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EVALUATION OF THERMAL STABILITY OF DOPED AN USING DSC AND ARC

P.P. Lee, R.R. Vandebeek and K.K. Feng

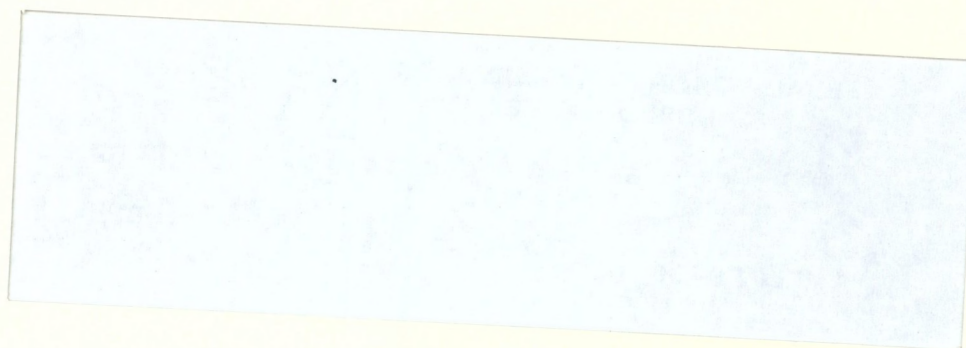
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by

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ABSTRACT

The thermal characteristics of AN (Ammonium Nitrate) and AN doped with small amounts of KNO_3 , NiO and CuO have been studied by ARC (Accelerating Rate Calorimetry) and DSC (Differential Scanning Calorimetry). ARC was used for detection of exothermic behaviour of the doped AN. DSC was used to characterize the crystal phase transitions. The doped AN samples were tested in both open and closed systems. An A.C.S. grade AN crystal was used in both instruments for comparison.

The chemical grade AN indicated self-heating above 195°C in ARC. In DSC, the chemical grade AN sample showed three crystal phase transitions between room temperature and the melting point (169°C), but the phase transition of III to II was not always observed.

The AN doped with KNO_3 , NiO and CuO were investigated by ARC. The onset decomposition temperature of NiO doped AN was detected at 235°C which is more thermally stable than KNO_3 doped AN and CuO doped AN. For KNO_3 doped AN, the first increase in self-heat rate occurred at 200°C and the onset temperature leading to ignition took place at 225°C . The CuO doped AN sample indicated self-heating at 215°C . The above doped AN samples were also tested by DSC. The crystal phase transitions of these products are of interest for practical use.

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INTRODUCTION

Ammonium nitrate(AN) has always been attractive in the explosives and propellants fields, because it is cheap and readily available. Its use is restricted in certain practical applications due to its hygroscopic nature and the phase change IV to III.

The phase change IV to III normally takes place at room temperature, and involves a volume change of 3.6% [1]. AN powder has seven distinct crystal phases below the melting point. Phases I and II are unambiguous and those transitions above phase V are not within the scope of this paper. The behaviour of AN at 32°C to 85°C appears to be irregular. AN doped with metal oxide is believed to form metal complexes which avoid the occurrence of phase III.

The thermal stability of AN has been extensively studied. When heated, the first step is the endothermic dissociation into ammonia and nitric acid. Concurrently, it decomposes exothermically and by a complex reaction mechanism into nitrous oxide and water. The molten mass of AN tends to reach a steady state temperature, which is a function both of the ambient pressure and of the heating rate [2]. An accelerating rate calorimeter (ARC) is used specifically for the determination of exothermic behaviour in larger size samples. The ARC records low initial temperatures for exothermic reaction due to heat accumulation effects.

The Canadian Explosives Research Laboratory is equipped to evaluate thermal hazards of energetic materials. ARC has been used for the purpose of assessing the thermal hazards of materials associated with exothermic reactions. Differential Scanning Calorimetry (DSC) is useful to compensate for the weakness that the quantitative results of endothermic reactions are not accessible by ARC. The purpose of the present study is two-fold, firstly, to study the crystal phase transitions of AN, AN doped with KNO_3 , NiO , and CuO below the melting point by using DSC, and secondly, to study the thermal stability of AN and doped AN above the melting point by using ARC.

EXPERIMENTAL

- 1) Materials: ACS grade AN was used as a standard. It was stored in a desiccator over silica gel. Three doped AN samples were obtained from the Defense Research Establishment Valcartier (DREV), and stored at room temperature. AN doped with 3.5% NiO is a green-coloured powder, AN doped with 5% CuO is a blue-coloured powder, AN doped with 7% KNO₃ is beige colour.
- 2) DSC: For the AN phase transition study, a Du Pont 910 DSC was used in conjunction with a Texas Instruments 9900 computer to identify and record the crystal phase transitions of AN and three related mixtures: NiO doped AN, CuO doped AN and KNO₃ doped AN. Each sample was tested in an open aluminum pan, crimped aluminum pan or hermetically sealed pan. All samples were heated at a constant heating rate of 20°C/min from an initial temperature of 35°C up to 350°C. Nitrogen gas was used as a purge with a controlled flow rate of 50 ml/min.
- 3) ARC: The thermal stability of three doped AN (KNO₃, NiO and CuO) samples were examined by ARC. An ACS grade AN crystal was used for comparison. The ARC, made by Columbia Scientific Industries [3,4], was used to study the thermal decomposition of AN above the melting point (169°C). It is designed to maintain the sample in an adiabatic condition. All measurements were conducted using wide-mouth cylindrical Hastelloy C bombs weighing approximately 49 grams each. Six stainless steel screws secured a thin metal disk and a Teflon gasket to a flange on the bomb. Approximately one gram of sample was placed in a 49 gram Hastelloy C bomb.

The step-heat method was employed in all the tests. First the sample and the bomb were heated to a starting temperature of 100°C and the calorimeter was allowed to thermally stabilize for 30 minutes. Then it was step heated 5°C. The self-heating rate was monitored at a threshold detection limit of 0.02°C/min. The process of "heat-wait-search" was continued until a self-heating rate greater than 0.02°C/min was detected. After the detection of an exothermic reaction, time and temperature data were collected until the end of reaction.

