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THE PHASE DIAGRAM OF KNO_3 to 40 kbars*

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Abstract—The phase diagram of KNO_3 was determined by differential thermal analysis to 40 kbars and 600°C. Three new polymorphs, KNO_3 V, VI, VII, were found. The melting curve passes through a broad maximum at 6·4 kbars, possibly through a second one at 11 kbars, and then rises steeply with increasing pressure. Above 15 kbars the phase diagram of KNO_3 is very similar to those of $RbNO_3$ and $CsNO_3$.

THE PHASE diagrams of six univalent nitrates (KNO_3, $RbNO_3$, $CsNO_3$, $TlNO_3$, NH_4NO_3 and $AgNO_3$) were determined by BRIDGMAN, first to 12 kbars and 200°C[1] and later to 50 kbars and 200°C.[2] This group of inorganic solids exhibits extensive polymorphism with some 25 known polymorphs. The crystal structure of some of these polymorphs is unknown and for others is incomplete. This makes the understanding of any systematic trends and relationships among these polymorphs difficult. Bridgman pointed out certain similarities in the phase diagrams of $RbNO_3$, $CsNO_3$ and $TlNO_3$. The phase boundaries between phases II and III in $RbNO_3$, between phases I and II in $CsNO_3$ and between phases I and II in $TlNO_3$† have very nearly the same slope, 9°C/kbar, in the P–T plane. Moreover, the 1 atm transition points are very close, viz. 164·4° for $RbNO_3$, 153·7° for $CsNO_3$ and 144·6° for $TlNO_3$.

This suggests similarity of the corresponding phases. Bridgman also argued that the III–IV phase boundary in KNO_3 belonged with the three discussed above. However, the slope in KNO_3 is markedly different, 40°C/kbar, and the crystal structures of the corresponding phases are known to be quite different.

Further relationships among the polymorphs of the univalent inorganic nitrates might be deduced from their melting curves.

The melting curve of KNO_3 was determined by BABB *et al.*[3] to 10 kbars and shows a broad maximum at 6·4 kbars. The melting curves of the five alkali nitrates to 10 kbars were recently determined by OWENS.[4] The melting curves of $LiNO_3$ and $NaNO_3$ show a similar behavior whereas the melting curve of $RbNO_3$ above 2 kbars very much resembles that of $CsNO_3$, both rise quite steeply with pressure. It would seem that the phase diagram of KNO_3 has no obvious similarities with the phase diagrams of the other univalent nitrates.

In the present experiments, pressures up to 40 kbars were generated in a piston-cylinder apparatus previously described.[5] Transitions were detected by means of differential thermal analysis (DTA).[6] Friction corrections were made by comparing the phase boundaries obtained on increasing pressure and on pressure release[6] and pressures are believed precise to $\pm 0{\cdot}5$ kbar. Chromel–alumel thermocouples were used and temperatures were read to a precision of ± 2°C. No corrections due to the pressure effect on the e.m.f. of the thermocouples were made as recent results[7] show the effect of pressure on alumel–chromel thermocouples to be negligible.

Reagent grade KNO_3, Baker's analyzed reagent with stated purity of 99·8 per cent was used. Samples were melted into aluminum capsules that were previously treated with concentrated nitric acid in order to form an adherent and protective oxide coating. The capsule design was described previously by PISTORIUS.[8] DTA signals were sharp and strong. Many of the experiments were

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† Phase notations are as in BRIDGMAN.[1]

carried through several compression–decompression cycles without any indication of sample or thermocouple contamination.

The phase diagram of KNO_3 is shown in Fig. 1. The coordinates of the various triple points and melting curve maxima are given in Table 1. Three new phases (KNO_3 V, VI, VII) were found. The melting curve of KNO_3I as obtained in the present experiments is in very good agreement with the extremely precise work of BABB *et al.*[3] to 9·5 kbars. Signals associated with the I–V phase boundary have been plotted but show substantial scatter.

