

VARIATIONS IN THE COOLING TRANSITIONS OF POTASSIUM NITRATE

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Because of questions concerning the suitability of potassium nitrate as a dynamic temperature standard for DTA, the relation between the experimental procedure and the resulting curves was ascertained for the Standard Reference Material KNO_3 . The material behaves differently *on cooling* in open pans than in cylindrical holders because confinement in the latter case initiates reversion to the room temperature form. Under the conditions of use as a dynamic temperature reference material, the curves are accurately reproducible.

Recently, Deshpande, Karkhanavala and Rao [1] in their thermal analysis studies called attention to the behavior of B.D.H. AnalaR potassium nitrate. As a result, they have questioned the suitability of potassium nitrate *in general* as a Standard Reference Material. The material, as is typical of many crystalline materials, may display pronounced variability of thermal behavior depending on its origin. This may be due to trace impurities, thermal or mechanical history or to a combination of factors.

For this reason, and as a result of earlier studies by various members of the Standards Committee of the International Confederation of Thermal Analysis (ICTA) and the National Bureau of Standards (NBS), the certification of the temperature transition [2] was based on selected batches of materials of known homogeneity. The materials were selected to provide reproducible ($\pm 0.5^\circ\text{C}$) crystallographic transitions or melting points. The dynamic transition temperatures given for each were based on mean values which were obtained on a variety of instruments [2]. Thus, the joint certification of these and similar materials serves to facilitate the communication of *reliable* data among research laboratories. Their thermodynamic enthalpy of transition data were *not certified*, and the Standard Reference Materials at present are not intended for this purpose. It was gratifying to find satisfactory agreement between the dynamic experimental temperatures and the equilibrium transition temperature [2].

There is an apparent dissimilarity between the AnalaR potassium nitrate and the ICTA-NBS Standard Reference Material, potassium nitrate. The latter undergoes two clearly defined transitions on cooling of a compacted sample. The peak areas on reheating have been found to be visually identical to those of the first heating. Deshpande *et al.* found little evidence that the AnalaR material

reverted to the low-temperature phase (III \rightarrow II) in their differential scanning calorimetry (DSC) work, even though it did show the reversion in their DTA apparatus.

The apparent lack of agreement in behavior of the same material in the two apparatuses points up the need for following ICTA's reporting recommendations [3]. The dissimilarities may be due to differences in the instrumentation programming rates, or to the state of sample compaction. On the other hand, the apparent differences may be influenced by other instrumental parameters. In the DSC instrument, both the temperature-measuring and the heat-sensing points are outside of and out of contact with the sample. If these points are significantly different in the DTA apparatus of Deshpande *et al.*, these differences must be taken into account. The most probable reason for the appearance of these transition peaks in the DTA is the cooperative self-heating which can occur in a large or in a more compact sample. On recycling the sample, an increase of about 15° apparently increases internal strain permitting the rearrangement to occur in particle after particle. The heat released is transferred to adjacent particles where it initiates reversion of that particle. In the uncompact specimen in the DSC, each particle transforms independently, transferring its heat to the contiguous heat sink. The internal strains in potassium nitrate have been well described by Kracek [4]. The KNO₃ (III) persists until the difference in potential energy between (III) and (II) becomes great enough to overcome the "internal friction", the constraints which tend to inhibit rearrangements. It is easy to infer that this measurable condition should be less reproducible than an equilibrium state, hence reversion would not take place simultaneously in an assemblage of particles.

Experimental

Using a single particle or shallow pan sample holder utilizing a three-thermocouple arrangement as described in reference 5, we have found that when a commercial sample of potassium nitrate was cycled between 80 and 140°, the I \rightarrow III transition was quite reproducible, but the III \rightarrow II transition varied over a small range of temperatures. Three of the curves are shown in Fig. 1. Note that the general direction of the shift in temperature of the III \rightarrow II transition was not consistent, the temperature of the third cycle being lower than the others. The other temperatures were within the range illustrated. Similar behavior, but by a large number of particles, may account for the effect seen by Deshpande *et al.* in the DSC experiment.

We have tested this hypothesis by heating about 5 mg of SRM potassium nitrate on a platinum sample pan in a R. L. Stone* DTA apparatus, and about 150 mg in a 4-mm Pyrex tube in a Du Pont 900* DTA apparatus, plotting the temperature difference in each case against the sample temperature.

