

THERMAL ANALYSIS OF SOME CRYSTAL HABITS OF PENTAERYTHRITOL TETRANITRATE

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ABSTRACT

The heat of fusion (ΔH_f) of the explosive pentaerythritol tetranitrate (PETN) varies as a result of the method used for its crystallization. Single crystals show a ΔH_f of 37.4 cal g^{-1} , but some samples have a ΔH_f as low as 31 cal g^{-1} . It is shown that the variation is not a function of surface area or impurity: it is the result of crystal imperfection. Calorimetric and X-ray data form the basis for the postulation of a disordered state of PETN. A scanning calorimetric method is presented for the determination of annealing rates of the disordered state, and the activation energy and preexponential for the process are determined ($E = 14.9 \text{ kcal mole}^{-1}$, $A = 1.2 \times 10^6 \text{ min}^{-1}$). It is concluded that the disorder is the result of the random inclusion within the lattice of inverted and strained PETN molecules. The effect of impurities on the system is discussed.

INTRODUCTION

The heat of fusion of a crystalline solid is a function of the amount of energy necessary to destroy the order of the crystal lattice. The internal energy of any given crystalline phase decreases as the degree of order or perfection of the lattice improves. Ideal heats of fusion can be calculated from equilibrium phase diagrams, and actual heats of fusion can be determined by scanning calorimetry. The application of such data to the study of an organic explosive is the subject of this article.

Bobolev and Karpukhin¹ presented a phase diagram for the system pentaerythritol tetranitrate (PETN)-*N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl). The system showed a simple eutectic with a eutectic temperature of 104°C and a mole fraction of PETN in the eutectic composition of 0.325. The heat of fusion (ΔH_f) for PETN, calculated from their data according to the van't Hoff equation, would be 39.8 cal g^{-1} . Values for the same diagram determined at this laboratory are as follows: eutectic temperature, 111°C ; mole fraction PETN in the eutectic composition, 0.323. The ΔH_f calculated from the latter values is 37.3 cal g^{-1} .

At least three general crystal habits of PETN can be recognized by microscopy: (1) "tetragonal" (Fig. 1), showing characteristic apex angles and little evidence of strain; (2) "needle" or "hour glass" (Fig. 2), having reentrant cavities from the ends and/or a high length to width ratio; and (3) "superfine" (Fig. 3), composed

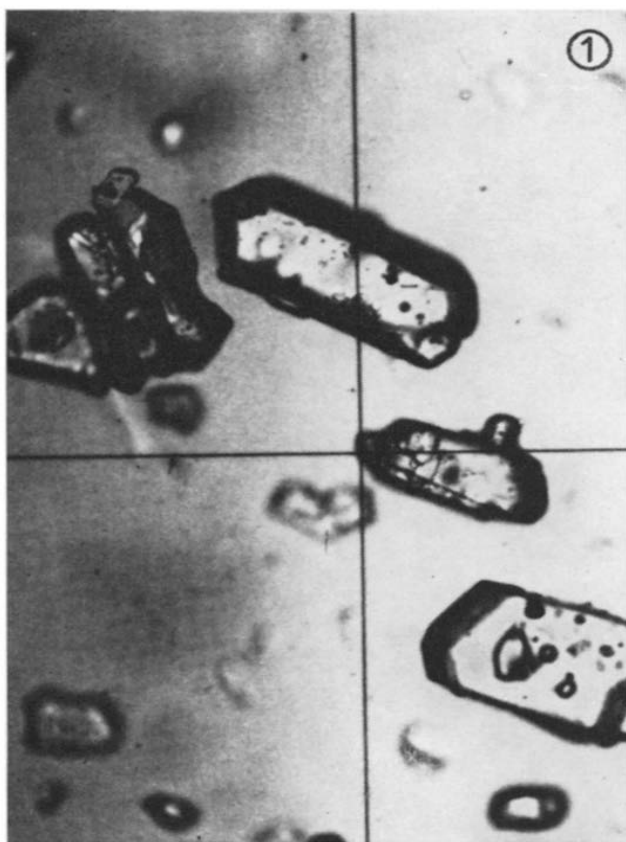


Fig. 1. "Tetragonal" PETN, sample RPS-3518 (200 \times).

largely of irregular plates. The heats of fusion of different samples of these crystal habits have been determined by scanning calorimetry.

