

for compacted glass. Over this period, an empirical technique has been developed for studying this property of the dense glass. Selected pieces weighing about 10 mg were put into 5 per cent HF solutions for 24 hours. The loss of weight was then determined. The method is necessarily approximate because of the variation in shapes and sizes of the samples. Only a few measurements have been made so far and the results are inconclusive. These experiments will be continued in the next period. Germanium will also be examined.

In the coming period, density columns covering the range of 4.0 to 5.0 will be prepared for the germanium samples. Infrared studies will be made on the compacted glass to determine if any significant structural changes have occurred. Further high-pressure experiments will be carried out in an attempt to prepare vitreous silica and germanium of even higher density. More accurate measurements of temperature will be made by the use of thermocouples in the high-pressure cells in order to obtain PVT relationships for both vitreous silica and germanium.

PART B

INTRODUCTION

During the third quarter of the contract period, emphasis has been given to the study of the decomposition and transformation of the naturally occurring polymorphs of Al_2SiO_5 . This departure from the expressed intention (second quarterly report) to focus on the substitution of Ga_2O_3 for Al_2O_3 in Al_2SiO_5 was made because of the consistent failure to produce any of the desired polymorphs from gel or mechanical mixtures in the Ga_2O_3 - SiO_2 system and the only limited success in the Al_2O_3 - SiO_2 system. Either reaction rates in both systems are too slow to reach what has been considered to be equilibrium at high pressures and temperatures in these systems or the assemblages found (Ga_2O_3 plus glass and corundum plus glass, respectively) do indeed represent equilibrium in the P-T region studied. The P-T conditions for the runs that have been made were based on the work of Clark *et al.*⁽¹⁾ (or an extrapolation of the results of that study), who concluded that the frequently found crystalline assemblage of Al_2O_3 and SiO_2 was metastable.

By studying the decomposition of natural kyanite, andalusite, and sillimanite, the stability regions can be determined from a different direction than that offered by the synthetic approach, and such information

1. S.P. Clark, Jr., E.C. Robertson, and F. Birch, *Am. J. Sci.*, 255, 628-640 (1957).

can then be used as a guide for future work with synthetic materials. As a result, a tentative curve for the decomposition of kyanite as a function of temperature and pressure has been determined, and some new observations on reaction paths and relative reaction rates for the decomposition of the polymorphs have been made. The data for kyanite are not in agreement with the previous work⁽¹⁾ in which kyanite and sillimanite were synthesized from kaolinite, andalusite, and sillimanite.

EXPERIMENTAL

High-Pressure Cell

The same cell type previously described in the second quarterly report was used. The cell assembly was the same as described recently in regard to diamond synthesis.⁽²⁾ The internal heater in most of the runs was a graphite cylinder separated from the sample by a cylinder of alumina. The sample was enclosed in Pt or 80 Pt-20 Rh foil.

Temperature and Pressure Measurement

Several runs have been made with the above cell with a thermocouple of which the Pt capsule containing the sample is a part. In these runs a plot of watts vs temperature was made and the reproducibility of the plot was found to be $\pm 50^\circ\text{C}$. With this information it is possible to make the runs without inserting a thermocouple in every run, and considerable time is saved without appreciable sacrifice of precision. Most of the runs are made this way with an occasional use of a thermocouple to check the watts vs temperature curve. No correction has been applied for the change of emf as a function of pressure.

The problem of an absolute pressure calibration is a difficult one, and we are in the unsatisfactory position of being able to state with certainty only the precision of the pressure measurement (± 2000 atm). The pressure calibration is made by measuring the change in resistance of Bi, Tl, or Ba wires with pressure at room temperature. The pressure transmitting medium adjacent to the wire is silver chloride. It obviously would be more satisfactory to have fixed points that could be determined under the same conditions as the runs.

2. Chemical and Engineering News, 24-25 (November 29, 1959).