In each case the first heating peak was about 2 degrees higher than the subsequent peaks. The subsequent heating peaks were reproducible to within 1 degree. The precaution recommended by ICTA-NBS is indeed warranted.

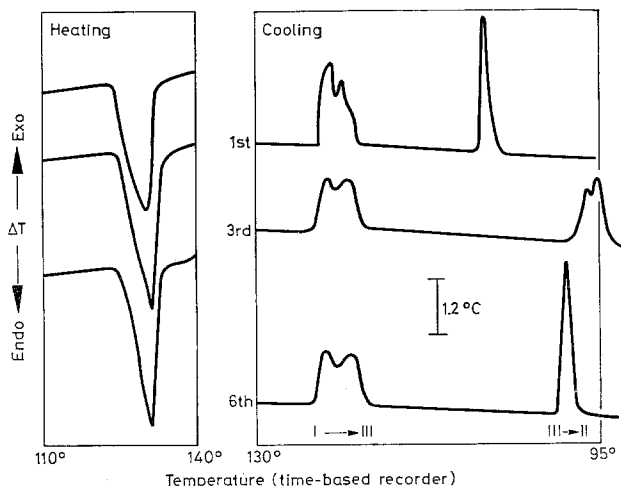


Fig. 1. Heating — cooling DTA curves of a single (ca. 15 mg) particle of Mallinckrodt A. R. potassium nitrate. Three representative curves were selected from the series to illustrate the variable behavior of the metastable state even under highly reproducible conditions.
Heating rate = 5°/min

The first cooling peak [KNO_3 (I) \rightarrow KNO_3 (III)] was reproducible in each case (126 and 125°, respectively for the extrapolated onset and peak) but the subsequent behavior differed greatly. For samples run in pan type sample holders, a few small peaks in the 115–105° range were observed. These presumably corresponded to transitions of individual particles. (14 particles weighed 70 μg .) The phenomenon was in no way reproducible. A set of three curves is shown in Fig. 2. Another non-reproducible characteristic of the open pan runs is the occasional appearance of an exotherm on reheating. Some of the KNO_3 (III) which survived the cooling reverted to KNO_3 (II) upon being heated enough to regain mobility. Differences in observed temperatures of transition is presumably related to the behavior which impelled the ICTA and NBS to recommend an initial heating.

In the compacted sample, where the heat evolved can be transferred more readily to another particle than to the heat sink (block), the [KNO_3 (I) \rightarrow KNO_3 (III)] transition was reproducible. Peaks were overlaid to the extent of being in-

* In no instance does the identification manufacturers' names imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

distinguishable. The $[\text{KNO}_3(\text{III}) \rightarrow \text{KNO}_3(\text{II})]$ (Fig. 3) transition showed evidence of single-particle transitions but these were superimposed upon a somewhat extended peak. Since the thermocouple responds most to the particles in

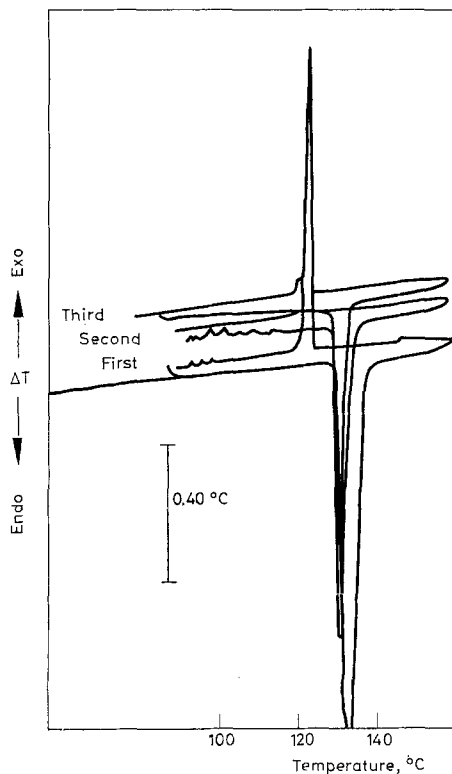


Fig. 2. Heating — cooling DTA curves of about 5 mg. Standard Reference Material potassium nitrate on a shallow pan sample holder. The second cooling transition is generally imperceptible. Heating curves are shown in a downward direction. Heating rate = $5^\circ/\text{min}$

immediate contact [6], these small peaks must represent the transition of these particles. Contact between particles is good because of the dimensional changes during transition. A specimen becomes cemented together because the cell wall limits expansion.

