

## DIFFERENTIAL SCANNING CALORIMETRY OF SODIUM AND POTASSIUM NITRATES AND NITRITES \*

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### ABSTRACT

Differential scanning calorimetry (DSC) experiments were performed with  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $(\text{Na,K})\text{NO}_3$ ,  $\text{NaNO}_2$  and  $\text{KNO}_2$  over the temperature range 350–990 K. Endothermic peaks, indicative of decomposition reactions, were observed to occur in the single salts above their melting points. The equimolar mixture of sodium and potassium nitrate did not decompose in the temperature range specified. The nitrites began to decompose at  $800 \pm 10$  K. Sodium nitrate began to decompose at  $840 \pm 10$  K and potassium nitrate began to decompose at  $820 \pm 20$  K. These results were compared with previously reported differential thermal analysis investigations of  $\text{NaNO}_3$  and  $\text{KNO}_3$ .

### INTRODUCTION

Nitrates and nitrites of sodium and potassium have often been used as heat transfer fluids in the metallurgical and chemical manufacturing industries [1,2]. These relatively inexpensive and low melting salts may also be used as thermal energy transfer media in solar [3,4] and nuclear energy [5] power plants in the future. These new applications require higher operating temperatures for the salts than have been required in the metallurgical or chemical industries [6]. For instance, continuous storage of a 50/50 mixture of sodium nitrate and potassium nitrate at 873 K for as long as 30 years has been suggested for the thermal energy storage section of a solar power plant [7].

At elevated temperatures, chemical reactions in sodium or potassium nitrate or nitrite have caused formation of insoluble materials, elevated melting points, and

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increased viscosity [7]. The temperature at which these deleterious reactions begin determines the usefulness of these salts as heat transfer fluids.

Sodium nitrate ( $\text{NaNO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ) may decompose via several paths. For instance, sodium or potassium nitrate may decompose to their corresponding nitrites ( $\text{NaNO}_2$  or  $\text{KNO}_2$ ) according to reaction (1) where M may be Na or K [8–11].



Reaction (1) has been observed as low as 568 K in  $(\text{Na,K})\text{NO}_3$  by Kust and Burke [11], but Freeman [9] observed reaction (1) above 873 K in  $\text{NaNO}_3$ . The difference between the studies may be attributed to technique. Kust and Burke used a sensitive electrochemical technique and Freeman used thermogravimetry.

The nitrites may in turn decompose to oxide ( $\text{M}_2\text{O}$ ) according to reaction (2).



According to refs. 12 and 13, reaction (2) occurs above 603 K for  $\text{NaNO}_2$  and above 683 K for  $\text{KNO}_2$ . Furthermore, the gaseous products,  $\text{NO}_2$  and  $\text{NO}$ , produced in reaction (2) may react with the remaining nitrite to produce nitrate [12,13] as in reactions (3) and (4).



The oxide produced in reaction (2) may also react with  $\text{NO}_2$  to form nitrate and nitrite [12,14] as in reaction (5).



At higher temperatures (above 873 K for  $\text{NaNO}_2$  and 1073 K for  $\text{KNO}_2$ ) the nitrites decompose completely to oxide [8] according to reaction (6).



In addition to decomposition to nitrite, the nitrates may also decompose directly to oxide ( $\text{M}_2\text{O}$ ) [8–10] according to reactions (7) or (8).



Reactions (1) through (8) cause sodium and potassium nitrates and nitrites to form mixtures of oxide, nitrate, and nitrite and evolve oxygen, nitrogen, and nitrogen oxide gas mixtures. These reactions may occur simultaneously, consecutively or overlap as they occur [9,15]. Determining the temperatures at which these reactions begin to occur (decomposition temperature) is very important for practical uses. However, one must remember that determinations of decomposition temperatures are dependent on the experimental technique and its sensitivity, and the sample's configuration [16]. For instance, the decomposition temperature for  $\text{NaNO}_3$  has been reported to be as low as 570 K [17] and high as 1029 K [18]. Determinations of the decomposition temperature for  $\text{NaNO}_3$  were based on observations of the

onset of weight loss [9,19], mass spectrometric indications of NO evolution [17], the occurrence of an endotherm in differential thermal analysis [18,20] and chemical identification of nitrite formation [21].

