Experiments were conducted in the hydrothermal units (with the charge sealed in platinum tubing) and in opposed anvil apparatus but the *p-T* range used was not as broad as for the main series. In the opposed anvil runs nickel rings 0.02-in. thick were used because it was found that the 0.01-in. rings had a tendency to blow out or become very thin on decomposition of the gel.

The main observations are (1) the gel is stable over an appreciable *p-T* range, (2) anatase crystallizes at lower *p-T* conditions than rutile, (3) the II phase crystallizes with some difficulty from the gel at higher pressures than anatase and rutile, (4) seeding is not effective and, (5) rutile crystallizes at lower temperatures than when other starting materials are used.

Discussion of Results

The first preparation of the II phase from anatase was not well-crystallized. Comparison of diffractometer traces with those of the II obtained from brookite emphasized this observation. The concentrations were determined by powder X-ray diffractometry (Klug and Alexander, 1948). TiO_2 not contributing to the X-ray diffraction maxima of the crystalline phases is estimated by difference and is designated SRO. A review of the structures of anatase, brookite, rutile and II showed that their oxygen layering schemes and distribution of titanium ions suggest a definite influence of structure on the relative difficulty of transitions. Results of this study are to be presented later. Pertinent here is that the complexity of atomic rearrangement for An-II is very much greater than for Br-II so that at temperatures which are low for this refractory oxide incomplete recrystallization from anatase could result, leaving a substantial amount of commingled residue of SRO. This is clearly demonstrated by the lower density of the II made from anatase and by the trend of concentration with time of reaction of anatase and II. The density, measured by the sink-float method, of II from anatase is 4.11 compared to 4.32 of II prepared from brookite. X-ray density is 4.330 and 4.329 respectively (Simons and Dachille, 1967). In Figure 3 are plotted the decrease in concentration of anatase with time of reaction at 42 kbars and 400°C, together with the increase of the II phase. The anatase was completely reacted after one day and the II phase increased slowly over a period of five days to about 50 percent of the sample. Measurements made for the Br-II reaction indicated a complete conversion to II in two days or less.

In view of the more precise results obtained with well-crystallized II in establishing the apparent boundary between the II and rutile fields (Figs. 1 and 2), it is believed that the SRO state which anatase, and, to

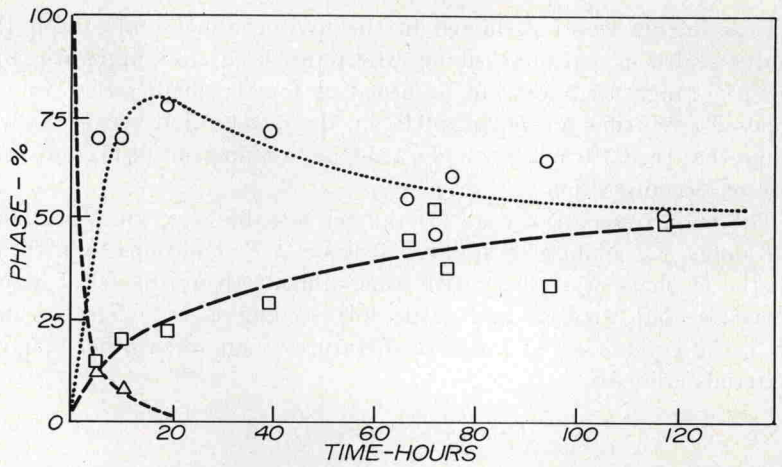

FIG. 3. The trend with time of the disappearance of anatase and of the slow crystallization of II. By difference, the amount of a short range order transition phase of TiO_2 is estimated. (△ = anatase; □ = II; ○ = SRO).

a lesser extent, brookite go through may be sensitive to local differences within the sample. The reactions then may follow metastable paths.

The essentially coincident triple points of Figures 1 and 2 favor the view that three TiO_2 phases coexist at such point either in a *stable or metastable* relation. Moreover, the extrapolations to atmospheric pressure of the An-Ru and Br-Ru boundaries determined in the opposed anvil experiments, intersecting the temperature axis at 605 and 720°C respectively, are in good agreement with the temperatures below which Rao *et al.* (1961) and Rao (1961) found effectively zero rates of conversion to rutile. It may be interpreted that below these temperatures rutile is not in its stability field or that reaction rates to rutile are immeasurably slow. However, the latter view requires such an abrupt decrease of the rate constants with a small decrease in temperature that there is question as to the validity of the kinetics argument. If the former view is taken, then the agreement of the An-Ru reaction boundary with that determined by Tu and Osborn (Osborn, 1953) gives support to the extrapolation and provides another example of the similarity of pressure effects of hydrothermal and opposed anvil systems (Fig. 4).

Our hydrothermal studies and those made with the gel starting material pose problems with respect to the significance of Figures 1, 2, and 4. If the results listed in Table 1 are referred to these diagrams it will be seen that rutile forms from oxides below 450–485°C at 2.1 kbars, well inside the respective anatase or brookite fields. Does this mean