RESULTS AND DISCUSSION

1) DSC

A) ACS AN:

The DSC scan of ACS AN in Figure 1 was compared to a similar scan produced by Langfelderova [5]. The general physical characteristics of each endothermic peak were very similar. The curve showed the endothermic peak (53.8°C) corresponding to the IV to III phase transition being accompanied by an exothermic peak with a temperature maximum at 75°C. The exothermic peak (75°C) indicates the formation of a metastable phase III [6]. The endothermic peaks located at 53.8°C, 90.8°C and 128°C were identified as phase transitions from IV to III, III to II and II to I, respectively. The endothermic peak located at 170.5°C was identified as the melting point of AN.

In studying the effect of the degree of confinement on the phase transition, three different sample pan types were used: An open top aluminum pan to simulate unconfined condition, a crimped aluminium pan to simulate limited confinement, and a hermetically sealed aluminum pan to simulate a high degree of confinement. Table 1 contains the results of the effect of confinement on the phase transitions of AN and doped AN. The results indicated that the small peaks at 75°C and at 90.8°C disappeared under unconfined and highly confined conditions; and the temperature of the melting point was similar under different confinements.

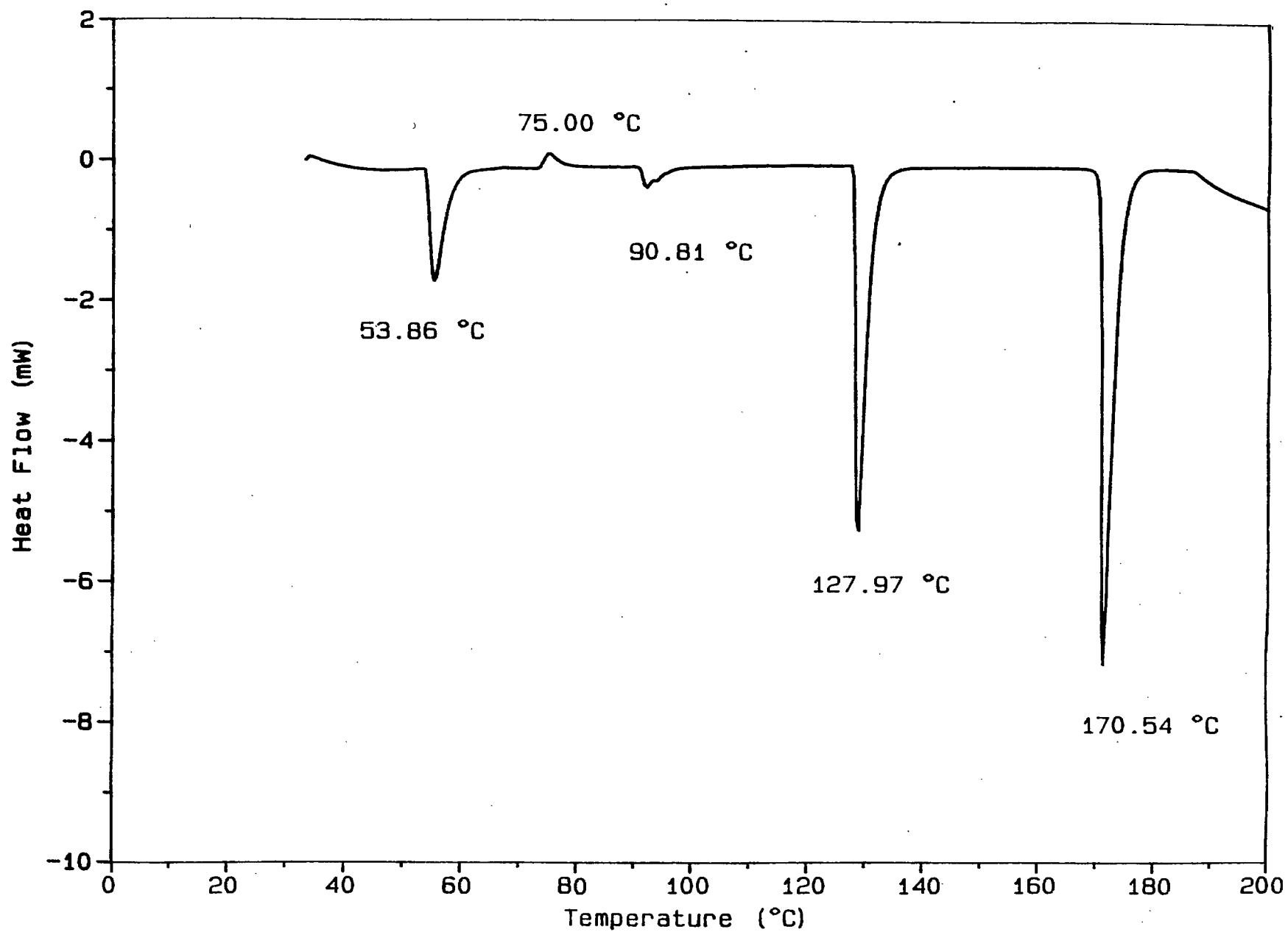


Fig. 1 - Typical DSC curve for ACS AN sample in crimped Al pan.

TABLE 1 - EFFECT OF CONFINEMENT ON THE PHASE TRANSITIONS OF AN AND DOPED AN.

| Materials | Phase Transition Temperature/°C | | |
|---------------------------|---------------------------------|--|-------------------------|
| | No Confinement | Limited confinement | High confinement |
| ACS AN | 53.0 128.0 169.8 | 53.9 75.0(exothermic) 90.8 128.0 170.5 | 55.5 129.4 170.3 |
| KNO ₃ doped AN | 121.3 129.7 158.0 | 116.1 128.2 157.6 | 118.6 129.1 156.9 |
| NiO doped AN | 57.0 127.6 140.0 155.0 | 56.9 125.3 143.9 154.3 | 58.9 128.6 141.7 |
| CuO doped AN | 59.5 130.8 169.3 | 57.0 129.6 168.5 | 61.1 132.5 155.3 |

Note: The above temperature is the onset temperature of the thermal curve.

B) KNO_3 doped AN

The first observable phase transition IV to II occurred at 116.1°C as shown in Figure 2 and differs from the behaviour of ACS AN. It is evident that a real nucleation of KNO_3 had taken place [7]. The second endothermic peak 128.2°C was assumed to represent the transition from phase II to I. The third endothermic peak, 157.6°C , is the point at which the mixture begins to melt. It appears that the melting point of AN is lowered by 13°C by the presence of 7% KNO_3 . The effect of confinement condition on the phase transition is shown in Table 1. There is no difference in endothermic peak under three confinement conditions.