EXPERIMENTAL

A Perkin-Elmer Model DSC-1B Differential Scanning Calorimeter was used to make all the quantitative thermal measurements. Samples were run in sealed cells (Perkin-Elmer Part Number 219-0062) to eliminate errors caused by the vaporization of the sample. Transition energies were measured with an analog computer-integrator designed and built by G. P. Watts and R. K. Spotts of this laboratory.

X-ray data were obtained with a North American Philips powder diffractometer, using $\text{CuK}\alpha$ radiation.

The superfine habit was prepared by rapidly pouring a relatively concentrated solution of PETN in acetone into water. The needle habit was prepared by precipitating PETN from an acetone or acetone-methanol solution by the addition of water. The tetragonal habit was obtained by slow addition of water to an acetone solution of PETN. The single crystals were obtained by slow cooling of a PETN-saturated acetone-water solution and by evaporation of an acetone solution.

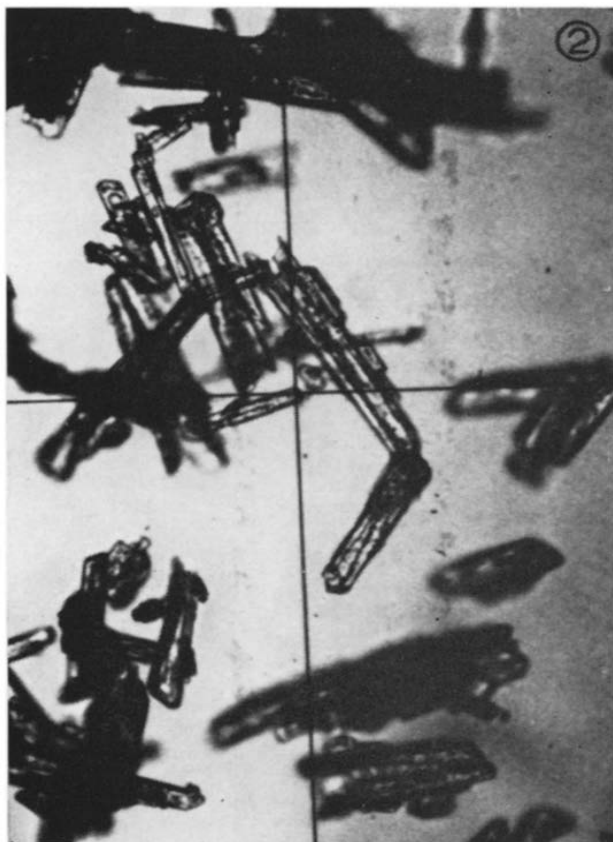


Fig. 2. "Needle" PETN, sample 25-88 (200 \times).

RESULTS AND DISCUSSION

Experimentally determined heats of fusion of PETN in the different crystal habits are shown in Table I. All error values in this report are standard deviations in units of cal g⁻¹. It can be seen that as the apparent perfection of the crystal increases the heat of fusion also increases. The single crystal value is not significantly different from the value calculated from our phase diagram.

Effect of specific surface on ΔH_f

A comparison of the results obtained from the needle-habit samples presented in Table I shows that surface area variations over a very wide range do not produce a significant difference in ΔH_f . A further search for surface-area effects and effects of physical attrition was made by ball-milling and ultrasonic grinding. A sample of tetragonal PETN with a ΔH_f of 37.2 ± 1.2 cal g⁻¹ was ball-milled to produce a powder with a surface area of 5350 cm² g⁻¹ that had a ΔH_f of 37.2 ± 0.2 cal g⁻¹. A sample of needle PETN with a ΔH_f of 36.0 ± 0.5 cal g⁻¹ was ground ultrasonically to produce a fine powder with a ΔH_f of 36.1 ± 0.1 cal g⁻¹. It can be concluded that surface area, *i.e.*, surface energy, is not responsible for the observed variations in the

heat of fusion of various PETN samples. It must also be concluded that grinding does not produce significant amounts of stored strain energy in crystals of PETN.