In this paper we report the results of the first differential scanning calorimeter investigation of the nitrates and nitrites of sodium and potassium and the equimolar mixture of sodium and potassium nitrates. In these DSC experiments the temperatures at which decomposition began in each salt was determined and the behavior of the five salts was compared.

## EXPERIMENTAL

A Perkin-Elmer differential scanning calorimeter (model DSC-2) was used to study  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $(\text{Na,K})\text{NO}_3$ ,  $\text{NaNO}_2$ , and  $\text{KNO}_2$  from 350 to 990 K. (The upper temperature limit of the DSC-2 is 999 K.) The samples were heated at a constant rate of  $10 \text{ K min}^{-1}$  from 350 to 990 K. The DSC was calibrated to within 0.05 K of the melting point of indium (429.78 K). The samples were made from reagent-grade powders that were dried at 393 K under vacuum for at least 16 h. Small (less than 30 mg) samples were encapsulated either in high-pressure stainless steel or gold plated stainless steel DSC pans, which were sealed by crimping. The gold plated stainless steel pans were used to provide an impermeable, unreactive barrier between the salt and the stainless steel. This procedure was developed after initial DSC experiments with the stainless steel pans indicated a reaction had occurred between the nitrites and the stainless pans. The reference pan was always empty. Two to ten experiments were performed with each salt.

## RESULTS

A large endothermic peak was observed for each of the five salts at the temperatures corresponding (within  $\pm 1 \text{ K}$ ) to the melting point of each salt [23]. Above the melting point of each salt [except for  $(\text{Na,K})\text{NO}_3$ ] endothermic reactions occurred. In some experiments the endothermic reactions were gradual. In other words, the differential energy required to heat the sample relative to the empty pan slowly increased, indicative of endothermic reaction(s) at elevated temperatures. Gradual endotherm decomposition reactions were also observed by Gordon and Campbell [20] who performed DTA experiments with the nitrates.

In other experiments endothermic reactions were observed where the DSC trace very abruptly went off-scale (greater than 10 mcal displacement). Usually the salts had leaked or exuded from their pans when abrupt endotherms occurred. The temperatures at which these endotherms began was reproducible within only 10 to 20 K. Figure 1 is an example of the DSC traces showing the melting and gradual decomposition endotherms. Both gradual and abrupt decomposition reactions were observed for all the salts except  $(\text{Na,K})\text{NO}_3$ . Unlike the single salts, no endothermic

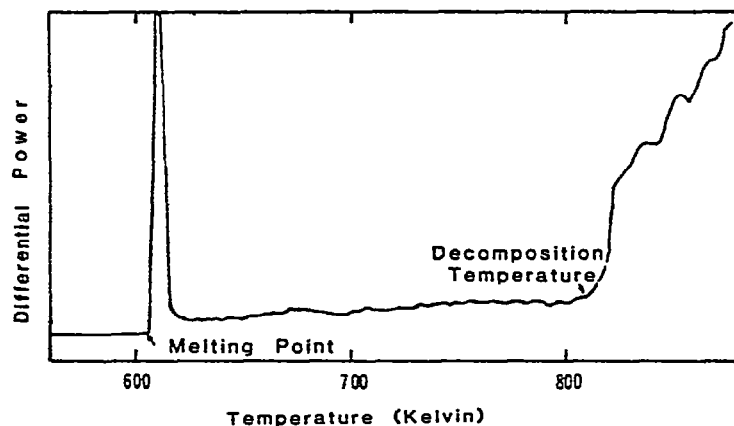


Fig. 1 Differential scanning calorimetry experiment with KNO<sub>3</sub> in a stainless steel pan.

decomposition peak was observed for (Na,K)NO<sub>3</sub> within the temperature range of the DSC. The temperatures at which the endothermic reactions began for the single salts are given in Table 1. Hereafter these temperatures are referred to as the DSC decomposition temperatures.

