

Decomposition of methane hydrates up to 15 kbar

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The decomposition curve of methane hydrate under pressure shows a break at 6.2 kbar indicating the formation of a second hydrate; at 5 to 6 kbar the decomposition temperature of the first hydrate reaches a maximum at 47.7 °C and the decomposition temperature of the denser hydrate increases to 57.3 °C at 15 kbar.

Methane hydrate $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ was first discovered by Villard.¹ It was studied by different researches^{2–5} at relatively low pressures (several hundreds of bars). Creation of a specially designed chamber⁶ has allowed data on methane hydrate decomposition to be obtained in the pressure range from 159 (17.0 °C) to 3970 (46.7 °C) bar using the pressure jump method. As for all guests which are gases under the starting conditions, the decomposition temperature of methane hydrate first sharply increases with increasing pressure. Then, as the gaseous phase is compressed, this increase is slowed down with a distinct trend to a maximum. According to ref. 7, the dissociation pressure of the hydrate at 0 °C is 26 atm. It was established by neutron diffraction analysis that methane forms a deuterohydrate with cubic structure I (CS-I).⁸

The cell and block-scheme of our experimental apparatus for the study of P, T diagrams by the DTA method under high pressures have been described earlier.^{9,10} The hydrate decomposition temperature was measured with a chromel–alumel thermocouple (the thermocouple readings were practically independent of pressure in the pressure range studied by the DTA method¹¹). The thermocouple was calibrated against the melting temperatures of reference materials. The pressure measurement with the manganin manometer was accurate to 1%. The manometer was calibrated against the melting of mercury under pressure.¹²

Distilled water and methane containing 99.99% of the main compound were used. As in the system with xenon,⁹ a non-ionogenic surfactant was added to speed up the gas dissolution. The surfactant concentration in the solution was 0.25% (preliminarily it was shown that the presence of such amounts of a surfactant did not affect the equilibrium within the accuracy of our studies¹³). For the same purpose, an inert material was added to the water (a SiC powder with a grain size of about 0.01 cm). The inertness of the material was confirmed by the identity of the melting and decomposition curves for ice and hydrate, respectively, with and without additives.

The results of our study are presented in Figure 1. There is a good agreement between our results and those of ref. 6 for the same pressure interval studied. At about 5.5 kbar the decomposition curve reaches a flattened maximum (47.7 °C). At about 6200 bar the decomposition curve undergoes a break and then increases again to 57.3 °C at 15000 bar. Following the bend in the decomposition curve, points of hydrate decomposition were noted at lower temperatures (denoted by triangles in Figure 1). These effects were small and disappeared completely after multiple heating.

On the basis of the data obtained it can be concluded that the CS-I hydrate formed in the system $\text{CH}_4\text{--H}_2\text{O}$ ⁸ is stable up to 6200 bar. At higher pressures it becomes metastable and transforms into a slightly denser structure. It would, of course, be tempting to suggest this structure to be the CS-II that is widely encountered under normal conditions. The hydrate number in CS-II at all of the voids completely filled (and this may be expected at the pressures used) is even somewhat lower (5.67) than in CS-I (5.75), *i.e.* the same quantity of water binds more methane in CS-II than in CS-I. However,

volumetric estimates do not confirm this suggestion. Indeed, according to ref. 8, for the CS-I methane hydrate at 5.2 K the parameter $a = 11.77 \text{ \AA}$, *i.e.* under these conditions the packing coefficient[†] $k = 0.532$. If we assume the same value of k for the hypothetical CS-II then under the same conditions the parameter would have been $a = 16.91 \text{ \AA}$. Hence, for the structure to be more stable under pressure than CS-I the condition $a < 16.91 \text{ \AA}$ must be fulfilled which seems to be very unlikely since for the deuterohydrates of argon and krypton of CS-II the parameter a under the same conditions $a = 17.01 \text{ \AA}$.

