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Transitiometric Determination of the Phase Diagram of KNO₃ between (350 and 650) K and at Pressures up to 100 MPa[†]

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A *P*, *T*-phase diagram for KNO₃ has been experimentally determined over the temperature range from (350 to 650) K and at pressures up to 100 MPa with the use of a scanning transitiometer. These new results are compared with those reported by other authors. The comparison shows that the pressures and temperatures of transitions among phases I, II, and III obtained in this study are in good agreement with those reported in the literature. In addition, a detailed analysis of these transitions was performed by measuring simultaneously the enthalpy and volume changes at selected pressures both by heating and cooling. The results demonstrate the reliability of scanning transitiometry to study phase transitions in complex systems at high temperatures and pressures. The present data will serve using KNO₃ as a calibrating and reference substance in subsequent high-pressure high-temperature studies by scanning transitiometry.

Introduction

It is well-known that KNO₃ can exhibit up to seven phase transitions, depending on the temperature and pressure ranges.^{1–5} Under atmospheric pressure KNO₃ presents three solid phases (I, II, and III).^{1–7} Phase II (orthorhombic crystal structure, space group *Pcmn*, *Z* = 4) is transformed by heating into phase I (rhombohedral crystal structure, space group *R3m*, *Z* = 1) at approximately 304 K and into a ferroelectric phase III (rhombohedral crystal structure, space group *R3m*, *Z* = 1) obtained by cooling^{6–8} of phase I.

Studies of the different phases present in KNO₃ at high pressure have used volumetric, thermodynamic, spectroscopic, photoacoustic calorimetry, and heat-flow calorimetric techniques, and the characterization of these phases requires the use of other techniques such as X-ray diffraction, Raman scattering, or infrared transmission spectroscopy.^{1,2,7,8} Font and Muntansell⁵ studied thermobarometrically the behavior of KNO₃ submitted to pressures up to 150 MPa using a metabolemeter, in which the effect of the pressure on the transitions among the different phases I, II, and III was analyzed. In this study, the endothermic transformation of the phase II into phase I took place through phase III, and coexistence was always observed with the phases

II and III, obtained by cooling phase I, which is metastable at room temperature.

The purpose of the present study is to determine the transitions among phases I, II, and III that KNO₃ exhibits over the temperature range from (350 to 650) K and at pressures up to 100 MPa, using scanning transitiometry.⁹ This technique, which combines calorimetry and PVT-methods, allows controlling the three most important thermodynamic variables (*p*, *V*, *T*) in simultaneous measurements of changes (or rate of such changes) of both thermal and mechanical contributions to the thermodynamic potential under precisely determined conditions. A transitiometric measurement consists in scanning one of the independent variables, keeping constant one of the other independent variables, while recording simultaneously the associated heat flux and the variations of the mechanical effect (variations of the dependable variable volume or pressure) resulting from the physicochemical change induced by the performed scanning.^{10,11}

Experimental Section

Description of the Apparatus. A schematic diagram of a scanning transitiometer used in the present study is presented in Figure 1. The instrument can be used to study phase transitions in simple and complex systems over the temperature range from (253 to 673) K under pressures up to 400 MPa.

The transitiometer consists mainly of two calorimetric detectors containing 622 (or 1244) thermocouples mounted differentially and connected to a nanovolt-amplifier. The calorimetric detectors were located in a calorimetric metallic block, in which temperature was digitally controlled within a precision of about (10^{−4} to 10^{−5}) K. The calorimetric block is surrounded by a heating–cooling shield. The temperature difference between the

