

elements comparable with those of RbNO_3 (orthorhombic, C -centered). They are $a = 16.07_8 \text{ \AA}$, $b = 9.94_1 \text{ \AA}$, $c = 7.67_8 \text{ \AA}$, $a : b : c := 1.617 : 1 : 0.687$ ($Z = 18$). JAMESON (1956) gives for this cell the constants $a = 16.12 \pm 0.04 \text{ \AA}$, $b = 10.12 \pm 0.04 \text{ \AA}$, $c = 7.75 \pm 0.01 \text{ \AA}$.

The standard deviation of the spacings for the small cell ($Z = 10$) is 0.00623, and that for the large cell ($Z = 18$), 0.01307, indicating a somewhat better fit of the indexing for the former. A check of the $\sin^2\theta$ values for $h00$, $0k0$, and $00l$ of JAMESON'S pattern against dense accumulations $\Delta \sin^2\theta$ on our bar graph (Hesse-Lipson procedure) showed a nearly complete lack of correspondence. Moreover, indexing of all lines of the pattern based on the large cell is not possible with $h + k = 2n$, a requirement for centering on C . In view of the above considerations it would seem preferable to adopt the smaller unit of structure.

From the indices listed in Table 1 it is possible to set up the following maximum restriction conditions:

$$\begin{array}{ll} h00 : h = 2n & hk0 : h + k = 2n \\ 0k0 : k = 2n & h0l : h + l = 2n \\ 00l : l = 2n & 0kl : k + l = 2n \end{array}$$

$$hkl : \text{no restriction.}$$

If these conditions are not fortuitous the space group is $P \frac{2_1}{n} \frac{2}{n} \frac{2_1}{n}$. With 10 molecules of KNO_3 per cell, however, space-group symmetry requires that triangular NO_3^- groups be placed on edges or corners of repeat units, which is not allowable. If one were to consider restrictions based on the best fit of data then h odd and $h + k$ odd must be allowed and the space groups should be either $P \frac{2}{m} \frac{2}{n} \frac{2}{m}$ or $Pmn2_1$. Again the former is rejected because of the triangular NO_3^- -group, but in $Pmn2_1$ several compact arrangements of 10 KNO_3 can be devised.

Although no one of four such arrangements based on $Pmn2_1$ gave agreement in intensity good enough to warrant its description here, certain features of one show promise for future study. If one were to place K^+ ions at 000 (two ions); $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ (four ions); and $\frac{1}{4} \frac{1}{4} \frac{3}{4}$ (four ions), then the calculated intensities of 002 , 202 , 400 , $230 + 222$, and 402 would be medium to strong and would compare roughly with the observed values. The 020 (observed weak) line would also be strong, but by placing several O atoms in equipoints in the glide-plane between the sets of 4 K^+ ions this line would be weakened. Further work will

be required before a complete description of the structure can be given.

The cell constants determined yield a Δv of transition of $0.060_4 \text{ cm}^3/\text{g}$ at 3 kbar which may be compared with $0.04474 \text{ cm}^3/\text{g}$ by BRIDGMAN (1916).

B. Transition rate

Our experimental arrangement is especially suitable for studying transition rates. This is accomplished by fixing the goniometer at the 2θ value corresponding to a high-pressure line, and applying the pressure to the sample as suddenly as possible with the chart running.

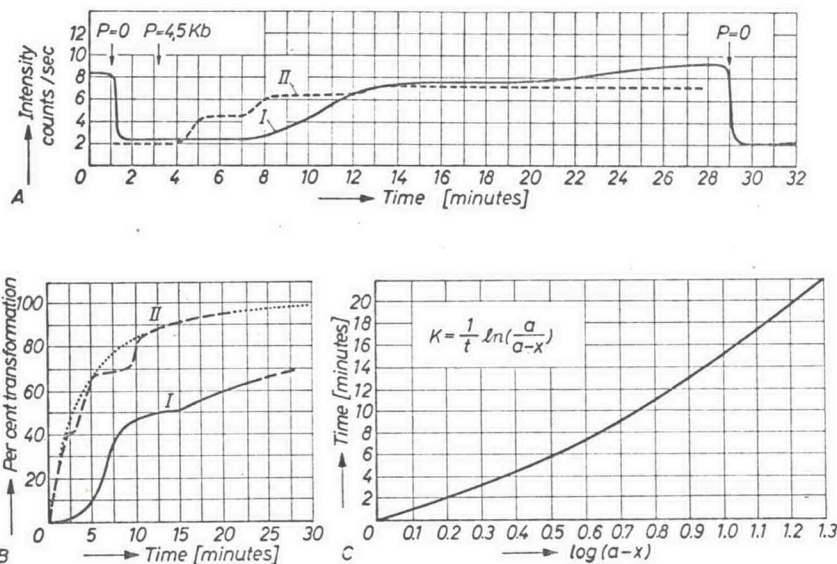


Fig. 4. A. Transformation rate of $\text{KNO}_3 \text{ II} \rightleftharpoons \text{KNO}_3 \text{ IV}$ as traced out by recording pen from growth of 230 peak. See text for explanation. Supported beryllium cylinder. Attenuation 2-1-4. Pellet $2.55 \times 0.4 \text{ mm}$.; B. Data of Fig. 4A plotted as per cent transformation vs time; C. Test of first-order kinetics for II-IV transition (see text). Plot is from data of Fig. 4B using dotted line

The final pattern is read in minutes horizontally and counts per second vertically. In this manner, as the high-pressure peak grows, the recording pen traces out directly the rate curve. Two such charts traced and reduced, are shown in Fig. 4A.

The rates have been investigated only in the supported beryllium pressure vessel since it is desirable to approach hydrostatic conditions in the sample as nearly as possible. In this instance a 2.55 mm sample was used. The attenuation used (scale factor = 2, multiplier = 1, time