New phase in the water–hydrogen system

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A new hydrogen hydrate denoted C\textsubscript{b} is discovered in the H\textsubscript{2}O–H\textsubscript{2} system at \(-20\) °C and hydrogen pressures near 5 kbar. Powder samples of the hydrate were quenched under high pressure to the liquid N\textsubscript{2} temperature and recovered to ambient pressure. Hot extraction in vacuum demonstrated that the hydrogen release from the quenched samples started immediately on heating above 77 K and completed at about 170 K. The total amount of the released hydrogen reached a molecular ratio of H\textsubscript{2}/H\textsubscript{2}O \(\approx 0.13\). An X-ray diffraction investigation at 80 K showed that the samples were single-phase and had a trigonal structure with \(a = 6.33\) Å and \(c = 6.20\) Å on hexagonal axes.

1. Introduction

Until recently, three hydrogen-rich crystalline phases, C\textsubscript{1} [1], C\textsubscript{2} [1] and sII [2], have been known in the H\textsubscript{2}O–H\textsubscript{2} system. These phases are called hydrogen clathrate hydrates, and their crystal structures are networks of hydrogen-bonded H\textsubscript{2}O molecules encasing guest H\textsubscript{2} molecules that only weakly interact with the network by van der Waals forces [1,2]. The available experimental data on phase relations in water placed in an atmospheric pressure of molecular hydrogen are presented in Fig. 1. The inaccuracy in the equilibrium phase boundaries of the sII field does not exceed the lines thickness. To illustrate the accuracy and measuring methods used to construct the boundaries of the C\textsubscript{1} and C\textsubscript{2} fields at higher hydrogen pressures, experimental points are shown in Fig. 1 along with the lines.

The equilibrium hydrogen solubility in the low-pressure hexagonal ice-I\textsubscript{h} is small and only reaches a molecular ratio H\textsubscript{2}/H\textsubscript{2}O of X\textsubscript{h} \(= 0.011(5)\) near the triple point of the Liq.+I\textsubscript{h}+sII equilibrium at \(P = 1.075(5)\) kbar and \(T = -10(1)\) °C [3]. The hydrogen content of the cubic sII hydrate varies with pressure and temperature, from X\textsubscript{sII} \(= 0.21(1)\) near the triple point [3] to X\textsubscript{sII} \(= 48/136 = 0.35\) at \(P = 2\) kbar and \(T < -90\) °C [4]. The C\textsubscript{1} phase has a diamond-like H\textsubscript{2}O sublattice and X\textsubscript{C\textsubscript{1}} = 1 at hydrogen pressures from 23 to 300 kbar [1].

The C\textsubscript{1} hydrate can be considered as H-filled high-pressure ice-II with a rhombohedral structure [1]. The hydrogen content of the C\textsubscript{1} phase at room temperature and hydrogen pressures 7.5–23 kbar lies in the range X\textsubscript{C\textsubscript{1}} \(= 0.1–0.25\), the most likely value being X\textsubscript{C\textsubscript{1}} \(= 1/6 = 0.17\) [1]. Assuming that the triple point at 3.6(1) kbar and \(+1(1)\) °C represents the Liq.+sII+C\textsubscript{1} equilibrium [5,6], volumetric results of Ref. [6] gave X\textsubscript{sII} \(= 0.32(2)\) and X\textsubscript{C\textsubscript{1}} \(= 0.10(2)\) near this point and along the sII → C\textsubscript{1} line at temperatures down to \(-22\) °C.

The sII → C\textsubscript{1} transformation is rather unusual, because it is accompanied by a decrease of the equilibrium hydrogen solubility in the solid phase at increasing pressure. The resulting emission of gaseous hydrogen is of interest, in the first place, for planetary science, as hydrogen and water are among the basic building materials of many icy satellites, and the sII → C\textsubscript{1} transformation could play a key role in their evolution.

To directly determine the hydrogen content of the C\textsubscript{1} hydrate, we have recently synthesized H\textsubscript{2}O–H\textsubscript{2} samples from the liquid at a hydrogen pressure of 18 kbar and room temperature (open triangle in Fig. 1) and quenched them under pressure to the temperature of liquid nitrogen [7]. An X-ray study showed the samples to be composed of a mixture of C\textsubscript{1} and ice-VI, which -- in the absence of hydrogen -- would have been the stable phase under the chosen T–P conditions of synthesis of the C\textsubscript{1} phase. Assuming that there was no hydrogen in the ice-VI phase, hot extraction gave X\textsubscript{C\textsubscript{1}} \(= 1/6\) for the C\textsubscript{1} phase [7] in agreement with the estimate in Ref. [1].