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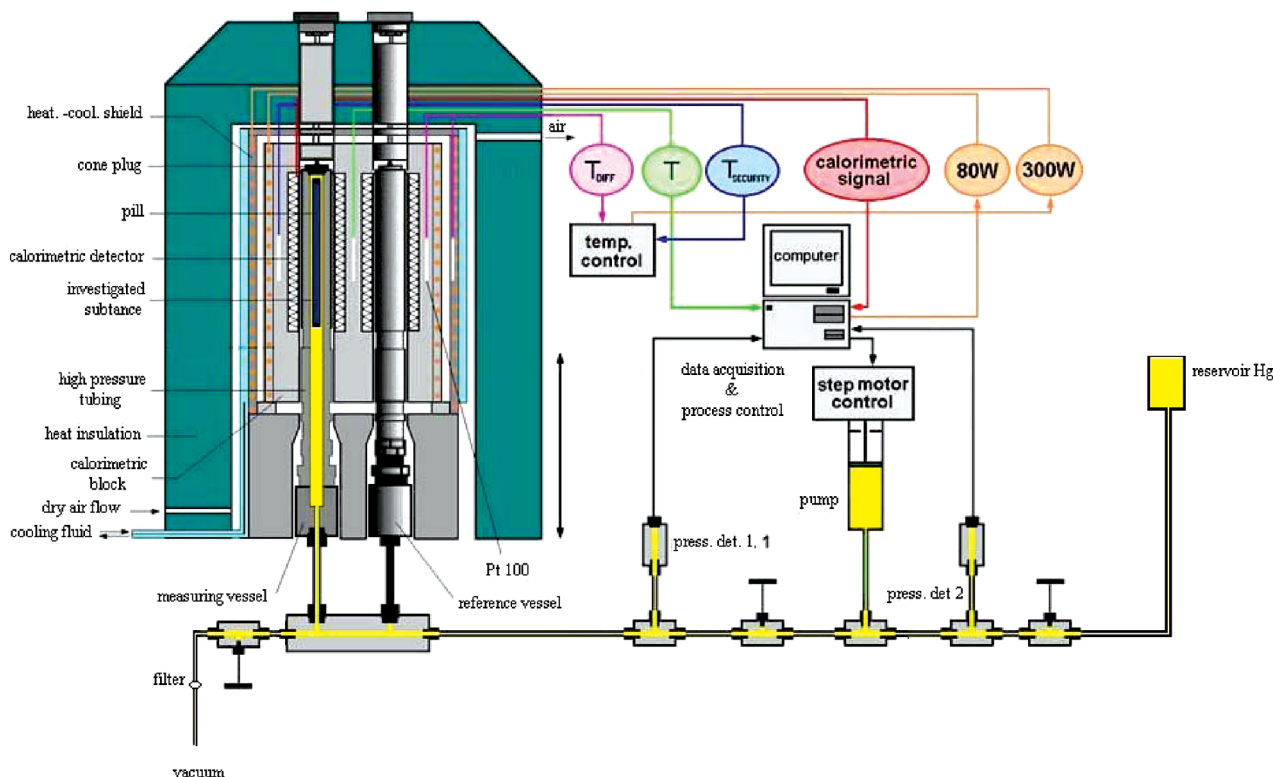


Figure 1. Schematic diagram of the transitiometer used in the present study.

metallic block and the heating–cooling shield was also controlled to stabilize the heat losses from the block and thus ensure a good homogeneity of its temperature, which was of importance for properly recording the heat fluxes in the calorimetric detectors over wide temperature ranges.

The measuring and reference calorimetric vessels were introduced into the calorimetric detectors through the holes in the thermal isolation. The calorimetric vessels were made of stainless steel 316 tubing with an internal diameter of 8 mm to withstand maximum pressures of 200 MPa; for measurements up to 400 MPa, the vessels were made of stainless steel 316 tubing with an internal diameter of 4.8 mm.

The sample under investigation was placed inside the measuring calorimetric vessel, which is connected to the high-pressure hydraulic system. The sample can be placed directly on the surface of mercury, which was used as a pressurizing fluid, or embedded in a flexible ampule. The displacement of the pressurizing fluid into the system was realized by means of a displacement pump controlled by a stepping motor with a total displacement volume of 10 mL; each motor step corresponds (as established by a weighing calibration) to a volume displacement of $(5.24 \pm 0.04) \cdot 10^{-6}$ mL. The pressure transducers 1 and 2 shown in Figure 1 were calibrated against a dead-weight pressure balance over a pressure range from (0.1 to 400) MPa. Pressure measurement uncertainties are estimated to be 0.15 % of the full pressure scale.

The pressure sensors, the stepping motor, the temperature controller, and the calorimetric amplifier were connected to a digital control module. An appropriate Labview type software allowed the independent control and recording of pressure p , temperature T , and volume V and recording of the heat flux q (see Figure 1). These four variables were recorded simultaneously during the whole experimental process. A more detailed description of the transitiometer can be found in the original references.^{12,13}

