Journal of Thermal Analysis, Vol. 6 (1974) 613—621

PHASE TRANSITIONS IN POTASSIUM NITRATE

V. V. DESHPANDE, M. D. KARKHANAVALA and U. R. K. RAO

Chemistry Division
Bhabha Atomic Research Centre Bombay 400085, India

(Received September 26, 1972; in revised form August 17, 1973)

It is shown that the heat of transition of the phase change II → I at 129° on heating KNO_3 is dependent on the thermal history of the sample, since it involves two steps, viz., II → III and III → I at 2° interval. During cooling, the latter step is fast and truly reversible, though with a temperature hysteresis. The former step is sluggish and is dependent both on temperature and time. Our results indicate that KNO_3 can be used for calibration purpose only if the material has not been heated beyond 128° in the immediately preceding three hours.

Potassium nitrate is one of the several substances recommended [1] as a standard reference material in thermal analysis. Hence we used it for calibrating DSC, in respect of the temperature and ΔH. Since the II → I transition of KNO_3 is generally recognised to be crystallographic in origin, the same sample was cycled a number of times between room temperature and 150*, especially between 80° and 150°, and the temperature and ΔH of the transitions were measured on the heating and cooling cycles. As the DSC curves exhibited some unexpected and unusual features, a systematic investigation of the phase transitions in KNO_3 was undertaken both by DTA and DSC, particularly to study the effect of thermal cycling.

Materials and method

1. KNO_3: B.D.H. (AnalaR) potassium nitrate from two different batches (No 70271 and 70708) was used.

Sample Type A refers to samples which had not been subjected to any preheat treatment, or if heated beyond 130° had remained at room temperature for more than 3 hrs.

Type B refers to samples heated to 120° and used immediately after cooling.

Type C refers to samples heated to 150° as recommended by the ICTA Committee on Standardisation [1].

All samples were less than 150 mesh (B.S.S.).

---

* Temperature is expressed in degrees Celsius.

2. DSC: The Perkin – Elmer model – 1B DSC was used. The curves were recorded in flowing nitrogen as well as oxygen (flow rate: 20 ml/min in both cases), at various heating/cooling rates (0.5° to 32°/min) and at different sensitivities (1 to 32 mcal/sec).

The sample size was about 15 mg.

The reproducibility of the instrument was very good. At any given heating rate the onset and peak temperatures were reproducible within $\pm 0.5°$ and ΔH values within ± 0.3 cal/g.

3. DTA: The DTA equipment was of our own design and described earlier [2] except that the furnace temperature was programmed using Redcroft temperature programmer capable of variation in heating/cooling rates from 1 to 20° per minute. The differential and furnace temperatures were recorded on a Rikadenki X – Y recorder. The DTA curves were recorded at a heating rate of 5°/min and uncontrolled cooling (effective cooling rate 2.5°/min in the range 150 to 80°), in static air as well as flowing N_2 (flow rate: 4.7 l/min).

The sample size was about 50 mg.

Results

DSC studies

(a) On initial heating all Type A and B samples showed a slightly asymmetric endothermic peak (Fig. 1) corresponding to the II → I transition with $T_0 = 129 \pm 2°$ and with $\Delta H = 11.6 \pm 0.3$ cal/g. The onset temperature (T_0) and the peak temperature (T_p) were determined following the recommendation of the Nomenclature Committee of the ICTA [3].

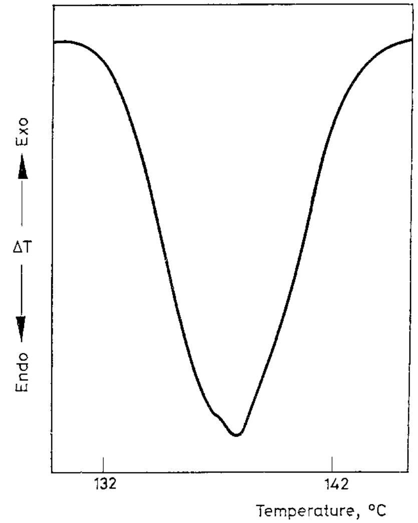

Fig. 1. DSC heating curve at 16 mcal/sec. and 16°C/min heating rate

(b) In case of Type C samples the values of ΔH was lower and ranged from 6 to 10 cal/g depending upon the time the sample was kept at room temperature after heating to 150°. However, if the time lapse between heat treatment to 150° and measurement exceeded three hours, then the peak became asymmetric and the same values of T_0, T_p and ΔH (11.6 cal/g) were obtained as reported at (a) above.