TABLE I
HEATS OF FUSION OF DIFFERENT PETN CRYSTAL HABITS

<i>Habit and Sample No.</i>	<i>Surface (cm² g⁻¹)^a</i>	<i>ΔH_f (cal g⁻¹)</i>
Superfine		
25-9	4700	31.7 ± 0.1
2689	4300	31.8 ± 0.2
2909	5400	33.2 ± 0.2
Needle		
25-88	3250	36.5 ± 0.3
25-159 ^b	4400	37.0 ± 0.1
25-81	16400	36.6 ± 0.3
25-157 ^b	18600	37.7 ± 1.2
Tetragonal		
RPS-3518	< 1000	36.8 ± 0.4
DB-2	< 1000	36.5 ± 0.5
Single crystals		37.4 ± 0.3

^aDetermined by gas permeability. ^bPrepared by reprecipitation of superfine 2689.

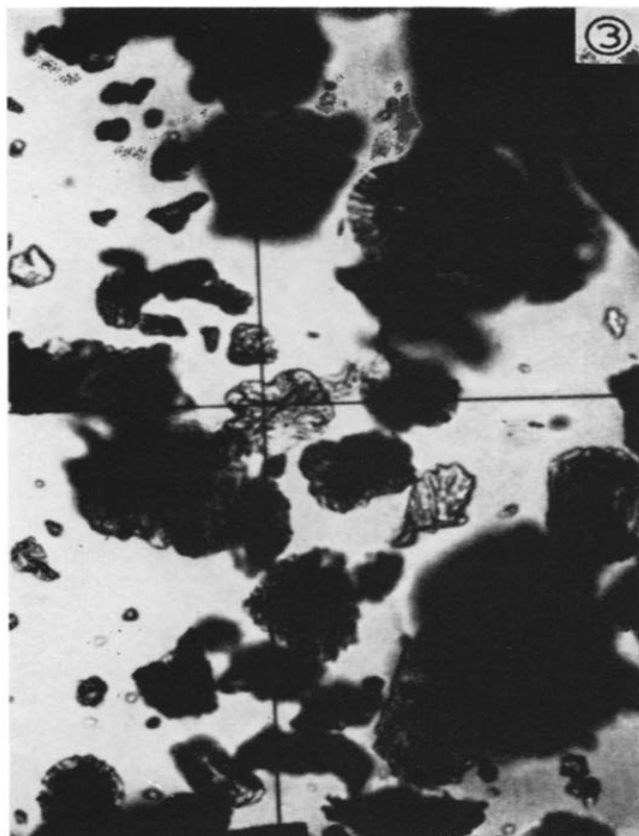


Fig. 3. "Superfine" PETN, sample 2689 (200×).

Effect of precipitation temperature on ΔH_f

The ΔH_f of superfine PETN depends on the temperature of the water used in the precipitation, as shown in Table II. The overall 4.5 cal g^{-1} change in ΔH_f cannot be accounted for by a change in purity, because all of the samples were prepared from the same batch of nominally pure PETN.

TABLE II

EFFECT OF WATER TEMPERATURE USED IN SUPERFINE PRECIPITATION ON ΔH_f OF PRODUCT

Water temperature (°C)	ΔH_f (cal g ⁻¹)
1	32.8 ± 0.3
18	35.0
50	35.9 ± 0.3
92	37.3 ± 1.0

Effect of sample purity on ΔH_f

PETN has an extremely low cryoscopic constant, making melting point a poor criterion of purity. When the cryoscopic constant is defined in terms of mole fraction, *i.e.*, $K_f = \Delta T_f/N_2$, the K_f for PETN is calculated to be $28.8\text{--}29.4^\circ\text{C mole}^{-1}$; experimentally, with tripentaerythritol octanitrate (triPEON) as second component, it was determined to be $30.6^\circ\text{C mole}^{-1}$. The equivalent K_f for water, a rather poor cryoscopic liquid, is $103.3^\circ\text{C mole}^{-1}$.