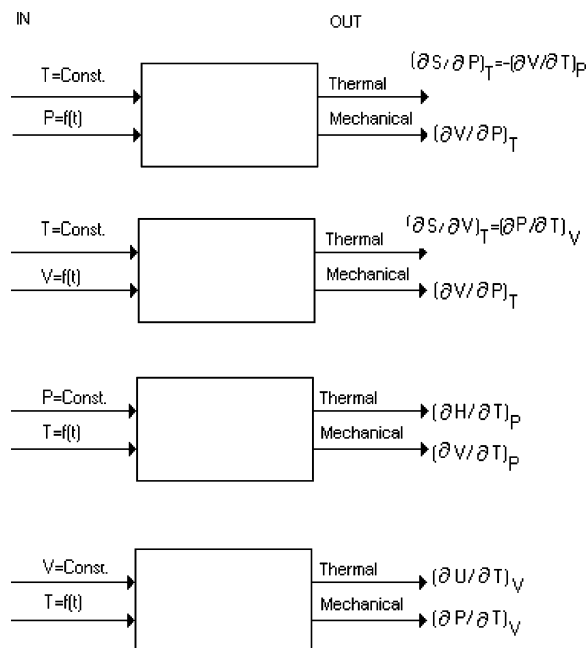


Figure 2. Thermodynamic scheme of scanning transitiometry principle. On the left-hand side are indicated the four possible thermodynamic modes (IN), and on the right-hand side are given the associated derived thermal and mechanical quantities (OUT) directly measured during the different variable scans as functions of time t .

Thermodynamic Principles of the Transitiometric Technique.

The thermodynamic principle of the scanning transitiometric technique is presented schematically in Figure 2. From the variations of the dependent variables and the associated heat flux, four thermodynamic situations can be created, in each case two thermophysical coefficients (thermal and mechanical) are determined accurately as a function of the scanning variable.

In the particular case of this study, where the pressure was kept constant and the temperature was varied linearly at the rate b as a function of time,

$$dp = 0 \quad T = T_0 + bt \quad dT = bdt \quad (1)$$

the thermodynamic derivatives were determined from the enthalpy function h , as described by expressions

$$dh(T, p) = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \quad (2)$$

$$dh(T, p) = dQ + V dp \quad (3)$$

By introducing conditions of eq 1 into eqs 2 and 3, the following expression is obtained

$$\left(\frac{dQ}{dt}\right)_p = q_p(T) = \left(\frac{\partial h}{\partial T}\right)_p b \quad (4)$$

where $q_p(T)$ is the heat generated or absorbed at isobaric conditions under the temperature scan with rate b . This is the fundamental thermodynamic principle for a temperature control scanning calorimeter (TCSC) at constant pressure,^{10,11} in which the temperature is the inducing variable as a function of time that allows to perform measurements of the enthalpy changes from temperature scans under isobaric conditions $(\partial h/\partial T)_p$. Simultaneously, from the recorded volume variations used to keep the pressure constant and from the rate of temperature variations the thermal expansion, $(\partial V/\partial T)_p$ is determined.

Procedures. KNO₃ was purchased from Aldrich (99.99 %) and used without any further purification. For the purpose of the phase diagram determination several cylindrical KNO₃ tablets of $(2.5 \pm 5 \cdot 10^{-3})$ kg were prepared under pressures of about 10 MPa. These tablets were dried under vacuum during 24 h at 373 K before use. The preparation of the KNO₃ in this manner resulted to be very convenient to carry out the experimental measurements, avoiding thus the encapsulation of the KNO₃ in metallic recipients.⁴

A KNO₃ tablet was placed inside the transitiometric vessel directly on the pressurizing fluid (Hg). Then, all of the systems were evacuated down to 0.01 Pa during 30 min. To make sure that the KNO₃ tablet was not modified under vacuum, a metallic filter containing a 0.45 μ m Teflon membrane was used. This membrane was weighted before and after the evacuation of the system to verify that there were no losses of the salt under vacuum. Results of several such tests showed that the KNO₃ tablets did not lose weight during the evacuation of the system.

Once the functionality of the KNO₃ tablets was verified, the determination of the transition temperatures for KNO₃ over the temperature range from (350 to 650) K was performed. The experiments were carried out under isobaric conditions for different pressures ranging from (0.1 to 77) MPa at a temperature scanning rate of 8 mK·s⁻¹.

For the purpose of a detailed transitiometric analysis of the transition lines between the three phases under pressures up to 100 MPa, a sample of KNO₃ of near 2.56 g was embedded in a flexible lead ampule, placed in the calorimetric vessel, and positioned (in the calorimetric detection zone) with the use of

