Formation and Composition of the Clathrate Phase in the H₂O–H₂ System at Pressures to 1.8 kbar

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The transition of the hexagonal ice phase I_h to the clathrate phase sII has been found in the H₂O–H₂ system at a pressure of about 1 kbar under conditions of an excess of gaseous hydrogen. The pressures of the $I_h \longrightarrow s$II and sII $\longrightarrow I_h$ transitions have been determined over a temperature range from –36 to –18°C, and the pressure dependence of the synthesis temperature of the clathrate phase from a liquid at pressures from 1.0 to 1.8 kbar has been constructed. The solubility of hydrogen in the I_h and sII phases and in liquid water has been measured. The concentration of hydrogen in the clathrate phase sII is about 1.2 wt % (10 mol %) near the boundary of the sII $\longrightarrow I_h$ transition, and it increases to 2 wt % (16 mol %) at a pressure of 1.8 kbar. © *2005 Pleiades Publishing, Inc.*

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Dyadin *et al.* [1] studied the H₂O–H₂ system by differential thermal analysis and found a region with anomalous behaviors of the melting temperature and the kinetics of melting of ice in an atmosphere of hydrogen at pressures from 1 to 3.6 kbar. They hypothesized that the clathrate phase of hydrogen hydrate was formed in this pressure range. Indeed, the clathrate phase sII of hydrogen hydrate was synthesized more recently [2, 3] from a liquid at a pressure of about 2 kbar and at –24°C. Lokshin *et al.* [3] studied the composition of this phase by neutron-diffraction analysis and found that H₂/H₂O = (32 + X)/136, where X varied from 0 to 16 depending on pressure and temperature.

The value of X = 16 corresponds to the dissolution of 3.8 wt % hydrogen in ice. Because of such a high concentration of hydrogen in ice at the pressure $P \approx$ 2 kbar, which is reachable within ice planet satellites, a study of the H₂O–H₂ system at $P \leq 2$ kbar is of considerable interest in either high-pressure physics and chemistry or planetology [2].

The aim of this work was to study experimentally the transition of the hexagonal phase I_h of low-pressure ice to the clathrate phase sII and vice versa and to study the transition from the liquid phase to the clathrate phase. The measurements were performed under conditions of an excess of molecular hydrogen. The transitions were determined from changes in the solubility of hydrogen in H₂O at pressures from 0.2 to 1.8 kbar.

The experimental setup was described elsewhere [4]. High-purity hydrogen (99.9999%) was prepared by the thermal decomposition of the hydride of the Ti–Fe–V alloy. The amount of hydrogen absorbed by a sample was determined volumetrically by measuring pressure and temperature in calibrated volumes of the measuring system. A modified van der Waals equation for strongly compressed hydrogen was used as the equation of state for the gaseous phase; this equation took into account the temperature and pressure dependence of coefficients [5]. Published data [6] on the pressure and temperature dependence of the molar volumes of liquid water and ice I_h were used. The molar volume of the clathrate phase sII was evaluated based on the published value [2] of the lattice parameter $a \approx 17.05$ Å of this cubic phase at $P = 2.2$ kbar and $T = -39°C$.

The sample of H₂O had a volume of about 1 cm³ and consisted of individual segments with characteristic sizes of about 5 mm. A steady-state pressure reached after changing temperature or total hydrogen amount in an autoclave was measured in the experiments. The drift of pressure lasted about 5 min, about 1 h, or 3–5 min in the absence of phase transitions, in the $I_h \longrightarrow s$II and sII $\longrightarrow I_h$ transitions, or in the synthesis of the sII phase from a liquid, respectively. With consideration for errors in the determination of various phase volumes in the H₂O–H₂ system, the concentration of hydrogen in condensed phases was determined to within ±0.05 wt %.

Figure 1 shows a typical solubility isotherm of hydrogen in water ice. The concentration of hydrogen in the I_h phase at $T = -22°C$ increased from 0.1 wt % at $P = 0.5$ kbar to 0.3 wt % at $P = 1$ kbar. A transition to the clathrate phase sII occurred at a higher pressure, and the amount of dissolved hydrogen increased to 1.2 wt %. As the pressure was increased to 1.8 kbar, the solubility of hydrogen in the clathrate phase monotonically increased to approximately 2 wt %.
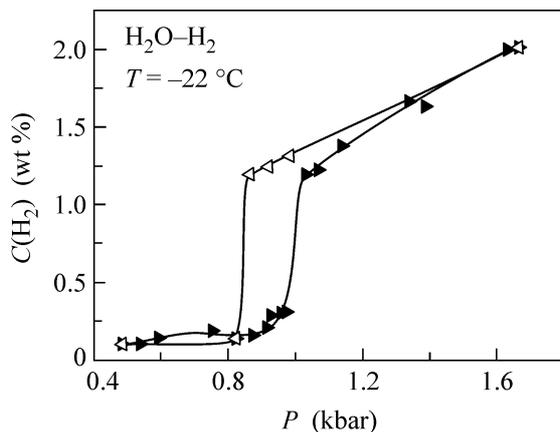
Fig. 1. Solubility of hydrogen in ice at –22°C. Closed and open triangles refer to increasing and decreasing pressure, respectively.

Fig. 2. Solubility of hydrogen in H_2O in the course of decreasing temperature at a pressure of 1.3 kbar.

