Phase Transitions in the Water–Hydrogen System at Pressures up to 4.7 kbar

Vladimir E. Antonov,*† Vadim S. Efimchenko,† and Marek Tkacz‡
Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District, Russia, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Using a volumetric technique, a T–P diagram of phase transformations between the hydrogen-rich clathrate hydrate (sII phase), hydrogen-filled ice II (C1 phase), and the liquid (L) is studied in the H2O–H2 system at pressures up to 4.7 kbar and temperatures from −22 to +15 °C. The volume and entropy effects of these transformations are established in the vicinity of the triple point of the L + sII + C1 equilibrium located at P = 3.6(1) kbar and T = +1(1) °C. The estimated molar ratios H2/H2O of phases at the triple point are X_L = 0.04(2), X_sII = 0.32(2), and X_C1 = 0.10(2).

Introduction

Figure 1 presents the available experimental data on phase relations in water1 (dashed lines) and in water placed in an atmosphere of molecular hydrogen (solid lines) at pressures up to 7 kbar. The melting line of ices in a H2 atmosphere was constructed by differential thermal analysis2 (thin solid line in Figure 1) at pressures up to 15 kbar and by optical microscopy3 at pressures 7–32 kbar. The experiments showed that the melting temperature of low-pressure hexagonal ice Ih in hydrogen nearly coincides with that in the absence of hydrogen at pressures up to 1 kbar. At about 1, 3.6, and also 25.5 kbar (not shown in Figure 1), the melting line of ices makes sharp bends signaling the formation of new solid phases rich in hydrogen.

The three hydrogen-rich H2O–H2 phases are called hydrogen clathrate hydrates, and their crystal structures are networks of hydrogen-bonded H2O molecules encasing guest H2 molecules that only weakly interact with the network by van der Waals forces. Neutron diffraction investigations showed that the hydrate formed in the pressure interval 1–3.6 kbar has an sII-type crystal structure.4 Its cubic unit cell is composed of 136 H2O molecules and, depending on the pressure and temperature, can accommodate from 27.25 to 486 guest molecules of H2, which gives a molar ratio H2/H2O of X = 0.200–0.353.

The hydrates stable at higher hydrogen pressures were denoted C1 and C2 and studied by Raman spectroscopy and X-ray diffraction.5 The C1 phase, which is expected to be stable at hydrogen pressures 3.6–25.5 kbar, was examined by X-rays at 21 kbar and 22 °C. The structure of its H2O sublattice was shown to be similar to that of rhombohedral high-pressure ice II (the stability field of this ice is labeled “II” in Figure 1). On the basis of results of the Raman studies, the hydrogen content of the C1 phase was assumed to be invariable within the examined T–P range and equal to X = 1/6, with the H2 molecules occupying each of the six accessible cages in the unit cell composed of 36 H2O molecules. Similar investigations demonstrated6 that the C2 phase had a diamond-like H2O sublattice and X = 1 at a hydrogen pressure of 31 kbar and room temperature.

Figure 1. T–P diagram of phase transitions in the H2O–H2 system with the H2 gas taken in access (solid lines) superimposed onto the equilibrium diagram of H2O1 (dashed lines; phase fields are labeled with the encircled symbols). The upper thin solid curve shows the melting line of water ices in a hydrogen atmosphere determined by differential thermal analysis.3 Three thick solid lines radiating from the L + Ih + sII triple point are constructed using a volumetric technique and represent phase equilibria between the L, Ih, and sII phases. The solid triangles6 and solid squares9 connected with the horizontal lines indicate the L → sII transitions, and the open square8 stands for the sII → L transition, all determined by optical microscopy in diamond anvils.

Phase relations in the H2O–H2 system are of significant interest, in the first place, for planetary science because hydrogen and water are among the basic building materials of many planets. In this connection, studies of the sII hydrogen hydrate are most attractive as its synthesis pressure is within the range of interior conditions of small, icy satellites, and transformations of the sII phase to other phases may play a key role in the evolution of these icy bodies.4 Using a volumetric technique, we have earlier examined transitions between the sII and Ih and L (liquid) phases in the H2O–H2 system7 and D2O–D2 system5,8 at pressures up to 1.8 kbar. The T–P–X diagrams of these systems proved to be very similar, and their comparative analysis allowed us to establish rather accurately the position of the Ih ↔ sII equilibrium line, the X(P) dependence for the sII phase, and the hydrogen contents of the sII and Ih and L phases at the triple point of the L + Ih + sII equilibrium.5 The constructed portion

* To whom correspondence should be addressed. E-mail: antonov@issp.ac.ru.
† Russian Academy of Sciences.
‡ Polish Academy of Sciences.