Small variations in purity would not be expected to have a significant effect on ΔH_f , and this has been found to be true. PETN 2689 was reprecipitated in the needle habit with and without the addition of 1% by weight of triPEON. ΔH_f with the impurity was $37.0 \pm 0.2 \text{ cal g}^{-1}$; ΔH_f without the impurity was $37.0 \pm 0.1 \text{ cal g}^{-1}$. The impurity is known to form a solid solution with PETN, and it was not present as a separate phase. Another batch of PETN was precipitated as the superfine habit with and without 1% of the same impurity. ΔH_f with the impurity was $33.6 \pm 0.4 \text{ cal g}^{-1}$; ΔH_f without the impurity was $33.2 \pm 0.2 \text{ cal g}^{-1}$. Therefore, impurities in the amounts to be expected in "pure" PETN cannot be responsible for the observed differences in heats of fusion.

TABLE III

 ΔH_f FOR IMPURE SAMPLES OF SUPERFINE PETN PRECIPITATED AT 18°C.

Mole fraction impurity (N ₂)	ΔH_f (cal g ⁻¹)
0.0	35.0 ^a
0.02	32.2
0.038	30.2
0.07	25.0 ^b

^aX-ray diffraction pattern of PETN I. ^bX-ray diffraction pattern of PETN II.

Although small amounts of impurity do not cause significant changes in ΔH_f , larger amounts have a profound effect. The effect of larger amounts of triPEON on ΔH_f is shown in Table III.

When PETN is crystallized rapidly from a supercooled melt, a metastable polymorph (PETN II) is formed. In the presence of impurities that form solid solutions with PETN II, conversion to the stable crystal structure (PETN I) is retarded. The heat of solidification of PETN in the liquid phase to produce PETN II was measured as $27.9 \pm 0.8 \text{ cal g}^{-1}$, appreciably lower than the heat of fusion of PETN I. X-ray diffraction results showed that larger amounts of impurity stabilized PETN II on precipitation from solution; therefore, the lower heats of fusion shown in Table III must be partly the result of the stabilization of PETN II in varying amounts. However, such stabilization by impurities cannot explain the low heats of fusion of pure superfine PETN shown in Tables I and II. Pure or slightly impure superfine precipitates appear to show X-ray characteristics of both PETN I and PETN II, but they do not show all of the characteristics of either structure. Therefore, it appears to be necessary to postulate a disordered state of PETN.

Type of disorder

The crystal structures of PETN I and PETN II have been compared by Cady². The PETN II structure differs from the PETN I structure by having molecules inverted and translated slightly in alternate layers. X-ray data show that there is a relationship between the disordered PETN I system and PETN II. Translations are forbidden, if the PETN I lattice is to be retained; therefore, we can assume that the observed disorder is the result of inversions. Inversion of random molecules in the PETN I lattice, retaining the original lattice spacing, would involve strain and reduce intermolecular interactions. Inclusion of such high-energy sites within the system would result in an observed decrease in heat of fusion. Therefore, it can be hypothesized that disorder in PETN involves the random inversion of molecules within the lattice.

If the above hypothesis is used, certain predictions can be made concerning the superfine system, and the hypothesis can be tested. The predictions are as follows: (1) an appreciable amount of activation energy should be required for the bond rotations required to convert a disordered site into an ordered site; (2) the annealing process involved in the conversion should be irreversible; and (3) if disordered sites are randomly distributed, the annealing process should be homogeneous, *i.e.*, not involve nucleation-growth. Annealing experiments to determine rates of conversion from disorder to order were used to test predictions (1) and (3), and heating experiments on single crystals were used to test prediction (2).

Single crystals of pure PETN were heated at 130°C to determine the amount of disorder that might be frozen into an ordered lattice. No significant difference could be observed after 15 min heating. ΔH_f (control) was $37.4 \pm 0.3 \text{ cal g}^{-1}$; ΔH_f (heated) was $37.3 \pm 0.4 \text{ cal g}^{-1}$. It can, therefore, be concluded that the process is either irreversible or slow, compared to the duration of the experiment.

Superfine samples 2909 (pure) and 2910 (containing 1% by weight triPEON) were annealed at 80, 110, 120, 125, and 130°C for various lengths of time up to 960 min, and the fraction annealed was determined from ΔH_f measurements. No significant changes could be measured in either of the samples at 80 or 110°C. Annealing data at 130°C were useless, because spontaneous generation of impurities led to the erratic production of a liquid phase. The average heat of fusion after annealing for 960 min at 120 or 125°C (35.3 cal g^{-1}) was taken as the final value for all calculations.