(c) Samples of Type A, B and C on second and all subsequent heating to 150° after cooling to 80° yielded ΔH value of 5.5 ± 0.3 cal/g, i.e., approximately half of the value obtained in the first heating. It was significant that in every case, on second and subsequent heating cycles, the T_0 and T_p of the endothermic peak were about 2° lower than those observed during the first heating.

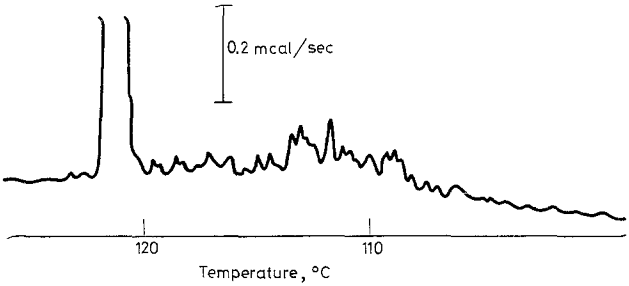

Fig. 2. DSC cooling curve at 1 mcal/sec. and 1°/min cooling rate

(d) A large temperature hysteresis was observed for this II → I transition. The temperature hysteresis was about 16° for a heating rate of 16°/min and about 8° for a heating rate of 1°/min.

(e) The most unexpected feature of the DSC curves was observed during the cooling cycles when only a single exothermic peak corresponding to the I → III transition was obtained. Attempts to get the second peak corresponding to the III → II transition failed.* Curves recorded under conditions of maximum sensitivity (1 or 0.5 mcal/sec), however, showed a large number of very small peaks over the temperature range 115–80° with an apparent maximum at 110° (Fig. 2). This is in complete disagreement with the earlier DTA observations and even with DTA results reported in this investigation.

DTA studies

(a) When Type A and B samples were initially heated up to 150° only one symmetrical peak was obtained with $T_0 = 129° \pm 2$ and $\Delta H = 11.6 \pm 0.5$ cal/g.

---

* Dr K. C. Patel of Sardar Patel University, Vallabh Vidyanagar, kindly obtained the DSC curves for KNO_3 on his Du Pont model 900 DSC thermoanalyzer with the same result, namely that no peak due to the III → II transition is observed with DSC.

These values are in agreement with those reported earlier [1, 4, 6]. On subsequent heating, the values of ΔH, T_0 and T_p depended on the temperature at which the immediately preceding cooling cycle was terminated (Table 1).

(b) On cooling from 150° to room temperature two exothermic peaks were observed at 122° and 102° corresponding respectively to the two known crystallographic transitions, viz., I → III and III → II transitions [6]. These temperatures are in reasonably good agreement with the values quoted earlier [6], but the ΔH values do not agree with the only reported [6] study of heats of transitions.

Table 1

16°/min	DSC 16 mcal/sec			5°/min	DTA 0.25 mV/cm		
Condition	T_0	T_p	ΔH cal/g	Condition	T_0	T_p	ΔH cal/g
1. First heating	131	135	11.6	1. First heating	129	139	11.6
2. First cooling	116	113	5.5	2. First cooling to room temperature (2 peaks)			
3. Second heating	129	131.5	5.4	1st	122	118	5.6
4. Second cooling	115.5	113	5.6	2nd	102	98	2.6
				3. Second and subsequent heating	129	139	11.6
				4. First cooling terminated at 110° and reheated	127	136	5.4

(c) If the sample was cooled to any temperature below 100° (i.e. after passing the second peak) and was reheated and cooled, the sample behaved like the initial sample and the observations at (a) and (b) above could be repeated. Unlike in the DSC the ΔH value of the transition at 129° was 11.6 cal/g and was independent of the time the sample was kept at room temperature or at any temperature below 100°.