Table 1. Experimental Transition Temperatures for the Transitions among Phases I, II, and III of KNO₃ and Literature Values

p/MPa	T/K			
	exp.	lit. ^a	lit. ^b	lit. ^c
Phase Transition I				
0.1	611.0	603.3	608.7	606.1
6.5	607.5	604.2	609.7	606.1
14.0	610.6	605.3	610.3	607.2
21.0	607.4	605.3	610.4	608.1
28.0	612.7	606.2	610.8	608.5
35.0	612.0	606.2	611.5	609.5
42.0	604.0	607.2	611.9	609.6
49.0	602.9	602.9	607.1	609.4
63.0	604.7	608.1	613.2	611.3
77.0	616.0	609.0	613.5	611.3
Phase Transition II				
0.1	404.4	399.8	403.7	401.0
6.5	402.4	397.3	402.3	401.0
14.0	403.8	395.9	400.1	400.9
20.0	400.0 ^d	395.3	397.3	399.0
21.0	398.7	395.2	396.8	398.4
28.0	400.5	394.3	395.6	397.7
35.0	400.0	392.9	392.6	395.6
42.0	398.5	392.3	391.0	394.9
49.0	397.0	389.6	389.6	392.4
50.0	394.0 ^d	389.5	389.8	392.5
63.0	394.2	386.1	386.4	389.5
75.0	388.5	383.8	385.9	387.6
77.0	392.0	383.1	385.6	387.3
100.0	383.5 ^d	383.7	379.8	381.3
Phase Transition III				
0.1	—	399.9	403.8	401.1
6.5	—	401.5	405.1	401.2
10.0	401.5 ^d	402.0	405.6	401.2
14.0	403.8	402.4	406.0	401.2
20.0	403.6 ^d	403.2	406.6	401.9
21.0	405.3	403.8	406.6	401.8
28.0	408.0	403.8	407.7	404.1
35.0	410.0	404.4	408.5	404.5
42.0	411.8	405.5	408.8	406.8
49.0	410.0	408.0	410.6	408.4
50.0	410.0 ^d	408.5	410.7	408.6
63.0	414.2	412.4	412.5	412.1
75.0	414.9	415.6	414.1	415.4
77.0	418.1	415.4	414.4	415.6
100.0	420.5 ^d	420.1	419.1	421.2

^a Adams et al.¹ ^b Schaffer and Mikkola.¹⁴ ^c Rapoport and Kennedy.⁴

^d Data measured at the Institute of Physical Chemistry, Warszawa, Poland.

a hastelloy spring support and a small quantity of high temperature oil. In this case the temperature scanning rate was 2 mK·s⁻¹.

Results and Discussion

P,T-Phase Diagram. Table 1 presents the transition temperatures of KNO₃ obtained by the transitiometric technique at different pressures from (0.1 to 77) MPa. This table presents three of the seven phase transitions exhibited by this salt. From our measurements it can be concluded that the global uncertainty of the data obtained for the temperatures of transitions of phases I, II, and III is ≈ 3 %, while the repeatability of the measurements is estimated to be ± 1 %. The results obtained in this study are compared with experimental data reported in the literature^{1,4,14} also listed in Table 1.

Figure 3 shows the relative deviations from literature values of the three phase transition temperatures of KNO₃ obtained in the present study over the temperature range from (350 to 650) K and at pressures up to 77 MPa. We observe that the literature values show a trend similar to that obtained in this work, and the general agreement between the different sets of data with

