Investigation to 6 kbar of Lambda and Solid-Liquid Transitions in Sodium Nitrate

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The solid-liquid and λ transition temperatures in $NaNO_3$ are investigated to 6 kbar by differential thermal analysis in hydrostatic apparatus. There is good agreement between the initial slopes predicted from thermodynamic data at 1 bar and the present experimental values of 7.0 ± 0.5 deg $kbar^{-1}$ for the lambda transition and 15.5 ± 0.7 deg $kbar^{-1}$ for melting. Negligible "curvature" is found for the trajectory of the λ transition, whereas $-d^2T/dp^2$ for the melting curve, $\sim$0.6 deg $kbar^{-2}$, provides a new, more precise constraint on the discontinuities in the interrelated thermodynamic quantities at the melting point as well as allowing the definite conclusion that the compliances $s_{13} < 0$.

The present investigation on the λ and solid-liquid transitions in sodium nitrate at high pressures was undertaken to improve existing high-pressure data and also to constrain further the interrelated 1-bar thermodynamic data near and at the transitions. For the λ transition, Klement's differential thermal analysis (DTA) data (*5*) to 5 kbar are marred by the $\sim$5° difference between heating and cooling signals; Rapoport's earlier DTA work (*11*) reported only cooling signals and were mostly only at higher pressures. For the solid-liquid transition, Owens' volume discontinuity data (*9*) were above $\sim$2 kbar, and Rapoport's DTA results were mostly only at higher pressures.

For the first run reported here, Baker AR material of specified 99.7% purity was dried overnight at 150°C under 1/2 atm of air, powdered in air, and $\sim$6 mg of sample loaded to $\sim$5-mm length in a 1.59-mm o.d. platinum tube of 0.13-mm wall thickness. The tubing was then sealed with an oxyacetylene torch and a Chromel-Alumel® thermocouple of 0.13-mm diam. wire and minimum bead size was mechanically attached to the sealed tube near the midpoint of the sample and silver conductive paint applied to the contact. Another similar thermocouple in contact with mullite thermocouple tubing and $\sim$2 mm away from the temperature-measuring junction served as reference junction. To promote isothermality, the sample and thermocouple assembly were surrounded by a gold sleeve of 5.59-mm o.d., which, in turn, was encased in a stainless-steel sleeve. The internally heated high-pressure apparatus, which uses argon as the pressurizing medium, is described elsewhere (*1*).

Pressure was read to ±5 bar from a 7-kbar Heise bourdon tube gage; other experiments (to be published) with sealed and unsealed capsules indicate that any pressure differentials caused by wall strength of the Pt capsules were less than the detection limit. Temperature was varied at rates from 0.1 to 1 deg sec^{-1} through the transitions, and both the emfs corresponding to the temperature and to the differential temperature were recorded on a 2-pen recorder with sensitivities of 0.20 and 0.008 mV cm^{-1}, respectively.

For the λ transition, there were abrupt and easily identified shifts in the differential pen, which agreed to within $\sim$0.5° on both heating and cooling, and which were taken as the temperature of this transition. The lack of appreciable hysteresis, as encountered in a previous investigation (*5*), can be attributed to the smaller sample size and more intimate thermocouple contact here. The signal corresponding to the onset of melting was not sharp, but the signal on cooling consisted of 1° or so of undercooling terminated by an abrupt freezing signal and followed by recalescence with a brief plateau apparently corresponding to the freezing temperature. The data so obtained in the initial run are shown in Figure 1 and represent two or more cycles at the given pressure, with reproducibility to within 0.5°. Data were obtained both when pressure was being stepwise increased and then decreased; the measurements were corroborative.

For the second run, Mallinckrodt AR material from a hitherto unopened bottle was dried in a Pyrex tube at $\sim$350°C for 24 hr under 1/2 atm of air. Then, in an argon-filled glove box with P_2O_5 present, the material was freshly powdered, loaded into a platinum capsule, the capsule then crimped, removed to air, sealed, and the DTA assembly prepared as before. Data from the second run, obtained as before, are also shown in Figure 1.