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of the equilibrium $T$–$P$ diagram of the H$_2$O–H$_2$ system is shown in Figure 1 by the thick solid lines.

In the present work, using another type of volumetric technique, we constructed the line of the sII ↔ C$_1$ transformation, which is the high-pressure boundary of the stability region of the sII phase, and estimated the hydrogen contents of the sII and C$_1$ and L phases near the second triple point of the L + sII + C$_1$ equilibrium. We also re-examined the position of this triple point because experimental results of ref 9 (open and solid squares in Figure 1) did not agree well with the melting curve of ices in the H$_2$O–H$_2$ system constructed in ref 2 (thin solid curve in Figure 1).

Experimental Details

The experiments were carried out in a piston–cylinder high-pressure chamber$^{10}$ with an inner diameter of 12 mm, in which gaseous hydrogen was compressed or decompressed by a movement of the piston. The movement was followed by a precise mechanical indicator providing the accuracy $\pm 1$ mm$^3$ in the determination of the volume change. The pressure was measured by a managanin wire gauge accurate to within $\pm 30$ bar. The temperature was regulated with an accuracy of $\pm 0.5 \, ^\circ$C by circulating the cooling liquid through the jacket of the high-pressure chamber.

Each studied sample of H$_2$O was 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 and desorption. The powder was poured into the high-pressure chamber cooled below $-23 \, ^\circ$C; the chamber was filled with gaseous hydrogen under a pressure of 1.5 kbar, and the gas was further compressed to 2.2–2.5 kbar. The sample was exposed to these conditions until its transformation to the sII phase was complete, and the volume or the temperature in the chamber was then varied as required. The preliminary cooling to $-23 \, ^\circ$C was necessary to avoid the melting of the starting sample of frozen water, which had no time to absorb enough hydrogen and to transform to the sII phase, on crossing the melting line of ice Ib (see Figure 1).

The mass of the H$_2$O samples was limited to $1.3-1.7 \, g$ so as not to damage the electrical leads inside the chamber by the densified ice powder at the maximum compression. The total mass of hydrogen in the high-pressure chamber was $0.4-0.45 \, g$. This gave a molar ratio of H$_2$/H$_2$O > 2; therefore, the hydrogen gas in the chamber was always in excess during our experiments.

The solubility of water in gaseous hydrogen was earlier shown to be vanishingly small at 27 $^\circ$C and pressures up to 6 kbar. We therefore assumed that the gaseous phase in our high-pressure experiments was pure hydrogen and used the equation of state of H$_2$ from ref 11 to describe its $P$–$V$–$T$ relations.

Results and Discussion

$T$–$P$ Phase Diagram. The obtained diagram of phase transformations in the H$_2$O–H$_2$ system is shown in Figure 2.

The sII ↔ C$_1$ transformation was examined by constructing isotherms of pressure, $P$, measured in the course of a stepwise increase and decrease in the total volume, $V$, of the H$_2$O–H$_2$ system. The volume itself could not be accurately measured and was counted from a value arbitrary chosen in each experiment. Changing the volume in the high-pressure chamber led to a temporal drift of the pressure. The drift lasted less than 5 min in the absence of phase transitions and about 20 min in the intervals of the sII → C$_1$ and C$_1$ → sII transitions. While constructing isotherms, the volume of the system was held constant until the pressure stopped changing and that final value was plotted in the figure. Representative isotherms $P(V)$ are shown in Figure 3a in a more convenient form, with the $P$-axis directed horizontally. The points of the sII → C$_1$ and C$_1$ → sII transitions indicated in Figure 2 were determined from an abrupt increase in the duration of the pressure drift arising after the increase and decrease in volume, respectively.

