Double clathrate hydrate of tetrahydrofuran and xenon at pressures up to 15 kBar

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The decomposition temperature of double clathrate hydrate of tetrahydrofuran and xenon increases from 13.5 to 124.5 °C as the xenon pressure increases from 1 atm to 15.1 kBar.

Tetrahydrofuran (THF) forms the clathrate hydrate $THF \cdot 17H_2O$ of cubic structure II (CS-II).[1] THF molecules (a maximum molecular dimension is 6.3 Å) fill only the large H-cavities. The free diameter of these cavities is about 6.6 Å, and the fraction of these cavities in the water framework of this structure is only one third. The remaining two thirds of the cavities are dodecahedral (D-cavities) with a free diameter of about 5.2 Å. They are vacant, and the hydrate structure is loose. Therefore, despite the good spatial correspondence of the H-cavity to the THF molecule, the hydrate as a whole has the low packing coefficient $k = 0.485$[2] and is relatively unstable: its melting temperature is only +4.3 °C at 1 atm.[3] This temperature is one of the highest melting temperatures for hydrates with this structure, but noticeably lower than that of analogous hydrates with other structures. Moreover, this hydrate is rapidly decomposed under high pressure to form hydrates with denser packing.[4]

The size of a xenon molecule (we chose this gas as an auxiliary component) is very close to the size of cavities of the CS-I water clathrate framework. When a hydrate is formed, xenon almost completely fills large cavities and a significant part (about 72%)[5] of small cavities ($k = 0.564$).[6] This is reflected in the stability of the xenon hydrate: first, it retains its structure when changing the pressure from 1 atm to 15 kBar[6] (unlike the above THF hydrate and argon and krypton hydrates, which form at least three hydrates in this pressure range[4,7,8]), and second, it reaches an extremely high (for simple clathrate hydrates) decomposition temperature (79.2 °C at about 9 kBar[6]).

The aim of this work was to study the stability of the double hydrate (in which each type of cavity is occupied by the guest molecules with the most appropriate size) under high pressures.

The high-pressure apparatus and the cell for differential thermal analysis (DTA) at high pressures of a gas (fluid) were
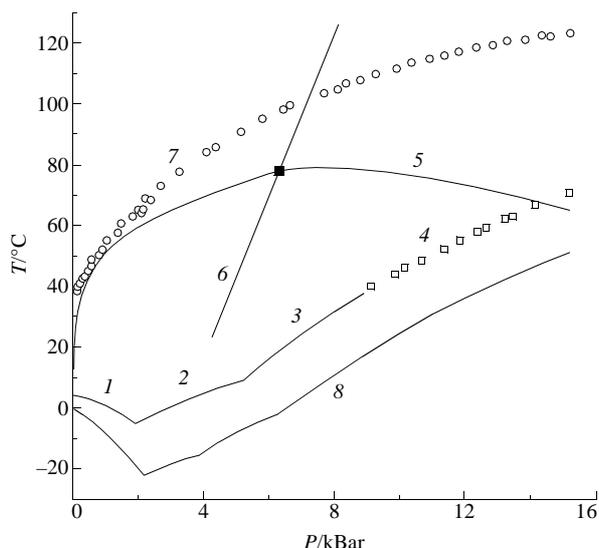

Figure 1 Phase equilibria in the THF–Xe–H₂O system: (*1*) melting curve of the THF·17H₂O hydrate, (*2*) melting curve of the THF·7H₂O hydrate, (*3*) melting curve of the THF·5H₂O hydrate (from ref. 4), (*4*) melting curve of the THF·5H₂O hydrate (this work), (*5*) melting curve of the xenon hydrate, (*6*) melting curve of solid xenon, (*7*) melting curve of the double THF·xXe·17H₂O hydrate and (*8*) melting curve of ices.

described previously.[6,7] The decomposition temperature of the hydrate was measured with a Chromel–Alumel thermocouple calibrated using standard reference compounds with an error of ±0.3 °C. The pressure was measured by a Burdon manometer (up to 2.5 kBar) and a manganin manometer (up to 15 kBar), which was calibrated against the melting of mercury. The pressure measurements were accurate to within 1%.

The starting aqueous THF solution with the molar ratio between components 1:17 (THF:water) was prepared using distilled water and tetrahydrofuran (purified from peroxides, dried, and distilled) by weighing. A known volume of this solution (about 0.03 ml) was transferred by a micropipette into a plastic ampoule for DTA, which was filled with silicon carbide powder with a grain size of about 0.01 mm,[7] using a micropipette. The gas reservoir was washed with xenon up to the moment of attachment of the ampoule with the THF solution to avoid evaporation of THF and thus changes in the composition of this solution. When the reservoir was filled with xenon, its pressure was chosen to ensure a two-fold excess of xenon with respect to the stoichiometric composition of the hydrate $THF \cdot 2Xe \cdot 17H_2O$ (about 2 atm). Under this pressure, the formation of the hydrate in the system was complete 10–20 min after decreasing the temperature below the equilibrium temperature of hydrate formation.