C) NiO doped AN

The first observable endothermic peak (56.9°C), as shown in Figure 3, is broad and not sharply defined. It did not appear that the sample transformed directly from phase IV to phase II, by passing phase III. Choi and Prask [8] have previously demonstrated the above using x-ray powder diffraction and indicated that a portion of the sample transformed from IV to III at 55°C . They also showed that at 60°C the phase II peak began to appear while the phase III peak was still increasing. Nevertheless, Choi and Prask indicated that the phase IV material was predominant.

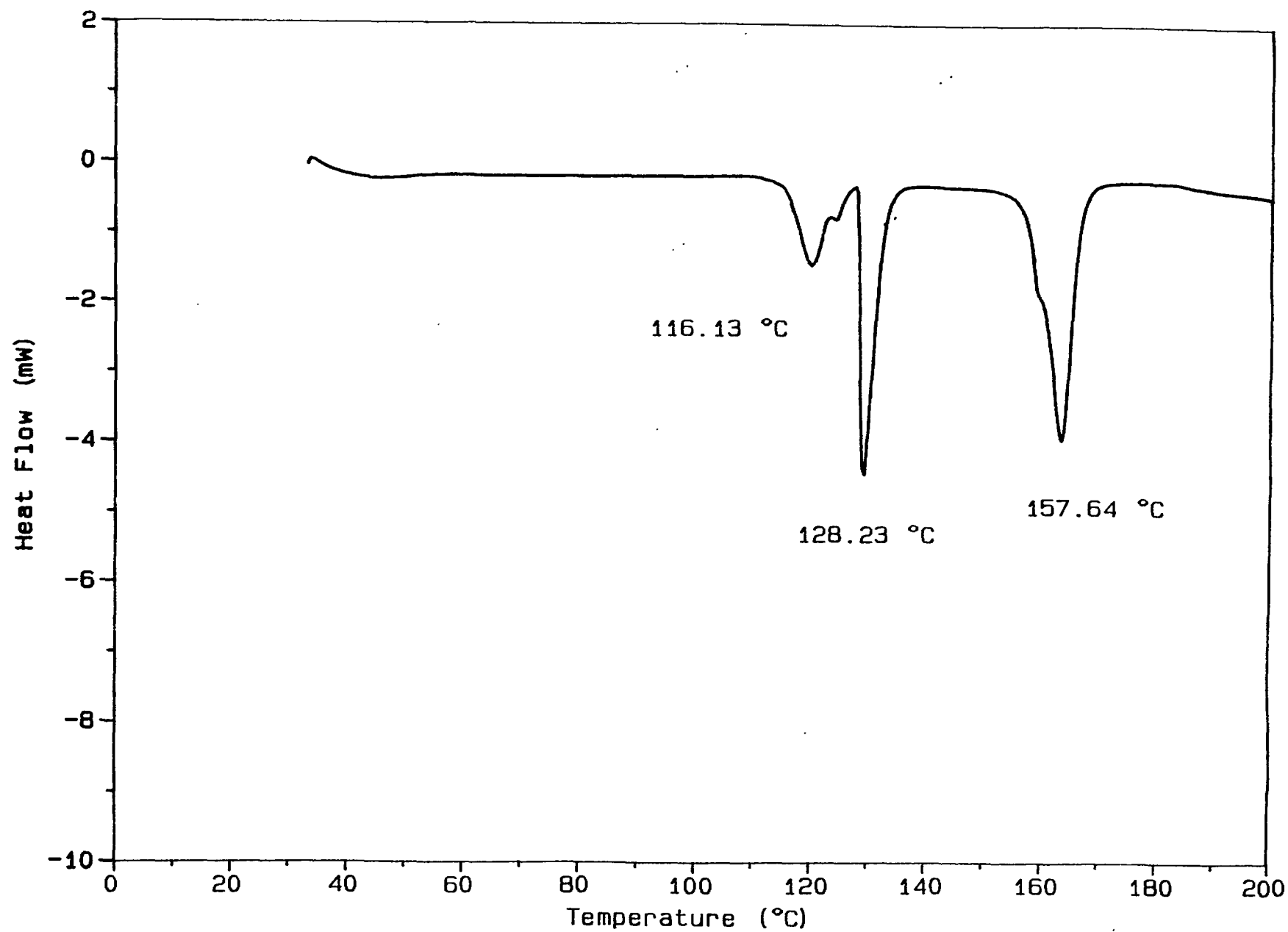


Fig. 2 - Typical DSC curve for KNO_3 doped AN sample in crimped Al pan.

