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A DSC Study of Low Temperature Phase Transitions in KH_2PO_4 and $NH_4H_2PO_4$.

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Abstract:

Low temperature phase transitions are known to occur in KH_2PO_4 and $NH_4H_2PO_4$ at 123K and 148K respectively[1]. The structure changes from tetragonal to orthorhombic in both cases[2]. Sharp reversible peaks corresponding to these changes were observed at reproducible temperatures using the PE DSC7. On the basis of the data obtained, the possibility of using the two substances as low temperature standards is considered.

Introduction:

Low temperature studies often provide valuable information for characterisation of materials such as polymers and most instruments have the facility of operating at temperatures down to 100K. There still exists,however, a lack of reference materials particularly in the region of153K - 100K. The standardization committee for Thermal Analysis has made available four sets of reference materials which cover the temperature range 180K to 1213K.

The aim of the present study is to find materials, preferably inorganic solids, which exhibit solid phase transitions as these are preferred by ICTA since not all instruments are able to cope with liquid samples[3]. KH_2PO_4 was chosen as this was already recommended by Redfern[4] in 1972, and then $NH_4H_2PO_4$ was also tested. The latter is a potassium dihydrogen phosphate type compound where a transition has been reported to occur at -125°C[1]. It is considered to belong to the class of antiferroelectric compounds whereas potassium dihydrogen phosphate is a known ferroelectric material.

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Procedure:

The Perkin-Elmer DSC7 was used for all measurements. The instrument was calibrated for temperature using the crystal transition in cyclohexane at -87.06°C. Cyclohexane is one of the materials recommended for temperature calibration in the DSC7 manual. Calibration for energy was made by measurements on accurately weighed samples of higt purity indium taken to have a latent heat of fusion of 28.45 J/g. A single point calibration was performed using the TASCAL programme in the PE7700.

Each solid was encapsulated in a 50 µl Al crucible and weighed on a Sartorius microbalance. The samples were then cooled and re-heated at 2°C/min, 5°C/min and 10°C/min. in the temperature range -80°C to -170°C.

The same samples were tested a few months later to determine the variation with time,if any, in the measurements of onset temperature and enthalpy.

Samples of differing weights were also used to determine how peak area varied with the mass of sample used.

The DSC7 system was operated using liquid N_2 as a coolant in the reservoir of the system. Helium was used as the purge gas with a flow rate of about 30 cm^3/min.

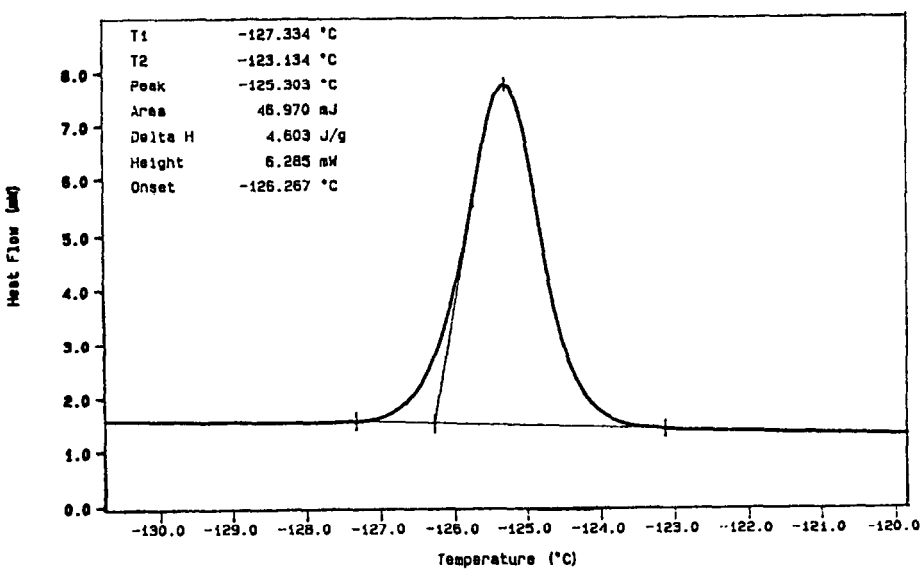

Fig 1 DSC curve of $NH_4H_2PO_4$ (Sample weight: 10.204 mg)

Results and Discussion:

The DSC curves of the transition obtained on reheating $NH_4H_2PO_4$ and KH_2PO_4 are shown in Figures 1 and 2.