The average decomposition temperature of sodium and potassium nitrite (800 K for both) was less than sodium nitrate (840 K) and potassium nitrate (820 K). However, the variability of the decomposition temperatures was large, therefore the DSC decomposition temperature ranges overlap.

The DSC traces were different for the nitrites when the stainless steel pans were gold plated and when they were not. A small exotherm beginning at  $690 \pm 20$  K was

TABLE 1

DSC and DTA experiments with nitrates and nitrites of sodium and potassium

Salt	Decomposition temperature <sup>a</sup>	Technique	Ref.
NaNO <sub>3</sub>	840 ± 10 K	DSC	This work
NaNO <sub>3</sub>	793 K	DTA	20
NaNO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	1006 K	DTA <sup>b</sup>	18
NaNO <sub>3</sub> -MgO	1029 K	DTA <sup>b</sup>	18
KNO <sub>3</sub>	820 ± 20 K	DSC	This work
KNO <sub>3</sub>	901 K	DTA	20
KNO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	958 K	DTA <sup>b</sup>	18
KNO <sub>3</sub> -MgO	1027 K	DTA <sup>b</sup>	18
(Na,K)NO <sub>3</sub>	> 990 K	DSC	This work
NaNO <sub>2</sub>	800 ± 10 K	DSC	This work
KNO <sub>2</sub>	800 ± 10 K	DSC	This work

<sup>a</sup> Temperature at which decomposition endotherm began.

<sup>b</sup> Salt was mixed with oxide powder.

observed when the nitrites were tested in stainless steel pans. No exotherms were observed when the nitrates were tested in stainless steel, nor when the nitrites were tested in gold plated pans. The exotherms did not affect the temperature at which endotherms were observed.

Other typical but unexpected behavior of the salts in the DSC was the relatively high noise level, baseline drift and unsteady baseline, as seen in Fig. 1.

## DISCUSSION

The DSC decomposition temperatures for the nitrites were much higher than the decomposition temperatures previously reported for the nitrites [8,12,13]. However, the chemical and gas analysis techniques used by others [12,13] to detect nitrite decomposition may have been more sensitive than the DSC. The DSC decomposition temperatures of  $\text{NaNO}_2$  and  $\text{KNO}_2$  were identical whereas in the earlier studies [12,13]  $\text{NaNO}_2$  was reported to decompose at a lower temperature than  $\text{KNO}_2$ . However, the two salts were not tested under identical conditions before this work, which may account for the discrepancies. No DTA results have been reported for  $\text{NaNO}_2$  or  $\text{KNO}_2$  for comparison with the present DSC results.

The average  $\text{NaNO}_2$  or  $\text{KNO}_2$  DSC decomposition temperature (800 K) was only 40 K less than average DSC decomposition temperature of  $\text{NaNO}_3$ , and 20 K less than the average DSC decomposition temperature for  $\text{KNO}_3$ . These four salts have not been compared before in any one experimental study. When one considers the range of the DSC decomposition temperatures, the nitrates and nitrites were not significantly different in the DSC. Since the nitrates decompose to nitrites which subsequently decompose, the DSC decomposition temperature for the nitrates may be determined by the stability of the nitrites. In other words, at 840 K in  $\text{NaNO}_3$ , the formation and decomposition of  $\text{NaNO}_2$  [reactions (1), (2), and (6)] may be the cause of the endotherm rather than reactions (7) and (8).

The equimolar mixture of sodium and potassium nitrate was more stable in the DSC than either of the nitrates singly. Kust and Duke [24] also observed that the equimolar mixture of sodium and potassium nitrate was slightly more stable than the single salts with respect to decomposition to oxide. Although no DSC decomposition endotherm was observed in this study, minor nitrite formation in  $(\text{Na,K})\text{NO}_3$  has been observed as low as 568 K [11]. Apparently Kust and Burke's technique [11] was more sensitive than the DSC technique. Nevertheless, of the five salts tested,  $(\text{Na,K})\text{NO}_3$  was the most stable with respect to decomposition.

