quenching as well as to the pre-pelleting procedure. (The transition for MnF_2 is much faster than the analogous one for PbO_2.)

PbO. The rather peculiar phase relations in this system, reported elsewhere[5], are due to the negative slope for the transition which also has the remarkably small enthalpy of transition of less than 0.25 cal/g for a reconstructive phase change. The shearing runs will convert litharge to massicot at room temperature only above the pressure required by the curve but not below it. Similarly, massicot will convert to litharge at room temperature at pressures below the curve by the action of displacive shear. Without this action the massicot will not revert to the stable form, as shown by the black-without-diagonal circle in the figure. A number of shearing runs in the region of 6000 bars at room temperature, using either litharge or massicot, showed that rapid changes to the appropriate form occurred. These runs are represented by the barred circle which falls on the extension of the p–t equilibrium line.

CaCO$_3$. The calcite–aragonite transition of this compound has been studied by others[7–9] and from their work it is reasonable to place the equilibrium pressure at room temperature in the region of 3000 bars. Jamieson used heat of solution data at temperatures below 100° C. MacDonald used the uniaxial high pressure apparatus and Clark used compressed nitrogen in an internally heated bomb. The high pressure experiments resulted in essentially the same p–t equilibrium although Clark's results place the pressures higher by about 1000 bars. Both workers had to restrict their data to runs made at temperatures above 250–350° C. The p–t line drawn in the $CaCO_3$ sub-diagram of Fig. 2 is an average of their results. Our shearing experiments show very plainly that calcite will remain unchanged at room temperature below the equilibrium pressure but will form aragonite in a few hours when above this pressure.

SiO$_2$. The quartz–coesite transformation is of considerable current interest. The equilibrium curve after Dachille and Roy[2], shown in Fig. 2, was based on runs from 350–650° C. Although considerable effort was made to produce coesite in shearing experiments at room temperature, no clear-cut evidence for coesite can be presented. At 70–100° C coesite is just detectable while it can be made well at 150° C and above. A very large number of shearing runs were made in the whole temperature range but none below the extrapolated curve produced coesite, while those above the curve did produce coesite easily.

From these results in five separate systems it becomes clear that the shearing action itself does not alter the equilibrium relations between the phases, at least not to an extent that it can be measured with our tools. Hence, the action of a mortar grinder and of a Wig-L-Bug is composed of two separable functions, each of them essential. The first is the generation of pressures of the order of 10–20,000 atmospheres sufficient to put substances in the stability field of a new polymorph. The second is to increase the rates of reaction due to the shearing stresses and/or the bond breakage involved. We shall turn our attention now to the question of the rates of the reactions involved.

INFLUENCE OF "DISPLACING SHEAR" ON RATES OF REACTIONS

In the above cases of polymorphism are several excellent qualitative examples of the effect of such shearing. A few data will be cited in each case, reserving the most extensive set on PbO_2 for later discussion.

MnF$_2$. A static pressure run of 60 hours at room temperature above the equi-

librium pressure will form none or very little of the II phase, but under the same conditions, the addition of shear will result in over 50 % conversion in only three hours. However, higher static pressures will drive the transition quite readily almost to completion at other conditions; for example, 72 hours, 25° C and 40,000 bars, or 10 minutes, 150° C, 80,000 bars.

PbO. Litharge only partially converts to massicot when held in the massicot field under static pressure at room temperature, but essentially complete conversion will occur at 9000 bars in four hours with the addition of shear. Freshly prepared massicot remains unchanged at room temperature at 2500 bars for 24 hours but the addition of shear produces 20 % litharge in only 30 minutes and more than 85 % in four hours. (It is of interest here to mention that in the equilibrium work on this transition under hydrothermal conditions—White, Dachille· and Roy (*op. cit.*)—massicot remained unchanged for days at 262° C and 10,000 psi, well within the litharge field. The addition of a small amount of mechanical action during similar runs served to "nucleate" the litharge.)

CaCO₃. Static pressure experiments on calcite at room temperature failed to form aragonite at 10,000 bars, very definitely in the aragonite field, after 24 hours. Even at this high pressure only 10–15 % of aragonite is formed at 150° C after 72 hours. The displacive shear experiments at room temperature and 4–5000 bars show plainly the formation of over 50 % aragonite in only 16 hours. The reverse reaction apparently is a more difficult one. Numerous shearing experiments in the calcite field to form calcite from well-crystallized natural aragonite failed at room temperature but were successful at 200° C and above. This reaction is usually accomplished only at 450–500° C at atmospheric pressure, and it remains very sluggish at static pressure near the equilibrium curve even at 400° C.

SiO₂. Our general experience has been that coesite forms very slowly at 325–375° C close to the equilibrium pressure. At 150° C and 17,000 bars no coesite was formed after 24 hours, but the addition of displacive shear at these conditions produced nearly 40 % conversion in various runs.

QUANTITATIVE STUDIES

Several quantitative studies on the rates of these reactions are now in progress. Some of the data on the PbO_2 system only will be presented here. In Fig. 3 is presented the percentage conversion *versus* time plot for three temperatures with static pressure held constant at 40,000 bars. Part of the conversion noticed at room temperature is no doubt due to the unavoidable shearing stresses applied in starting a "static" run. In Fig. 4 we present a plot of· percentage conversion *versus* time for runs made at room temperature at three different pressures, but with the addition of displacive shear. In Fig. 5 percentage conversion in 10 minutes *versus* static pressure is shown for two temperatures. Fig. 6 compares the percentage conversion in 10 minutes for different pressures under shear conditions at room temperature and 300° C. In Fig. 7 we present some results of a rate study (Hoffer, Dachille and Roy)[10] on a reaction in a ternary system: 2 jadeite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2$) ⇆ nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) + albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). An example of the influence of shear is evident in the 60 % conversion to jadeite at 350° C and about 14,000 bars, conditions for which static runs produce less than 10 % jadeite. The typical activation energy "wall",