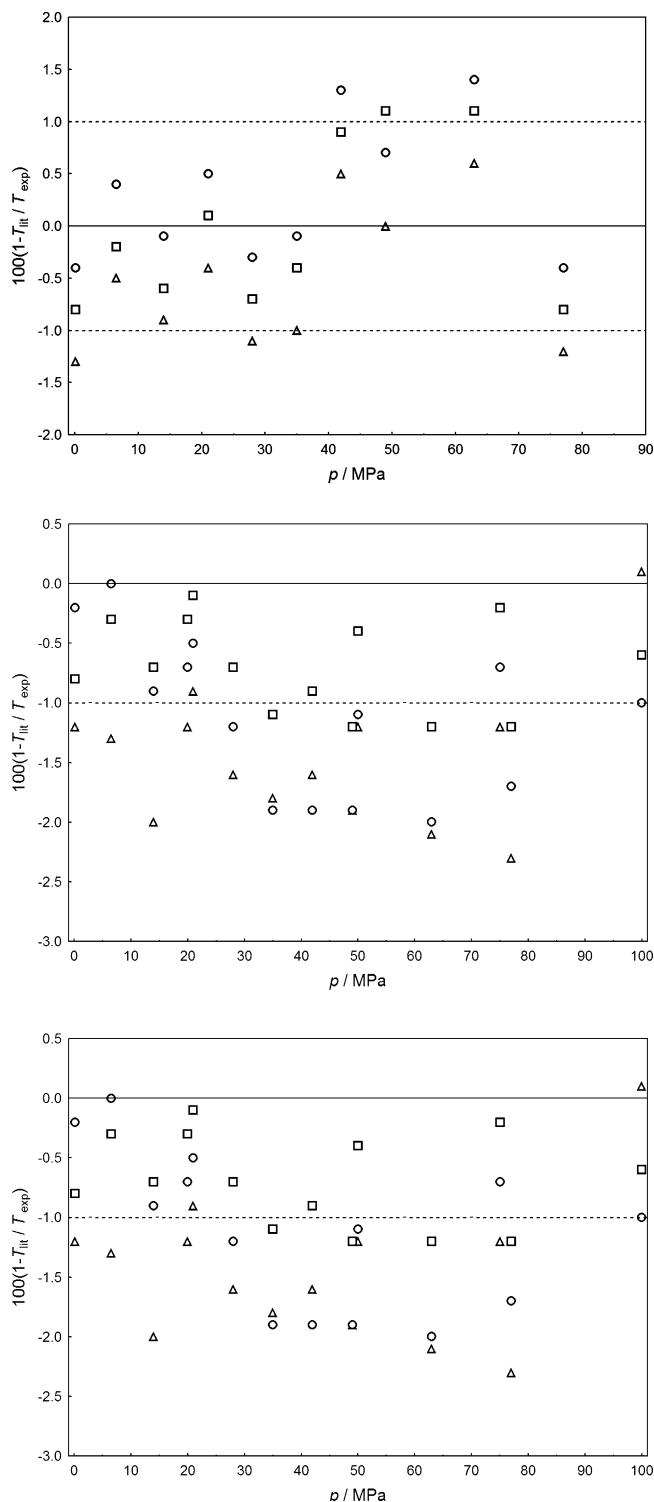


Figure 3. Comparison of this work's experimental data with literature data of the three phase transition temperatures of KNO_3 . Plots of the relative difference $\text{Diff} = 100 (1 - T_{\text{lit}}/T_{\text{exp}})$: top, phase I transition; middle, phase II transition; bottom, phase III transition. Δ , Adams et al.;¹ \circ , Schaffer and Mikkola;¹⁴ \square , Rapoport and Kennedy.⁴

ours is within $\pm 1\%$, although our transition temperatures for the three KNO_3 phases are in general slightly above than those reported in the literature. Notwithstanding, it is worth mentioning that the measurements of the phase transitions reported in literature were obtained using experimental techniques different to the transitiometric one used in the present study.

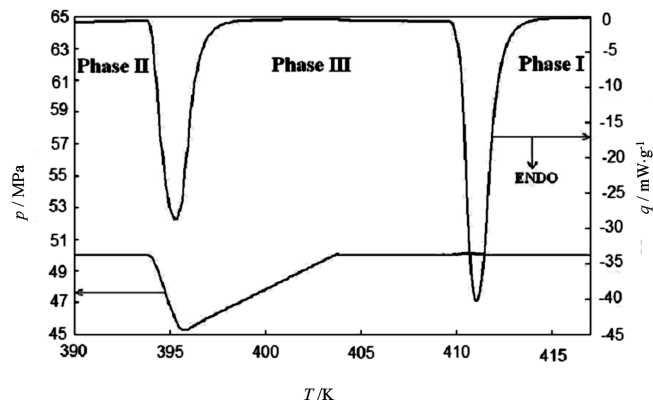


Figure 4. Transitiometric traces obtained for KNO_3 under the 50 MPa pressure by heating at a rate of $2.00 \text{ mK} \cdot \text{s}^{-1}$.

Table 2. Thermodynamic Data for the Transition in KNO_3 from Phase III to Phase I Obtained in the Transitiometer by Isobaric Heating at a Rate of $2.00 \text{ mK} \cdot \text{s}^{-1}$

p MPa	T K	ΔH_{tr} $\text{J} \cdot \text{g}^{-1}$	ΔV_{tr} $\text{mm}^3 \cdot \text{g}^{-1}$
100 ± 0.15	420.5 ± 0.2	29.08 ± 0.44	13.35 ± 0.27
75 ± 0.11	414.5 ± 0.2	29.96 ± 0.44	13.44 ± 0.44
50 ± 0.08	409.8 ± 0.2	28.62 ± 0.44	13.30 ± 0.44
20 ± 0.03	403.6 ± 0.2	28.10 ± 0.44	13.50 ± 0.44
10 ± 0.02	401.5 ± 0.2	27.97 ± 0.44	13.33 ± 0.44