(d) When the thermal cycling was confined to the range 105° – 150° (i.e., if the cooling cycle was terminated just before the second peak at 102°) the ΔH value of the endothermic peak at 127° on heating and the exothermic peak at 122° on cooling were equal (5.5 ± 0.3 cal/g). This value is the mean of four heating and cooling cycles and is in good agreement with the value obtained on DSC for second and subsequent heating cycles.

(e) None of the above observations were affected when the atmosphere was changed from static air to flowing nitrogen.

(f) These observations were independent of whether the sample had received any preheat treatment or not.

Discussion

Sequence and temperatures of transition in KNO_3

KNO_3 is reported [4–9, 11–13] to undergo the following crystallographic phase transitions when thermally cycled between room temperature and 140°.

$$\text{Phase II (Orthorhombic)} \xrightarrow{129^\circ} \text{I (Trigonal)}$$

$$\text{II} \xleftarrow{105^\circ} \text{III} \xleftarrow{120^\circ} \text{I}$$

Trigonal
(Ferroelectric)

The results obtained show several disparities which cannot be explained.

(1) In the DSC curves the transition from the ferroelectric phase III to the normal phase II is not observed as a noticeable peak though it is clearly observed in the DTA curves (Fig. 3). Obviously in the DSC the III → II transition somehow gets inhibited. The cause for this behaviour is not clear, but it seems that the rate of cooling, rate of heat conduction out of the sample, and the temperature gradients within the sample may be contributing factors. This is inferred from DTA studies using different rates of heating, different sample holders and sample holder blocks. It is relevant to note that Miekk–Oja [7] from a calorimetric study has found that if the rate of cooling is less than 0.35°/min the two transitions merge and appear as a single peak. This, however, does not appear to be the cause in the

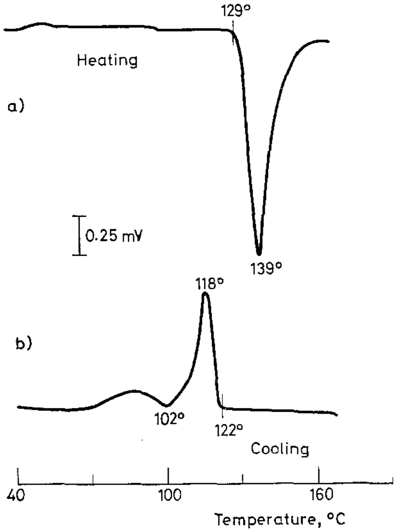

Fig. 3. DTA curves (a) heating at 5°C/min rate, (b) cooling uncontrolled

present case, since on second and subsequent heating and cooling the ΔH is constant at 5.5 cal/g, whereas if the two transitions were to have merged a single exotherm with a ΔH of 11.8 cal/g should have been observed on cooling, just as it is in the heating cycle.

(2) Only in the DSC studies the III → II transformation appears to be dependent upon the time the sample is kept at room temperature or at temperatures below about 80°. The samples cycled between 87° and 150° gave consistent but low values of ΔH for the forward transition irrespective of the rate of heating. These results suggest that the transformation could be sluggish. However the DTA studies clearly show that the transformation is rapid since the sample heated immediately after cooling just beyond the end of the second peak, i.e., after cooling to about 100° gave ΔH value of 11.8 cal/g for the endothermic peak at 129°.

That these disparities are inherent in the two techniques and not caused by the experimental conditions is demonstrated by the fact that no difference was observed in the DTA curves recorded with nitrogen flowing over the samples as in DSC or conversely in the DSC curves recorded in flowing oxygen to simulate the oxidising conditions normally prevalent in DTA in static air atmosphere. Thus it has to be concluded that the results obtained were not influenced by the environment, though according to Forestier and Kiehl [8] the transformation temperature of KNO_3 is influenced to some extent by the ambient gas.

(3) The endothermic peak at 129° exhibits a pronounced asymmetry only during the first heating. Garn [9] observed asymmetric and multiple peaks in the DTA endothermic peak at 129° which he attributed to large particle size. Menis [10] also attributes the multiple peaks to single particles transforming in the appropriate directions. To test this hypothesis DSC and DTA curves were recorded with samples of $+60$ mesh size, which confirmed the observations of Garn [9] and showed splitting (often multiple) of the 129° peak on first heating, while the -300 to $+350$ mesh size samples did not. Nevertheless in the DSC curves of even the -300 to $+350$ mesh material the asymmetry was retained. The effect of particle size is being systematically investigated.

