

Composition of Tetrahydrofuran Hydrate and the Effect of Pressure on the Decomposition¹

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The decomposition temperature of the structure II clathrate hydrate of tetrahydrofuran has been followed to pressures above 3 kbars, where the hydrate is found to decompose incongruently in the regions of stability of ices III and II, with no evidence of formation of a denser hydrate. From measurements of liquid solution densities and of volume changes at hydrate decomposition the density of the hydrate was obtained. Comparison with the X-ray lattice dimension indicates that at least 98% of the large cages are occupied, the principal uncertainty being in the lattice parameter. A similar treatment is made of Tammann and Krige's data (23) for chloroform hydrate. Analysis of the results of 18 composition determinations of structure II hydrates shows no statistical evidence of departure from the ideal composition of 17 mol of water per mol of hydrate former.

La température de décomposition du clathrate hydraté de structure II du tétrahydrofurane a été suivie jusqu'à des pressions supérieures à 3 kbar; il a été trouvé que dans ces régions de stabilité des glaces III et II l'hydrate se décompose d'une façon aberrante sans preuve de formation d'un hydrate plus dense. A partir des mesures de densité des solutions liquides et des changements de volume à la décomposition de l'hydrate, il a été possible d'obtenir la densité de l'hydrate. La comparaison avec la dimension du réseau obtenu par rayons X indique qu'au moins 98% des grandes cages sont occupées, l'incertitude principale étant dans le paramètre réticulaire. A partir des données de Tamman et Krige une analyse similaire est effectuée pour le chloroforme hydraté. Les analyses des résultats se rapportant à 18 déterminations de composition d'hydratés ayant la structure II ne montrent aucune preuve statistique d'écart par rapport à la composition idéale de 17 mol d'eau par mole de générateur d'hydrate.

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Among the diverse molecules now known to form "gas hydrates" of von Stackelberg's structures I and II (1) are a number of ethers and ketones which are distinguished from the classical gas-hydrate formers by their solubility in water and by the possibility of hydrogen bonding with the host water molecules of the clathrate structures. Ethylene oxide (2, 3) and trimethylene oxide (4) form hydrates of type I. Structure II hydrates are formed by dimethyl ether (1), by trimethylene oxide, tetrahydrofuran, 2,5-dihydrofuran, propylene oxide, and 1,3-dioxolane (4, 5) and by acetone (6, 7) and cyclobutanone (5, 8). With the exception of the study by Glew and Rath (9) of the variable composition of ethylene oxide hydrate, there appears to be no accurate information about the degree of occupancy of the cages or the heat of formation of these hydrates.

Trimethylene oxide (4) and acetone (8) hydrates decompose incongruently. Of the other structure II hydrates only tetrahydrofuran hydrate melts appreciably above 0 °C. This hydrate is

therefore most easily distinguished from ice and has been chosen for further study.

Tetrahydrofuran hydrate was first reported by Palmer (10) who found from melting point *vs.* concentration curves a composition of between 13 and 16 molecules of water per molecule of tetrahydrofuran (THF), with a probable formula of THF·14H₂O. Erva (11) obtained a congruent melting point of 4.38 °C at an approximate composition of THF·16H₂O. Several nugatory irregularities in the melting points of solutions of higher THF content were interpreted as peritectic points of lower hydrates (11) or in terms of discrete association complexes in liquid solution (12). They are more likely to be related to the incorporation of different amounts of air in different hydrate samples.

Among several indirect methods (13) of determining the composition of clathrate hydrates, one which is particularly applicable to the hydrates of water-soluble molecules depends on comparison of measured hydrate density with the composition-dependent density calculated from the X-ray unit cell dimensions. Glew and Rath (9) have used the results of flotation mea-

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measurements of the density of ethylene oxide hydrate in conjunction with the lattice parameter to obtain compositions of this hydrate. We have determined the density of THF hydrate from measurements of the volume change at hydrate decomposition and of the density of the liquid solution. Volume, capacitance, and thermal-analysis measurements were made to high pressures to determine the effect of pressure on the hydrate-solution equilibrium and to look for evidence of a transformation of the hydrate to a denser crystallographic form. Heats of formation of the hydrate were estimated from the results.