Table 3. Thermodynamic Data for the Transition in KNO_3 from Phase I to Phase III Obtained in the Transitiometer by Isobaric Cooling at a Rate of $-2.00 \text{ mK} \cdot \text{s}^{-1}$

p MPa	T K	ΔH_{tr} $\text{J} \cdot \text{g}^{-1}$	ΔV_{tr} $\text{mm}^3 \cdot \text{g}^{-1}$
100 ± 0.15	417.5 ± 0.2	-29.82 ± 0.44	-13.33 ± 0.27
75 ± 0.11	412.2 ± 0.2	-29.52 ± 0.44	-13.23 ± 0.44
20 ± 0.03	400.7 ± 0.2	-28.70 ± 0.44	-13.59 ± 0.44
10 ± 0.02	398.6 ± 0.2	-28.36 ± 0.44	-13.47 ± 0.44

These discrepancies can be attributed either to the purity of the KNO_3 ($< 99.99\%$ in the present work) used by the other authors or to the numerical values of the melting temperatures used for comparison, when obtained from graphical interpolation. Nonetheless, regardless of these discrepancies, the results of the comparison show that the transitiometric technique is appropriate to determine the phase transitions of this kind of salts over wide ranges of pressure and temperature.

Detailed Analysis of the Transition Lines among Phases I, II, and III. An interesting aspect of first-order transitions, like the ones observed among the three phases, is the slope (i.e., the Clapeyron slope) of the corresponding equilibrium curves. According to the Clapeyron equation the slope dT/dp for the equilibrium of the first-order transitions is determined by the signs of variations of both enthalpy and volume. Thus, the transitiometric technique permitting to determine the two quantities simultaneously under precisely determined thermodynamic conditions is advantageous for such an analysis. However, the present status of the technique permits making such measurements only when the sign of the change of a mechanical variable (volume/pressure) observed during the phase transition under investigation is the same as in single phases. For example, during heating under isobaric conditions, the pressure control system expands the internal volume of the system to compensate both the positive thermal expansion and the positive volume variation associated with the phase transition. Because of some technical problems, when the sign of the change of the mechanical variable observed during the

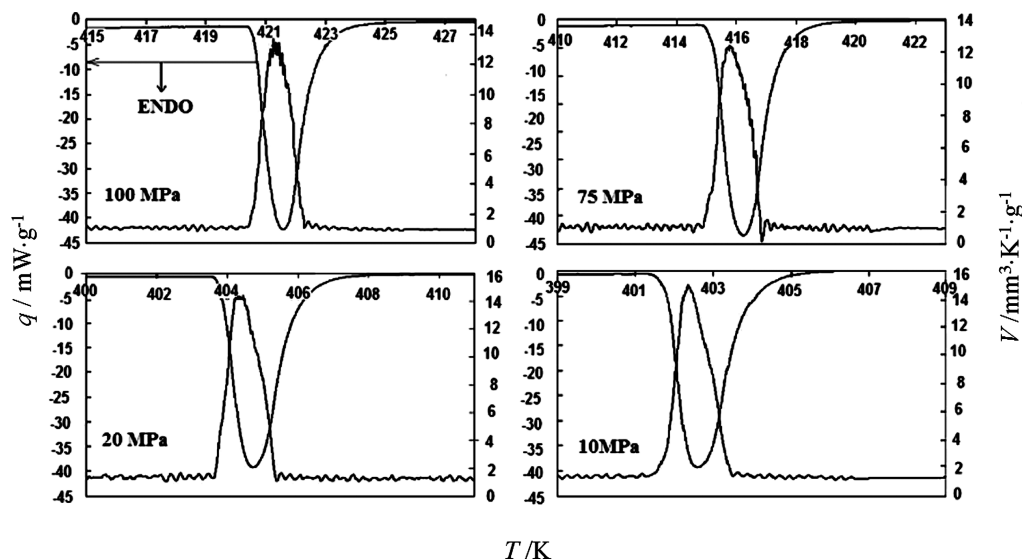


Figure 5. Transitiometric traces for the transition between phases III and I of KNO_3 obtained by isobaric heating at selected pressures at a rate of $2 \text{ mK} \cdot \text{s}^{-1}$: left-hand scale, endothermic heat flux (enthalpy) change q ; right-hand scale, volume change.