Also, the general peak shape of the $\text{III} \rightarrow \text{II}$ transition is variable from run to run because initiation of the transition is almost random. Similarly, the temperature of initiation is not constant. The four runs at $5^\circ/\text{min}$ yielded (corrected to SRM KNO_3) onsets of 106, 103, 105 and 108° , respectively.

Interruption of some subsequent runs before the second exotherm yielded heating curves substantially smaller than those obtained with greater cooling. The specimen shown in Figure 3 was allowed to stand at room temperature overnight,

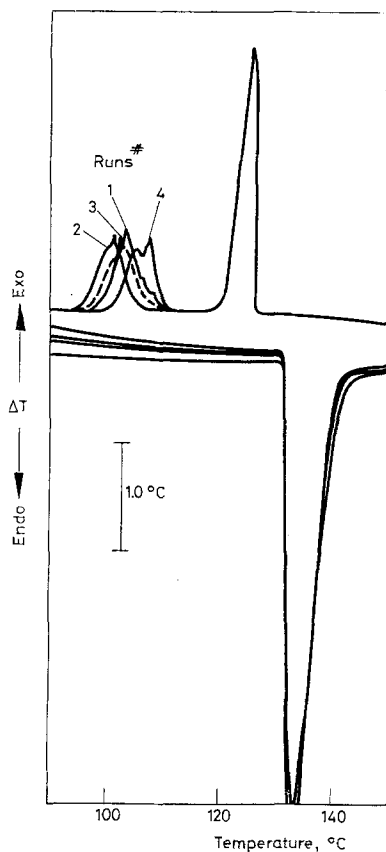


Fig. 3. Heating — cooling DTA curves of about 150 mg of SRM potassium nitrate in a cylindrical sample tube with centered thermocouple. The II → I and I → III transitions are reproducible, but the III → II transition shows considerable variability. Heating rate, 5.0°/min

then cycled at 2°C/min through the whole transition region twice, the cooling cycle was then interrupted at about 124°, the sample actually reaching about 120° before the heating program was regained. The peak (Fig. 4) on reheating has approximately one-half the area of those obtained after greater cooling. This is in agreement with Deshpande *et al.*, Harmelin [7] and, forty years earlier, Kracek [4]. The second peak on cooling has less area than the first, was less well defined,

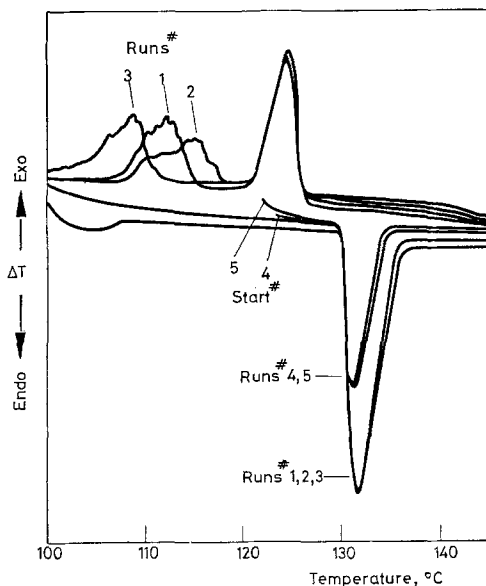


Fig. 4. Heating — cooling DTA curves of about 150 mg of SRM potassium nitrate in a cylindrical sample tube. The III to I transition is reproducible in temperature and area. Heating rate, $2.0^{\circ}/\text{min}$

and its extrapolated onset and peak temperature were, respectively, 114, 117 and 110° , and 111, 114 and 108° , including a final cooling after the two interrupted cycles.

Discussion

The results on the samples compacted in the sample tube resemble those on the single large particle. The single large particle has sufficient mass and extra energy for its transformation to be seen clearly on the recording system. Whether by chance it is a single crystal, or, in the more likely case, a number of adjoining domains, the transformation is not likely to be reproducible in temperature because of random initiation in some region of the particle. The sample in the sample tube is comparable; the particles are not simply in point contact. Because of the dimensional changes during the heating transition the material is cemented together, providing good physical and thermal contact and probably an excellent site for initiating the transformation. Under these circumstances, when the intermediate to low transformation is initiated, the heat released is transferred to adjoining particles, increasing the mobility of its ions. With the system nucleated in the low form, reversion takes place easily and heat from each particle's reversion furthers the process. The second transition, then, is self propagating because of the compaction and thermal contact between particles.

