constant = 4) allowed easily constructed curves (irregularities due to background scatter must be averaged out) and yet did not introduce a serious lag from the time constant.

An interesting feature of curve I is the levelling off of intensity part way along so that two stages of peak-height growth result. Furthermore, the reverse rate appears faster than the forward rate, thus producing an asymmetrical curve. A second experiment confirmed this phenomena even though the length of time to reach a final level was somewhat less. Such differences might be explained by sample preparation, or in variations in size of the beryllium disk between sample and piston, thereby creating differences in friction and of actual pressure on one sample as compared to the other. Also noted in the second experiment are three stages of growth instead of two.

When the curve has tapered off so that further growth is impractical to follow continuously, one can scan part of the pattern to ascertain the completion of the conversion. With curve I at the end of 20 minutes, 60 per cent ofmaterial was NK O_3 the IV; with curve II after 10 minutes, 80 per cent of the material had converted to the high-pressure form.

One ratê carried out in an identical manner with NH_4I showed only slight asymmetry. Several other rate experiments with NH_4I, RbI, and cerium, however, showed neither asymmetry nor growth stages. It has been suggested that the asymmetrical shape of the KNO_3 II $\rightleftharpoons$ KNO_3 IV curve is the result of friction release and adjustment of the pressure within the vessel. One would then have to explain why such adjustment does not take place with release of pressure, and why such phenomena have not been observed in rate studies with this apparatus on other materials. No reasonable explanation for the growth stages or asymmetry of the curve can be suggested that is compatible with the irreversible nature of the step-wise transformation. It has been observed with NH_4I that the slight asymmetry of the curve produced under conditions very near the phase boundary is eliminated and replaced by completely symmetrical curves when the transformation pressure is exceeded by 50, 100, or 200 per cent. Our work with rates on NH_4I and a few other materials has shown with certainty that the rate is dependent on the amount of excess pressure above the equilibrium value that is applied.

The pressure of Fig. 4 is 4½ kbar, or 50 per cent above the transformation pressure. Perhaps with internal pressure of 6 or 8 kbar the asymmetry of the curve would disappear. A study of this rate at lower pressures is more time consuming but further work in this direction is certainly desirable.

Figure 4*B* is a plot of the data from curves I and II, of Fig. 4*A*, in terms of per cent transformation vs time. It was desirable to see if the transition obeyed first-order kinetics, that is, if the amount being transformed at any given moment in time was proportional to the amount of unconverted material remaining in the vessel. The law is stated as

$$K = \frac{1}{C}\frac{dC}{dt},$$

where K is a constant, and the amount, C, at any instant can be replaced by $(a-x)$, a being the initial amount, and x the amount transformed at time t. Rearrangement and integration between the time limits 0 and t yields the "kinetic equation"

$$K = \frac{1}{t}\ln\frac{a}{(a-x)}.$$

A plot of log $(a-x)$ against t should be a straight line if the data conform to first-order kinetics. As seen in Fig. 4*C*, the data for curve II plotted in 1-minute intervals yield a line with very slight curvature which is concave upwards. It should be noted that the growth stages, which in themselves show departure from first-order kinetics, were ignored in the above test. The data represent the general growth curve depicted by the dotted line fitted to curve II. The time lag before the growth and the subsequent shape of the curve in experiment I show obvious departure from first-order kinetics.

From the data obtained thus far it does not appear that the rate of transformation of KNO_3 II $\rightleftharpoons$ KNO_3 IV is in accord with first-order kinetics even though an approach to such is indicated by the slight curvature of curve II. Since the differences between curve I and curve II is likely to be tied in with experimental factors it will be necessary to obtain curves under identical, more precisely controlled pressure conditions before reliable quantitative rate data may be presented.

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