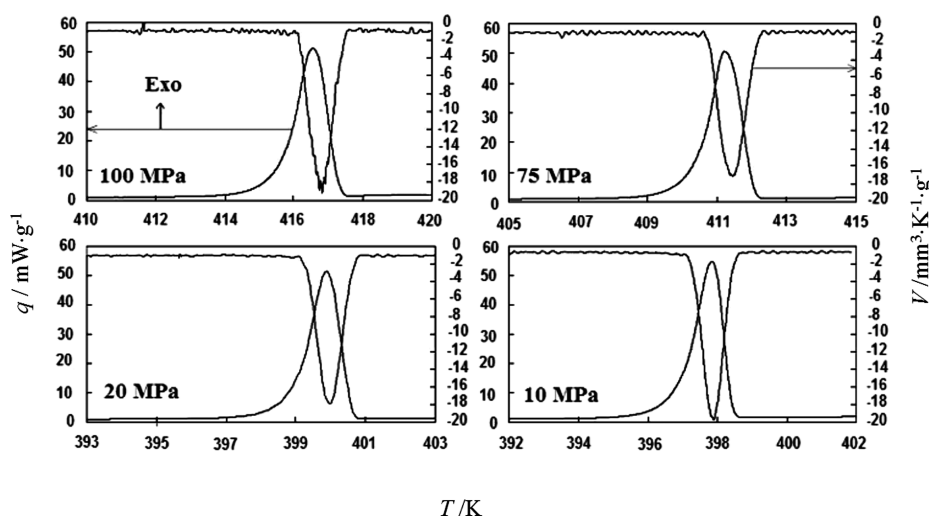


Figure 6. Transitiometric traces for the transition between phases I and III of KNO_3 obtained by isobaric cooling at selected pressures at a rate of $-2 \text{ mK} \cdot \text{s}^{-1}$: left-hand scale, exothermic heat flux (enthalpy) change q ; right-hand scale, volume change.

Table 4. Thermodynamic Data for the Transition in KNO_3 from Phase II to Phase III Obtained in the Transitiometer by Heating at a Rate of $2.00 \text{ mK} \cdot \text{s}^{-1}$ without Pressure Control

p MPa	T K	ΔH_{tr} $\text{J} \cdot \text{g}^{-1}$	ΔV_{tr} $\text{mm}^3 \cdot \text{g}^{-1}$
100 ± 0.15	383.5 ± 0.2	20.97 ± 0.31	-11.39 ± 1.14^a
75 ± 0.11	388.5 ± 0.2	22.25 ± 0.33	-11.93 ± 1.19^a
50 ± 0.08	394.0 ± 0.2	24.19 ± 0.36	-12.79 ± 1.28^a
20 ± 0.03	400.0 ± 0.2	26.90 ± 0.40	-14.01 ± 1.40^a

^a Estimated from the Clapeyron equation based on the measured $\Delta_{\text{tr}}H$, p , and T for that transition.

transition is opposite to that in single phases, the compensation cannot be performed correctly, because the dynamic change of the direction of both the stepping motor and the gear box cannot be perfect. Figure 4 presents an example of transitiometric traces obtained on heating at a rate of $2 \text{ mK} \cdot \text{s}^{-1}$ with the pressure compensation system set for positive variations of the mechanical variables. The temperature scanning started at 50 MPa and was correctly controlled when the system was under a single phase II. At the beginning of the transition to phase III, the pressure dropped, because the volume decreased importantly.

On further heating, the pressure increased to the set value of 50 MPa due to the positive thermal expansion of phase III. At the transition from phase III to phase I, the pressure was correctly controlled, because this time the volume change was positive. It is also worth noting from Figure 4 that the both transitions are endothermic. For the above reasons, the transitiometric analysis of the transition from phase III to phase I could be performed correctly at selected isobars, while for the transition from phase II to phase III only temperature, pressure, and the heat of transition could be measured; however, the heat of transition could be affected by the pressure variations.

Table 2 presents the thermodynamic data for the transition in KNO_3 from phase III to phase I obtained in the transitiometer by isobaric heating under selected pressures at a rate of $2.00 \text{ mK} \cdot \text{s}^{-1}$. Table 3 presents the thermodynamic data for the transition of KNO_3 from phase I to phase III obtained in the transitiometer by isobaric cooling under selected pressures at a rate of $-2.00 \text{ mK} \cdot \text{s}^{-1}$. Figures 5 and 6 present examples of transitiometric traces obtained by heating and cooling at selected pressures respectively for those transitions. From the data obtained, it is worth noting that on both heating and cooling the volumes of the transitions do not depend on pressure within