The uncertainty in the coordinates of the I-V-L triple point is estimated to be of the order of 1–2 kbars. The melting curve of KNO_3V shows a probable maximum at 11 kbars. The melting curve of KNO_3VI rises steeply with increasing pressure in a similar manner to the melting curves of $RbNO_3$ and $CsNO_3$. The III–IV, VI–IV and VII–IV transformations display thermal hysteresis and supercooling behavior which seem to be an inherent property of the KNO_3 IV phase. The IV–III transformation rate is very slow below 200°C and no DTA signals were obtained. Above 200°C the transformation is sufficiently rapid to yield sharp DTA signals. No DTA signals could be obtained for the II–III transition below 70°C because of the slowness of the transition at lower temperatures. Transformation rates in the KNO_3 system were studied in more detail by DAVIS and ADAMS.[9,10] The heat of transition for the II–III transformation decreases with pressure.[1] The KNO_3 IV–KNO_3 VI phase boundary has a slope of 6°C/kbar as compared to 9°C/kbar in the diagrams of $RbNO_3$, $CsNO_3$ and $TlNO_3$.[1]

Thus, because the phase diagram of KNO_3 above 15 kbars strongly resembles that of $RbNO_3$, $CsNO_3$ and $TlNO_3$, it is suggested that KNO_3 VII encountered at 30 kbars is structurally similar to the phases found by BRIDGMAN[2] in $RbNO_3$ at 24 kbars and in $CsNO_3$ at 27 kbars.

The structural data for KNO_3 I, II, III and IV

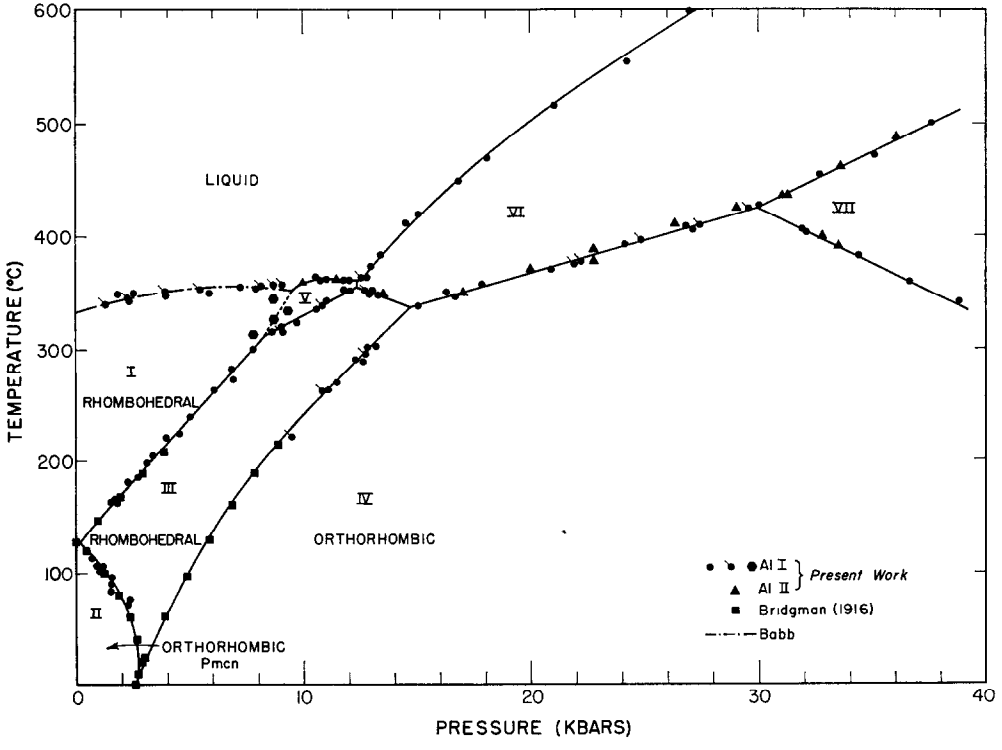

FIG. 1. The phase diagram of KNO_3 showing data of BRIDGMAN, BABB and our results from four runs in two different Al capsules.

Table 1. *Triple points and melting curve maxima in the* KNO_3 *phase diagram*

Phases	Pressure kbars	Temperature °C	Source
I–II–III	0·12	128·3	BRIDGMAN[1]
II–III–IV	3·0	21·3	BRIDGMAN[1]
I–III–V	8·0	306	Present work
I–V–L	9·6	352	Present work
III–V–VI	12·4	355	Present work
V–VI–L	12·4	361	Present work
III–IV–VI	14·6	338	Present work
IV–VI–VII	30·0	424	Present work
	Melting curve maxima		
KNO_3I	6·4	355	BABB[3]
KNO_3V	11·0	363	Present work

were recently reviewed by DAVIS and ADAMS.[10] No structural data are available on KNO_3 V, VI and VII nor for the high-pressure polymorphs in $RbNO_3$ and $CsNO_3$.

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