In the present work, we initially planned to complete the investigation of phase relations in the H\textsubscript{2}O–H\textsubscript{2} system by studying the hydrogen content and crystal structure of C\textsubscript{1} samples synthesized near the line of the sII → C\textsubscript{1} transformation (the synthesis conditions are shown by the open rhombs in Fig. 1) and quenched to the N\textsubscript{2} temperature. Quite unexpectedly, we produced a new hydrate...
with the structure never observed in the high-pressure ices or gas hydrates studied so far.

2. Experimental details

Three samples of the new hydrate denoted C0 were produced using a monostatic device [8] made of beryllium bronze, with an inner diameter of 8 mm, in which gaseous hydrogen was compressed by a moving piston. The hydrogen pressure was measured with an accuracy of ±0.5 kbar, the temperature ±3 ºC. The samples were made of distilled water frozen and powdered in an agate mortar under liquid nitrogen prior to the high-pressure experiment in order to speed up the kinetics of hydrogen absorption. Approximately 300 mg of the powder was placed into the high-pressure chamber cooled to −20 ºC and the chamber was filled with gaseous hydrogen under a pressure of 1.5 kbar. The hydrogen pressure was then raised to 2.5 kbar at −20 ºC and kept constant for 30 min that transformed the sample to the sII phase [6]. The gas was further compressed to a pressure near 5 kbar (open rhombs in Fig. 1) and kept constant for 1 h. According to Ref. [6], the procedure used should have completely transformed the sample to the higher hydrate, which was expected to be the C1 phase. After the hydrogenation was over, the monostasis was immersed in liquid nitrogen, cooled to 77 K in about 3 min and disassembled. When not in use, the H2O–H2 samples thus produced were stored in liquid N2 to avoid hydrogen losses.

The crystal structure of the obtained H2O–H2 samples was studied by powder X-ray diffraction at ambient pressure and 80 K using a Siemens D500 diffractometer equipped with a home-designed nitrogen cryostat that permitted loading the powder samples without their intermediate warming. The diffraction data were analyzed with a computer program [9] based on the Rietveld profile refinement technique. The hydrogen content and thermal stability of the samples were examined by hot extraction into a pre-evacuated volume.

The studies of the quenched H2O–H2 samples were supplemented by in situ volumetric measurements of an isotherm at −18 ºC and an isochor at hydrogen pressures near 6 kbar using a piston-cylinder high-pressure chamber with an inner diameter of 12 mm [10]. The pressure was measured with an accuracy of ±0.03 kbar, the temperature ±0.5 ºC, the volume ±1 mm3. The procedure applied to convert the starting powder of ice-Ih to the sII phase was the same as in the case of the monostatic device. After the formation of the sII phase at 2.5 kbar at −20 ºC was completed, the volume and the temperature in the chamber were varied as required.

3. Results and discussion

Fig. 2 shows an X-ray diffraction pattern of one of the H2O–H2 samples prepared in the present work (a) and, for comparison, a pattern of a C1 sample from Ref. [7] (b). The C1 sample was composed of a mixture of approximately equal amounts of the C1 phase and high-pressure ice-VI, and was also contaminated with ice-Ih condensed on the surface of the sample when it was loaded into the X-ray cryostat. As one can see, our new H2O–H2 sample did not contain the C1 phase or ice-VI. The ice-Ih impurity manifested itself by three weak lines at 2θ = 22.8, 24.3 and 25.9 º. The sample holder gave a weak line at 2θ = 27.6 º. All other lines in Fig. 2a can be indexed to a hexagonal unit cell with a = 6.633 Å and c = 6.20 Å. The (00l) lines with l = 1, 2 and 4 are absent that implies the reflection condition l = 3n, where n is an integer. None of the known phases of ice or gas hydrates can give such a diffraction pattern.

The diffraction patterns of other two C0 samples studied in the present work looked similar. However, the unit cell parameters of different samples did not fully coincide and differed within ±0.01 Å. The line intensities also varied from sample to sample, so the crys-
tal structure of the C₀ phase could not be reliably determined on the basis of the available powder diffraction results. Our very preliminary results of a profile analysis of the measured X-ray patterns can be described as follows.