A first-order plot of the 120°C data for PETN 2909 (pure), each point representing the mean of at least three determinations, is shown in Fig. 4. A rate constant for the process of $7.23 \times 10^{-3} \text{ min}^{-1}$ is obtained from a least-squares fit of the data. The rate constant at 125°C was determined to be $9.17 \times 10^{-3} \text{ min}^{-1}$. The activation energy for the process computed from these results is $14.9 \text{ kcal mole}^{-1}$; the pre-exponential is $1.2 \times 10^6 \text{ min}^{-1}$. The significant factors to note are, first, that an

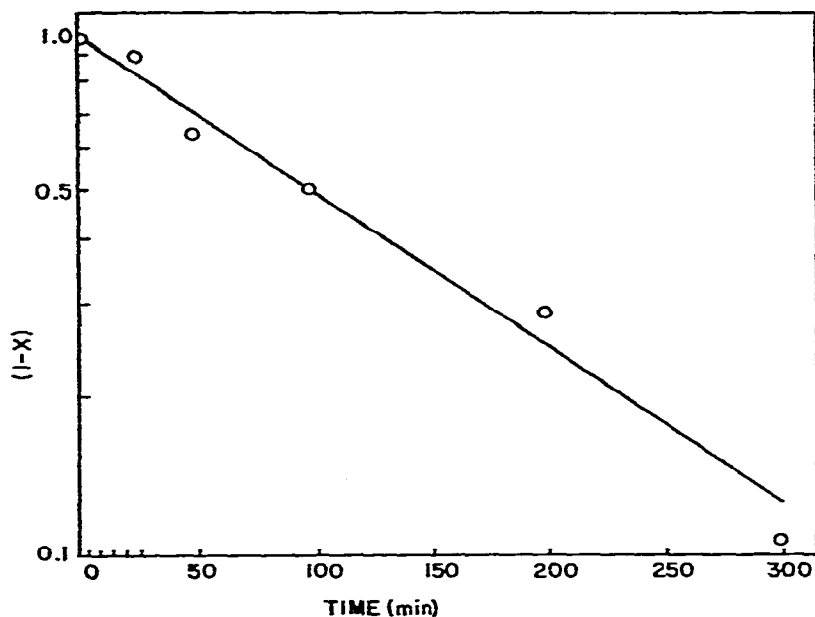


Fig. 4. First-order plot of annealing data obtained at 120°C with PETN 2909. The fraction converted, x , was calculated as follows: $x = \frac{\Delta H_f - \Delta H_f(\text{start})}{\Delta H_f(\text{final}) - \Delta H_f(\text{start})}$.

appreciable activation energy is associated with the process, and, second, that the process is first order, *i.e.*, it does not involve nucleation-growth. These data are consistent with our hypothesis of a random distribution of disordered PETN molecules within the PETN I lattice.

