Melting and Pre-Melting Phenomena
in Alkali Metal Nitrates

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Data for the heat content, heats and entropies for the solid-state transition (276° C.), and for fusion (307° C.), gained by the method of phase-transition drop calorimetry, are reported. The thermal data confirm that the solid-state transition in NaNO₃ has unusual features. The change persists from 180° to 280° C., and appears about 60% complete at 270° C. This, and the relatively small magnitude of the thermal effects ΔS_{tr}, 0.32 deg.$^{-1}$ mole^{-1}), are examined relative to the nature and extent of the solid-state transition. A comparison of the fusion and pre-fusion parameters for a related series of nitrate and chloride salts is presented and discussed relative to a "premonition of melting" effect as evidenced by such continuous solid-state transition regions. The lower melting point and smaller change in volume on fusion also appear interrelated.

THE VALUE of the heat of fusion of sodium nitrate has been a subject of dispute for many years. Two recent determinations of this quantity, although less discrepant than many of those reported previously, serve to point out the need for resolving this problem. Such an evaluation is long overdue. Sodium nitrate is used as a solvent in fused salt cryoscopy (17, 18), and uncertainty in the heat of fusion is reflected in the cryoscopic constant. The apparent number of foreign particles produced by the addition of a solute is influenced by this uncertainty.

Table I lists ΔH_f values for sodium nitrate as obtained from calorimetric investigations. (Considerably less precise values obtained from freezing-point experiments with binary systems have not been included.) Goodwin and Kalmus (9) report values of 3690 cal./mole and 45.3 cal./gram; the latter, although obviously an incorrect transcription of 43.5 cal./gram, has been used in interpreting cryoscopic measurements. The value reported by Mustajoki (29) is advocated by Kelley in his 1960 compilation (23) of high-temperature data. (The work of Sokolov and Shmidt (40) apparently was not available for consideration at that time.) The discrepancy between the two most recent values for ΔH_f (29, 40) is 3%. The high-temperature calorimetric assembly used in this laboratory (10, 41), as modified, is capable of determining heats of fusion within 1.5%, which reduces the uncertainty in ΔH_f and related thermodynamic quantities.

One other consideration prompted this investigation—the determination of the nature and extent of the solid-state transition in sodium nitrate in the vicinity of 280° C. A number of previous workers (26, 28, 29) have noted this transition in thermal investigations, but others—especially those using calorimetric techniques—have failed to observe it (40), or have interpreted it incorrectly (9). The problem is essentially this: differential thermal analytical techniques are capable of detecting very small discontinuities in heat capacity, but can indicate only approximately the changes in heat content to which they refer. Drop calorimetry, on the other hand, provides a direct measure of heat content, but by reason of experimental limitations (too rapid passage of the sample through the region of the transition temperature, for example, or relative smallness of the energy involved in the change) may fail to detect the transition entirely. The two techniques are essentially complementary, differential analysis being most suitable for detecting a transition, and (integral)

calorimetry for assessing the magnitude of the energy changes involved.

As an illustration of the dilemma, Mustajoki (29) and Miekk-oja (28), using (DTA), observed a transition in the vicinity of 275° C., and assigned to it (by graphical integration) a ΔS_f value of 1.7 cal. deg.$^{-1}$ mole^{-1}. This is a change of considerable magnitude, yet Sokolov and Shmidt (40) failed to detect it. The calorimeter used in the present investigation is capable of measuring entropy changes greater than $150/T$ cal. deg.$^{-1}$ mole^{-1}—that is, greater than 0.3 cal. deg.$^{-1}$ mole^{-1} in the vicinity of 275° C.—and is suitable for investigating this transition.

EXPERIMENTAL

Apparatus and Techniques. The high-temperature calorimetric assembly and its operation are described in detail elsewhere (10, 18, 41). Hermetically-sealed platinum crucibles were used to contain the sodium nitrate (Fisher A.C.S. certified reagent grade, oven-dried at 130° C.) and the copper calibration samples. The sodium nitrate was premelted, and the lower half of the crucible embedded in ice to obviate decomposition during the sealing operation. The sodium nitrate was the same grade as that used in this laboratory for cryoscopic studies; cooling curves indicate negligible impurities.

