

## 5.2. *Monobromoacetic Acid*

The temperature-pressure coefficients and heats and entropies of phase change in monobromoacetic acid, calculated from the high-pressure data, are given in table 7 for the fusion of C III, and for the transitions C I to C II and C II to C III. Although reaction occurred when this sample was melted and subjected to high pressures, it is felt, from an analysis of the piezometric data, that the acid retained its purity during the experiments at 45°C and below. No previous high-pressure studies on this compound have been reported.

## 6. POLYMORPHIC FORMS OF MONOBROMOACETIC ACID UNDER PRESSURE

It will be noted in table 7 that the solid transitions of monobromoacetic acid occurred at increasingly lower pressures as the temperature was increased. Such negative temperature-pressure coefficients are unusual. BRIDGMAN [19, 20] did not find any organic compound in which negative temperature-pressure coefficients occurred for two consecutive crystal transitions. Crystalline transitions with negative coefficients occur infrequently; examples are found in the transitions between forms I and II of urethane, ethylurethane, acetamide, benzene, and ammonium thiocyanate. Inorganic compounds have been reported which have several crystalline transitions with negative temperature-pressure coefficients; i.e., the potassium acid sulfate transitions C II to C III, C II to C IV, and C III to C IV.

In related polymorphic studies at ordinary pressures [1], monobromoacetic acid was obtained in only one crystalline form, although monochloroacetic acid exists in at least three. Although three forms of the monochloro acid exist at ordinary pressure and three forms of the monobromo acid at elevated pressures, no comparison of the phase diagrams of the solid forms of these acids can be made on the basis of corresponding states. This is because two of the three crystalline forms of monobromoacetic acid at the elevated pressures cannot exist in equilibrium with liquid at ordinary pressures. No polymorph of monobromoacetic acid was observed which would have melted at a higher temperature at atmospheric pressure.

The comparatively low pressures associated with the solid transitions in monobromoacetic acid suggest the possibility of x-ray or neutron diffraction studies of the crystal structure of the high-pressure forms.