Effect of impurity on rate of annealing

The behavior of PETN with 1% by weight triPEON is considerably different

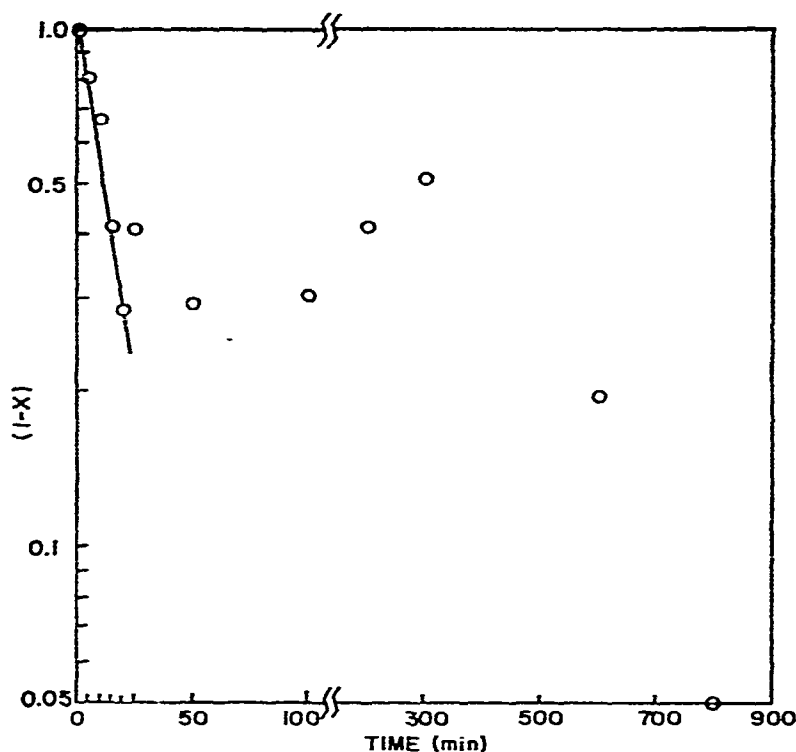


Fig. 5. First-order plot of annealing data obtained at 120°C with PETN 2910 (1% triPEON). Note change of scale on the abscissa. —, least-squares treatment of 0–20 min data.

from that of pure PETN. PETN 2910 annealed essentially to completion in 60 min at 125°C; its rate constant was determined to be 0.052 min^{-1} . The first-order plot of the 120°C data is shown in Fig. 5. The sample anneals to 60–70% of the maximum value within the first 20 min with a rate constant of 0.065 min^{-1} . It appears that the process then essentially stops, and the data become extremely erratic. The activation energy and preexponential calculated from the early data are essentially zero, as the difference between the 120 and 125°C rate constants cannot be considered significant. Such a process could involve a transition through a molten phase which, at the lower temperature, terminates when melting ceases because of the increased stability of the solid.

The phase diagram of the PETN–triPEON system has been studied by DTA and hot-stage microscopy, and the PETN-rich portion of the diagram is shown in Fig. 6. The PETN I–triPEON solid solution solidus line was established from DTA curves of PETN–triPEON precipitates prepared by evaporation of an acetone solution while grinding in a remote mortar. Examples of the DTA curves are shown in Figs. 7 and 8. The changes in the first deviations from the baseline are obvious. A PETN II–triPEON solid-solution field exists in the diagram; however, the system is extremely sluggish in attaining equilibrium, and the position of the solidus line could not be established.

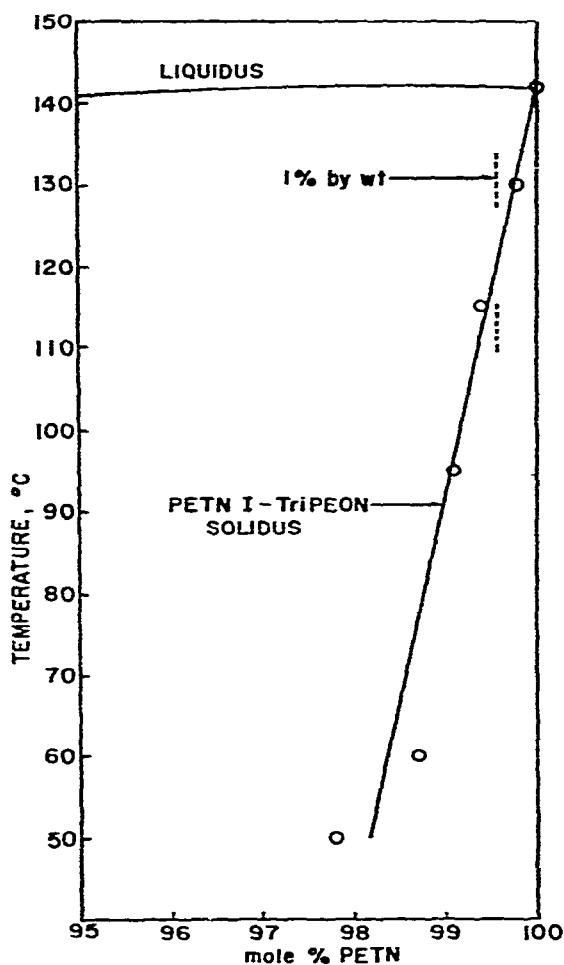


Fig. 6. PETN-rich portion of PETN-triPEON phase diagram.