Kracek [4] points out the reason for the easy interconversion of the high and intermediate forms. These have similar structures, uniaxial and optically negative. The substantial difference in structure of the low temperature form, orthorhombic and hence biaxial, suggests that major repositioning of ions must take place. Nucleation of KNO_3 (II) would be difficult in either species.

One of the major points made by Deshpande *et al.* is that the transformation of the low to the high form is a two-step process, via the intermediate form. They based this largely upon the reversibility of the III \rightarrow I transition and partly upon the shape of the DTA curve. The latter is because of the superheating; Kracek showed that both the intermediate and the low temperature forms superheated. Deshpande's hypothesis would appear to be tenable from the DTA evidence alone, but Kracek had found from his dilatometric experiments that the intermediate form could not be kept in existence at any temperature near the transition to the high form, if atmospheric pressure was used. Nor could he coax the low temperature form into the intermediate form at atmospheric pressure.

Only at high pressure can the intermediate and the low forms transform reversibly, and only at those pressures could the intermediate form be kept near the high transition temperature without change.

The simplest way to ascertain whether or not there is a transient existence of KNO_3 (III) on heating is to measure the ferroelectric property of the specimen as it is heated slowly through the transition. The reaction consumes moderate heat, so some finite existence of any intermediate can be expected long enough to obtain polarization measurements.

The persistence of the KNO_3 (III) far into the region of stability of the room temperature phase has been noted also by Nolta, Schubring and Dork [9], who were able to observe the progress of the reversion by measuring the decay of the remanent polarization of the (ferroelectric) KNO_3 (III). The state persists to sub-ambient temperature at high cooling rates. In spite of the great disparity in energy levels, the material does not transform quickly.

Conclusions

The work of Deshpande *et al.* draws special attention to the possible variability of reagent-grade materials and hence to the advisability of certification as Standard Reference Materials of only specific, well-tested batches of the selected materials. The SRM batch has not been certified as a calorimetric standard, nor should *any* inference be made concerning the suitability of any other potassium nitrate as a reference material. It appears that KNO_3 is a suitable temperature standard when used as it was specifically intended and when all precautions and suggestions are carefully heeded.

Taking account of the several pieces of information the conclusions to be reached are that:

1. Heating the low form causes a direct transition to the high form.
2. On cooling, the high form ordinarily transforms first to an intermediate

- metastable form, the individual particles of which may persist through extended cooling.
3. In the absence of physical restriction, the metastable particles revert to the stable low temperature phase independently.
 4. If the particles are under constraint, the expansion causes a joining-together of the particles. This interface both enables easy transfer of heat and provides a continuous surface for growth of the low form.
 5. A large particle has such constraints built in, and hence behaves like a sample in a cavity unless, like some of Kracek's samples, the strain is large enough to cause fracture.

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RÉSUMÉ — En raison de l'emploi du nitrate de potassium comme étalon de température en ATD, on a étudié l'influence des conditions d'expérience sur les courbes obtenues. Le comportement de ce corps est différent si on effectue le refroidissement dans des capsules ouvertes ou dans des creusets cylindriques. Dans ce dernier cas, le manque d'espace initie le retour à la forme stable de la température ambiante. Dans les conditions d'emploi comme matériau de température étalon, les courbes sont exactement reproductibles.

ZUSAMMENFASSUNG — Zur Überprüfung der Eignung von Kaliumnitrat als dynamische Temperatur-Eichsubstanz für die DTA, wurde der Zusammenhang des Versuchsvorganges und der erhaltenen Kurven für das Standard-Referenz-Material KNO_3 untersucht. Die Substanz verhält sich bei der Kühlung in offenen Tiegeln und in zylindrischen Behältern unterschiedlich, da in letzteren die Begrenztheit die Reversion zur Zimmertemperatur-Form in Gang setzt. Unter den für das dynamische Temperatur-Referenz-Material gegebenen Bedingungen sind die Kurven gut reproduzierbar.

Резюме — Соотношение между методикой проведения опыта и полученными кривыми доказало пригодность нитрата калия в качестве стандарта для ДТА при динамических температурных условиях. Вещество по-разному ведет себя при охлаждении в открытой ячейке и в цилиндрическом держателе, превращаясь в последнем случае в форму, характерную для комнатной температуры. Полученные кривые надежно воспроизводимы