The experimental data on the decomposition of hydrates in the THF–Xe–H₂O system are presented in Figure 1 (the data of this work are designated by points, and the published data[4,6] are shown by lines). Curve *1* presents congruent melting of the $THF \cdot 17H_2O$ hydrate. As can be seen, the hydrate is destabilized by the pressure: its melting temperature decreases to –5.8 °C at 2 kBar.[4] At higher pressures, this hydrate transforms to the $THF \cdot 7H_2O$ hydrate (curve *2*), which refers to the cubic structure I (CS-I)[4,9] in which the ratio of the number of greater T-cavities† (filled with THF molecules) to the number of vacant D-cavities is 3:1. The $THF \cdot 7H_2O$ hydrate (as all hydrates with this structure) is already stabilised by the pressure and melts at 10 °C at $P = 5.3$ kBar.[4] The pentahydrate (curve *3*),[4] which is most likely not a clathrate,[10] is stable at higher pressures. Our experimental data show that the melting curve of this hydrate below 15 kBar exhibits no specific features; the curve is a smooth continuation of the melting curve[4] for the $THF \cdot 5H_2O$ hydrate, and the decomposition temperature of this hydrate reaches 72.2 °C at 15.1 kBar.

As would be expected,[11] in the presence of xenon, the melting temperature of the double hydrate significantly increases (from 4.3 °C for the simple $THF \cdot 17H_2O$ hydrate[3] to 13.5 °C for $THF \cdot xXe \cdot 17H_2O$ at a xenon pressure of 1 atm; under these conditions, the decomposition temperature of the xenon hydrate with the CS-I structure is –10.4 °C[12]). This difference increases with pressure. As already mentioned, the $THF \cdot 17H_2O$ hydrate is destabilised by the pressure, and the difference in the melting (decomposition) temperatures reaches 74 °C at 2 kBar. This difference also increases in comparison with the $THF \cdot 7H_2O$ hydrate, reaching 83 °C at 5.2 kBar. As compared to the non-clathrate pentahydrate, although the difference in the melting

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† The free space of the T-cavity can be approximated by the flatten ellipsoid with free diameters of 5.3 and 6.4 Å. The D- and H-cavities are isometric, and the free space in them is satisfactorily approximated by the sphere.[2]
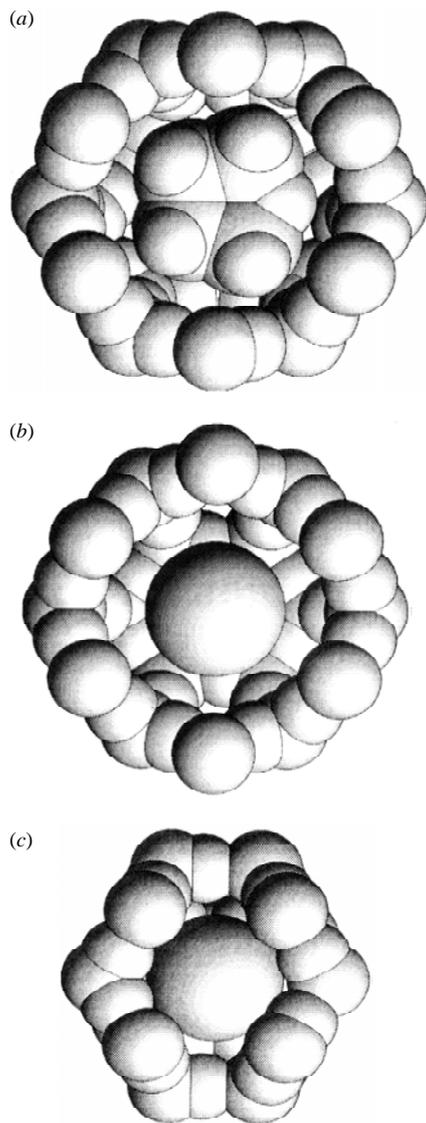
(*a*)

(*b*)

(*c*)

Figure 2 Arrangement of guest molecules in cavities: (*a*) tetrahydrofuran in the H-cavity, (*b*) xenon in the T-cavity and (*c*) xenon in the D-cavity.

molecule corresponds better to the large H-cavity in the CS-II structure than the size of the xenon molecule corresponds to the T-cavity in CS-I, and the xenon molecule effectively occupies the D-cavity in both structures. Evidently, the packing coefficient in the double compound should be higher than that of any clathrate hydrates with classical structures in which different types of cavities are filled with the same guest molecules. If we assume that the unit cell parameters of the double THF·2Xe·17H$_2$O hydrate are similar to those of the simple THF·17H$_2$O hydrate (17.29 Å at 0 °C[13]), its packing coefficient $k = 0.619$[‡] is really higher than that of the xenon hydrate (see above) and is the highest for known clathrate hydrates with classical structures.[2] This fact explains the efficient stabilisation of the hydrate phase by pressure and the highest decomposition temperature of this hydrate among the known gas hydrates.

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temperatures decreases, it remains significant (52 °C) at 15 kBar. Within the entire range of pressures studied, the double hydrate melts at temperatures higher than the xenon hydrate, and this difference noticeably increases with pressure. The relative sizes of guest molecules and cavities in which they are located are shown in Figure 2. As can be seen, the size of the THF

‡ The following reference values were used for calculating the packing coefficient: the van der Waals radii of oxygen $R_O = 1.29$ Å, hydrogen $R_H = 1.16$ Å and xenon $R_{Xe} = 2.18$ Å; the hydrogen bond length $l_H = 2.80$ Å. Based on these data, we calculated the volume occupied by a water molecule in the hydrate $V_{H_2O} = 14.12$ Å^3 (ref. 2) and the molecular volumes $V_{Xe} = 43.40$ Å^3 and $V_{THF} = 73.24$ Å^3.