Figs. 7 and 8 show that energy is being absorbed by the sample at an increasingly greater rate as temperature increases between the first deviation from the baseline and the sharp melting endotherm. This indicates that the system possesses two degrees of freedom through that range, temperature and pressure. Since there are two components, the system must consist of two phases through that temperature range. These phases could be either (1) PETN I-triPEON solid solution and melt, or (2) PETN II-triPEON solid solution and PETN I-triPEON solid solution; however, a solid-state transition to produce the second system has never been observed microscopically.

It should be noted that the ΔH_f of a superfine PETN specifies that it is a metastable phase, *i.e.*, it would be unstable with regard to liquid at any point on the equilibrium solidus line. Therefore, impure superfine PETN must begin to melt and/or to produce a more stable solid phase at, or before, the indicated PETN I-triPEON solidus line.

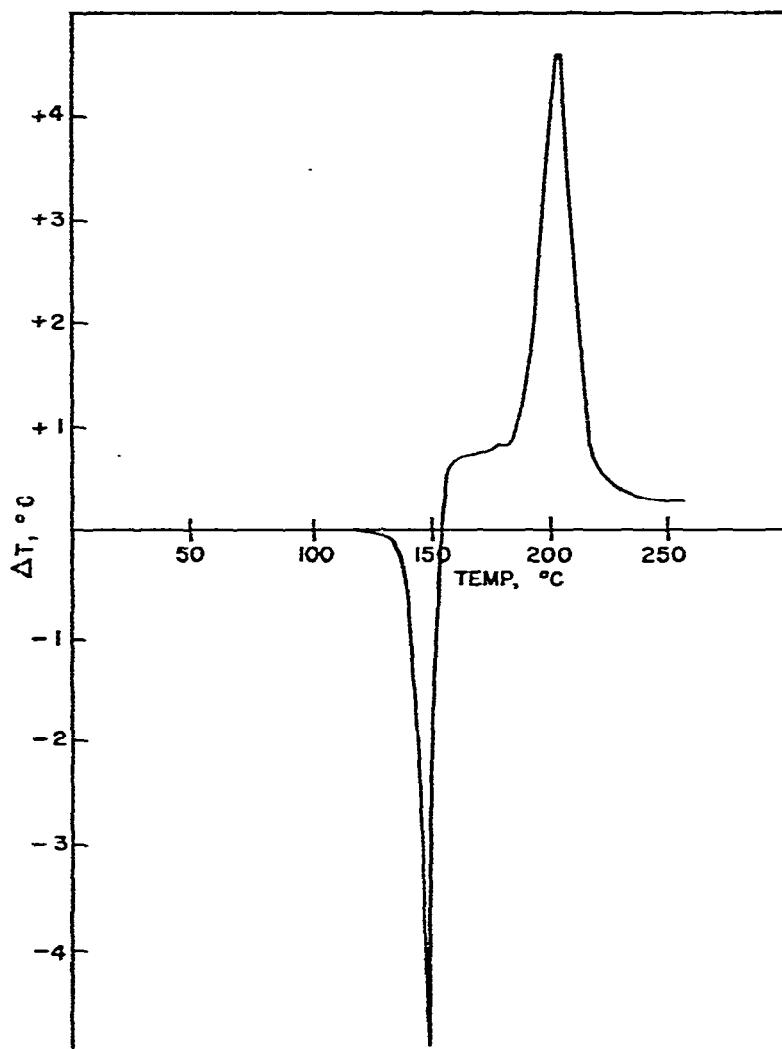


Fig. 7. DTA curve from 0.65 mole % triPEON in PETN, run at $4^\circ/\text{min}$.

Any liquid phase formed at the annealing temperature would not solidify on cooling, at the end of the annealing time, to form a solid with the same ΔH_f as superfine PETN. In order to illustrate this point, superfine PETN with a ΔH_f of $31.8 \pm 0.2 \text{ cal g}^{-1}$ was melted. It solidified on cooling with the evolution of $27.9 \pm 0.8 \text{ cal g}^{-1}$ to form PETN II. The PETN II, on standing at room temperature, converted to PETN I that had a ΔH_f of $36.5 \pm 0.4 \text{ cal g}^{-1}$. The addition of 1% triPEON did not stabilize the PETN II phase at room temperature.

