

$P = 1$ bar the temperature was very slowly raised from 124°C . The transition began at 127°C and was essentially complete in $2\frac{1}{2}$ min. No phase III was observed. Figure 2 shows the rate curve and the slight temperature shift during the transition. In one experiment, in which the piston was left out of the vessel,* the II-I transformation went to completion in about one minute. In another experiment, in which approximately 500 bars had been applied

phase I peak occurred here. Phase III grew to a maximum, leveled off, and then rapidly died out as phase II appeared.

Figure 4 shows rate curves during which phase III appeared both at the beginning and at the end of the experiment. At the start, about 125°C , phases I and III both grew simultaneously at the expense of phase II, and shortly thereafter phase III disappeared. Why phase I did not grow more when phase III disappeared is not

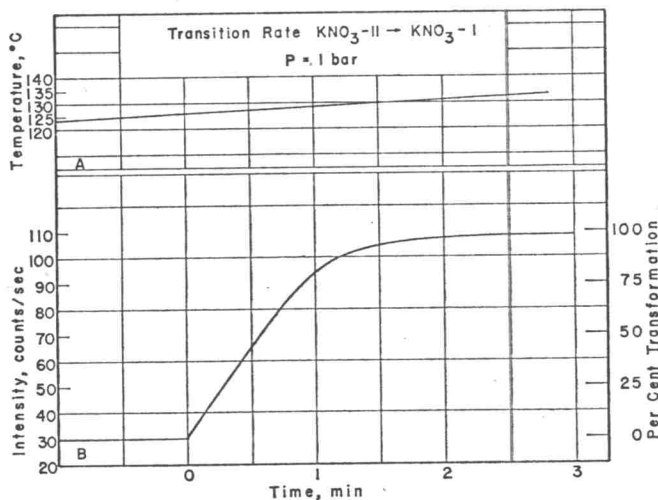


FIG. 2. Transition rate $\text{KNO}_3\text{-II} \rightarrow \text{KNO}_3\text{-I}$ at 1 bar; (a) variation of temperature during the rate, and (b) rate curve representing growth of the strong 014 peak with time. $\text{MoK}\alpha$ radiation.

to the sample, the transition commenced at $t = 115^\circ\text{C}$ and took about $3\frac{1}{2}$ min to run to completion.

It was not possible in any of the runs to record the I-II rate without the appearance of phase III. An example of the rate curves recorded when phase III appeared is found in Fig. 3. At a temperature slightly less than 125°C the peak representing phase I dropped off suddenly, leveled off, and then grew some again. At 120°C it dropped off again, this time permanently, while another peak, representing phase III began to grow. Actually the growth of phase III might have begun earlier, as indicated by the dashed line of Fig. 3, since a drop in intensity of the

understood. This is strange when it is seen that phase III grew an additional amount at the time when phase I was diminished at the end of the experiment.

The appearance of phase III, as shown in Figs. 3 and 4, illustrates the well-known phenomenon that in a chemical or polymorphic transition the phase that first appears, as the P - t environment is changed, may not be the one which is most stable in that environment. The appearance of phase III at the end of the experiments mentioned took place at temperatures below that of the established phase boundary; at these temperatures phase III considered to be metastable.

$\text{KNO}_3\text{-II} \rightleftharpoons \text{KNO}_3\text{-III}$

At a pressure of 500 bars the transition II-III took place in less than 2 min and began at

* To avoid applying even a few bars pressure on the sample.