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INFLUENCE OF "DISPLACIVE-SHEARING" STRESSES ON THE KINETICS OF RECONSTRUCTIVE TRANSFORMATIONS EFFECTED BY PRESSURE IN THE RANGE 0-100,000 BARS

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Earlier results showed that ordinary laboratory grinders and mixers were able to convert several phases (*e.g.* PbO_2 , MnF_2 , CaCO_3 , BeF_2 , etc.) into their respective high-pressure forms, which at equilibrium require 10-15,000 atmospheres at room temperature. Hence, experiments were devised to attempt to separate the effect of hydrostatic pressure from those of shearing stresses and "bond-breakage".

A study of the influence of shearing stresses superimposed upon quasi-hydrostatic pressures of up to 100,000 bars at temperatures below 550°C has been made possible by the development of a simple apparatus. This consists of the Bridgman uniaxial-type apparatus—with a provision for continuous rotation of the bottom piston very slowly back and forth through a 2° arc. The sample is heated externally; and displacive-shearing runs with pressure and temperature automatically controlled can be made for periods exceeding several days if desired. The results clearly separate the influence of "hydrostatic" pressure itself upon reaction rates from the effect of the added "displacive-shearing" stresses. Further, from the results it becomes clear that equilibrium relations between phases are not altered by the shearing stresses. The influence of this type of stress is illustrated for the transformations $\text{SiO}_2 \text{ qtz} \rightleftharpoons \text{SiO}_2 \text{ coesite}$; $\text{PbO}_2(\text{MnF}_2)_{\text{rutile}} \rightleftharpoons \text{PbO}_2(\text{MnF}_2)_{\text{orthorhombic}}$; $\text{PbO}_{11\text{tharge}} \rightleftharpoons \text{PbO}_{\text{masseicot}}$; $\text{CaCO}_3 \text{ calc.} \rightleftharpoons \text{CaCO}_3 \text{ arag.}$ and the formation of $\text{NaAlSi}_2\text{O}_6$ (jadeite). Reactions which cannot usually be made to proceed below $300\text{--}350^\circ\text{C}$ can be performed at temperatures between $0\text{--}150^\circ\text{C}$.

Increases in rates of reaction of two or three orders of magnitude can be attained at a given pressure and temperature. It is not clear whether this should be ascribed to strain energy stored in the lattice or merely to breakage of bonds.

INTRODUCTION

It has recently been thoroughly demonstrated in our laboratory¹ that the combination of pressure, "shearing stresses" and bond breakage found in a variety of laboratory grinders is very effective in forming high-pressure phases of all types. These results are briefly summarized first. Using ordinary "automatic" laboratory grinders it was possible to convert the low pressure forms of PbO_2 , MnF_2 , CaCO_3 , PbO , Sb_2O_3 , and BeF_2 into their corresponding high pressure polymorphs in a matter of hours of grinding at room temperature. The identification of the phases was established in all cases by powder X-ray diffractometry. Furthermore, the same effects, *i.e.* with neither fewer nor more substances, could be obtained by using the common vibrator-shaker mills (trade name: Wig-L-Bug) used in spectroscopic laboratories or dentists' offices. From earlier independent phase-diagram studies of these phases in our laboratory, it was shown that if the high-pressure phases were being formed in their respective regions of thermodynamic stability, then the pressures involved in these simple laboratory devices are of the order of 15,000 bars.

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hydrostatic pressure by runs in our apparatus. This has been done for some eight or nine substances. In Fig. 2 we have combined some of the information obtained on five phases. The general pattern of the data is as follows: On each sub-diagram is presented as a heavy line the equilibrium $p-t$ curve (determined in separate studies in

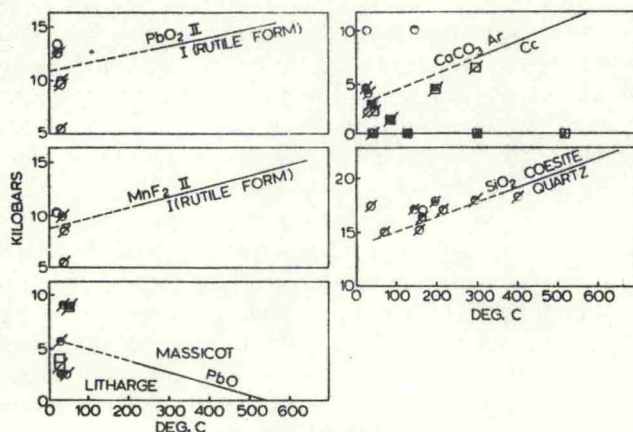


Fig. 2. The $p-t$ equilibrium lines for five polymorphic pairs determined by phase equilibrium studies are shown as heavy lines. Note that the equilibrium work ends at temperatures near 300°C . The light dashed lines are extensions to low temperature of the equilibrium curves, and are independent of the results of the shearing experiments shown with diagonal bars. It can clearly be seen that within the limits of experimental error the application of these shearing stresses does not displace the position of equilibrium. Symbols: black filling for high-pressure forms. In respective plots squares are for massicot or aragonite, circles are for litharge or calcite, starting materials.

these or other laboratories). It will be noticed that this $p-t$ phase boundary usually is determined experimentally only in the region above about 300°C ; below this the line is extrapolated down to room temperature as a dashed line. Note that the experimental runs with the displacive shear apparatus are not the basis for drawing the curve. We are attempting to present in each case a comparison between the extrapolated curve and the displacive shear runs. All such runs are shown with a diagonal across the symbol. Each of the phases in Fig. 2 can be briefly discussed in turn:

PbO₂. The equilibrium curve reported by White, Dacheille and Roy⁵ was based on points from $300-550^{\circ}\text{C}$. It will be recalled that grinding in a mortar or Wig-L-Bug easily produces the high pressure form at room temperature. However, it can clearly be seen that shearing runs at 9-10,000 bars (below the extrapolated equilibrium curve) failed to convert the rutile form; as soon as the hydrostatic ambient pressure is raised to 12,000 bars (above the curve) conversion to the high form takes place rapidly. In general, therefore, the data from the shearing runs fit rather well with the equilibrium data within experimental limits.

MnF₂. The study by Azzaria and Dacheille⁶ has shown that this phase acts as a nearly perfect model for PbO₂ with two structurally analogous polymorphs in equilibrium along a $p-t$ line which is close to that for PbO₂ itself. Here again the shearing experiments fit in with the extrapolated curve. The presence of small amounts of one phase in the stability field of the other is attributed here both to failure of