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PRESSURE-TEMPERATURE STUDIES OF ANATASE,
BROOKITE RUTILE, AND $\text{TiO}_2(\text{II})$: A DISCUSSIONJOHN C. JAMIESON AND BART OLINGER, *Department of the
Geophysical Sciences, University of Chicago,
Chicago, Illinois 60637.*

ABSTRACT

Recently published thermochemical data show that anatase is everywhere metastable with respect to rutile and the alpha-lead dioxide form of titanium dioxide in the pressure-temperature region studied by Dachille *et al.* (1968). The same probably could be stated for brookite. This indicates that the reaction boundaries of Dachille *et al.* (1968) are not the approximations to equilibrium phase boundaries that they reported.

Recently Dachille *et al.* (1968) have reported studies on the pressures and temperatures of conversion of anatase or brookite to rutile and to $\alpha\text{-PbO}_2$ form of TiO_2 (called $\text{TiO}_2(\text{II})$). They also studied the conversion of the latter to rutile. In all cases only one-directional transitions were achieved. While the authors do state clearly that this lack of reversal means that metastable transitions may be occurring, we feel that this point has not been sufficiently emphasized or explored. In particular, we disagree with their statements that "phase boundaries" reported by them approximate equilibria on the high temperature side. Indeed, the reaction boundaries reported by Dachille *et al.* (1968) are almost certain to bear no approximation to equilibrium phase boundaries.

The true equilibrium relations of anatase and rutile may be roughly estimated using the recent determination of ΔG° , the change in Gibbs Free Energy, for this reaction reported by Navrotsky and Kleppa (1967) and molar volumes, V , quoted by Robie *et al.* (1966). The former authors have already stated that anatase is metastable with respect to rutile under all conditions of pressure and temperature. Using $\Delta G^\circ \simeq P_0 \Delta V$, where ΔG° (anatase to rutile) = -1.27 kcal/mole at 298°K and -1.04 kcal/mole at 968°K , as reported by Navrotsky and Kleppa (1967), $P_0 = -32$ kbar and -26 kbar respectively. In other words, hypothetical negative pressures would be needed to stabilize anatase. Therefore, the reaction boundary for anatase-rutile reported by Dachille *et al.* (1968) is probably 20 kbar or more above equilibrium. Similar calculations may be made using the Enthalpy measurements of $\text{TiO}_2(\text{II})$ by Navrotsky *et al.* (1967). At 298°K , ΔH° for anatase-rutile (Navrotsky and Kleppa (1967)) is -1.24 kcal/mole while at 294°K , ΔH° for $\text{TiO}_2(\text{II})$ -rutile (Navrotsky *et al.* (1967)) is -0.76 kcal/mole. This implies that under ambient conditions rutile is the stable modification and in addition, $\text{TiO}_2(\text{II})$ is itself

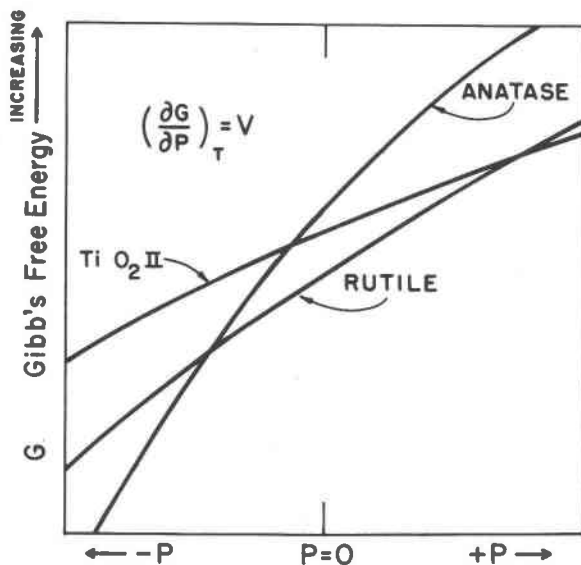


FIG. 1. A schematic plot of Gibb's Free Energy, G , of anatase, rutile, and TiO_2II to illustrate only how the relative stabilities of these phases vary with positive and hypothetical negative pressures.

stable with respect to anatase. No possible entropy contributions can alter these conclusions. Figure 1 illustrates hypothetically the free energies of the three phases as a function of pressure relative to rutile. Note that the slopes of these curves are determined by the thermodynamic relationship $(\partial G/\partial P)_T = V$. This explains the lack of reversed reactions obtained by Dachille *et al.* (1968) because in their anatase "field" anatase is everywhere the least stable form with respect to TiO_2II and rutile. Also, it explains why rutile alone was never observed to transform to any other phase. As to the TiO_2II —rutile equilibrium we have discussed it elsewhere (Jamieson and Olinger (1968)). That paper was not available to Dachille *et al.* (1968) due to the time of manuscript submission. There we concluded that no reliable estimate could be made of the true equilibrium of these two forms. However, a rigorous lower bound of 60 kbar was found for the pressure necessary to stabilize TiO_2II with respect to rutile at room temperature. Our conclusion from this and the preceding analysis of anatase is that the entire study of Dachille *et al.* (1968) was performed in the rutile stable field of (P, T) and that the reaction boundaries reported are no indication of equilibrium behavior.