The I = 3n extinction condition is satisfied for six trigonal space groups, which can be considered in pairs: P3₁ and P3₂; P3₁2₁ and P3₂12; P3₁2 and P3₂12. The groups in each pair differ from each other only by the direction of the screw axis rotation. This direction is indistinguishable from the powder diffraction data, so we restricted ourselves to only three groups, P3₁ and P3₁2 and P3₂12. We started modelling the structure of the C₀ phase using the more symmetrical P3₁2 and P3₂12 groups. The P3₁2 group provided a significantly better agreement with the experimental data than the P3₂12 group, so the P3₂12 group was ruled out. Using the P3₁ group and, correspondingly, varying 9 positional parameters instead of 3 did not noticeably improve the fit, so we had no reason to assume that the symmetry of the C₀ structure was lower than P3₁2.

The proposed description of the oxygen sublattice in the space group P3₁2 allowed the most satisfactory fit to the line intensities for all three studied C₀ samples and gave a reasonable value of 2.78 Å for the O–O interatomic distances. The profile fit shown in Fig. 2a by the thin solid line is calculated assuming that the oxygen atoms occupy three types of crystallographically non-equivalent positions in the unit cell of the C₀ phase. These are the 3a₁ positions with the positional parameter x = 0.23 and occupancy ω = 1; the 3b positions with x = 0.75 and ω = 1 and the half-filled 3a₂ positions with x = 0.10 and ω = 0.5. The 6 oxygen atoms/unit cell occupying all 3a₁ (x = 0.23) and 3b (x = 0.75) sites form channels along the c-axis. These channels accommodate the half-filled 3a₂ oxygen sites and one can expect that these 3a₂ sites serve as stoppers transforming the channels into the chains of voids. If every such void is occupied with one H₂ molecule, the hydrogen content of the hydrate reaches an H₂/H₂O ratio of 1.5/7.5 = 0.2. The total number of the oxygen atoms in the unit cell of the C₀ phase, 7.5 atoms/unit cell, corresponds to a density of about 1 g/cm³.

We find it necessary to note again that the results of profile analysis discussed above can only be considered as preliminary ones. The fitting parameters were chosen so as to equally well describe three diffraction patterns of different C₀ samples. The line intensities in these patterns being different, this gave us rather poor profile factors of Rₚ = 14%, Rₑ = 18% and χ = 0.14 with the expected Rₑ = 5%. Nevertheless, we believe that the proposed P3₁2 model reflects some intrinsic features of the C₀ structure and could make a starting point for its future refinements.

Fig. 3 demonstrates a significant difference in the thermal stability of the C₀ and C₁ phases in vacuum. If heated at 25 °C/min, the C₁ phase starts evolving hydrogen at ≈ 140 K and completely decomposes at ≈ 200 K. The hydrogen release from the C₀ phase begins immediately on heating above 77 K and completes at ≈ 170 K. The maximum amount of hydrogen evolved from the C₀ samples reached X₀ = 0.13. However, in view of the instability of the samples at a nearly N₂ temperature, the equilibrium hydrogen content of the C₀ phase could be higher under the synthesis conditions (Pₑ ≈ 5 kbar and T = −20 °C). In particular, it could reach X₀ = 0.2 corresponding to the complete H₂ filling of voids in the proposed P3₁2 water sublattice of this hydrate.

It is interesting to mention that a heating of the C₀ sample to 100 K for 10 min, which removed the major portion of the hydrogen (see Fig. 3a), did not change the intensity distribution in its X-ray pattern at 80 K compared to that measured before the heating, and the lattice parameters of the C₀ phase only decreased by about 0.01 Å. After further heating to 140 K resulting in the loss of nearly all hydrogen, the C₀ phase transformed to metastable cubic ice Ic.

According to the T–P diagram of the H₂O–H₂ system presented in Fig. 1, the C₀ phase was synthesized inside the stability range of the C₁ phase. We think that the diagram is incomplete. It should include the stability region of the C₀ phase, and our samples were synthesized inside this region.