The temperature dependences of pressures of the sII → C$_1$ and C$_1$ → sII transitions in Figure 2 are approximated with thin dashed lines, and the thick solid line representing the sII ↔ C$_1$ equilibrium is plotted in the middle between them. The line of

![Figure 2](image-url)

![Figure 3](image-url)
the sII ↔ C1 equilibrium thus constructed crosses the melting line of ices determined in ref 2 (thin solid curve in Figure 1) exactly at the point 3.6 kbar and 1 °C, where the curve makes a sharp bend.

This bending point was assumed to well reproduce the point of invariant equilibrium of the liquid with the sII and C1 phases because the melting temperature of most substances is very close to the temperature of phase equilibrium between the solid and liquid. The observed intersection of the three independently determined phase boundaries at one point strongly corroborates this assumption.

We also constructed two isochors intersecting the melting curves of the sII and C1 phases near the L + sII + C1 triple point. The isochors are shown in Figure 4. The smooth curves fitting these isochors are copied to Figure 2 as dash-dot lines.

On the upper isochor in Figure 4, there is a step at temperatures 5–9 °C. The position of this step well agrees with the melting curve of the C1 phase constructed in ref 2 and drawn with a thick solid line in Figure 2. The good agreement between the melting conditions determined by different techniques suggests that the melting curve from ref 2 should be accurate as a whole, and it should well represent the C1 ↔ L equilibrium. Furthermore, the melting curve of the sII phase measured in ref 2 should accurately reproduce the sII ↔ L equilibrium near the L + sII + C1 triple point; otherwise, it would not meet with the other two equilibrium lines at this point.

At the same time, it was mentioned in ref 2 that melting of the sII phase was a very slow process, and the equilibrium was not achieved in some DTA experiments. In fact, we earlier observed a certain overheating of the sII phase in the DTA measurements at pressures below 1.8 kbar (compare the melting curves plotted by the thin and thick solid lines in Figure 1). To check whether the DTA curve well represents the sII ↔ L equilibrium in the range of the shallow maximum located at 3.0–3.4 kbar, we constructed an isochor crossing this melting curve, \( T_m(P) \), at a pressure of 3.3 kbar. The isochor is shown at the bottom of Figure 4. As one can see, it is close to a straight line and shows no stepwise anomalies. This implies a zero volume effect, \( \Delta V_m \), of melting and therefore justifies the occurrence of a maximum on the melting curve. (Clapeyron’s equation with \( \Delta V_m = 0 \) gives \( \frac{dT_m}{dP} = \Delta V_m/\Delta S_m = 0 \) because the change in entropy, \( \Delta S_m \), is always positive on melting.)

Correspondingly, we extended the equilibrium melting curve from ref 5 up to the L + sII + C1 triple point (thick solid line in Figure 2) so that it asymptotically approached the melting line from ref 2 near its maximum.

The melting point of the sII phase from ref 9 (open square in Figure 1) is located rather far above the melting line thus constructed and should therefore be considered as a nonequilibrium result. As for the reverse transition—crystallization of the sII phase from the liquid at decreasing temperature—it always requires significant supercooling.

At pressures up to 1.8 kbar, the sII phase crystallizes together with ice Ih, some 4 °C below the melting curve of this ice shown in Figure 1 by the dashed line. The effect of simultaneous crystallization of the sII phase and metastable ice Ih was explained in ref 8. Namely, the growing particles of ice Ih should supersaturate the surrounding of water with hydrogen, thus providing more favorable conditions for the nucleation and growth of the hydrogen-rich sII phase. In its turn, the growing sII phase depletes the water of the dissolved hydrogen, therefore facilitating the nucleation and growth of the hydrogen-poor ice Ih. The formation of the sII phase on cooling the liquid to −24 °C at pressures near 2 kbar observed in ref 6 (solid triangles in Figure 1) agrees with results of refs 7 and 8. The formation of the sII phase at the same temperature and pressures up to 6 kbar (solid squares in Figure 1), deep inside the stability region of the C1 phase, needs further investigation.

**Volume and Entropy Effects of Phase Transitions near the L + sII + C1 Triple Point.** The volume effect of the sII → C1 transition was determined from the experimental isotherms \( \Delta V(P) \).