In the $\text{CH}_4\text{--H}_2\text{O}$ system as well as in the $\text{Xe--H}_2\text{O}$ system the CS-I hydrate is formed at ambient pressures. In the methane system a second hydrate appears at pressure higher than 6200 bar. The hydrate-2 decomposition temperature very slightly depends on pressure and reaches only 57.3 °C at 15250 bar (from 47.3 °C at 6200 bar). One can expect (Figure 1) the hydrate-2 decomposition line must intersect the ice VI melting curve at 16.2–16.5 kbar and most likely it is the upper limit of the crystallization field of the methane hydrate. We observed the similar picture in the $\text{Xe--H}_2\text{O}$ system.⁹ This phenomenon might be explained by the fact that the complementarity of the guest molecule and cavity (even in the best case for the classic water clathrate structures) is yet not enough for the formation of the closest packing with the packing coefficient about 0.74. Therefore, under certain conditions the density of clathrate structures becomes equal to that of the fluid phase (phases) which causes the destabilization of the hydrate as is the case with the CS-I hydrates of SO_2 ,¹⁴ CH_4 and the CS-II hydrate of

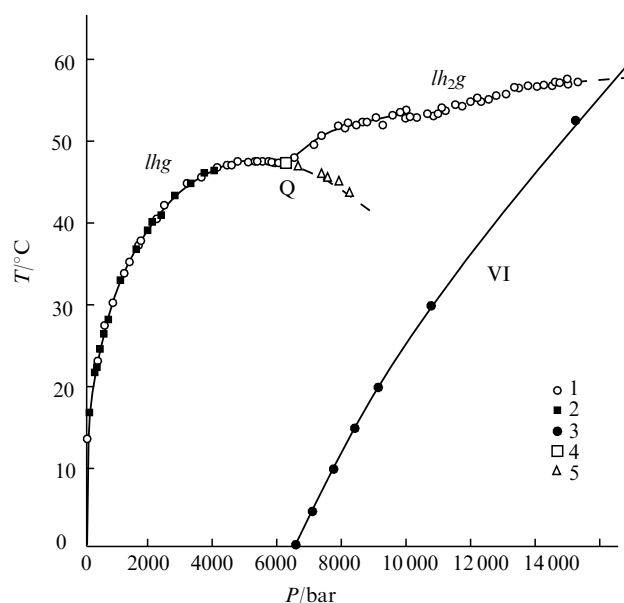


Figure 1 Fragment of the P, T -phase diagram of the methane–water system. 1 is liquid phase rich in water, g is gaseous (fluid) phase rich in methane, h_1 is hydrate of CS-I, h_2 is novel hydrate. (1) our data, (2) data of ref. 6, (3) melting points of ice VI, (4) quadruple point lh_1/h_2g , (5) decomposition points of metastable phase (CS-I hydrate at $P > 6200$ bar).

Ar.¹⁰ However, studying the Ar–H₂O system showed, that at the pressures high enough ($P > 9600 \text{ bar}^{10}$) the formation of a third, very dense hydrate with unknown framework is possible (non-clathrate nature of the hydrate in this system is highly unlikely) and the upper stability limit for this hydrate is overshadowed. However, it is difficult to say now whether the formation of these hydrates is typical. Thus, the available knowledge¹⁵ allows one to conclude that the most plausible upper stability limit for the most stable hydrates of the classic structures concerned will be pressures of the order of 16–20 kbar. Above these pressures selfclathrate ices VI–VIII will be more stable.

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[†] To calculate the packing coefficient we used the following reference value: van der Waals radii of hydrogen $R_H = 1.16 \text{ \AA}$, oxygen $R_O = 1.29 \text{ \AA}$, carbon $R_C = 1.71 \text{ \AA}$, the length of the H-bond H–OH = 2.80 Å. Based on these initial data, the volume occupied by a water molecule in the hydrate $V_{H_2O} = 14.12 \text{ \AA}^3$, and the volume of a methane molecule $V_{CH_4} = 27.19 \text{ \AA}^3$.

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