

Fig. 3. Comparison of the extent of conversion effected at a constant pressure of 40,000 bars in the  $\text{PbO}_2$  I  $\rightarrow$  II transition at 25, 150, and 400°C under static uniaxial pressure conditions. In this and subsequent diagrams reproducibility of X-ray method and from run to run is  $\pm 10$  percent.

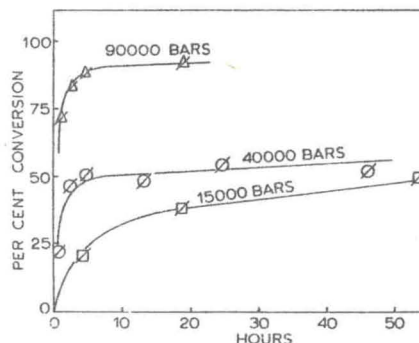


Fig. 4. Comparison of the extent of conversion of  $\text{PbO}_2$  I  $\rightarrow$  II at a constant temperature of 25°C at 15,000, 40,000 and 90,000 bars under displacing shear + uniaxial pressure conditions. Note that the effect of shearing on conversion at 40,000 bars may be estimated to be at least equal to that of 200°C. Points at 40,000 bars for two and four hours are averages of several runs.

and the influence of temperature at any one pressure or pressure at constant temperature are illustrated here also.

These data need hardly any comment as to the general influence of shear, pressure and temperature on this reaction. It appears that the addition of displacive shear at room temperature and 40,000 bars is about equal to the effect of using 200°C under static conditions, a conclusion very similar to one made by Bridgman<sup>11</sup> many years ago, without perhaps as many data available, when he stated "... in general one can expect to find transitions by the shearing method 100° to 150° below the temperature at which they become suppressed by internal viscosity for the volume method." Increases in conversion of 50–200 times can be found under the various conditions of reaction. Quantitative treatment of the influence of pressure on activation energies of these reaction and influence of shear on these rates is deferred to later publications.

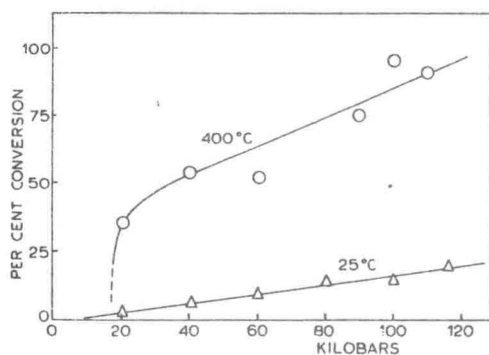


Fig. 5. Effect of temperature on the conversion  $\text{PbO}_2$  I  $\rightarrow$  II versus pressure for 25° and 400°C. Constant time of reaction is 10 minutes. Compare with the more rapid conversions due to the effect of shearing as shown in Fig. 6.

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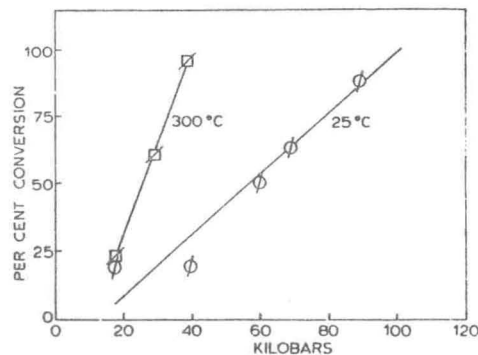


Fig. 6. Combined effect of temperature and shearing on the conversion of  $\text{PbO}_2$  I  $\rightarrow$  II versus pressure for 25° and 300°C. Constant time of reaction is 10 minutes.

The question of the mechanism for this increase in reaction rate with shear is still a moot one. One can conceive at least two explanations. The first is merely that when the shearing stress exceeds the ultimate strength of the material, bonds are broken, and in the reorganization of this matter the phase stable at the ambient

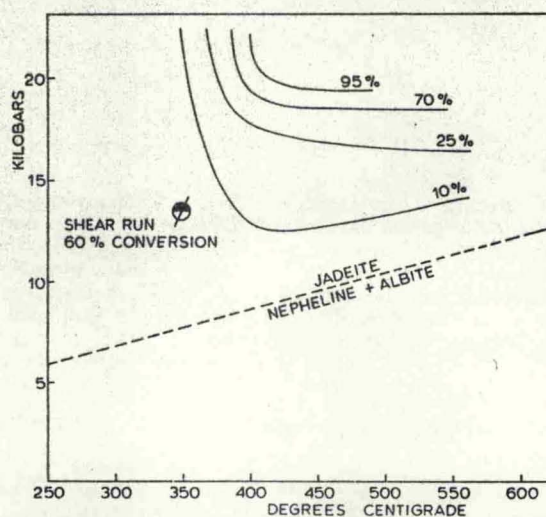


Fig. 7. Albite + Nepheline  $\rightarrow$  2Jadeite. This reaction has been studied at a large number of pressures and temperatures in the region above the extension of the  $p$ - $t$  equilibrium line of Robertson *et al.*<sup>12</sup>. The percent conversion in 40 hours of reaction is shown as contours for 10, 25, 70 and 95 percent conversion. Note that the addition of shearing increases the conversion to over 60% in a region of very low yield.

high pressures is nucleated and then continues to grow because of the pressure. One may contend that the actual amount of bond breakage due to comminution is really not enough in the apparatus used. On the other hand, to virtually every piece some shearing stress or torque is applied. The crystals respond by being strained—mutual displacement of ions from their equilibrium position—and the amount of energy stored as strain energy in the sample may, therefore, be quite considerable, and this strain energy could serve as a chemical tunnel through the activation energy wall. In an attempt to check this, oriented sections of single crystals of quartz and calcite have been subjected to this shearing action. Very little reaction was noted, and what coesite or aragonite was present was found to have no structural relation to the original quartz or calcite. This would tend to speak against the strain theory except for the fact that the efficient transmission of the shear to even a very thin plate is impossible. Only the surfaces appear to convert at all.

If the bond breakage picture is correct, new devices employing this principle will be important in industrial high pressure syntheses.

#### ACKNOWLEDGEMENT

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