

The pressure,  $P_{1/2}$ , at which the sample is one-half solid, was obtained by drawing a line from the point  $1/2 (t_a + t_b)$ , on the horizontal P line, with a slope equal to the average of those for the liquid and solid curves.

The intersection of this line with the experimental liquid-solid curve gives  $P_{1/2}$ . The difference,  $(P_{1/2} - P)$ , is assumed to be the same as the pressure change,  $(P - P_0)$ , that would be caused by adding a like amount of impurity to the pure substance,  $P_0$ . Equation 1 was then used to calculate the amount of impurity.

#### 4. MATERIALS AND PIEZOMETRIC DATA

##### 4.1. Dichloroacetic Acid

The preparation of the sample of dichloroacetic acid used in this work has been described previously [1]; its purity had been determined cryoscopically to be 99.8 mole percent. It was alternately melted and frozen at least four times under high vacuum to remove dissolved gases before transfer to the piezometric vessel as described in 2.1. Before the sample was transferred, the piezometric vessel was heated for 16 hours at a pressure of  $10^{-5}$  mm Hg to remove adsorbed water. Despite these precautions, some reaction occurred during the high pressure experiments. To minimize this reaction, the experiments were made at the lower temperatures first. The reaction was accelerated when the sample was heated to 60°C.

Eleven piezometric experiments were performed: five experiments at 15°C and two each at 30°, 45°, and 60°C. In experiments at 15°, 45°, and 60°, a search was made for solid-solid transitions at pressures to about 4900 kg/cm<sup>2</sup>. No transitions below this pressure were observed for this compound other than fusion. A summary of the piezometric data for dichloroacetic acid is given in table 1. From the data of experiment 11, an impurity of about 0.35 mole percent was calculated, in reasonable agreement with the value of 0.2 mole percent from the cryoscopic measurements on the original sample. Calculations for succeeding experiments at 30° and 60°C indicated that the impurity had increased to 0.6 and 1.7 mole percent, respectively; no calculation of purity was made for experiments 17 and 18, at 45°C, because of the much larger pressure changes during fusion.

The temperature-pressure phase diagram for dichloroacetic acid obtained from the data in table 1 is shown in figure 2. The open circles