As seen from Figure 3a, the isotherms measured at increasing and decreasing pressure do not coincide in the interval about 0.5 kbar above the sII → C1 transition. The observed difference apparently reflects the incompleteness of this transition at increasing pressure. Below the reverse C1 → sII transition, the isotherms do not coincide either; only in this case they go parallel to each other and do not converge. Consequently, the difference between the isotherms in this pressure range should rather be attributed to a certain systematic error accumulated during the whole cycle of the pressure increase and decrease (e.g., caused by a slight gas escape from the high-pressure chamber). We therefore assumed that the C1 → sII transition was nearly complete right below the interval of the steep volume increase. The volume effect of the transition was determined as shown in Figure 3b. Within the experimental error, the magnitude of this effect calculated per 1 g-mol of H2O did not depend on the temperature in the examined interval from −21 to −4 °C. Taking into account that the linear fit to the experimental points of the C1 → sII transition (dashed line in Figure 2) passed through the L + sII + C1 triple point at a nearby temperature of +1 °C, the mean value of \( \Delta V_{sII-C1} = 2.01(3) \text{ cm}^3/\text{mol} \) was ascribed to the C1 transition. The observed difference \( \Delta V \) was ascribed to the C1 transition. The observed difference \( \Delta V \) was calculated from the experimental isotherms \( \Delta V(P) \) of the three lines of phase transitions radiating from the triple point.

The volume effects of the C1 ↔ L and L → sII transitions could not be determined from experiment, and we calculated them using the additive relations for the three changes in volume, \( \Delta V_i \) and \( \Delta S_i \), accompanying phase transitions around the L + sII + C1 triple point:

\[
\sum \Delta V_i = 0 \quad \text{and} \quad \sum \Delta S_i = \sum \left(\frac{dT_i}{dP}\right) / \Delta V_i = 0
\]

Using experimental values of \( \Delta V_{sII-C1} \) and the slopes \( \left(\frac{dT_i}{dP}\right) \) of the three lines of phase transitions radiating from the triple point, these two equations give the two missing changes in volume, \( \Delta V_{sII-C1} \) and \( \Delta V_{l-Ih} \). The obtained values of \( \Delta V_i \) and \( \left(\frac{dT_i}{dP}\right) \) are \( \Delta S = \left(\frac{dT_i}{dP}\right)/\Delta V_i \), and changes in enthalpy \( \Delta H = T \Delta S \) near the L + sII + C1 triple point are listed in Table 1. For comparison, Table 1 also presents analogous data for phase transitions near the L + Ih + sII triple point taken from ref 8.

An analysis of the available experimental data made it possible to produce estimates of the molar volumes and
TABLE 1: Parameters of Phase Transformations in the H₂O–H₂ System near the Triple Points of the L + sII + C₁ Equilibrium (Data of the Present Work) and L + I₀ + sII Equilibrium (Ref 8)∗

<table>
<thead>
<tr>
<th>triple point</th>
<th>transition</th>
<th>ΔV₂, cm³/mol</th>
<th>dV₂/dP, kbar⁻¹</th>
<th>ΔS₂, J/K mol</th>
<th>ΔH₂, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>L + sII + C₁</td>
<td>sII − C₁</td>
<td>−2.01</td>
<td>89</td>
<td>−2.3</td>
<td>−0.62</td>
</tr>
<tr>
<td>(3.6 kbar, 294 K)</td>
<td>C₁ − L</td>
<td>1.66</td>
<td>6.5</td>
<td>25.6</td>
<td>7.01</td>
</tr>
<tr>
<td></td>
<td>L − sII</td>
<td>0.35</td>
<td>−1.5</td>
<td>−23.3</td>
<td>−6.39</td>
</tr>
<tr>
<td>L + I₀ + sII</td>
<td>I₀ − sII</td>
<td>−4.33</td>
<td>128</td>
<td>−3.38</td>
<td>−0.89</td>
</tr>
<tr>
<td>(1.07 kbar, 263 K)</td>
<td>sII − L</td>
<td>2.05</td>
<td>8.5</td>
<td>24.1</td>
<td>6.34</td>
</tr>
<tr>
<td></td>
<td>L − I₀</td>
<td>2.28</td>
<td>−11.0</td>
<td>−20.7</td>
<td>−5.44</td>
</tr>
</tbody>
</table>

∗ The changes in volume (ΔV), entropy (ΔS), and enthalpy (ΔH) are calculated per 1 g-mol of H₂O.

