morphs.) Applying the Clapeyron equation with the usual assumptions of negligible differences of compressibilities (and thermal expansion), a first estimate of the enthalpy of the transition is calculated as 5.6 ± 0.3 kcal. per mole at room temperature. This value is of the same numerical range as those for the graphite-diamond (Rossini and Jessup, 1938) or the olivine-spinel (Dachille and Roy, 1960) reconstructive transitions.

havior of the two polymorphs. A geological connotation is that the very rare occurrence of huttonite might be related to its instability in the more accessible portions of the earth's crust where pressures and temperatures would be those of the thorite stability field.

Nb_2O_5

It was found that the shearing modification was useful to bring about the first and complete reversal of the Nb_2O_5-I (high-tem-
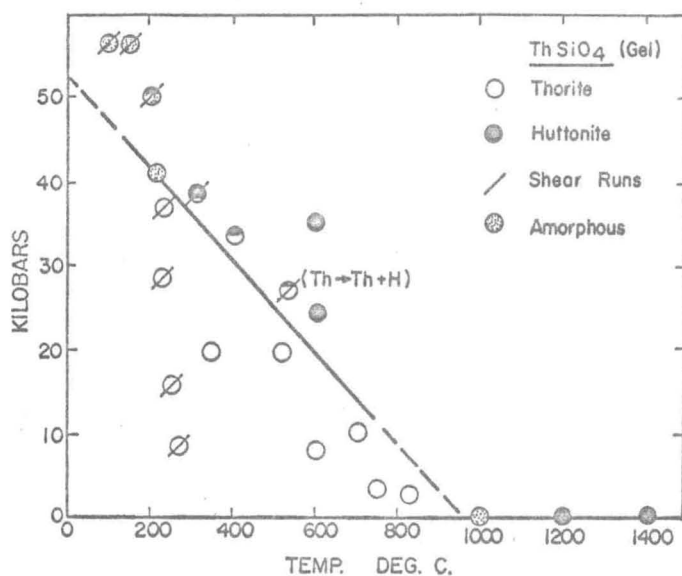

Fig. 1.—P-T diagram based on static and shear runs using $ThSiO_4$ "gel" starting material

It still has not proven possible to convert the huttonite to thorite by hydrothermal or shearing treatment in the thorite stability field, and this fact might justify withholding acceptance of figure 1 as the true equilibrium diagram. However, in a number of mortar runs in air of 3–20 hours' duration the noticeable breakdown of huttonite to an amorphous material was observed, whereas thorite was reasonably more persistent. Mechanical mortars have been found to generate pressures of the order of 10–20 kilobars (Dachille and Roy, 1960) in addition to the very considerable shearing stresses so that the conditions of these runs at room temperature fit very definitely in the thorite-phase field and might explain the comparative be-

perature) form to the III (low) form, at a temperature of only 350° C. at 7 kilobars pressure. This reversal also could be achieved, but to much lesser extent, under static conditions at considerably higher pressures and temperatures, but it never could be realized under the most intense hydrothermal conditions (Shafer and Roy, 1958). This further establishes the existence of Nb_2O_5 III as the stable low-temperature phase contrary to the suggestion of Holtzberg, Reisman, Berry, and Berkenblit (1941).

PbO_2-I→II QUANTITATIVE RESULTS

A more than qualitative picture of the influence of shear on the rate of reaction may

be obtained from a study of figures 2 and 3 summarizing the results of a large number of runs on the conversion of PbO_2 I→II. In these runs the starting material was the I (rutile) form of PbO_2, without the addition of any form of "mineralizer." Its conversion with time to the II (orthorhombic) form at
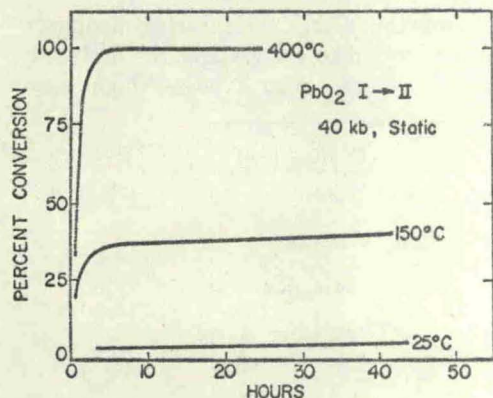

FIG. 2.—Isotherms at 40 kilobars for PbO_2 I→II transition showing the variation of conversion with time of run under static conditions.

different conditions of pressure and temperature was estimated by the use of integrated intensity ratios of selected X-ray diffraction lines of the two phases and an appropriate calibration curve obtained with the use of mixtures of the two phases. One set of runs was made at 40 kilobars under static conditions at three different temperatures—25°, 150°, and 400° C. Another set at the same temperatures and pressure but with the addition of displacive shearing shows very clearly the increase in conversion which results. (An intensification of shearing stresses under the application of higher pressures was shown by the increased conversion of a set of runs at 25° C., 90 kilobars. This might be expected as a consequence of the applied stresses having to overcome the gain in shear strength of material under pressure previously demonstrated by Bridgman [1935].)

From the data of figures 2 and 3, an approximate value of the activation energy of the reaction PbO_2 I→II both for the static and the shearing conditions may be calcu-

lated. This is done by assuming that the first-order reaction "constant" for each temperature (in each series) is directly proportional to the conversion to PbO_2 II in the same interval and, therefore, according to the Arrhenius relation, conversion is thus proportional to $e^{-A/KT}$. By calculating or by graphical means the activation energy, A, is found to be about 3.5 kcal/mole for the static runs and about 1.4 kcal for the displacive-shearing runs.[2] The reaction rates for the shearing runs therefore would be of the order of four to thirty times greater than for the equivalent static runs in the temperature range of 30°–500° C.

From the studies described above and in the references, it is seen that the presence or absence of shearing stresses is an important variable in determining the actual as-
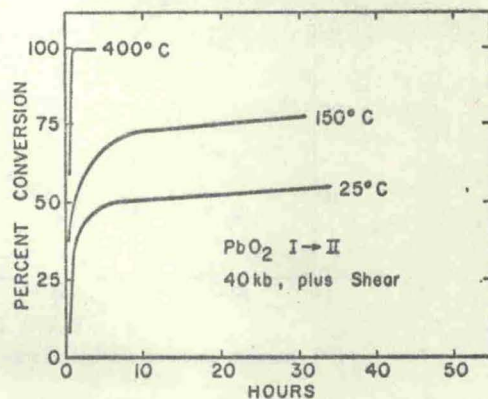

FIG. 3.—Isotherms as in fig. 2 but for shear conditions.

semblages in rocks or in experimental samples which may or may not have been brought to equilibrium.

[2] These values essentially give the magnitude and relative comparison of the activation energies. Greater precision cannot be attached to them because of the inherent difficulties of kinetic studies in solid-state reactions and the limitations of X-ray methods of quantitative analysis of phases.