

FIG. 3. Example of determination of temperature and volume change of decomposition of THF hydrate.

Densities of liquid solutions near 4 °C were measured with a quartz pycnometer of 11 ml capacity designed after Kirshenbaum (15) and calibrated with mercury and water at 4 °C. The bath temperature was regulated to  $\pm 0.01$  °C and measured with a platinum resistance thermometer.

## Results

### Solution Densities

The densities of a solution of composition THF·16.98H<sub>2</sub>O at four temperatures near the hydrate decomposition point at 1 atm are given in Table 1, along with a single measurement of a more dilute solution. The accuracy is considered to be  $\pm 0.00003$  g/cm<sup>3</sup>, with a relative accuracy with respect to temperature change of the first solution of  $\pm 0.00001$  g/cm<sup>3</sup>. These data are sufficient to define the dependence on composition and temperature necessary for determination of the density at the decomposition temperature and over the range of possible hydrate compositions considered below. The appreciable decrease of density with increase of temperature is not surprising, since Wada and Umeda (16) found that THF lowers the temperature of maximum density of water. Extrapolation of their results suggests this temperature to be about -15 °C for a composition of THF·17H<sub>2</sub>O.

### Phase Equilibria of THF Hydrate

Figure 4 (heavy line) shows the region of stability of THF hydrate. At pressures below 3.05 kbar the hydrate melts congruently to a liquid of greater density, the curvature of the temperature-pressure line being determined by the larger compressibility and thermal contraction of the liquid. This part of the hydrate de-

TABLE 1. Densities of THF solutions

Composition	Temperature (°C)	Density (g/cm <sup>3</sup> )
THF·16.98H <sub>2</sub> O	4.03 <sub>5</sub>	0.99730
	4.13 <sub>3</sub>	0.99726
	4.31 <sub>1</sub>	0.99719
	4.67 <sub>5</sub>	0.99706
THF·17.99H <sub>2</sub> O	3.98 <sub>0</sub>	0.99768

composition curve intersects the freezing curve of ice III in the presence of liquid of hydrate composition at -19.8 °C and 3.05 kbar. At higher pressures the hydrate (h) "melts" incongruently to give ice III and a peritectic liquid (l), the dependence of decomposition temperature on pressure becoming increasingly great as ice III is formed in greater proportion. The decomposition curves in this region were not well enough defined to distinguish between the h → III + l and h → V + l curves, ice V (as shown by its melting behavior) having been obtained in most pressurizing runs within the region of stability of ice III. When the ice formed is V, the melting of the hydrate remains congruent to about -21.4 °C and 3.12 kbar. At lower temperatures the equilibrium decomposition is to ice II and THF-rich liquid. Dielectric studies (to be published elsewhere) show the hydrate to be stable to at least 3.5 kbar at -62 °C.

There was no evidence of formation of a denser hydrate.

### Melting of Ice in the Presence of THF

Over its full range, the curve corresponding to eutectic melting of ice I in the presence of hydrate (Fig. 4) lies about 1° below the melting curve of ice I given by Bridgman (17). This suggests that the eutectic composition shows little variation over this pressure range from its value (0.9 mol% THF (11)) at 1 bar and that the partial molar volume of water ( $V_1$ ) in the eutectic liquid is not much different from the molar volume of pure water ( $V_1^0$ ) at the same pressure. The increasing depression of the freezing point of ice III with increase of pressure corresponds to increasing THF content of the eutectic solution, which reaches the hydrate composition at the intersection with the hydrate melting curve. On the other hand, the increasing depression of the freezing point of ice V, 5° at 6.2 kbar, is due to an increasing value of  $V_1^0 - V_1$ , where  $V_1$  refers to the liquid of the same composition as the hydrate.

