dichloroacetic acids were studied at pressures to 5000 atmospheres. The only previous study of a halogenated acid under pressure was by BRIDGMAN [3], who obtained the stable form and one of the metastable modifications (mp 50°C at 1 atm.) of monochloroacetic acid, but observed no solid-solid transitions.

Interest in these acids arose from a comparison of the melting points, at atmospheric pressure, of the halogenated fatty acids. The mono-, di-, and tri-halogen derivatives of an acid in which halogen atoms are substituted for hydrogens at the same carbon atom show a regularity in the melting point, with the iodine derivative melting higher than the bromine derivative, which in turn melts higher than the chlorine derivative [1, 2]. An exception to this rule is that monochloroacetic acid melts higher than monobromoacetic acid. A search was undertaken for an additional solid form of this acid with a melting point, at atmospheric pressure, higher than that of monochloroacetic acid.

In the high-pressure experiments described here, the phase diagrams to 2500 atmospheres in the region 10° to 90°C were established for monobromo- and dichloroacetic acids. Two additional forms of monobromoacetic acid were obtained which exist only under pressure. These two forms are of especial interest as they have negative temperature-pressure coefficients. This is the first organic compound reported to have two successive solid transitions with negative temperature-pressure coefficients.

2. PIEZOMETRIC METHOD

The name "piezometric" was proposed by TIMMERMANS [4] to describe the method for the determination of phase equilibria in which the substance is maintained at a constant temperature while the volume of the system is slowly increased and the resulting pressures are observed. During a phase transition the pressure remains constant because the change in volume of the substance compensates for the change in volume in the system. From the ΔV and P data thus obtained, the T–P phase diagram for the substance and the changes in enthalpy and entropy during solid-solid and liquid-solid transitions may be calculated.

Deffet, in a series of papers from the Université Libre [5, 9], starting in 1935, described the application of the piezometric method to compounds and mixtures. The present apparatus and procedure are essentially those described by Trappeniers[10], except as discussed below.