In any case, it is very unlikely that the C₁ phase was formed at ≈ 5 kbar and −20 °C. It is most probably transformed to the C₀ phase in the course of lowering the temperature to 77 K and pressure to 1 bar. In the first place, a similar procedure saved the C₁ phase in the samples prepared at a higher pressure of 18 kbar and +20 °C [7], therefore no C₁ → C₀ transformation could occur at liquid N₂ temperature and lower pressures. Secondly, the diffraction patterns of the C₀ samples showed no traces of the C₁ phase, while the complete C₁ → C₀ transformation in the course of the rapid cooling to the liquid N₂ temperature was not likely. Finally, as seen from Fig. 4, cooling the C₁ phase from 5 kbar and −20 °C brings it into the stability region of ice-II in the T–P diagram of water without hydrogen [11]. The C₁ phase is actually ice-II filled with H₂ molecules weakly interacting with the H₂O network [1]. Consequently, even if the C₁ phase lost some hydrogen at decreasing hydrogen pressure, its H₂O sublattice would have remained unchanged rather than transformed to a new structure, the more so that ice-II without hydrogen can be recovered to ambient pressure at liquid nitrogen temperature [12]. To know more about the T–P stability region of the C₀ phase, we supplemented volumetric results of Refs. [6,7] with measurements of an isotherm at −18 °C and hydrogen pressures up to 8 kbar and an isochor at pressures near 6 kbar. Both curves are shown in Fig. 5. The isochor is also plotted in Fig. 4 together with isochors measured in Refs. [6,7].

P–V isotherms in the H₂O–H₂ system were earlier measured at pressures up to 4.7 kbar [6]. Similar to those, the isotherm presented in Fig. 5 was constructed in the regime of a step-wise increase in the total volume, V, of the system. Changing the volume led to a temporal drift of the pressure. The drift lasted about
20 min in the interval of the phase transition at $P_{H_2} \approx 3.8$ kbar and <5 min outside this interval. The volume was held constant until the hydrogen pressure stopped changing, and the final value was plotted in the figure.

As one can see from Fig. 5, the isotherm measured at $-18\,^\circ C$ and pressures $2.5-8$ kbar only shows one discontinuity at $P_{H_2} \approx 3.8$ kbar attributable to a phase transformation. This can only be the sII $\rightarrow$ C0 transformation and not sII $\rightarrow$ C1 as considered earlier [6]. As seen from Fig. 4, the isochors constructed at pressures from $\approx 4.5$ to $\approx 7.5$ kbar and $T \geq -18\,^\circ C$ only have steps near the melting curve. These suggest that the C0 phase is formed from the sII phase and does not transform to the C1 phase at hydrogen pressures up to $7.5$ kbar and temperatures from $-18\,^\circ C$ to the melting temperature. Correspondingly, the triple point at $3.6(1)$ kbar and $+1(1)^\circ C$, which was earlier considered to be the point of the Liq. $+$ sII $+$ C1 equilibrium [5,6], is the invariant Liq. $+$ sII $+$ C0 point. The line radiating downwards from this point in the $T$-$P$ diagram of the H2O–H2 system (Figs. 1 and 4) is the equilibrium line of the reversible sII $\rightarrow$ C0 transformation.

Results of the present paper show that the C0 phase is stable below the melting curve, which ascends to $\approx 25\,^\circ C$ at 7.5 kbar. According to [1], the C1 phase is stable at temperatures above 22(3) $^\circ C$ and pressures above 7.5 kbar. The line of the C0 $\leftrightarrow$ C1 transformation should therefore cross the melting curve at a pressure near 7.5 kbar. If the available experimental melting points of ices in a hydrogen atmosphere shown in Fig. 1 are fitted by smooth curves separately at pressures below 8 kbar and above 6 kbar, this gives a bent at $\approx 7$ kbar and $\approx 20\,^\circ C$ (see thin solid curves in Figs. 1 and 4). One can speculate that this is the triple point of the Liq. + C0 + C1 equilibrium. (Note that the suggested location of the triple point at a pressure of 7 kbar does not contradict the observed absence of the C0 $\rightarrow$ C1 transformation at pressures up to 7.5–8 kbar because of the baric hysteresis characteristic of phase transformations between different hydrogen hydrates [3,6].)

4. Conclusions

A new hydrate denoted C0 is discovered in the H2O–H2 system. The trigonal crystal structure of this hydrate has no analogue among the structures of high-pressure phases of ice and the large variety of gas hydrates studied so far. The occurrence of the C0 hydrate necessitated a revision of the $T$-$P$ diagram of the H2O–H2 system in the pressure range of a few kilobars. Our experimental results suggest that the C0 hydrate is stable in the $T$-$P$ region below 8 kbar, which was earlier considered as part of the stability field of the C1 hydrate. Constructing the high-pressure boundary of the C0 stability field requires further in situ measurements at hydrogen pressures above 8 kbar and temperatures below $-20\,^\circ C$. The work on extending the operability of our volumetric technique to this $T$-$P$ range is in progress.

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