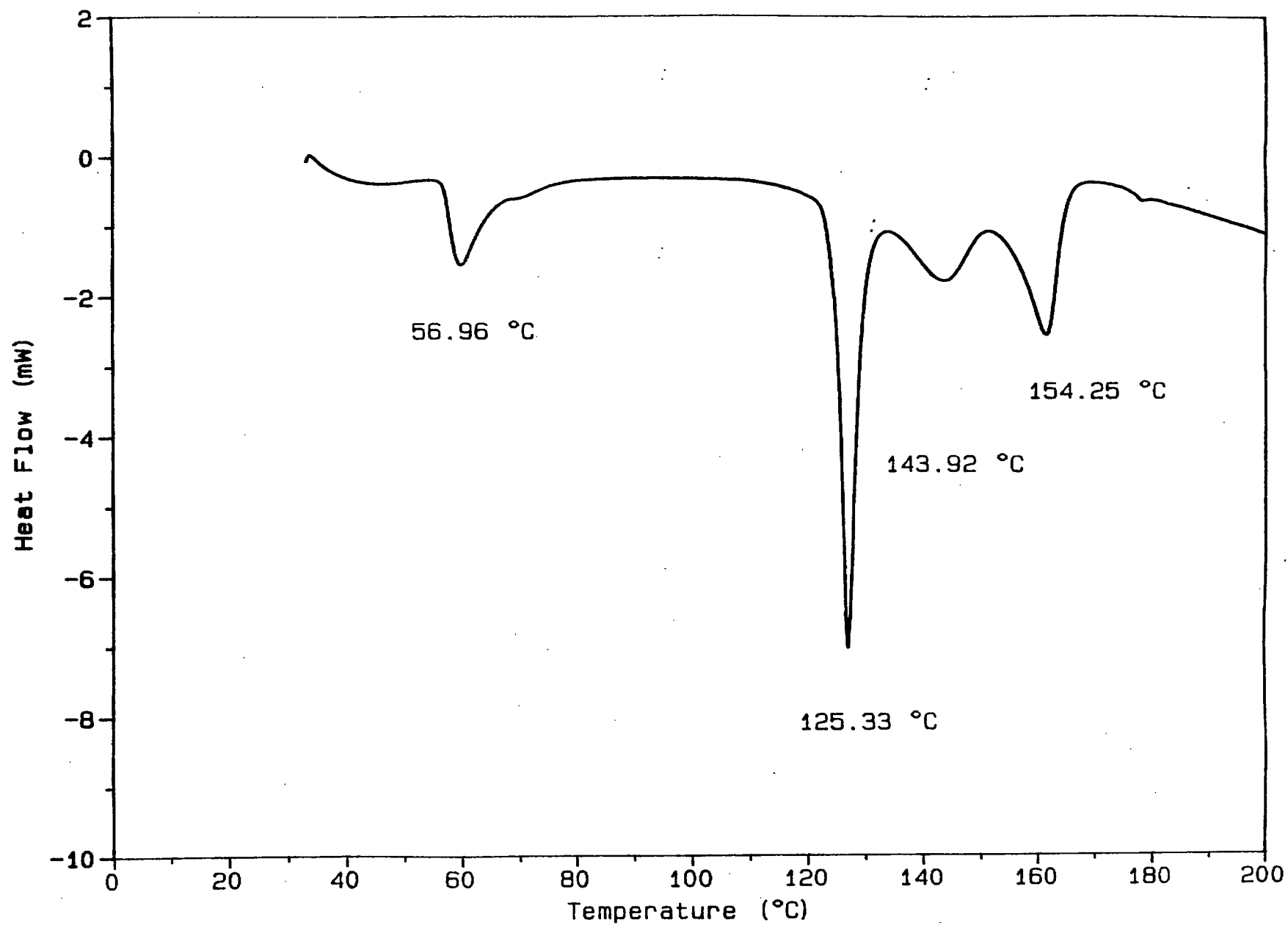


Fig. 3 - Typical DSC curve for NiO doped AN sample in crimped Al pan.

The endothermic peak (125°C) represented the II to I transition. This occurred at slightly lower temperature than the equivalent transition observed for ACS AN. The melting point of NiO doped AN is 154.3°C which is lower than that of standard AN. The mixture possibly forms a metal-amine coordination compound. There is another weak endothermic peak (about 140°C) before the melting point. This peak may correspond to phase transition II to I due to crystal orientation.

The effect of confinement conditions are shown in Table 1. The peaks of the NiO doped AN sample under no confinement are essentially identical to that of the sample in the crimped pan. Under a high degree of confinement in a hermetically sealed pan, the weak endothermic peak (about 140°C) has disappeared. This may be attributed to a particle size increase by recrystallization in the phase II to I transition process.[7]

D) CuO doped AN

It has been reported that the transformation III to II occurs less frequently and to a much lesser extent [9] when CuO forms an amine-metal complex with AN. This observation has been verified by Choi & Prask [8]. In Figure 4, a single transition peak (57°C) was observed. It indicated that the phase III to II transition is small and that phase IV is transformed virtually completely to phase II.

The endothermic peak (129.6°C) in Figure 4, was assumed to represent the phase II to I transition. There is a double peak character before the peak at 129.6°C. This phenomenon is the result of an inhomogeneous distribution of the CuO additive. The melting point of the mixture is 168.5°C which is similar to ACS AN.

Table 1 shows the results of changing the degree of confinement on CuO doped AN. It indicates that the high degree of confinement in a hermetically sealed pan decreases the onset melting point from 168.5°C to 155.3°C.