A smooth decrease in the concentration of hydrogen in the clathrate phase was observed in the course of decreasing pressure at all of the test temperatures. For example, as can be seen in Fig. 1, at $T = -22$°C, the composition decreased from 2 wt % at $P = 1.8$ kbar to 1.2 wt % at $P \approx 0.8$ kbar; thereafter, a transition to the ice phase I_h occurred.

Figure 2 shows the isobar of hydrogen solubility in liquid water and the sII phase at $P \approx 1.3$ kbar. The amount of hydrogen dissolved in the liquid increased from 0.2 wt % at +16°C to 0.4 wt % at –18°C. After the transition to the clathrate phase, the solubility of hydrogen increased to 1.9–2.0 wt %.

The phase transition points in the $H_2O–H_2$ system determined in this work were plotted in the $T–P$ diagram, which is shown in Fig. 3. The pressure of the transition of ice I_h to the clathrate phase sII is about 1 kbar, and it only slightly depends on temperature. The pressure of the reverse transition of the sII phase to ice I_h decreased with temperature from 0.9 kbar at –18°C to 0.5 kbar at –36°C. The synthesis of the clathrate phase from the liquid occurred at a temperature 5–7°C lower than the melting temperature of ice I_h at the same pressure in the absence of hydrogen.

In the tested range of temperatures to –36°C, a maximum concentration of hydrogen in ice I_h was about 0.3 wt %; this concentration was reached at the pressure $P \approx 1$ kbar near the boundary of a transition to the clathrate phase sII (closed circles in Fig. 3). The concentration of hydrogen in the sII phase changed from approximately 1.2 wt % near the boundary of a transition to ice I_h (to the right of open circles in Fig. 3) to 2 wt % at a pressure of 1.8 kbar.

The solubility of hydrogen in the I_h and sII phases over the given temperature and pressure ranges was not studied previously. Lokshin *et al.* [3] evaluated the hydrogen content of the sII phase at temperatures lower than –73°C based on the most likely interpretation of
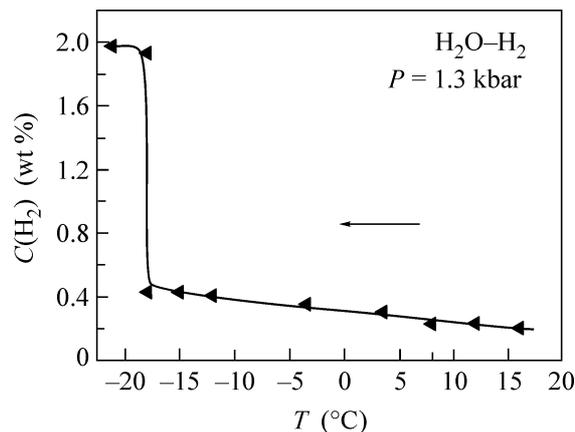
the neutron-diffraction patterns of $D_2O–D_2$ polycrystals measured at two pressures of 1 bar and 2 kbar over a temperature range from –233 to –73°C. According to this evaluation, the concentration of hydrogen in the sII phase of the $H_2O–H_2$ system can vary within a range from 2.5 wt % ($H_2/H_2O = 32/136$) to 3.8 wt % ($H_2/H_2O = 48/136$).

A minimum value of 1.2 wt % obtained in this work for the concentration of hydrogen in the sII phase is lower than a value of 2.5 wt % by a factor of about 2; according to Lokshin *et al.* [3], the latter value is required for the stability of the clathrate structure sII. The linear extrapolation of the solubility isotherms of
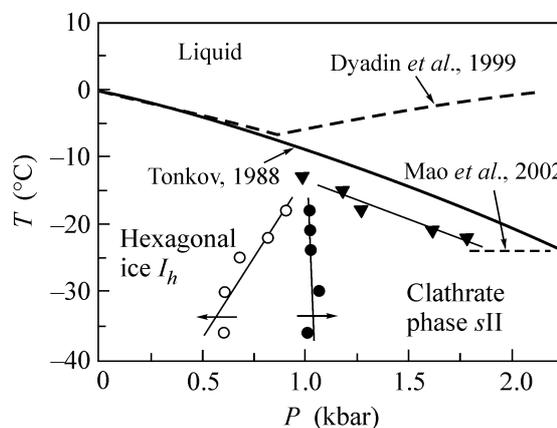
Fig. 3. $T–P$ diagram of the $H_2O–H_2$ system. Closed and open circles refer to $I_h \longrightarrow sII$ and $sII \longrightarrow I_h$ phase transition points, respectively. Closed triangles indicate the conditions of the synthesis of the sII phase from a liquid with decreasing temperature (this work) and the dashed horizontal segment refers to published data [2]. The dashed curve shows the melting line of the clathrate phase sII determined by Dyadin *et al.* [1] and the solid line shows the melting temperature of ice I_h in the absence of hydrogen [7].

hydrogen in the sII phase (e.g., see Fig. 1) to a maximum pressure of 3.6 kbar (according to Dyadin *et al.* [1], this is the maximum pressure at which this phase can exist) gave a value of about 4 wt %. This value is close to an estimated value of 3.8 wt % found by Lokshin *et al.* [3] for the maximally possible hydrogen concentration in the sII phase.

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