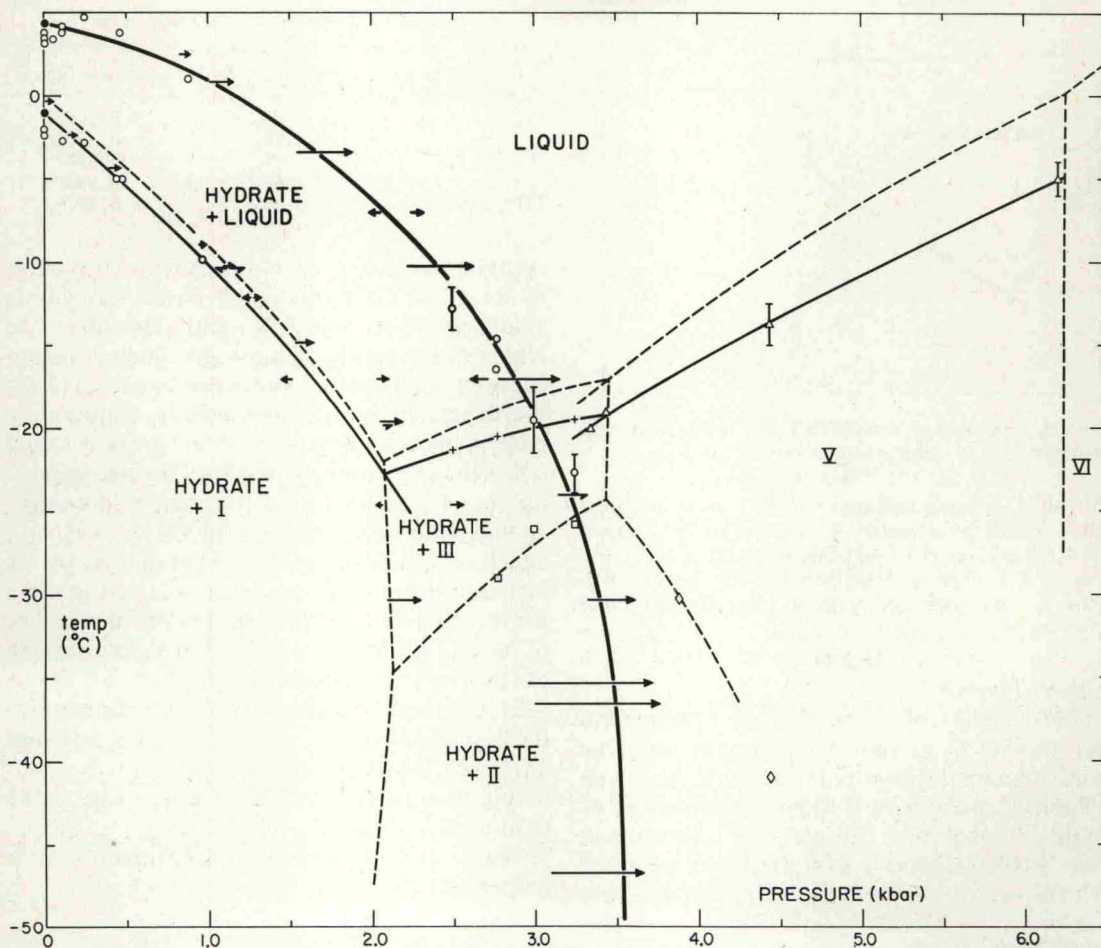


FIG. 4. Phase diagram of the THF-water system. The heavy line is the decomposition curve of THF hydrate, light lines are water-rich eutectic points (to left of heavy line) or melting points of ice in the THF·17H<sub>2</sub>O system (to right), and broken lines are Bridgman's phase boundaries in the water system.

#### Dependence of Decomposition Temperature on Pressure

The decomposition temperature of THF·16.69-H<sub>2</sub>O given by the mid-points of the thermal steps in the temperature *vs.* time curves were measured at 17 pressures between 1 and 1400 bars. The results (Fig. 5) are given, to a standard deviation ( $\sigma$ ) of 0.080°, by

$$[1] \quad t(^{\circ}\text{C}) = (4.126 \pm 0.035) \\ - (2.280 \pm 0.139) \times 10^{-3} P \\ - (1.150 \pm 0.112) \times 10^{-6} P^2$$

where  $P$  is the pressure in bars.

The temperatures at the mid-points of the

corresponding volume changes were measured at 14 pressures (Fig. 5) and are given, with  $\sigma = 0.093^{\circ}$ , by

$$[2] \quad t(^{\circ}\text{C}) = (4.279 \pm 0.082) \\ - (2.375 \pm 0.259) \times 10^{-3} P \\ - (1.169 \pm 0.176) \times 10^{-6} P^2$$

No reduction of variance was achieved by the inclusion of terms in  $P^3$  in the least squares analyses.

The mid-points of the decomposition curves were chosen for greatest accuracy of the pressure dependence of the melting points. Equations 1 and 2 are expected to underestimate the melting