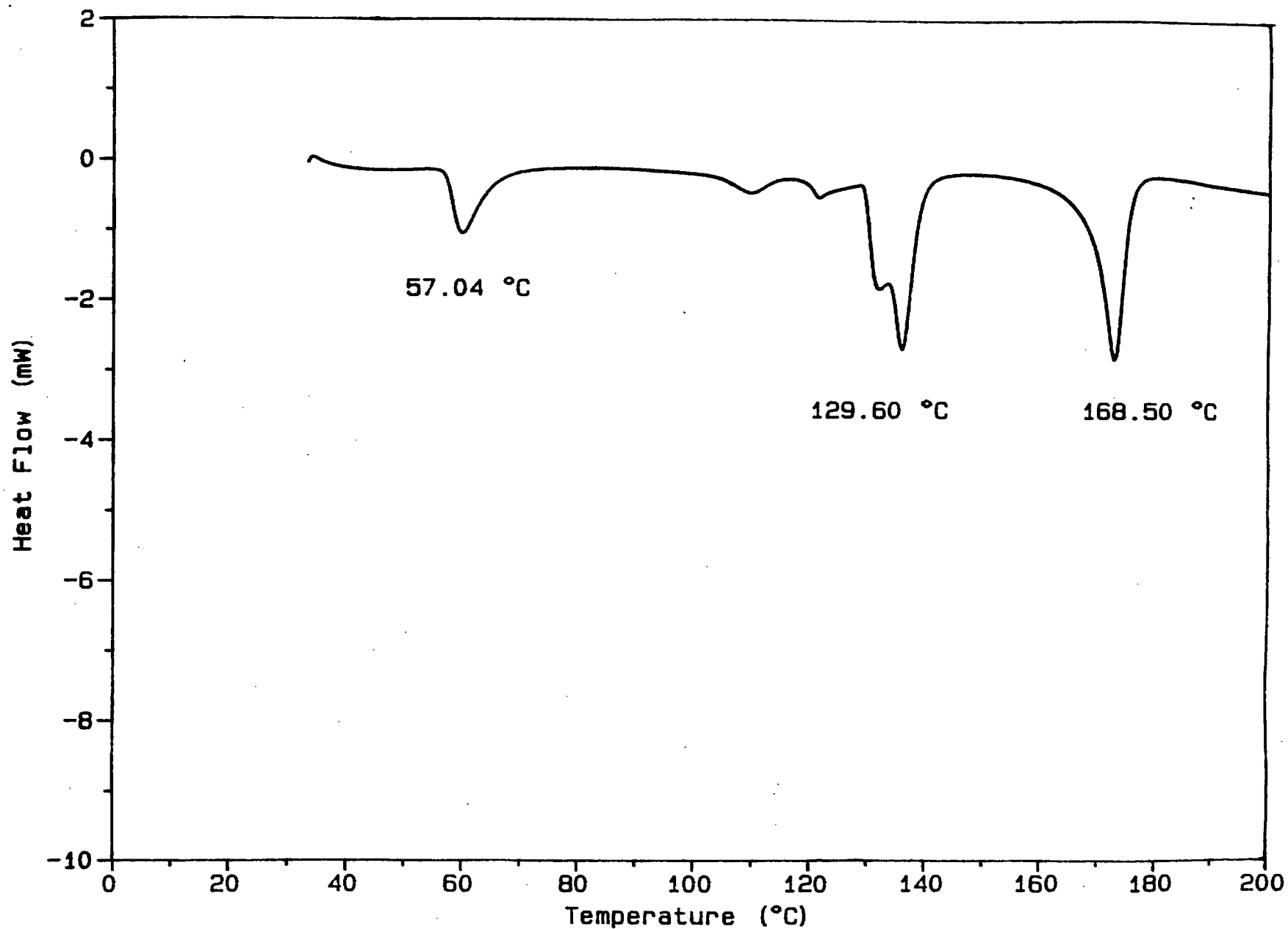


Fig. 4 - Typical DSC curve for CuO doped AN sample in crimped Al pan.

2) ARC

A) ACS AN

For ACS AN, the first self-heating was detected at a temperature of 195°C and terminated after a short time. The exotherm leading to ignition was detected at 218°C (the average of three repetitions). A plot of the self-heating rate as a function of $1/T$ is shown in Figure 5 and the data are detailed in Table 2. Total weight loss after reaction was 98%.

B) KNO_3 doped AN

When KNO_3 doped AN was heated to 170°C (just above the m.p.) and cooled, it separated into two layers with two different colours, white and beige. The first increase in self-heating rate occurred at 200°C and the onset temperature leading to ignition took place at 220°C - 230°C with an average temperature of 225°C. In the early stages of decomposition, the reproducibility of the onset temperature was poor, but the values became more consistent at a rate above 0.1°C/min as shown in Figure 6. The amount of residue after reaction is approximately 14%.

C) NiO doped AN

For the NiO doped AN, self heating was detected at 220°C. The initial onset temperature of the major exotherm was found to average 235°C for the three tests shown in Figure 7. Weight loss averaged 94%.

D) CuO doped AN

The third sample tested (CuO doped AN) indicated self-heating at 215°C. The initial temperature for the major exothermic reaction was 225°C and the decomposition curves are shown in Figure 8. Total weight loss was 94%.

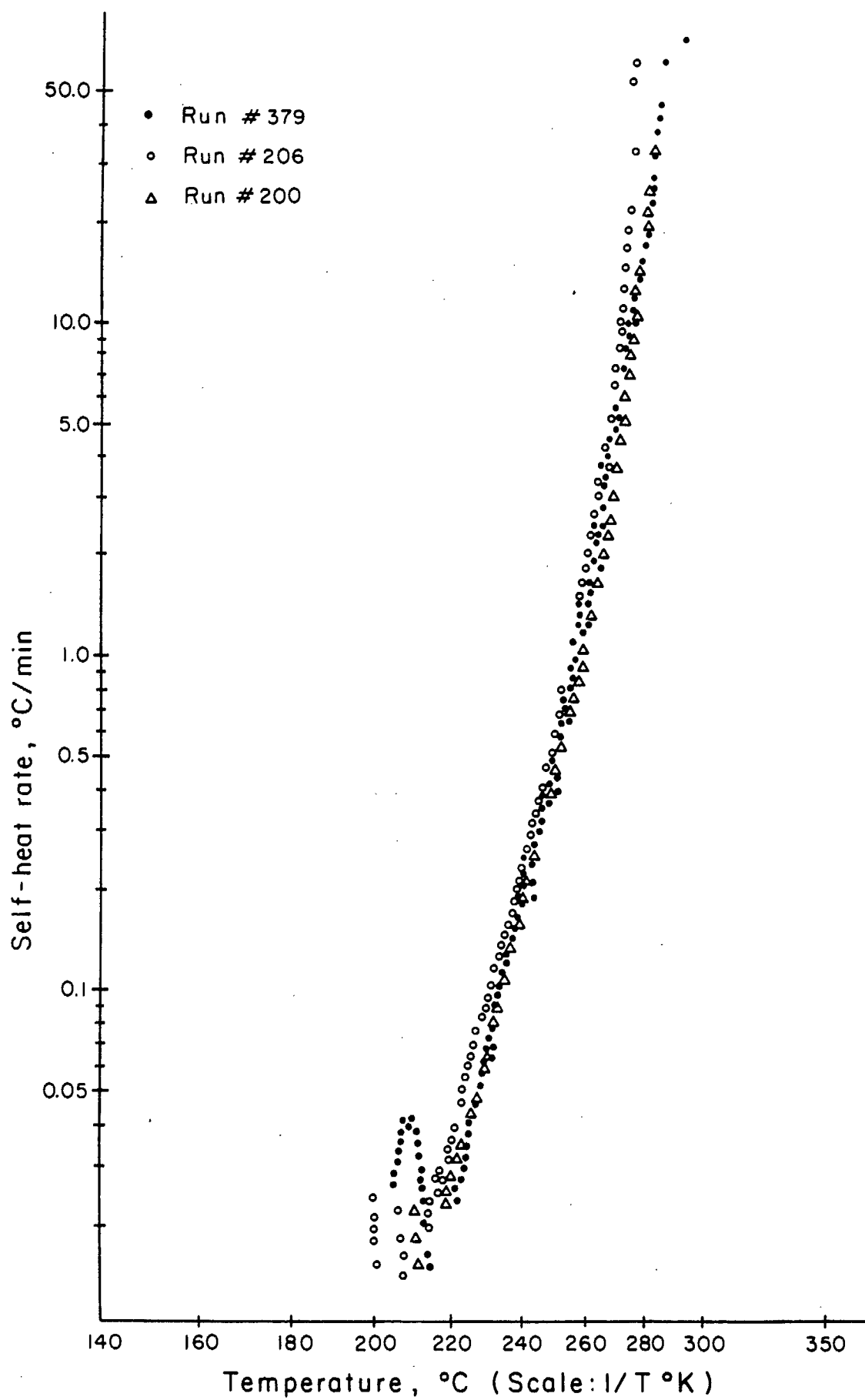


Fig. 5 - Thermal decomposition of ammonium nitrate.

