

$t = 118^\circ\text{C}$ . As the temperature was increased slowly to  $130^\circ\text{C}$  the III-I transition took place. The temperature maximum of  $143^\circ\text{C}$  was attained after which the temperature was lowered slowly. At  $128\text{--}130^\circ\text{C}$  the reverse transition I-III took place and immediately (at about  $t = 120^\circ\text{C}$ ) the transition III-II began, but slowly. At this pressure the III-II transition went to completion in approximately 13 min.

Essentially the same transition sequence was observed at a pressure of 1500 bars. Here the initiation of the II-III transition took place at  $113^\circ\text{C}$ , the III-I transition at  $145^\circ\text{C}$ , the I-III transition again at  $145^\circ\text{C}$ , and the III-II transition somewhere near  $115^\circ\text{C}$ . This latter point was not accurately determined because the transition III-II proceeded so slowly that after  $\frac{1}{2}$  hr only a small amount of phase II had appeared. After 10 hr there was still about 10 per cent of phase III remaining. During the 10 hr period, however, the pressure had dropped to about 500 bars due to leaks in the pressure system; had the pressure remained constant during this time, less of the transformation might have taken place.

Other similar experiments performed support the conclusion that the metastability of phase III is prolonged at low temperatures when pressure is increased and that the duration of the persistence of phase III increases with lowering temperature and increasing pressure along the negative slope of the II-III phase boundary. Because of the effect of lower temperatures in the phase II field as pressure is increased this phenomenon is not wholly unexpected. The separation of the effects of pressure and temperature on the kinetics of this transition cannot be made with certainty. The rate IV-III (with the phase boundary  $dt/dP$  positive) was also sluggish at 3000 bars and  $100^\circ\text{C}$ , but since the rate here is between different phases a comparison cannot be made.

One transition across the II-III boundary was studied at constant temperature. At  $t = 93^\circ\text{C}$  the pressure was abruptly raised to 3000 bars. The transition II-III took place within  $1\frac{1}{2}$  min. Upon release of the pressure to zero (nominal) the reverse transition III-II went to completion in 7 min. It is interesting to note the lack, in this experiment, of the persistence of phase III that was seen under similar  $P$ - $t$  conditions but with pressure constant and temperature variable.

#### GRAIN ORIENTATION RESULTING FROM TRANSFORMATION

Preferred orientation of grains in the powder pellet was very striking during the rate study of  $\text{KNO}_3\text{-II} \rightleftharpoons \text{KNO}_3\text{-III}$ . With the forward rate, the pattern of phase III was quite consistent from experiment to experiment but after completing the reverse process the resulting aragonite-type phase II yielded an anomalous pattern. In two cases the 111 (relative intensity  $I/I_0 = 100$ , normally) and 021 ( $I/I_0 = 56$ , normally) peaks were completely missing. The 221 ( $I/I_0 = 41$ , normally) and 041 ( $I/I_0 = 20$  normally) peaks were very weak. On the other hand, the unresolved lines 040 and 220 showed an intensity of 90-100 whereas usually each line should show  $I/I_0$  less than 10. Line 211 was also unusually strong.

These results might indicate an orientation of the crystals with the 010 and 110 cleavages, or both, normal to the direction of applied load, thus indicating the lack of true hydrostatic stress conditions within the pressure vessel.

A similar orientation effect was noticed upon completion of the rate  $\text{KNO}_3\text{-I} \rightarrow \text{KNO}_3\text{-II}$ . In this case, however, the strong lines were either 130, 112, or 022, or some combination of these (all are unresolved with molybdenum radiation).

Such orientation phenomena indicate that the transition of a calcite-type structure (i.e., I and III) to the aragonite-type structure (II) is not of the "single-crystal" variety, but is one involving complete breakdown of crystal units and reconstruction of those of the new phase, a concept wholly in harmony with the accepted nature of the calcite-aragonite transition.

#### ORDER OF TRANSITION

All of the rate curves of the study are non-linear; that is, the curves show a marked tail-off near completion of the transition.

Using a general rate theory (with the variables defined to conform to solid-state transitions) modified by PESSEN,<sup>(7)</sup> it can be concluded that the rate of transformation at any instant, for most of these transitions, is equal to a constant times the quantity of reactant phase remaining raised to a power between 1 and 2 (i.e., the transition order lies between 1 and 2).

It is suspected that such tail-off is the result of