Similar starting materials and drying techniques were used by Owens (*9*), Rapoport (*11*), and also Kleppa and McCarty (*7*) in their determination of the heat of fusion.

Polynomial regression analysis was performed on 51 observations of the freezing signal and 95 observations of the λ transition. For the melting curve, values for the 1-bar intercept, the initial slope dT/dp, and the curvature are, respectively, 304.1 ± 0.5°C, 15.5 ± 0.7 deg $kbar^{-1}$, and $-0.3 \pm 0.1_5$ deg $kbar^{-2}$. Extension of the regression analysis to third order made only slight changes in the second order term. For the lambda transition, the 1-bar intercept and the slope are 273.9 ± 0.5°C and 7.0 ± 0.5 deg $kbar^{-1}$, with no higher order terms indicated. The internal consistency between the two runs is within 1°, except that the data for the λ transition from the second run may be systematically as much as 1° higher than those from the first run. The uncertainties quoted are the standard deviation to which have been added estimated experimental uncertainties, exclusive of any undetected systematic errors.

An in situ thermocouple calibration was made with lead of 99.999% purity from Fairmount Chemical Co. sealed in a 1.6-mm o.d., 0.2-mm wall thickness capillary and positioned in the high-pressure assembly as the samples had been. At 1 bar with temperature varied from 2 to 40 deg min^{-1}, the onset of melting was detected at 327°C, but the temperature of the plateau on freezing, after undercooling and recalescence, was consistently

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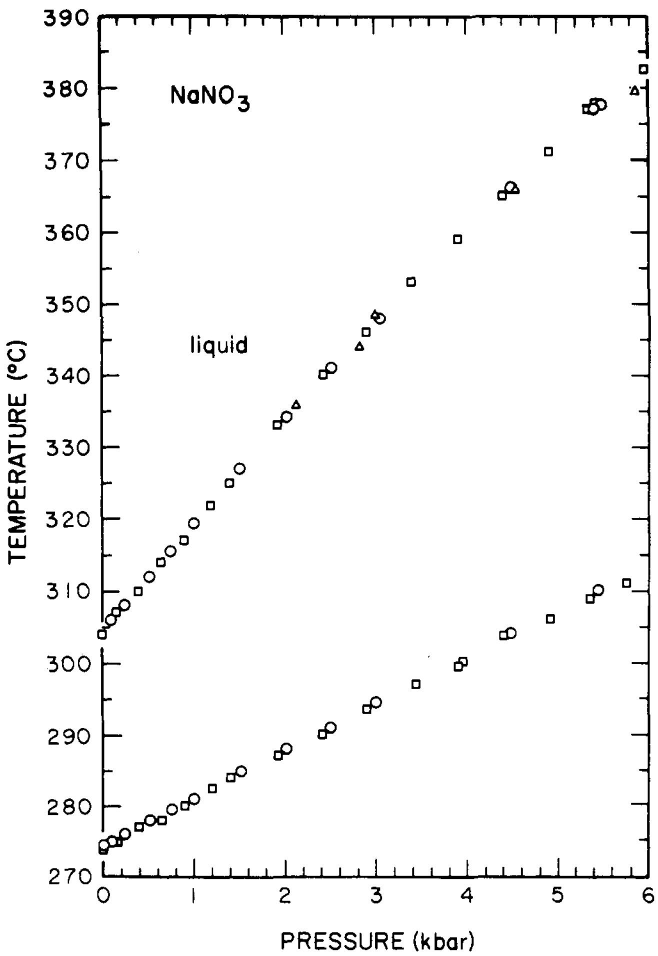

Figure 1. Data for solid-liquid transition (upper curve) and lambda transition (lower curve) in sodium nitrate

□ First run
○ Second run
△ Owens (9)

324°C. The maximum differences between measuring and reference junctions before onset of a transition were always less than 1°. The melting signal was accepted for the calibration; this compares favorably with 327.5° for lead on the IPTS of 1968 (*12*). Thus, temperatures shown in Figure 1 are reckoned to this accuracy. No correction was attempted for the effects of pressure on thermocouple emf, which should be minimal. The slopes of the phase boundaries, of course, are independent of absolute calibration.