As noted previously (18), the water equivalent of the calorimeter showed a slight linear dependence on the initial temperature of the capsule, a source of error minimized by constructing calibration and sample capsules as similar in heat content as possible.

25° Correction. Enthalpy changes were corrected for the small temperature difference between the final calorimeter temperature and 25° C. C_p values for this correction (in all cases smaller than 1% of the total enthalpy

Table I. Status of Heat of Fusion Data
for Sodium Nitrate to 1957

Year	T_f(° K.)	ΔH_f(Kcal. mole^{-1})
1909 Goodwin and Kalmus (9)	581.2	3.690
1934 Kelley (21)	583	3.760
1955 Sokolov and Shmidt (40)	579.6	3.596
1957 Mustajoki (29)	579.2	3.490

chage) were obtained from tne accurate data reported by Mustajoki (29).

Results. Heat content changes are shown graphically as a function of temperature in Figure 1. There changes can be represented as:

$$H_T - H_{298.15} = 39.63T - 14300 \ (\pm 0.87\%)[483.7 - 548.4° \text{ K.}]$$

$$H_T - H_{298.15} = 44.64T - 16870 \ (\pm 1.18\%)[554.0° - 573.4° \text{ K.}]$$

$$H_T - H_{298.15} = 31.22T - 5570 \ (\pm 0.61\%)[597.8° - 747.2° \text{ K.}]$$

whence

$$\Delta H_{tr} = 174 \text{ cal. mole}^{-1} \ (T_{tr} = 549.2° \text{ K.})$$

$$\Delta H_f = 3520 \text{ cal. mole}^{-1} \ (T_f = 580.0° \text{ K.})$$

$$\Delta S_{tr} = 0.32 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta S_f = 6.08 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

DISCUSSION

Mathematical Treatment of Calorimetric Data. The data shown in Figure 1 might well have been represented below the melting point by one straight line had not the existence of a transition point been indicated by DTA. The assumption of a transition, however, and the representation of the data by two straight lines reduces the experimental scatter from 1.4 to 1.0%. This in itself does not justify the assumption; it is necessary to examine the squared residuals (separately and pooled) about the two lines, as compared with those about one line. Such an analysis (1) indicates that a transition is 93% probable. Another significant point also emerges: Almost all of the reduction in squared residuals results from fitting separate means (rather than separate slopes) for the two lines. The two sets of data warrant two lines having the same slope, but displaced parallel to one another. (An example of the other alternative is provided by sodium ferrite, $NaFeO_2$: at 870° K. this salt undergoes a transition in which heat is neither absorbed nor emitted. The transition is revealed by a change in the slope of the heat content vs. temperature graph, that is, by a variation in heat capacity.) This analysis coincides with the results from DTA (29). The heat capacities of sodium nitrate before and after the transition are virtually identical.

Heat and Entropy of Fusion. The heat of fusion obtained in this investigation is intermediate in value between the two previous "best" values, and is recommended for thermochemical calculations. Cryoscopic measurements using $NaNO_3$, with lithium, rubidium, cesium, and thallous nitrates and sodium fluoride and chloride as solutes (17), also yield a value for the heat of fusion which is in excellent agreement, within experimental error, with that obtained in this study.

Table II contains a survey of recent thermochemical measurements, and fusion and prefusion parameters for $NaNO_3$ recommended from this survey. The heat capacity values recommended differ markedly from those obtained in this investigation. This discrepancy does not affect the heat of fusion significantly, since it results from differentiation of calorimetric heat-content data.

Inspection of Table III shows that the entropy of fusion of sodium nitrate is comparable in magnitude with those of the alkali halides, but (with the exception of $LiNO_3$) larger than any of the other alkali nitrates. The significance of this is considered below, in connection with solid-state transitions.