Both the rate curve and the phase diagram (Figs. 5 and 6) show that the 1% triPEON system becomes unstable at a temperature very close to 120°C . Partial liquefaction is almost certain, and recrystallization to a solid phase stable at the annealing temperature is possible. The characteristics of the phase diagram and the

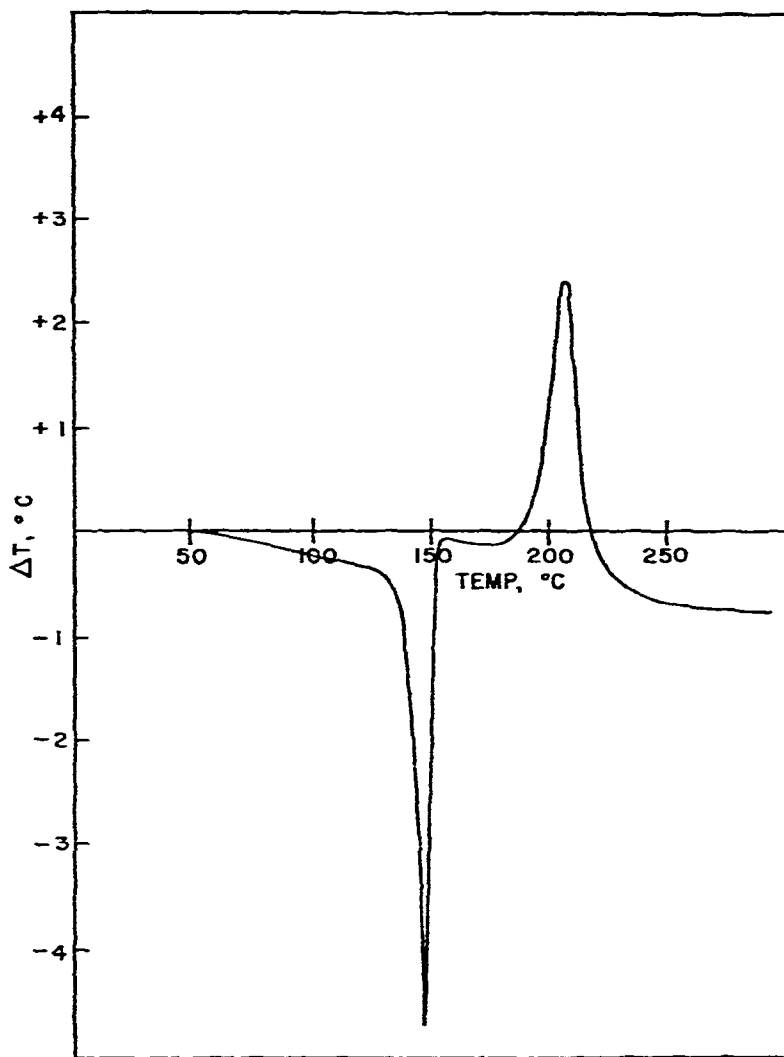


Fig. 8. DTA curve from 2.32 mole % triPEON in PETN, run at 4 $^\circ$ /min.

rate for attainment of equilibrium undoubtedly explain the observations; however, a complete explanation for the discontinuity in Fig. 5 cannot, at present, be proposed.

It should be noted that both of the samples used for annealing rate studies, 2909 and 2910, contained approximately 0.8% acetone trapped in relatively large occlusions. Since this is a characteristic of all superfine samples, it had to be tolerated. Low annealing rates at the lower temperatures seem to preclude the possibility that this impurity has a major effect on rates.

CONCLUSIONS

Variations in the heat of fusion of PETN according to precipitation method are primarily a function of disorder in the normal PETN I lattice. The disorder is the

result of the random inclusion within the lattice of inverted and strained PETN molecules. The lattice energy increase resulting from these inclusions is reflected in a decreased heat of fusion. Impurities in solid solution may decrease annealing rates at lower temperatures and/or stabilize the normally metastable polymorph of PETN, but the effect of impurities is primarily a function of the phase diagram of the system in question.

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