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PRESSURE-TEMPERATURE STUDIES OF ANATASE, BROOKITE, RUTILE AND TiO_2(II): A REPLY

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Phase relationships among the TiO_2 polymorphs have been the subject of experimental work and speculation for a long time. It is probably agreed upon by all, and certainly in this laboratory, that rutile is the only stable phase at or near one atmosphere. All approaches based on direct reversible phase equilibrium methods have so far failed to give definitive solutions to equilibrium among the various phases. Our recent study was concerned with kinetics (and mechanisms) and their possible relation to "equilibrium." (See also Simons, 1967.)

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In the report in which the synthesis of TiO-II was described for the first time (Dachille and Roy, 1962) as well as in a later report (Simons and Dachille, 1968) it was clearly stated that there was insufficient evidence for any statement on equilibrium. In the present paper commented on by Jamieson and Olinger this is repeated at least three times and the point is emphasized by the explicit use of the term "reaction boundaries" in every relevant figure. There is no doubt whatsoever of the interesting p-T dependence of certain reaction rates in the interconversion of the various TiO_2 phases. These are what are summarized in the "reaction boundaries" of the figures. Unfortunately, in discussing the results incorrect statements regarding the possible equilibrium relations among TiO_2 polymorphs crept in, in one or two places. Jamieson and Olinger have properly pointed out and provided a valuable comment on a possible TiO_2 *stable* equilibrium diagram. Indeed it will be seen that the latter is similar to our previous diagrams for isostructural phases: PbO_2 and MnF_2 undergoing analogous transitions (White, Dachille and Roy, 1961; Azzaria and Dachille, 1961).

Kinetic anomalies such as those observed by us (and not specifically treated by Jamieson and Olinger), their significance and possible relation to stable or metastable equilibria remain a subject for further study.

It should be mentioned that the Magnet Cover brookite used by us was processed mechanically to reduce the impurity level to 1% (Simons and Dachille, 1967; Simons, 1967).

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