Solid-State Transition. The solid-state transition confirmed by these results in unusual in a number of ways:

It does not occur abruptly, as do the transformations in solid $KNO_3(26, 28)$ $RbNO_3(31)$, and $CsNO_3(30)$. The additional energy required to effect a transition in any of these salts is absorbed over a temperature interval smaller than 10° C. With $NaNO_3$ (28, 29), the first indications of a change in heat capacity occur at 180° C., but the absorption of energy does not begin to diminish until 276° C. The resulting C_p vs. T curve is considerably skewed, while those for the other alkali nitrates—and even for the melting process in $NaNO_3$—are relatively quite symmetrical.

This broad cusp-shaped peak in the heat capacity curve (often called a Λ-transition) is observed with other substances—e.g., the ammonium halides (14, 42, 43) and the alkali borohydrides

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Table II. Melting and Premelting Parameters for $NaNO_3$

	T_{tr}	T_f	ΔS_{tr}	ΔS_f	$C_p(T_{tr})$	$C_p(s)$ (T_f)	$C_p(l)$ (T_f)
This work	549.2	580.2	0.3	6.1	39.6–44.6	44.6	31.2
Sokolov and Shmidt (40)	...	579.6	0.0	6.2	...	...	...
Miekk-oja (28)	549.2	...	1.6	...	...	...	...
Mustajoki (29)	549.2	579.2	1.7	6.0	88.4	36.0	36.8
Recommended Value	549.2	580	0.3	6.1	88.4	36.0	36.8

Table III. Comparison of Phase-Transition Properties for Alkali Nitrates and Chlorides

	Nitrates					Chlorides				
	T_f	T_{tr}	ΔS_f	ΔS_{tr}	$\Delta S_f + \sum(\Delta S_{tr})$	T_f	T_{tr}	ΔS_f	ΔS_{tr}	$\Delta S_f + \sum(\Delta S_{tr})$
Li	525(23)	443(38)	11.66(9)	(Small)	11.7	880(21)	838?(24)	5.36(21)	?	5.4
Na	580(23)	549(29)	6.1	0.3	6.4	1073(23)	...	6.38(23)	0.0	6.4
K	611(23)	401(23)	4.58(9)	3.49(9)	8.1	1043(23)	298(13)[a]	5.85(23)	0.0	5.85
Rb	581(23)	433(31) 492 563	1.91	2.15(31) 1.56 0.41	6.0	990(21)	298(13)[b]	4.4(21)	0.0	4.4
NH₄	443(8)	305(8) 357 398	2.94(8)	1.24(8) 0.90 2.54	7.6 7.6	793(37)[c]	458(23)	...	2.05(23)	...
Cs	679(30)	424(30)	4.96(30)	2.1(30)	7.1	918(20)	742(20)	5.41(20)	0.78(20)	6.2

[a] 2×10^4 kg./cm.². [b] 5.5×10^3 kg./cm.². [c] 2.62×10^4 mm. Hg.

(44, 45). In these cases spectroscopic and thermodynamic evidence support the view that the gradual transitions are associated with increased torsional oscillation by the polyatomic ion (48), rather than with the onset of free rotation (36). Similar arguments apply to $NaNO_3$. (Ammonium iodide is a possible exception, but with only single-axis, and not three-dimensional, free rotation of the NH_4^- ion allowed.)

No significant discrepancy is observed between heating and cooling curves, but there is evidence of an abnormal dependence on the rate at which these processes are carried out. For example, a sample of $NaNO_3$ heated rapidly (1.6° C. min.$^{-1}$) appears to transform some 9° higher than one heated infinitesimally slowly (28). With still more rapid heating the transition usually escapes detection (3).

Comparatively little supporting evidence is available to confirm the $NaNO_3$ transition. This contrasts with other nitrates, which usually display a variation in electrical conductance (e.g., $AgNO_3$ (6), KNO_3 (15) or in molar volume (e.g., $AgNO_3$ (6) in the vicinity of the transition temperature. The lack of evidence reflects the smallness of the structural rearrangement involved: cf. $LiNO_3$, in which a previously unrecorded transition has been revealed by ultraviolet absorption spectroscopy (38). Although almost entirely spectroscopic, the evidence for $NaNO_3$ is considerably more diverse: the transition has been observed in Raman (33, 34) infrared (12), ultraviolet (38), and x-ray (39) absorption studies.