Experimental Methods

The initial measurements were made to define the region of stability of THF hydrate in the pressure-temperature plane. The decomposition of the hydrate was followed by the capacitance, conductance, and volume changes which accompanied increase of temperature or pressure through the decomposition region. Some experiments were also made with pressure decreasing. The cell used was that previously described (Fig. 1(b) of ref. 14), with essentially the same methods of control and measurement of temperature and pressure. The electrical measurements were normally made at 20 kHz. The driving piston was coupled to a slow-speed motor to effect rotational oscillation through $\pm 4^\circ$ and thereby to reduce piston friction. Volume changes were measured in terms of displacement of this piston which was monitored to 10 μm . by a dial gauge.

Solutions were prepared from conductivity water and THF which had been distilled over calcium hydride. Analysis by vapor phase chromatography showed the THF to contain 0.1% of volatile impurity. Compositions ranged from $\text{THF}\cdot 17.0\text{H}_2\text{O}$ to $\text{THF}\cdot 16.8\text{H}_2\text{O}$. Hydrate was normally prepared by cooling to below 0°C and conditioning at $+2^\circ\text{C}$ and 1 atm for about 12 h, followed by over-night conditioning at a temperature and pressure near the starting point of the decomposition measurements.

Most hydrate samples showed relatively small capacitance and volume changes associated with the melting of ice; conductance was particularly sensitive to such eutectic melting. For these samples both ice and hydrate melting data were recorded. Since the measuring thermocouple was outside the pressure vessel (14) in these measurements, melting points were taken as the temperatures at the onset of melting, upon which there was usually agreement to within a few tenths of a degree among the parameters measured. Figure 1 illustrates such warming curves. Measurements with varying pressure refer to equilibrated temperatures, but the transitions tended to occur over a range of pressure and to show hysteresis when the pressure change was reversed (Fig. 2). Nevertheless, the hydrate and ice melting points appear to have been generally defined to better than 1° and 100 bars.

Considerably more accurate determination of the variation of hydrate decomposition temperature (and

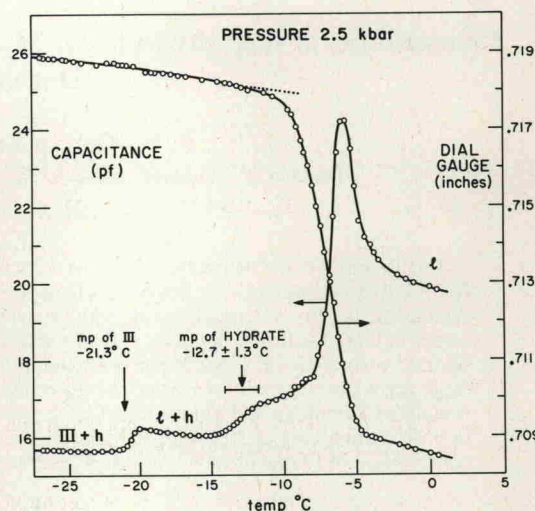


FIG. 1. Illustration of capacitance and volume changes at temperatures of phase changes in the THF-water system.

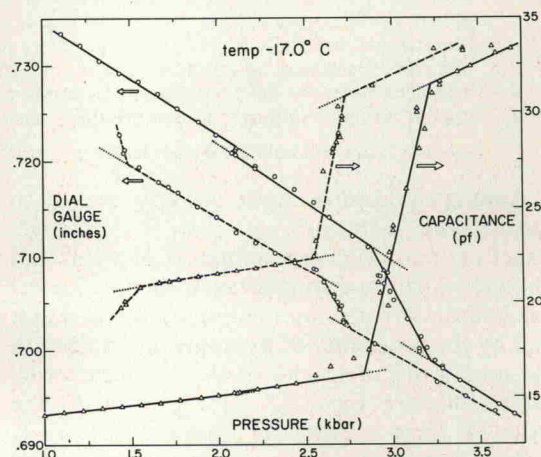


FIG. 2. Capacitance and volume changes at pressures of hydrate decomposition (pressure increasing, solid lines) and formation (pressure decreasing, broken lines).

volume) with pressure to 1400 bars was realized by insertion of a calibrated Chromel-Alumel thermocouple into the center of the sample, the insulated leads, swaged in a stainless steel tube, being brought out through the lower electrode and piston. Since the presence of the thermocouple interfered with the electrical measurements, the decomposition temperature was determined from the dilatometric and thermal (temperature vs. time) measurements only, as the mid-points of the volume changes or of the thermal steps. An example is shown in Fig. 3. All such measurements were made with a sample of composition $\text{THF}\cdot 16.69\text{H}_2\text{O}$ at a heating rate of about $0.2^\circ/\text{min}$.