The rates were measured in a beryllium cylinder mounted on a Norelco X-ray goniometer, a detailed description of which has already been presented (DAVIS and ADAMS[5]). The vessel was modified for heating to 300°C by winding the cylinder with No. 22 (B. & S. gauge) Nichrome-V wire. The heating coil was separated from the vessel wall by a thin layer of Alundum cement; another layer of this cement was applied over the furnace to act as thermal insulation against heat loss to the atomsphere. The temperature was measured by means of a Chromel–alumel thermocouple placed in a hole directly beneath the lower piston. Temperatures were determined from readings on a Leeds–Northrup portable potentiometer with which one scale division corresponded to 0·02 mV.

Previously (DAVIS and ADAMS[5]) the KNO_3 was mixed with starch in an attempt to obtain better pressure distribution throughout the sample. However, since this might also affect the rate, only pure KNO_3 was used in the present study. The sample material was pressed into pellets $4{\cdot}6 \times 1$ mm and placed at the bottom of the cylinder bore under a similar pellet of beryllium metal.

The transition rates were measured by fixing the goniometer at the 2θ value expected for a high-pressure or high-temperature line while the chart recorder is operating, then applying the pressure or temperature to start the transition. There was some difficulty experienced in boosting the temperature over the phase boundary and then being able to stop it from rising further. Since some creep of the temperatu was unavoidable, an accurate record of the variation of the temperature on the sample during the progress of a transition has been included with the rate curves.

RESULTS

KNO_3-II $\rightleftharpoons$ KNO_3-IV

Forward and reverse transitions for this rate have already been described (DAVIS and ADAMS[5]). The conclusions concerning these rates are summarized as follows:

(1) The rate curve is assymetrical. In two experiments the forward change required 14–30 min for completion and the reverse change only seconds.

(2) The forward change appears to take place in steps, whereas the reverse apparently does not (possibly because of the rapidity of the rate the steps were not seen).

(3) Except for the step intervals one of the rate curves approached first-order kinetics, but it is apparent that factors, such as nucleation, strain energy, and grain growth, may affect the order of the rate.

KNO_3-III $\rightleftharpoons$ KNO_3-IV

Phase III is the high-temperature phase (see Fig. 1) and therefore the forward rate, as written in the above heading, occurs with lowering temperature. As the temperature is raised the IV–III change takes place quite slowly. At a pressure of 3000 bars and a temperature rising from 50 to 85°C, only about 20 per cent conversion took place in 15 min. Upon raising the temperature to 105°C the reaction went to completion in 10 min. It is assumed that much of the change took place in the several minutes required to raise the temperature to the 105°C value.

For the reverse (III–IV) rate no transformation had taken place after 17 min at 3000 bars and 29°C. At this pressure the temperature was not low enough to permit the formation of phase IV again. When the pressure was suddenly dropped to zero, phase II appeared leaving about 10 or 20 per cent of phase III remaining.

KNO_3-I $\rightleftharpoons$ KNO_3-II

Examination of the phase diagram, Fig. 1, shows that the stability fields of phases I, II, and III meet at a triple-point at 113 bars and 128·3°C.* The only place possible to measure the rate of the KNO_3-I $\rightleftharpoons$ KNO_3-II transition is near this point, and it has been very difficult to obtain records not showing the appearance of phase III. It is fortunate that the strong peak of phase III lies less than one degree (2θ) from the strong peak of phase I; otherwise accurate recording of the appearance of these two phases simultaneously and in closely following intervals would have been difficult. The up-temperature transformation often went to completion without the appearance of phase III. For example, at

* As measured by BRIDGMAN.[6]