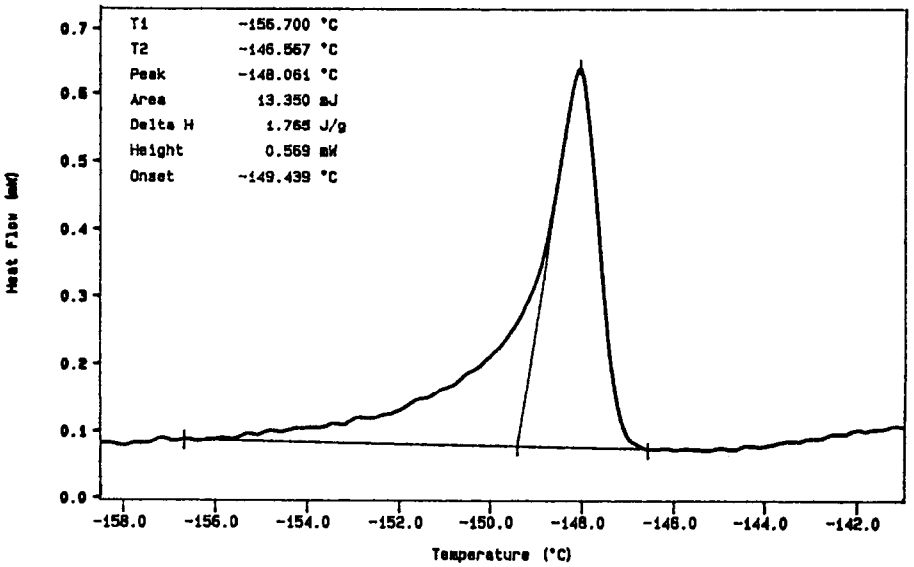

Fig 2 DSC curve of KH_2PO_4 (Sample weight: 7.563 mg)

The reproducibility in temperature of the transition in $NH_4H_2PO_4$ obtained on cooling and re-heating several times is demonstrated in Figure 3.

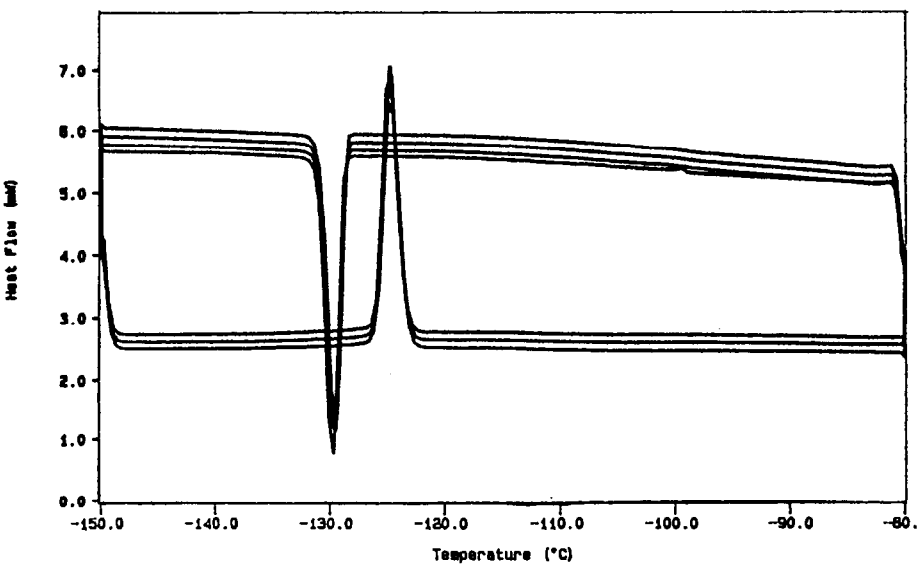

Fig 3 Cooling and reheating DSC curves of $NH_4H_2PO_4$ (Sample weight: 8.110 mg)

Table 1 Values of Onset Temperature and Enthalpy for $NH_4H_2PO_4$.

$NH_4H_2PO_4$	Weight of sample mg.	Onset Temperature T(C)	Delta H (J/g)
Date of measurement June 25th	10.204	-126.3	4.603
	8.110	-127.0	4.771
	6.432	-127.4	4.805
	4.271	-127.0	4.744
Rate of heating 10C/min	2.066	-127.4	4.663
	10.204	-125.2	4.724
Date of measurement	10.204	-125.2	4.697
August 12th	10.204	-125.1	4.695
	8.110	-125.9	4.921
Rate of heating	8.110	-126.0	4.961
10C/min	8.110	-126.0	4.887
Date of measurement	10.204	-125.5	4.740
August 12th	10.204	-125.6	4.714
	10.204	-125.6	4.666
Rate of heating 2C/min			

The transition in KH_2PO_4 occurs with a change in baseline and thus a change in the heat capacity. The peak shape also makes its use as a potential standard less attractive than $NH_4H_2PO_4$. Hence further measurements were made on $NH_4H_2PO_4$. Table 1 shows the values of Onset Temperature and Enthalpy for $NH_4H_2PO_4$.

Figures 4 and 5 demonstrate the variation in these two parameters with the number of independent measurements made.