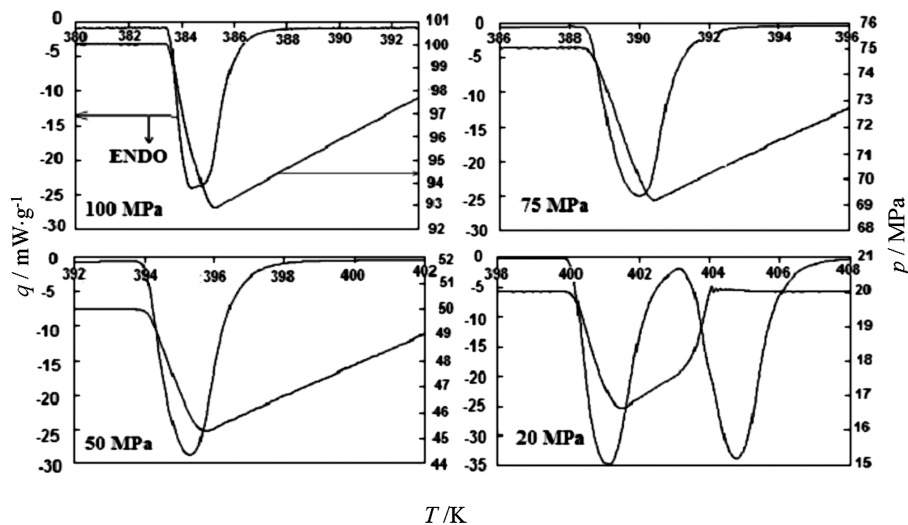


Figure 7. Transitiometric traces for the transition between phases II and III of KNO₃ obtained by heating at selected pressures at a rate of 2 mK·s⁻¹ without pressure control: left-hand scale, endothermic heat flux (enthalpy) change q ; right-hand scale, pressure variation.

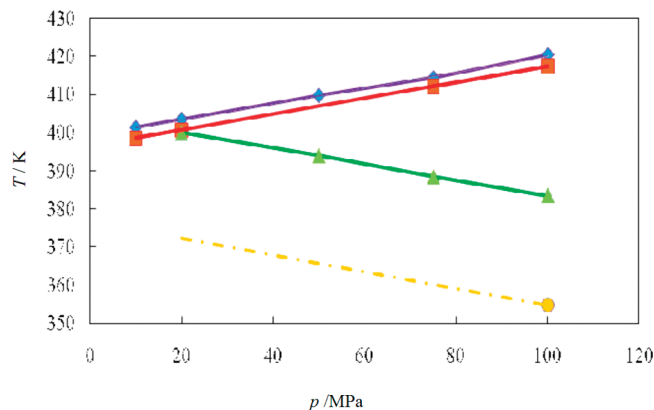


Figure 8. T - p diagram showing the transition curves between the three selected phases of KNO₃: ♦, phase III to phase I; ■, phase I to phase III; ▲, phase II to phase III; ● and dotted line, phase III to phase II.

the experimental error, while the absolute values of the enthalpies of the transitions increase with pressure slightly above the experimental error, which is not typical for the first-order transitions.

Table 4 presents the thermodynamic data for the transition of KNO₃ from phase II to phase III obtained in the transitiometer by heating under selected pressures at a rate of 2.00 mK·s⁻¹, but without pressure control, and Figure 7 presents selected transitiometric traces obtained under such conditions for that transition. The volume variations at selected pressures have been estimated from the Clapeyron equation based on the experimental data for $\Delta_{\text{tr}}H$, p , and T for that transition. Noticeably, in this case the absolute values of both heat of transition and volume change importantly decrease with pressure increase, which is often encountered for the first-order transitions. Unfortunately, on cooling only under pressure of 100 MPa, the transition from phase III to phase II could be experimentally observed, giving rise to an important decrease of the transition temperature.

All transition curves determined transitiometrically in the present study are presented in Figure 8. We observe that the slope of the equilibrium curve between phases III and I is positive, whereas between phases II and III it is negative. Noticeably, the transitions between phases III and I and I and

III have a rather narrow metastability region of only near 2.9 K. On the contrary, on the basis of the results obtained for 100 MPa, such a metastable region for the transitions between phases II and III and III and II is rather large, near at least 28.6 K.

Conclusions

In this work, the transitiometric technique was successfully used to determine the phase diagram of KNO₃ over the temperature range from (350 to 650) K and at pressures up to 100 MPa. Under these temperature and pressure conditions, the transitions among the three phases I, II, and III of the KNO₃ were obtained; they are three of the seven phase transitions that this salt exhibits at higher temperatures and pressures due to its polymorphism. Both the comparison of the transition temperatures for the three phase transitions of the KNO₃ with values reported in the literature and the detailed analysis of the transition curves demonstrate that the transitiometric technique can be used to study the phase transitions in different complex systems and that the potassium nitrate can serve as a calibrating or reference substance in such studies.

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