The decomposition temperatures obtained in this investigation for  $\text{NaNO}_3$  and  $\text{KNO}_3$  ( $840 \pm 10$  and  $820 \pm 20$  K, respectively) were, with one exception, lower than the reported DTA decomposition temperatures (Table 1). The exception was in the case of  $\text{NaNO}_3$  for which Gordon and Campbell [20] reported a decomposition temperature of 793 K. It should be noted that the results reported by Sweeney [18] correspond to observations of salt samples mixed with alumina and magnesia. Although the oxides were supposedly inert, the oxide additions raised the melting

points relative to the pure nitrates and the oxides may have also affected the decomposition process.

In the present study, sodium nitrate and potassium nitrate were equally stable. Other investigators [10,18,20] report potassium nitrate more stable than sodium nitrate. However, Sweeney's [18] DTA results (see Table 1) showed that sodium nitrate was as stable as potassium nitrate, as in the present work.

Although the DTA and DSC techniques are similar, the sample configurations differed significantly. The DTA experiments were performed with open crucibles whereas the DSC experiments were performed with capsules creating different atmospheric conditions above the salts. The atmosphere surrounding the salts influences the reactions that occur [8]. For instance, reactions (3)–(5) where NO and NO<sub>2</sub> react with the salts, were more likely to occur in the DSC experiments than in the DTA experiments. Therefore one may anticipate differences between the DSC and the DTA experiments.

The DSC experiments provide no information as to which reaction(s) have occurred. The DTA decomposition temperatures of Gordon and Campbell [18] were the temperatures at which "slight bubbling" began as gases were being released. Reactions (1), (2), (6) or (8), described in the Introduction, may have caused gases to be released.

The untypically noisy traces that were obtained with the DSC were peculiar to the salt samples above their melting points. The noise may be a consequence of limited decomposition such as Kust and Burke [11] observed in (Na,K)NO<sub>3</sub>.

Two phenomena may have contributed to the salt leakage out of some of the DSC capsules: overpressurization and wetting. As decomposition proceeded and gases were released, the pressure inside the DSC capsules may have risen high enough to break the crimped seal allowing the salt to leak. Alternatively, the molten salts in the DSC experiments may have wetted the surfaces of the DSC pans and crept out between the top and bottom of the DSC capsule. Sweeney [18] observed the phenomena of creep and he mixed oxide powders with nitrates to prevent the salts from wetting or creeping out of his DTA containers. When the salt crept out, it chemically attacked the DSC sensors and caused baseline drift.

The small exothermic peak (at  $690 \pm 20$  K) observed when nitrite samples were heated in stainless steel pans may have been caused by a reaction between the samples and the chromium oxide surface layer on the stainless steel. The exotherm was not observed when gold plated stainless steel pans were used. Chromium oxide and KNO<sub>3</sub> have been observed to react and form chromates [25,26]. In this investigation auxiliary experiments were conducted in which small amounts of Cr<sub>2</sub>O<sub>3</sub> were added to NaNO<sub>2</sub> in gold-plated stainless steel pans and analyzed by DSC. A small exothermic peak was observed in the NaNO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> experiments, in the same temperature range ( $690 \pm 20$  K) as the nitrites in stainless steel DSC pans. Udupa [26] observed that the decomposition temperature of KNO<sub>3</sub> was lowered by adding chromium oxide. In contrast to Udupa, no change in the DSC decomposition temperature was observed no matter which kind of pan was used.

## CONCLUSIONS

Differential scanning calorimetry experiments were performed to compare the decomposition of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $(\text{Na,K})\text{NO}_3$ ,  $\text{KNO}_2$  and  $\text{NaNO}_2$ . Endothermic decomposition reactions occurred above the melting points of the single salts. Sodium nitrate began to decompose at  $840 \pm 10$  K and potassium nitrate at  $820 \pm 20$  K in the DSC. The nitrites began to decompose at  $800 \pm 10$  K in the DSC. The equimolar mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$  had enhanced stability relative to the single salts and did not decompose below 990 K, the upper temperature limit of this study.

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