FIG. 5. Pressure dependence of decomposition temperature from thermal (○) and volume (△) measurements and of change of piston displacement (●) at decomposition. (The decomposition temperatures from volume measurements are displaced upward by 0.3 °C.)

point of the hydrate at 1 bar because of the central position in the sample of the measuring thermocouple. This appears to be less true of eq. 2, possibly because of some lag of the piston behind the change of volume.

The linear coefficients in eqs. 1 and 2 may be combined to yield

$$[3] \quad \left(\frac{dt}{dP}\right)_{P \to 0} = -(2.301 \pm 0.122) \times 10^{-3}$$

degrees per bar, the error quoted, like those of eqs. 1 and 2, being the standard error.

Volume Change of Hydrate Decomposition

Seventeen measurements of the change of dilatometer gauge reading for THF·16.69H$_2$O at pressures between 1 and 1400 bars (Fig. 5) gave

$$[4] \quad \Delta s \text{ (in.)} = -(0.00972 \pm 0.00021)$$
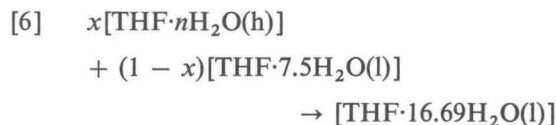$$- (8.22 \pm 0.35) \times 10^{-6} P$$

The value of σ (0.00057 in.) was scarcely improved, and the constant term hardly affected, by inclusion of a term in P^2.

Division of Δs for $P = 1$ bar, by the length of the column of liquid solution at 4.4 °C gave

$$[5] \quad \Delta v/v = \Delta s/s = -(0.01470 \pm 0.00034)$$

for the relative change of volume. From Table 1 the density of liquid THF·16.69H$_2$O at 4.4 °C may be taken as 0.99705 ± 0.00004 g cm^{-3}, whence the change of volume is -5.496 ± 0.129 cm^3 per mol of THF·16.69H$_2$O.

This volume change is not quite the desired volume change for congruent melting of 1 mol of hydrate of composition THF·nH$_2$O, since $n > 16.69$. Some melting of the hydrate occurs over the whole temperature between the THF-rich eutectic temperature and the final melting point. Examination of the volume *vs.* temperature curves shows that a contribution to the *measured* volume change is first detected about 1° below the temperature of final melting. Erva's data (11) show the liquid composition to be THF·7.5H$_2$O at this temperature. The measured volume change then corresponds to

$$[6] \quad x[\text{THF} \cdot n\text{H}_2\text{O(h)}]$$
$$+ (1 - x)[\text{THF} \cdot 7.5\text{H}_2\text{O(l)}]$$
$$\to [\text{THF} \cdot 16.69\text{H}_2\text{O(l)}]$$

where $x = 9.19/(n - 7.5)$ is the fraction of THF present in the hydrate at the onset of melting.

Reaction 6 may be considered as the sum of the processes of melting x mol of hydrate and of mixing x mol of liquid THF·nH$_2$O with $(1 - x)$ mol of liquid THF·7.5H$_2$O. The volume change of mixing is zero for an ideal solution. The density measurements of THF–water solutions at 25 °C by Critchfield *et al.* (18) give zero for this volume change, with n near 17, to within the experimental accuracy of 0.02%. We ascribe the whole of the measured volume change to the melting of x mol of hydrate and put for the melting of 1 mol

$$[7] \quad \Delta V(\text{h} \to \text{l}) = \frac{-5.496}{x}$$
$$\pm \frac{1}{x} \sqrt{30.25(1 - x)^2 + 0.0640}$$

The error estimate[2] has been conservatively written to include an uncertainty in the correction $(1/x)$ of the order of magnitude of the correction itself and the original standard error of the measured volume change has been expanded to the 95% confidence level.

[2]The error in x is assumed to be $x(1 - x)$ and in the measured volume change 1.96×0.129 cm^3.