Thus, whilst the assumptions of Garn [9] and of Menis [10] have a certain validity, and are the obvious cause for the multiple splitting of the DTA peak in the coarse sample, the asymmetry of the DSC peak of the sample with a very fine and narrow range of particle size leads us to believe that there are two very close transformations and not one as hitherto believed [11–13]. This is further supported by the observations that (i) for the second and subsequent heating the ΔH value of the endotherm at 127° is 5.5 cal/g in the DSC curves of all samples and is almost half of the ΔH value observed on first heating of any fresh sample, (ii) this value of 5.5 cal/g is the same as that for the exothermic peak observed both in DTA and DSC at about 122° during cooling, which exothermic peak is unquestionably due to the transformation of the high temperature trigonal phase I to the ferroelectric phase III, (iii) for samples not allowed to transform to phase II but reheated from this phase III, i.e., cycled between 110–150° the DTA curves also showed a single symmetric endotherm on heating and a single exotherm on cooling, both with the same ΔH value of 5.5 cal/g, (iv) for a constant heating rate the onset and peak temperatures of the endotherm obtained on second and subsequent heating in the DSC curves, or of the endotherm obtained in the DTA of samples cycled between 110–140°, were about 2° lower than the corresponding values on the first heating.

It has therefore to be concluded that on heating a fresh sample of KNO_3 the original phase II does not transform to phase I directly, but that it transforms to an intermediate phase, which immediately transforms to phase I. This intermediate phase is presumably the ferroelectric phase III since the ΔH on second heating (cf. (ii) and (iii) above) is identical with that observed for the I → III transition on cooling though with a large temperature hysteresis of about 5 to 15° depending on the rate of cooling.

Heats of transition

The total ΔH for these II → III → I transformations in the forward direction is undoubtedly 11.6 ± 0.3 cal/g. This has been verified by several workers [4, 6]. This heat must distribute itself between the two transformations observed during cooling. Following this expectation Rao and Rao* distributed the ΔH of 12 cal/g observed during the heating and reported [6] values of 8.2 and 3.8 cal/g for the I → III and III → II transitions based upon the relative areas of the two exothermic peaks. In the present investigation these values could not be corroborated, the calculated values of ΔH for these two transformations being 5.5 and 2.3 cal/g respectively. However the ratios of ΔH for the two transitions as reported [6] and as observed here are about the same.

Since the ΔH value of 5.5 ± 0.3 cal/g for the III → I transition is consistent on the heating and cooling cycles, then by difference the ΔH of the II → III transformation should be 6.1 cal/g.

This raises two questions, (i) why is the ΔH for the III → II transformation as observed in DTA during the cooling so much less, and (ii) why is this transformation smeared out in DSC. The DSC results, which have been repeated more than a dozen times suggest that the III → II transformation is both time and temperature dependent. If this be so then it is not impossible that somehow during DTA only a certain fraction of III transforms sharply to II giving rise to the smaller value of ΔH. The remaining supercooled phase III could then transform gradually to II, thereby smearing out the heat effect. Gray [14] suggested that the low value could be due to variation in the specific heat of phase III. The values of specific heat obtained [15] can account for only a small part of the missing 3.8 cal/g. It is not clear why a similar phenomenon is not observed in DSC. This aspect is being investigated.

---

* Private communication.

It is possible that this apparently sluggish and time dependent III → II transformation may be responsible for causing in the DTA and DSC study [4] the relatively large spread in the reported values of ΔH for the II → I transformation which ranges from about 10.3 to 12.7 cal/g. Since the thermal history of the sample used in that study [4] has not been recorded, it is not possible to seek any correlation with the reported values of ΔH.

Effect of thermal history

It is evident from this study that it is very essential to characterize the sample in terms of its thermal history. While the time interval between the pretreatment of heating to 150° [1] and the measurement is not critical in DTA, somehow it becomes very important for DSC measurements, particularly if the pretreatment is given *in situ* in the DSC sample holder.