The change in ordering to which ΔS_{tr} corresponds has accordingly been postulated through interpretation of variations in lattice frequency assignments. In view of thermochemical evidence that the transformation persists from 180° to 280°, a comparison of spectra at 270° C.—at which the transformation is $\sim 60\%$ complete—and at 300° C. is likely to prove inconclusive. Although occasionally based on the assumption of a sharp transition point, certain conclusions seem warranted. The high-temperature phase of solid sodium nitrate contains energetically librating, rather than freely rotating, nitrate ions. Additional support is provided by the continuity of the "normal" heat capacity curve through the transition. A far smaller value of the normal heat capacity would be found upon the attainment of rotational freedom. Several workers

(12, 39) have suggested a parallel with calcite, which undergoes a Λ-transition at 975° C. This is demonstrably a calcite $\rightarrow$ aragonite transition. The low-temperature form of sodium nitrate is isomorphous with calcite, and a rearrangement to the aragonite structure would require that each disordered nitrate group should, in the course of oscillation, rotate by 30° about the c-axis. Such a transition may occur over a range of energy input, and may be expected to be small in energy consumption. X-ray evidence also indicates that, unlike calcite, in which the transition is accompanied by a cubic $\rightarrow$ hexagonal rearrangement, no change in the packing scheme occurs in solid $NaNO_3$ (39). This explains in large part the difficulty encountered in detecting the transition other than by thermal and spectroscopic methods.

The heat of transition obtained in this investigation is 0.17 (± 0.15) kcal. mole^{-1} and gives an entropy of transition of 0.3 (± 0.3) cal. deg.$^{-1}$ mole^{-1}. This value is considerably smaller than those recorded by previous workers (28, 29) as shown in Table II. This discrepancy may reflect the difficulty encountered in studying a rate-process by drop calorimetry. Nevertheless, it is considered unlikely that the present value underestimates the magnitude of the change. The low-temperature portion of the graph shown in Figure 1 should, DTA indicates, be represented by a curve with a slight upward slope; we have expressed the data, within experimental error, by a straight line and thus exaggerated the intercept.

The entropy change involved in the calcite $\rightarrow$ aragonite transformation is 0.9 $\pm$ 0.3 cal. deg.$^{-1}$ mole.$^{-1}$ (2, 21). Since the $CaCO_3$ transition involves also a change in packing, it is hardly surprising that the entropy change should be larger than for $NaNO_3$; at least some of the differences may be ascribed to increases in vibrational entropy and in orientational randomization.

The sums of the entropies of fusion and transition for compounds which show solid-state specific-heat maxima are very similar to and comparable in magnitude with entropies
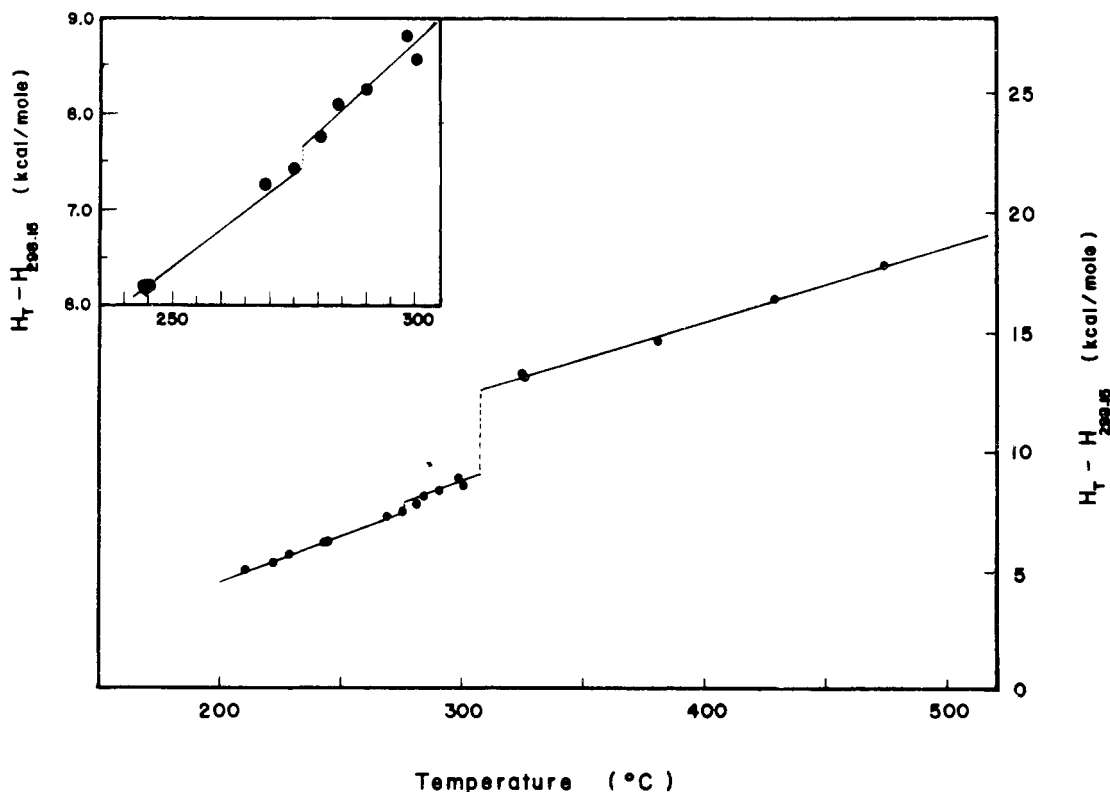