Hydrate Composition

The molar volume of $THF \cdot nH_2O(l)$ at $4.4°$ may be written as

$$[8] \quad V(l) = \frac{72.10 + 18.015n}{0.99716 + 0.000364(n - 16.98)} \ cm^3$$

and that of the solid hydrate as

$$[9] \qquad V(h) = \frac{Nna^3}{136} \ cm^3$$

where N is Avogadro's number and a is the dimension of the cubic unit cell which contains 136 water molecules. Unfortunately, a is not accurately known at the decomposition temperature of the hydrate. Von Stackelberg and Meuthen's value (2) of $17.18 \ Å$ at $-10 °C$ appears to be uncertain by as much as $0.10 \ Å$. The more accurate values of Sargent and Calvert (5), $viz.$, $17.13 \pm 0.03 \ Å$ at $-163 °C$ and two values of 17.170 ± 0.004 and $17.162 \pm 0.007 \ Å$ at $-137 °C$ (the errors are σ's), refer to much lower temperatures. The values (5) for the closely related hydrate of dihydrofuran, almost identical with those of THF hydrate at $-137 °C$, include $17.22 \pm 0.01 \ Å$ at $-40 °C$. Extrapolation of the combined data for THF and dihydrofuran hydrates to $4 °C$ gives $17.24 \ Å$, to which we assign a maximum uncertainty of $\pm 0.03 \ Å$.

In Fig. 6 volumes given by eq. 7 and by the difference between eqs. 8 and 9 are plotted against n for values of a between 17.21 and 17.27 Å.
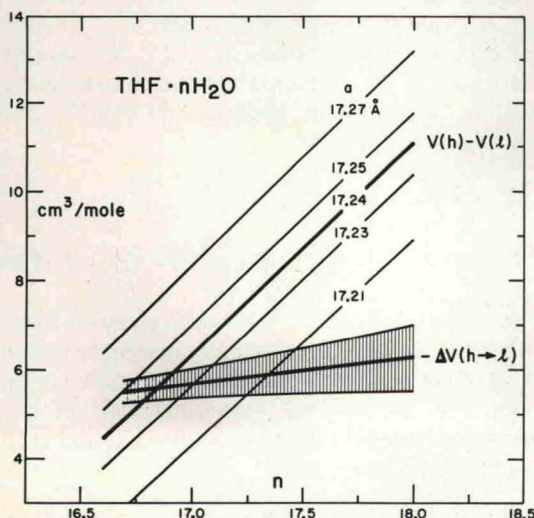
The most probable value of n is 16.86. For the

FIG. 6. Dependence of volume change at decomposition on composition of THF hydrate.

range of lattice parameters allowed, values between about 16.4 and 17.5 are formally permitted. It is unlikely, however, that THF (maximum diameter 5.9 Å (2)) can occupy the small cages of free diameter 4.9 Å and therefore that n is less than 17. It may also be noted that $a = 17.21 \ Å$, for which n is 17.34 ± 0.20, is much less likely than $a = 17.23 \ Å$, with $n = 17.01 \pm 0.16$. We conclude, at about the 90% confidence level, that at least 98% of the large cages are occupied.

Effect of Air on Hydrate Properties

Under the conditions of our experiments, in which the only air present was that initially dissolved in the liquid, the effect of air on the volume changes discussed above may be shown to be negligible. Saturation with air at 1 atm affects the density of liquid water only in the sixth decimal place (19) and therefore may be assumed to have a negligible effect on the density of the THF solution. If the air present in the solution (assumed to be the amount soluble in water at $4 °C$) is entirely taken into the small cages of the hydrate, the hydrate density is increased by $0.000034 \ g/cm^3$ and the volume change of melting reduced by only $0.013 \ cm^3/mol$.

It is well-known that some hydrates grown in the presence of air incorporate large quantities of air in their cages, with a consequent increase of stability (see refs. 13 and 20, for example). A simple experiment showed this to be true of THF hydrate. A sample of $THF \cdot 16.79H_2O$ was slowly frozen and conditioned in an ice bath for several hours. The warming curve obtained in an air-jacketed glass vessel showed the great bulk of the sample to melt at $4.45 °C$. With further warming the remaining crystals gradually melted with the evolution of air bubbles and only completely disappeared at $5.0 °C$. It is likely that the presence of air accounts for Palmer's report (10) of two maximum melting points at 5.07 and $5.37 °C$. The available data suggest that the melting point of THF hydrate containing little or no air lies at $4.4 \pm 0.1 °C$.

Heats of Decomposition

The enthalpy change of congruent melting at negligible pressure is given by

$$[10] \qquad \Delta H(h \to l) = \frac{T\Delta V(h \to l)}{\left(\dfrac{dt}{dP}\right)_{P \to 0}}$$

The pressure coefficient of the melting point is