with endothermic minima at 568 K and 671 K. The temperature of the phase transition of  $(\text{NH}_4)_2\text{SO}_4$  was 225 K (Fig. 7).

Derivatograms for 300–1000 mg of  $(\text{NH}_4)_2\text{SO}_4$  in static and dynamic air atmospheres, showed a decomposition resulting in three endothermic minima at 604, 633 and 676 K. The beginning of the decomposition was highly dependent on the heating rate: using  $2$  K  $\text{min}^{-1}$  heating rate, the process began at about 493 K, and with  $10$  K  $\text{min}^{-1}$ , at about 543 K (Fig. 7).

Peak temperatures obtained in DSC and derivatographic measurements for the decomposition of  $(\text{NH}_4)_2\text{SO}_4$  differed significantly from one another. The course of  $(\text{NH}_4)_2\text{SO}_4$  decomposition was influenced by the conditions of thermal treatment (sample mass, static or dynamic atmosphere, rate of heating, etc.). It may be assumed that these processes, which take place in the derivatograph at higher temperatures, proceed in the DSC instrument at lower temperatures.

To follow the decomposition of  $(\text{NH}_4)_2\text{SO}_4$  step by step, a  $0.5$  K  $\text{min}^{-1}$  heating rate and 4–8 mg sample were used for DSC. At the first heating, a shoulder appeared at about 480 K followed by a very high endothermic peak at about 500 K, which ended at 523 K (Fig. 8). The average value of the endothermic effect was  $\Delta H = 122.5$  kJ  $\text{mole}^{-1}$ . The  $\text{NH}_3$  evolution, as



registered with the Dräger tube, decreased at the same time as the endothermic effect ended.

When a heating rate of  $5 \text{ K min}^{-1}$  was used for DSC, the process began only in that temperature range in which the first part of the decomposition ended at the  $0.5 \text{ K min}^{-1}$  heating rate (Fig. 8). Accordingly, the first endothermic peak appeared at about 491 K and the next only at 523 K; the  $\text{NH}_3$  evolution continued without a break. Throughout the first part of the decomposition, on cooling, an exothermic peak was present at 453–463 K. When the decomposition in the range 300–523 K was complete, there was no exothermic peak on cooling. It may be assumed that this exothermic heat effect was due to an unstable compound which disappeared on further heating. The development of the peak at 480 K was enhanced by repeated heating.

In one series of experiments, the above limit of the successive heating temperature was raised gradually by 20 K (first to 453 K, then to 473 K, and so on) (Fig. 9). When the  $(\text{NH}_4)_2\text{SO}_4$  was heated to 473 K, a new small exothermic peak appeared at about 409 K on cooling; the next heating at 411 K resulted in a small endothermic peak. Raising the temperature to

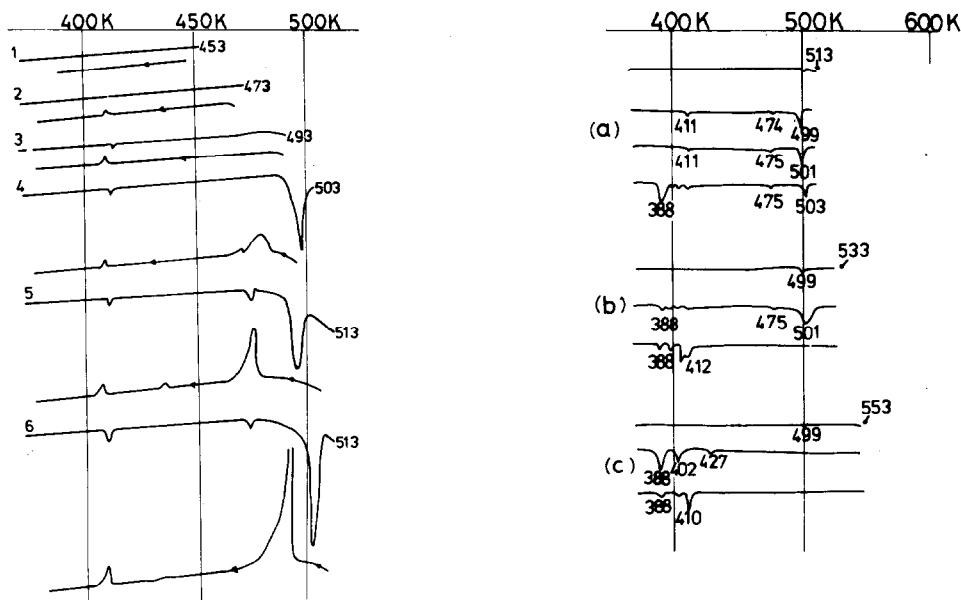


Fig. 9. Cyclic DSC thermograms of  $(\text{NH}_4)_2\text{SO}_4$  to illustrate the result of gradually increased heating.  $m = 5.88 \text{ mg}$   $(\text{NH}_4)_2\text{SO}_4$ ;  $v = 5 \text{ K min}^{-1}$ ; sensitivity  $= 0.84 \text{ mJ sec}^{-1} \text{ in}^{-1}$ , in argon (1–4) and in air (5–9) after standing overnight.

Fig. 10. Characteristic cyclic DSC thermograms of  $(\text{NH}_4)_2\text{SO}_4$  in air on heating to (a) 513 K; (b) 533 K; (c) 553 K.

503 K resulted in a new endothermic peak at 498 K. The size of the peak areas at 498 and 411 K showed an increase for both peaks.

Similarly to the DSC results for  $\text{NH}_4\text{NH}_2\text{SO}_3$  and  $\text{NH}_4\text{HSO}_4$ , when  $(\text{NH}_4)_2\text{SO}_4$  was investigated with cyclic heating in an atmosphere of air, new endothermic effects appeared at about 393 and 415 K (Fig. 10).

When the thermal treatment in the derivatograph was continued to 603 K, on further heating, a new endothermic peak appeared on the DTA curve at 469 K. When the above limit was 653 K, on repeated heating a shoulder appeared at 492 K on the former endothermic peak of 469 K.

The weight loss, as calculated from derivatographic TG curves, was 7.0% at 604 K and 13.0% at 643 K (Fig. 7). This indicates that the process does not take place either in DSC or the derivatographic experiments in one step. On the basis of the weight loss of  $(\text{NH}_4)_2\text{SO}_4$ , two equations can be postulated. According to eqn. (1), the theoretical weight loss is 12.3%. The equation calculated from the present findings for the first step is



with a theoretical weight loss of 6.43%.

The peaks at 498 and 411 K may be explained by enthalpy changes of the double salt  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{HSO}_4$ , the former peak being associated with the incongruent melting point, the latter with its polymorphic transition [2]. Namely, during thermal treatment  $(\text{NH}_4)_2\text{SO}_4$  produces  $\text{NH}_4\text{HSO}_4$ , but this new compound immediately forms a double salt with the main component,  $(\text{NH}_4)_2\text{SO}_4$ . Upon continued heating, the amount of  $\text{NH}_4\text{HSO}_4$  increases and when the ratio becomes disadvantageous, the formation of the double salt ceases. The endothermic peaks at about 393–420 K are due to different combinations of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  formed on exposure to the corresponding thermal treatments.

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