TABLE 2
THERMAL DECOMPOSITION OF DOPED AMMONIUM NITRATE SAMPLES

| RUN # | SAMPLE WT. (gm) | Ø | INITIAL DATA | | AT 0.1 °C/min | | AT 2 °C/min | | AT MAX. RATE | | Δ T _{AB} (°C) | WT. LOSS (%) | 2 °C/min TO MAX RATE TIME (min) |
|---------------------------------|--------------------|------|------------------------|----------------------------|---------------|---------------|-------------|---------------|------------------------|----------------------------|---------------------------|-------------------|--|
| | | | T ₀ (°C) | m ₀ (°C/min) | T (°C) | m (°C/min) | T (°C) | m (°C/min) | T _m (°C) | m _m (°C/min) | | | |
| AMMONIUM NITRATE (A.C.S. GRADE) | | | | | | | | | | | | | |
| 200 | 1.5237 | 8.9 | 218.75 | 0.028 | 235.37 | 0.101 | 267.42 | 2.066 | 289.25 | 102.000 | 76.48 | 98.2 | 3.15 |
| 206 | 1.5058 | 9.0 | 215.46 | 0.022 | 233.08 | 0.107 | 262.54 | 2.050 | 286.73 | 112.666 | 75.45 | 98.1 | 3.24 |
| 379 | 1.5134 | 8.8 | 221.66 | 0.026 | 234.26 | 0.098 | 264.25 | 2.000 | 291.92 | 110.500 | 75.14 | ---- | 3.92 |
| AN + KNO ₃ (TP-8619) | | | | | | | | | | | | | |
| 380 | 1.0406 | 12.7 | 231.57 | 0.029 | 241.60 | 0.103 | 261.27 | 2.033 | 290.98 | 107.714 | 60.43 | 87.3 | 3.16 |
| 384 | 1.0670 | 12.2 | 224.53 | 0.022 | 239.18 | 0.100 | 263.72 | 2.000 | 291.44 | 170.000 | 68.01 | 83.3 | 2.83 |
| 389 | 1.0130 | 12.8 | 219.33 | 0.030 | 236.95 | 0.100 | 261.37 | 2.105 | 279.18 | 105.000 | 67.82 | 87.6 | 3.01 |
| AN + H ₂ O (TP-8629) | | | | | | | | | | | | | |
| 383 | 1.0370 | 13.1 | 232.72 | 0.024 | 246.75 | 0.104 | 272.28 | 1.935 | 294.14 | 59.500 | 65.10 | 91.5 | 3.13 |
| 386 | 1.0520 | 12.2 | 236.45 | 0.039 | 243.07 | 0.102 | 266.61 | 2.000 | 283.82 | 120.500 | 59.31 | 94.8 | 2.94 |
| 387 | 1.1135 | 11.9 | 236.07 | 0.024 | 238.68 | 0.108 | 267.15 | 1.909 | 294.74 | 47.500 | 61.44 | 95.1 | 3.73 |
| AN + CuO (TP-8630) | | | | | | | | | | | | | |
| 385 | 1.0160 | 12.2 | 221.97 | 0.047 | 233.99 | 0.102 | 259.52 | 2.105 | 290.04 | 126.666 | 68.07 | 93.5 | 3.32 |
| 388 | 1.0945 | 11.8 | 226.49 | 0.029 | 234.10 | 0.106 | 259.13 | 2.000 | 282.67 | 105.833 | 58.54 | 93.7 | 3.33 |
| 390 | 1.1068 | 11.8 | 226.40 | 0.031 | 235.42 | 0.107 | 265.56 | 1.937 | 287.79 | 117.500 | 68.06 | 93.7 | 3.53 |

$$\phi = 1 + \frac{C_v (\text{bomb}) M (\text{bomb})}{C_v (\text{sample}) M (\text{sample})}$$

Where C_v is the specific heat and M is the mass.