In the case of brookite, Rao *et al.* (1961) found an approximate heat of transformation to rutile to be -100 ± 75 cal/mole at $715^\circ \pm 10^\circ\text{C}$. In

the absence of specific heat data, it is not possible to relate this to ΔH° at 298°K for comparison with anatase, rutile and TiO_2II . Using an identical technique Rao (1961) reported -100 ± 50 cal/mole for the heat of transformation of anatase to rutile. Hence, the equilibrium behavior of brookite with respect to rutile and TiO_2II should be qualitatively like that of anatase as the heats of transformation to rutile are the same within the error of Rao's techniques. Molar volume considerations dictate qualitatively that pressure should increase the stability of brookite with respect to anatase, but decrease its stability with respect to TiO_2II and rutile. It should be noted that natural samples of brookite from Magnet Cove, Arkansas, were used by Dachille *et al.* (1968) for the brookite to rutile and brookite to TiO_2II reactions. In addition, they note that TiO_2II was prepared from brookite in order to determine "more accurately" the TiO_2II -rutile phase boundary. Rao *et al.*, (1961) gave an analysis presumably of samples from Magnet Cove which showed an impurity content no less than 4%, and stated that no purer brookite was available. Shannon and Pask (1965) have shown that the temperature of conversion of anatase to rutile to a given concentration in a given time may vary 200C° depending on the atmosphere surrounding the sample or on its impurity content. Under these conditions it is difficult to interpret the brookite conversion data using any standard kinetic theory.

Rao *et al.* (1961) and Rao (1961) found that below 610°C and 715°C anatase and brookite, respectively, converted to rutile at an extremely slow rate—the "infinite-time temperatures." Dachille *et al.* (1968) argue that if rutile is not unstable below these temperatures, then the rate constants must decrease abruptly with small decreases in temperatures. They then state that if the rate constants decrease abruptly, then the validity of the kinetic argument should be questioned. Rao *et al.* (1961) and Rao (1961), though, state that both transformations obey regular transformation rate laws and fit the Arrhenius equation. The rate constants do not decrease "abruptly" or abnormally below the temperatures above mentioned, and therefore no question of the validity of the kinetics argument should be raised. The "infinite-time temperatures" mentioned in Rao's papers were determined from linear extrapolations tangent to conversion-fraction-versus-temperature exponential curves and were in no way meant to be interpreted as real, or, in this case as a means of relating to phase equilibrium temperatures.

The reaction diagram of Dachille *et al.* (1968) for the conversion of anatase may be understood when it is realized that here is a case of competing processes. The metastable (everywhere in the range of their study) anatase has differing activation energies, Q for transitions to rutile and TiO_2II ; the activation energy for the reaction of anatase to TiO_2II is less

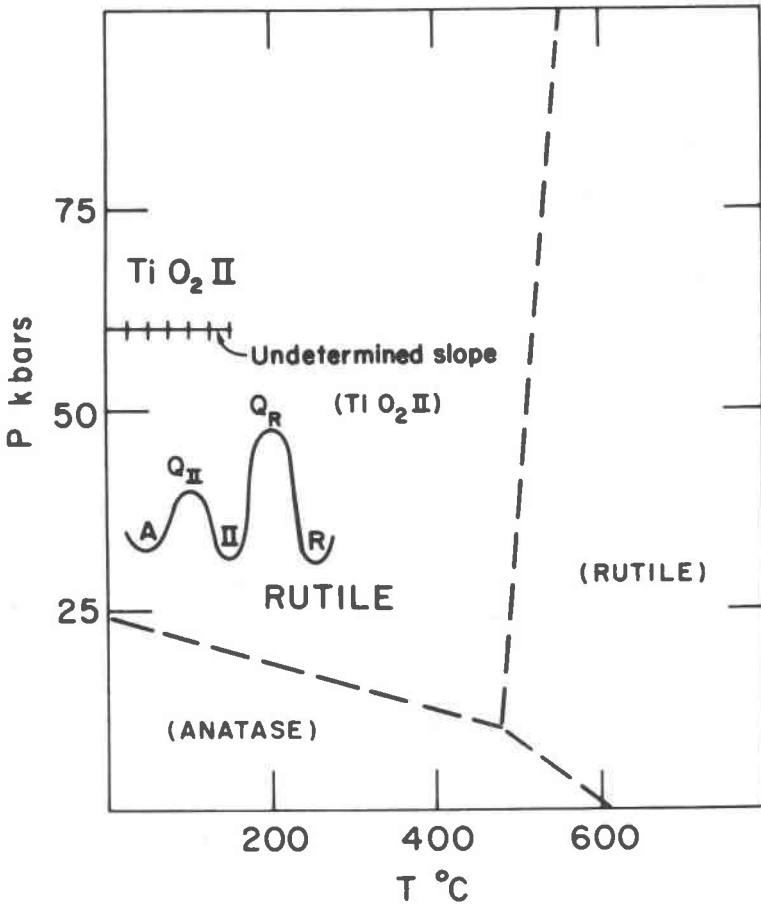


FIG. 2. The cross-hatched line represents the lowest possible pressure rutile and TiO_2II could be in equilibrium at 298°K . No upper limit could be determined (Jamieson and Olinger (1968)). The superimposed dashed lines are the metastable reaction boundaries determined by Dacheille *et al.* (1968)-their "reaction field" labels are in parentheses. In the figure is also shown schematic activation energy, Q , relationships for anatase (A)- TiO_2II (II)-rutile (R) conversion. Anatase is everywhere metastable with respect to TiO_2II and rutile.

than that to rutile. At low temperatures only anatase conversion to TiO_2II is observed. In the neighborhood of 500°C , the activation energy to rutile is overcome and both TiO_2II and rutile are observed, precisely as reported by Dacheille *et al.* (1968) as a region 75°C in width where the two products were formed. At still higher temperatures, of course, conversion to rutile will be predominate. This is summarized by Figure 2.

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PRESSURE-TEMPERATURE STUDIES OF ANATASE, BROOKITE,
RUTILE AND $\text{TiO}_2(\text{II})$: A REPLY

FRANK DACHILLE, P. Y. SIMONS¹, AND RUSTUM ROY, *Materials Research Laboratory and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania 16802.*

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.)

¹ Present address: E. I. du Pont de Nemours and Company, Parlin, N. J.