KNO_3 as a reference standard

Since KNO_3 is suggested as a reference standard it needs to be emphasized that at least for temperature calibration of the DSC and DTA equipment the recommendations of ICTA Committee should be followed (allowing for a time lapse of about 3 hours for DSC measurements) as that procedure permits obtaining extremely reproducible onset and peak temperatures. However, for calibration of the DSC in terms of ΔH, only fresh samples which have not been heated beyond 128° in the immediately preceding three hours should be used. For DTA measurements this precondition does not seem to be essential yet it is considered advisable.

*

The authors' thanks are due to Dr. H. G. McAdie, Chairman, ICTA Committee on Standardisation, Dr. O. Menis (National Bureau of Standards), Dr. A. P. Gray, and Prof. C. N. R. Rao for helpful discussion of the data. The authors are grateful to Dr. K. C. Patel for obtaining the DSC curves on the Du Pont thermoanalyser which has enabled an inter-instrumental comparison of the DSC data.

References

1. H. G. McAdie, Thermal Analysis (Proc. of the 3rd ICTA, Davos, 1971), Birkhäuser, Basel, 1972. Vol. 1, p. 591.
2. M. D. Karkhanavala, V. V. Deshpande and A. B. Phadnis, J. Thermal Anal., 2 (1970) 259.
3. R. C. Mackenzie, Thermal Analysis (Proc. of the 3rd ICTA, Davos, 1971), Birkhäuser, Basel, 1972. Vol. 1, p. 609.
4. P. A. Einhorn, Thermal Analysis (Proc. of the 2nd ICTA, Worcester, 1968), Academic Press, New York—London, 1969. Vol. 1, p. 149.
5. J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 2, 809.

6. K. J. Rao and C. N. R. Rao, J. Material Sci., 1 (1966) 238.
7. H. Miekk-Oja, Ann. Acad. Sci. Fennicae, A1 (1941) 65.
9. H. Forestier and J. P. Kiehl, Comp. Rend., 230 (1950) 2288.
9. P. D. Garn, Anal. Chem. 41 (1969) 447.
10. O. Menis, Private Communication.
11. D. A. Edwards, Z. Krist., 80 (1931) 159.
12. E. Cohen and H. L. Bredee, Z. Phys. Chem., A140 (1929) 391.
13. F. C. Kracek, J. Phys. Chem., 34 (1930) 225.
14. A. P. Gray, Instrument Division, The Perkin-Elmer Corporation, Norwalk, Connecticut, USA — Private Communication.
15. V. V. Deshpande, M. D. Karkhanavala and U. R. K. Rao — to be published.

Résumé — Lors du chauffage de KNO_3, on montre que la chaleur de la transition de phase II → I à 129°C dépend du passé thermique de l'échantillon. Deux étapes successives interviennent dans un intervalle de 2°: II → III et III → I. Pendant le refroidissement, cette dernière étape est rapide et réellement réversible bien qu'elle s'effectue avec une hystérèse de température. La première étape est retardée et dépend de la température et du temps. Les résultats présentés indiquent que KNO_3 ne se prête à l'étalonnage que s'il n'a pas été chauffé au-dessus de 128° pendant les trois heures qui ont précédé l'expérience.

Zusammenfassung — Es wurde gezeigt, daß beim Erhitzen von KNO_3 die Übergangswärme der Phasenumwandlung II → I bei 129° vom thermischen Vorleben der Probe abhängt, da diese zwei Stufen enthält, nämlich II → III und III → I in einem Abstand von 2°. Während der Kühlung ist die zweite Stufe schnell und wirklich reversibel, obgleich eine Temperaturhysterese zu beobachten ist. Die erste Stufe ist verzögert und sowohl temperatur- als auch zeitabhängig. Die Ergebnisse zeigen, daß KNO_3 für Eichzwecke nur in dem Falle verwendet werden kann, wenn das Material in den unmittelbar vorangehenden drei Stunden nicht über 128° erhitzt worden war.

Резюме — Показано, что тепловой эффект фазового изменения II → I при 129° C в случае нагревания $КИO_3$ зависит от предварительной термической обработки образца, т. к. этот переход включает две ступени II → III и III → I, при интервале 2°. При охлаждении вторая ступень протекает быстро и обратимо, хотя и с температурным гистерезисом. Первая ступень протекает медленно и зависит как от температуры, так и от времени. Результаты показывают, что KNO_3 можно использовать с целью калибровки только в том случае, если его не нагревать выше 128°.