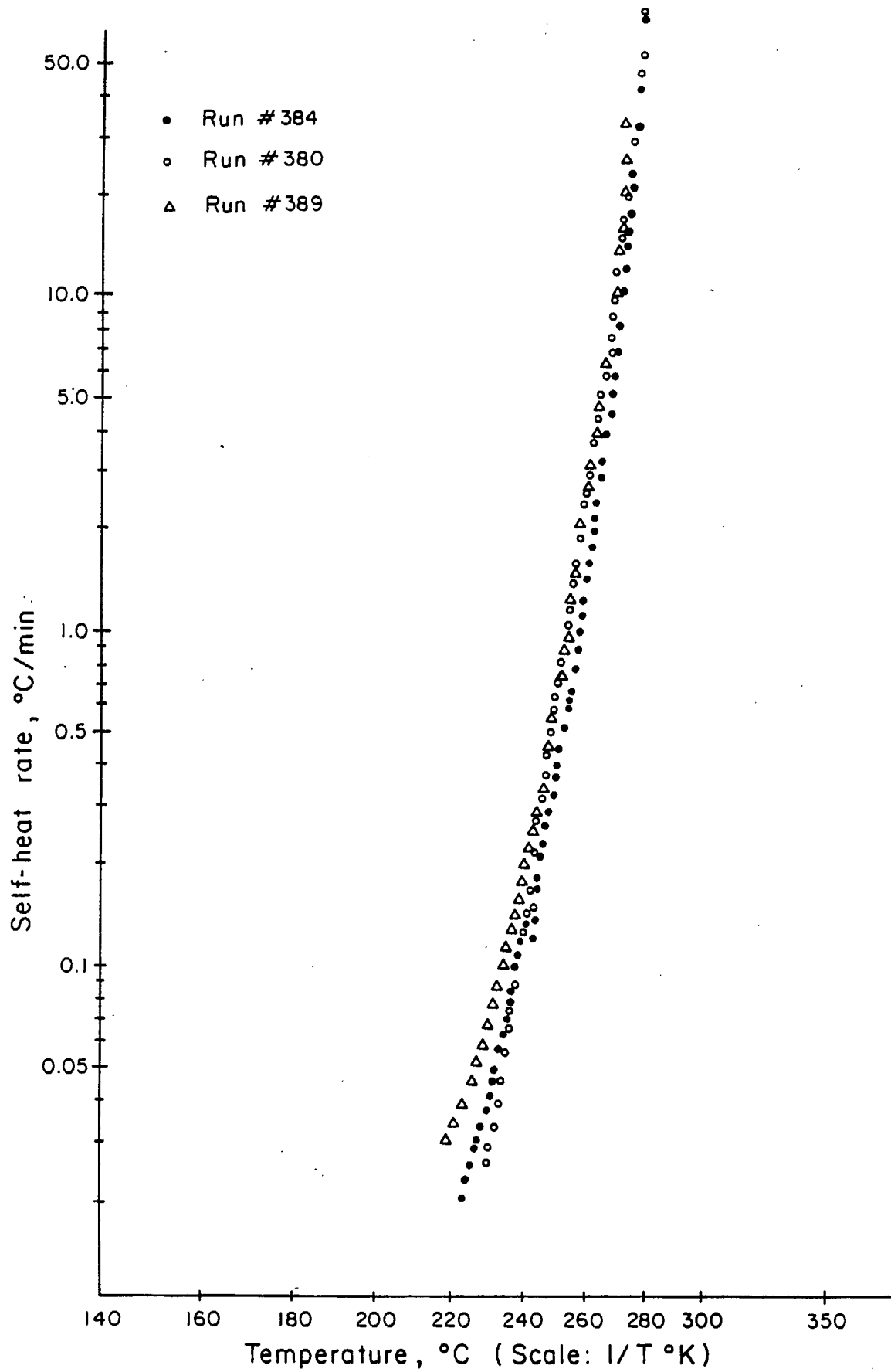


Fig. 6 - Thermal decomposition of KNO_3 doped ammonium nitrate.

After the melting point, and before the exotherm leading to ignition, the doped AN samples showed instability with slow increase in self-heating rate as a general phenomenon. Usually the self-heating rate fluctuated at the region of detection limit and it varied slightly for each test. The reaction profile for the initial decomposition is complicated, probably as a result of the properties of the metal-amine complex in the doped AN.

All AN samples ignited as the pressure built up and the cover disks were distorted after reaction. When the reaction rate is too fast, the thermocouple cannot accurately track the temperature. Therefore temperature was determined on the basis of a self-heating rate of 2°C/min and it was defined as before ignition. The time from before ignition to maximum rate was about 3 minutes; short duration of this period should raise some concern in hazard evaluation.

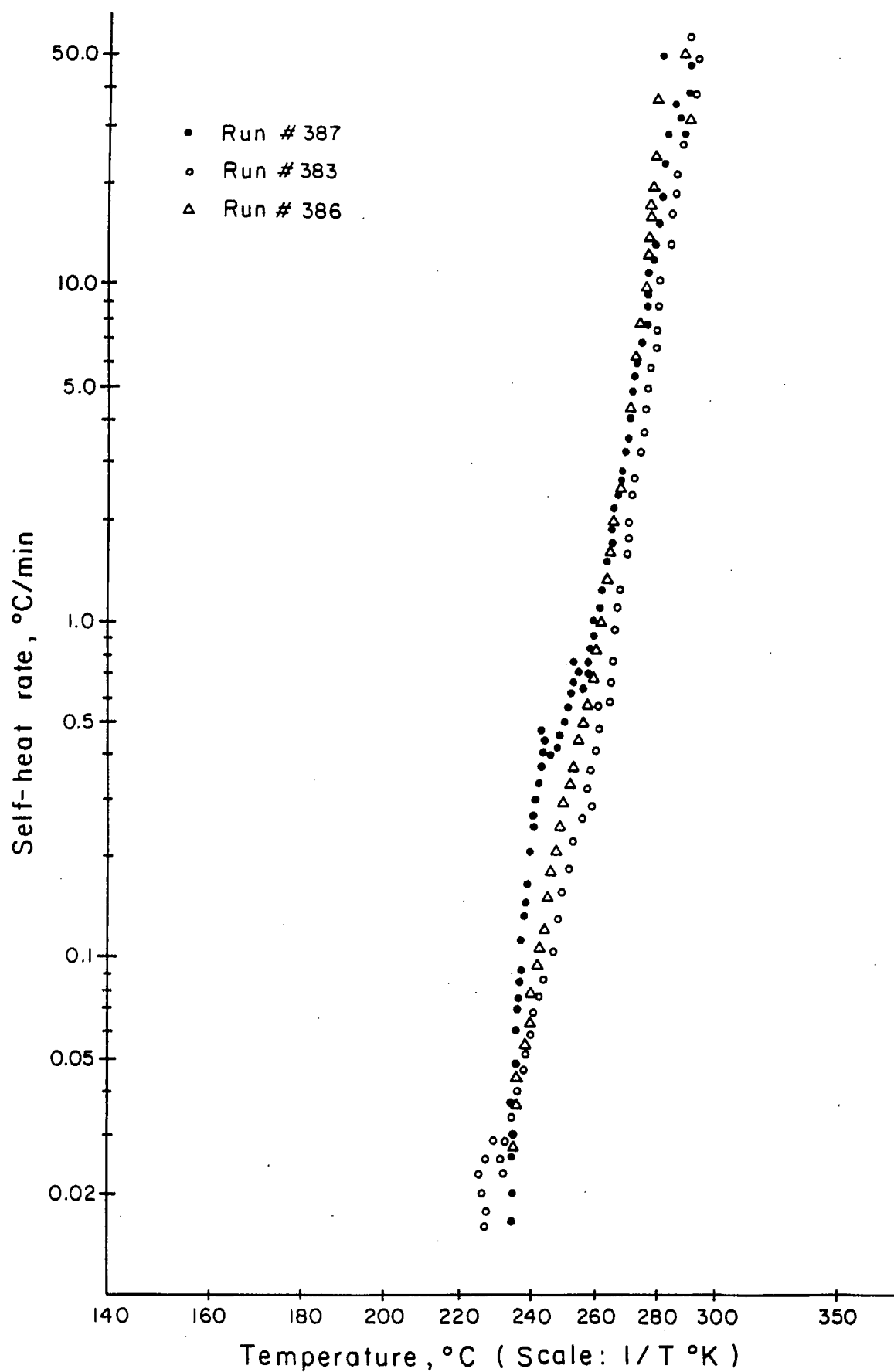


Fig. 7 - Thermal decomposition of NiO doped ammonium nitrate.

