

long runs, no transitions of rutile to other phases were observed. Similarly, no conversion to brookite was observed when a prepared II was the starting material. Therefore, the boundaries separating the phase fields on the diagram do not represent equilibrium positions but probably approximate them on the higher temperature side. Furthermore, metastable relations may be involved with anatase and brookite, and perhaps even the II phase. What the boundaries definitely show are the conditions at which enough of the product of a "forward" reaction was observed after 1-5 day runs in a quenched charge by powder X-ray diffraction analysis.

The definition of the boundary between the II and rutile fields was poor in runs starting with anatase and brookite. There was a region about 75°C in width in which two product phases, II and rutile, appeared together with or without residual starting material. Of course, a residue of starting material is often observed in slow reactions. The presence of two product phases over a broad p-T range might be attributed to the metastable nucleation and growth of one or the other phase, and/or to transitory variations of pressure sufficient to sustain stable growth for finite intervals. Once formed, the slowness of reactions could allow a phase to remain in identifiable amounts in a metastable field.

It was found that the boundary could be determined more accurately by removing one of the reaction steps. Brookite was converted completely to a well-crystallized II phase in the region of 40 kbars and 400-450°C in 48 hours or less. This product was recharged and used to determine points near the apparent II-rutile reaction boundary. However, a more convenient but equally effective procedure was to form the II phase from brookite with 2-3 days reaction in the "active" region and then to shift the conditions to the final temperature and pressure for an additional three or more days. Using this method the apparent reaction boundary from II to rutile shown in Figures 1 and 2 was determined. A graphical fit of this line to yield a triple point in both the "anatase" and "brookite" diagrams is possible. This may be fortuitous, but that it could have significance with regard to the existence of actual triple points in stable or metastable phase diagrams should not be dismissed. The positions of the apparent triple points are at 9.5 kbars, 484°C for the anatase, and 7.8 kbars, 475°C for the brookite series.

Hydrothermal experiments. Charges of approximately 10 mgms were sealed with or without water into 1.5 mm O.D. platinum tubing by welding with a carbon electrode. Table 1 lists a few runs made at 2.1 kbars.

The results showed that the annealed and "unannealed" anatase be-

TABLE 1. RUNS IN HYDROTHERMAL APPARATUS

| St. Mat. | Temp. $\pm 5^\circ\text{C}$ | Time days | Results |
|-----------------------------------|-----------------------------|-----------|---------------|
| Annealed An +H ₂ O | 400 | 16.6 | An |
| Annealed An, no H ₂ O | 485 | 7.9 | An |
| Annealed An +H ₂ O | 485 | 7.9 | Ru |
| Annealed An, no H ₂ O | 640 | 7.9 | An |
| Annealed An +H ₂ O | 640 | 7.9 | Ru |
| An +II _B | 400 | 16.6 | no change |
| An +II _B | 462 | 6 | Ru |
| II _A +H ₂ O | 400 | 11 | An |
| II _B +H ₂ O | 400 | 11 | no change |
| II _A +H ₂ O | 400 | 11.9 | no change |
| II _A +H ₂ O | 450 | 9.8 | 50% Ru+50% II |
| II _B +H ₂ O | 450 | 9.8 | 50% Ru+50% II |
| II _A +H ₂ O | 515 | 9.8 | Ru |
| II _B +H ₂ O | 515 | 9.8 | Ru |
| Ru+H ₂ O | 400 | 11.9 | Ru |
| Gel+brookite seeds ^a | 255 | 6.0 | An |
| Gel+TiO ₂ II seeds | 250 | 6.0 | An |
| Gel+TiO ₂ II seeds | 373 | 6.0 | An+Ru |
| Gel | 373 | 6.0 | An+Ru |
| Gel | 440 | 9.0 | Ru |

^a Seeds amounted to less than 6% by weight.

II_A=II prepared from anatase.

II_B=II prepared from brookite.

haved in the same manner and that the presence of excess water apparently lowered the temperature of conversion to rutile to a value less than 485°C. However, even doubling the time at 400°C failed to form any rutile under the same pressure. Under "dry" conditions the 1/1 anatase-brookite mixture was inert at 400°C but converted to rutile at 462°C and 2.1 kbars.

The II prepared from anatase and brookite in opposed anvils appeared to be quite resistant to alteration under water pressure at 450°C and below, although one of four runs at 400°C was converted to anatase.

Experiments with the gel starting material. The gel preparation is based on that of Czanderna *et al.* (1957), but using 30 percent hydrogen peroxide and concentrating the gel at 110°C. Spectrochemical analysis showed only trace concentrations of Si, Mg, Fe, Mn and Ca. The solids content of the gel was 52 percent. The high residual concentration of ammonia in the gel was not determined quantitatively. It was amorphous with respect to Debye-Scherrer X-ray diffraction.