The previous high-pressure investigations suggested that the 1-bar transition temperatures were 275-276°C [Klement (*5*)], 275°C (*11*) or 275.5°C (*10*) (Rapoport); and 306°C [Owens (*9*)], 310.6°C (*11*) or 307°C (*10*) (Rapoport), with Rapoport (*11*) using material from the Owens' stock. It does not seem that these temperatures were ever determined directly or by very precise extrapolation.

In further comparison with the previous high-pressure data, Klement's results (*5*) for the λ transition appear to lie slightly higher in temperature than the present results, although not beyond the hysteresis encountered in the earlier work; Rapoport's actual data (*11*) for the λ transition essentially do not overlap the present results, thus precluding comparison. The actual melting data of Owens (*9*) in the present pressure range are also shown in Figure 1, where it can be seen that there is essential agreement. Likewise, it does not seem that Rapoport's actual data (*11*) disagree with the present results. For the fusion curve, it thus appears that the present data at the lowest pressures correspond to a lower melting point than was assumed by the previous workers.

For the trajectory of the λ transition, the present data are compatible with the constraints developed (*6*) from the thermodynamic data at 1 bar. For the melting curve, the initial slope $dT/dp = \Delta V/\Delta S$ agrees, within experimental uncertainties, with the value(s) calculated from the heat of fusion (3696 ± 32 cal mol^{-1}) determined by Kleppa and McCarty (*7*) and the volume discontinuity (4.32 cm^3 mol^{-1}) suggested by Schinke and Sauerwald (*13*) (other determinations of these quantities are cited in these papers). For the "curvature," $-d^2T/dp^2$,

$$-\frac{d^2T}{dp^2} = (\Delta S)^{-1}\left\{-\left(\frac{\partial \Delta V}{\partial p}\right)_T - 2\left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p + \left(\frac{dT}{dp}\right)^2 \frac{\Delta C_p}{T}\right\}$$

The $(dT/dp)^2\ \Delta Cp/T$ term (*4, 7*) much smaller than the others, is $\lesssim$ 0.02 cm^3 mol^{-1} kbar^{-1}. The thermal expansion of the liquid is taken from Barton et al. (*2*) (who cite unpublished theses) and that of the solid from Kracek (*8*) and others (*6*) and yields $-2(dT/dp)(\partial\Delta V/\partial T)_p \lesssim -0.24$ cm^3 mol^{-1} kbar^{-1}. For the dominant term involving the difference between the isothermal compressibilities, there is a precise value of 18 ± 1 Mbar^{-1} for the isothermal compressibility of the liquid from Barton et al. (*2*); the adiabatic compressibility ($\equiv 2s_{11} + 2s_{12} + 4s_{13} + s_{33}$) of the solid is estimated from the elastic compliance data synthesized by Hearmon (*3*). It may be concluded that $s_{13} < 0$, to obtain agreement between the experimental and calculated curvatures; previously (*6, 3*), the sign of s_{13} had not been established. The isothermal compressibility of the solid is then estimated as $\sim 9\frac{1}{2}(\pm 1 - 2?)$ Mbar^{-1}, where the adiabatic → isothermal compressibility correction term, $\{(\partial V/\partial T)_p{}^2\ (T/Cp \cdot V)\}$, is only ≈ 0.5 Mbar^{-1}. Thus $-(\partial\Delta V/\partial p)_T \sim 0.36$ cm^3 mol^{-1} kbar^{-1}. Combining these contributions, $-d^2T/dp^2 \sim 0.5$ deg kbar^{-2}, with an uncertainty of the same magnitude—but consistent with the experimental value(s) given above.

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