Temperature (°C)

Figure 1. Heat content changes as a function of temperature

Table IV. Comparison of Phase-Transition Properties for a Series of Inorganic Sodium Salts

Salt	ΔT_f	ΔT_{tr}	ΔS_f	ΔS_{tr}	$\Delta V_f/V_s$
NaF	1285(23)	...	6.25(23)	0.0	0.27(25)
NaCl	1073(23)	...	6.38(23)	0.0	0.26(5)
NaNO₃	580(29)	549(29)	6.1	0.3	0.11(6)
NaCN	837(21)	172(4)	5 (21)	0.9(4)	
		288		2.4	
	583(36)		7.4(21)		0.07(36)
NaBH₄	(>700)(19)	190(19)	...	1.2(19)	...
NaSH	...	358(46)	...	2.0(46)	...
NaOH	592(7)	566(7)	2.56(7)	2.69(7)	...
Na₂TiO₃	1303(32)	560(32)	12.9(32)	0.7(32)	...

of fusion of compounds which have no solid-state transitions. This observation is borne out by recent data for the alkali nitrates (Table III): ΔS_f for the series (LiNO₃ execpted) shows a variation of 53% but $[\Delta S_f + \sum (\Delta S_{tr})]$ varies at the most by 14%. The compensating effect of ΔS_{tr} is seen especially with RbNO₃: 68% of the total change in entropy occurs in the solid phase. LiNO₃ resembles other lithium salts in its exceptional behavior, presumably because of the highly polarizing nature of the Li⁻ ion. The resulting interactions apparently produce a "smeared" cubic packing arrangement (as opposed to the highly localized hexagonal close-packing of the other alkali nitrates) in the melt (16). Table III shows that the total entropy changes for the alkali chlorides also conform to the similitude relationship. In this series, however, the constancy is almost entirely a property of ΔS_f. With the exception of ammonium chloride, the solid-state transformations are thermodynamically insignificant. The reason for this is that the transformations are discontinuous, and correspond to a definite structural change (from body-centered to face-centered cubic in the case of CsCl, for example (11, 27).

A comparison of melting and pre-melting parameters of sodium salts (Table IV) enables two general conclusions to be drawn. Salts with polyatomic anions exhibit continuous solid-state transition regions. This is also true for polyatomic cations—cf. NH₄Cl and, especially, NH₄NO₃ (Table III). This "premonition of melting" is obviously an important preliminary to the fusion process.

The lower melting-point and smaller change in volume on fusion found with polyatomic anions are interrelated. Pairing or clustering in the melt, to a greater extent than is possible in the crystal lattice, is often postulated to account for these observations. Further, no simple relationship exists between T_f and T_{tr}, or between ΔS_f and ΔS_{tr} in this series of inorganic salts.

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