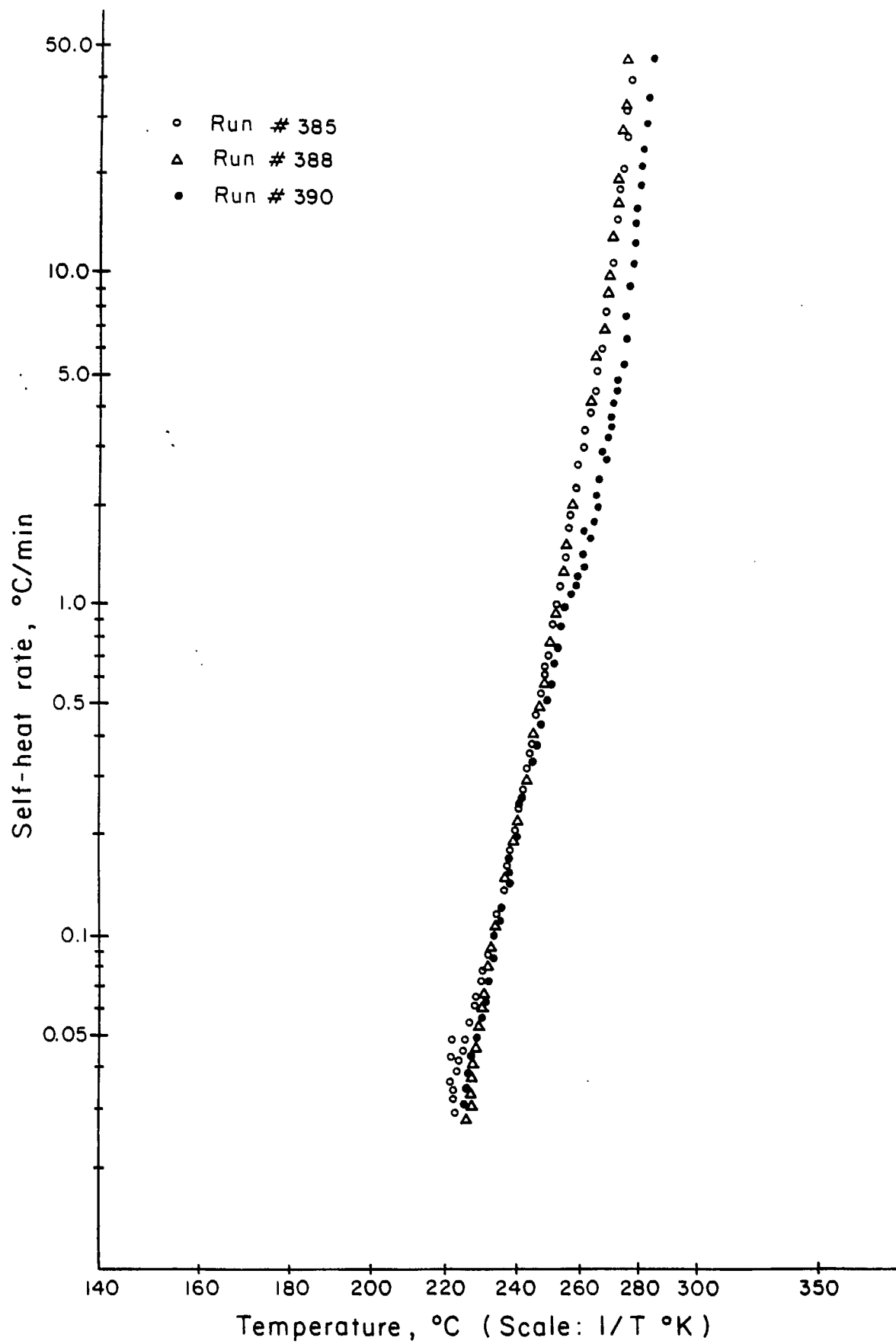


Fig. 8 - Thermal decomposition of CuO doped ammonium nitrate.

CONCLUSION

Doping affects significantly the phase transition results IV to III and III to II and the temperature of the melting point, in comparison with undoped AN. Addition of 7% KNO_3 to AN caused the initial phase transition to disappear and only phase transition IV to II is detected. The point at which the material begin to melt decreased from 170°C to 157°C . The first observable endothermic peak of NiO doped AN or CuO doped AN occurred at 57°C in contrast with the peak at 53°C (IV to III) for ACS AN. Previous investigations [8] have indicated that the peak at 57°C contains both the IV to III and IV to II phase transitions. Doping AN with NiO reduces the melting point from 170°C to 154°C .

The endothermic peaks of doped AN samples in the open aluminum pan under no confinement condition are essentially identical to that of the sample in the crimped pan under limited confinement. The temperature of the melting point of NiO doped AN and CuO doped AN samples is decreased in a hermetically sealed pan under high confinement condition.

The onset decomposition temperature of NiO doped AN is 235°C by ARC, which is higher than that for KNO_3 doped AN and that for CuO doped AN. However, when overall decomposition patterns are compared, more variation is found between successive runs for NiO doped AN. One advantage of the NiO doped AN over the KNO_3 doped product is the reduced amount of solid residue in the combustion products.

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REFERENCES

1. E. Enoksson; Symp. Chem, Probl. Connected Stabil. Explos., 6 (1982) 487.
2. G. Feick and R.M. Hainer; J. Am. Chem. Soc., 76 (1954) 5860.
3. D.I. Townsend and J.C. Tou; Thermochim. Acta, 37 (1980) 1.
4. J.C. Tou and L.F. Whiting; Thermochim. Acta, 48 (1981) 21.
5. H. Langfelderova and P. Ambrovic. Thermochim. Acta, 56, (1982) 385.
6. R.N. Brown and A.C. McLaren; Proc. Roy Soc. (London), A266 (1962) 329.
7. I. Konkoly-Thege; J. of Thermal Analysis, 12 (1977) 197.
8. C.S. Choi and H.J. Prask. Journal of Applied Crystallography, 13, (1980) 403.
9. W. Engel; Propellants, Explosives, Pyrotechnics, 10 (1985) 84.