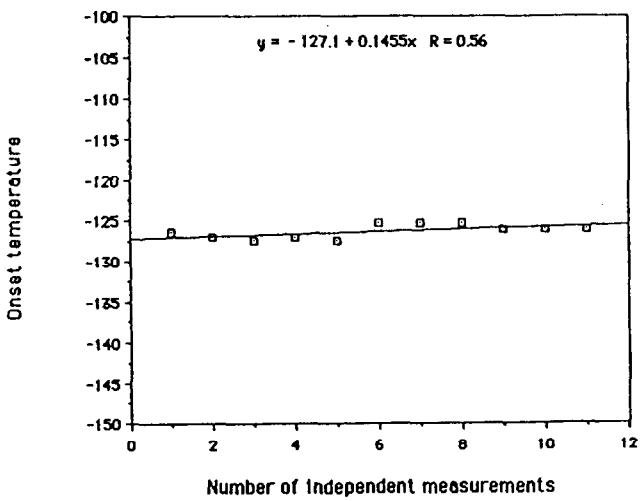

Figure 4 Variation of T(onset) with the number of independent measurements

Table 2 Fluctuation in ΔH values for KH_2PO_4

KH_2PO_4	Weight of sample mg.	Onset Temperature T(C)	Delta H (J/g)
Rate of heating	7.794	-149.4	1.885
	7.563	-149.4	1.767
	6.232	-151.0	1.560
5C/min	4.060	-149.1	1.559
	1.658	-149.2	1.317
	0.889	-149.2	1.249

In Figure 4 the scatter in onset temperature is described by a line of best fit where slope is 0.1455 and the standard deviation is 0.84. The value of the latter is reduced where samples of the same weight are used. Clearly more measurements are required using the same weight and fresh samples to test the variation more precisely.
In Figure 5 the scatter in ΔH values is described by a line of best fit where the slope 0.0029 and the standard deviation is 0.074. The small deviations in ΔH values make i reasonable to consider $NH_4H_2PO_4$ as a calibrant also for enthalpy.(c.f Table 2 which shows the fluctuation in ΔH values for KH_2PO_4).
The enthalpy value as calculated still needs to be compared to the literature value. In both cases there is a linearity of response of peak area to the differing weights of th samples used(Figures 6 and 7).

Conclusion:

The preliminary observations made on the low temperature transitions in KH_2PO_4 an $NH_4H_2PO_4$ have shown that it may be possible to consider $NH_4H_2PO_4$ as a new refere material both for temperature and enthalpy calibration.

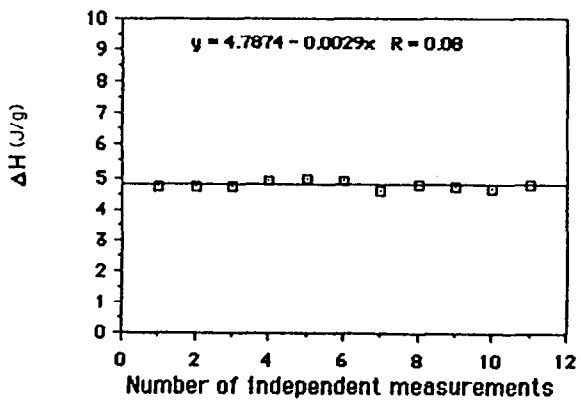

Figure 5 Variation of Delta H with the number of measurements

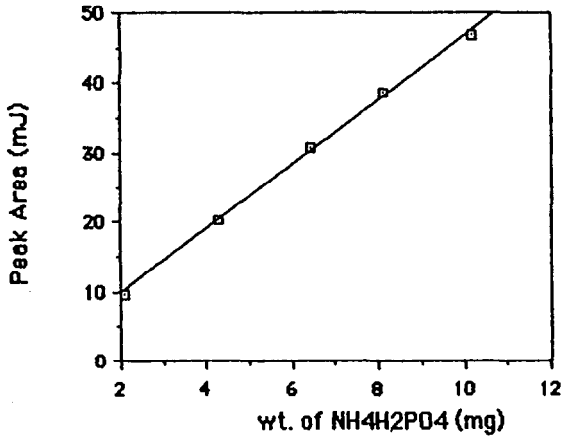

Figure 6 Variation of Peak Area vs. wt. of $NH_4H_2PO_4$

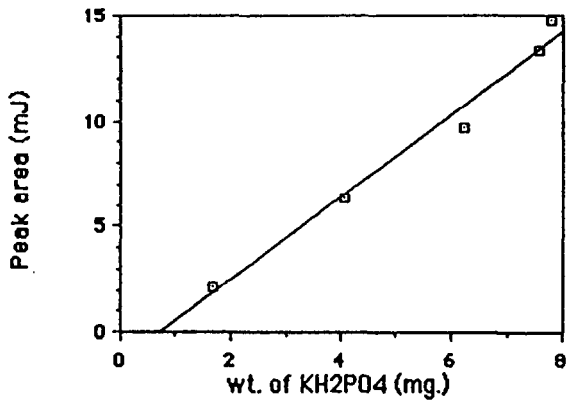

Figure 7 Peak area vs. wt. of KH_2PO_4

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