TABLE 2: Molar Ratio (X = H₂/H₂O) and Molar Volume (V) of Phases in the H₂O–H₂ System at the Triple Points L + sII + C₁ (Estimates of the Present Work) and L + I₀ + sII (Results of Ref 8)

<table>
<thead>
<tr>
<th>phase</th>
<th>X</th>
<th>V₂, cm³/mol</th>
<th>X</th>
<th>V₂, cm³/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.04(2)</td>
<td>16.31</td>
<td>L</td>
<td>0.017(5)</td>
</tr>
<tr>
<td>sII</td>
<td>0.32(2)</td>
<td>21.77</td>
<td>sII</td>
<td>0.207(5)</td>
</tr>
<tr>
<td>C₁</td>
<td>0.10(2)</td>
<td>(15.21)</td>
<td>C₁</td>
<td>0.107(2)</td>
</tr>
<tr>
<td>I₀</td>
<td></td>
<td></td>
<td>I₀</td>
<td>0.117(5)</td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td></td>
<td>H₂</td>
<td>20.73</td>
</tr>
</tbody>
</table>

Figure 5. Pressure dependences of the molar volumes of gas-free ice II and of ice II filled with helium and hydrogen (the C₁ phase). The solid square stands for the C₁ phase of hydrogen hydrate at 22 °C. The circles and the solid line drawn through them show the experimental results for heavy ice II at −48 °C fitted with a Birch–Murnaghan equation. The dashed curve is calculated for ice II at 22 °C using the parameters of the equation of state determined in ref 15 (see text). The two solid segments labeled “Londono 1992” are for He-filled heavy ice II. The solid star indicates our estimate of the volume of the hydrogen hydrate C₁ at the L + sII + C₁ triple point. The crossed square is discussed in subsection “Molar Volumes...” the half-blackened squares in subssection “Hydrogen Content...”. The inset compares the data for D₂O14 and H₂O17,18 ice II. of V_C1 in this pressure region could be achieved via an analysis of the P−V−T relations of the “parent” phase of ice II15,16 and helium-filled ice II17,18 studied in more detail.

The solid line in Figure 5 is a third-order Birch–Murnaghan fit to the experimental isotherm (open circles) of the molar volume of heavy ice II at −48 °C determined by neutron diffraction. The dashed line represents the isotherm at 22 °C calculated using a Birch–Murnaghan equation with the same bulk modulus K₀ = 109 kbar and its first derivative K₀′ = 10 as at −48 °C, while the zero-pressure volume was increased from V₀(−48 °C) = 15.42 cm³/mol to V₀(22 °C) = 15.74 cm³/mol, in accordance with the polynomial fit15 to the room-pressure experimental data. As one can see from Figure 5, the experimental point for the C₁ hydrogen hydrate (solid square) is close to the dashed line. If the C₁ hydrate is considered as a hydrogen-filled ice II, this suggests a small volume effect of hydrogen uptake by ice II.

The magnitude and sign of this effect cannot be assessed because of the large uncertainty in the extrapolation of the molar volume of ice II to 21 kbar and 22 °C (see the vertical error bar crossing the dashed line). What can definitely be said is that the effect is small compared to the volume expansion caused by the hydrogen dissolution in liquid water. In fact, if the hydrogen hydrate had X_C₁ = 1/6 as suggested in ref 3 and β ≈ 8 cm²/mol H₂ as water does, its molar volume would exceed that of ice II by a value of 4βX_C₁ ≈ 1.3 cm³/mol. The maximum possible difference in the volumes of the C₁ phase and ice II at 21 kbar and 22 °C is smaller by an order of magnitude. To illustrate this, the crossed square in Figure 5 shows the molar volume of the C₁ phase that it would have in the case of β = 8 cm²/mol H₂.

Cavities in the crystal structure of ice II can also be filled with He atoms. Figure 5 presents two isotherms of the molar volume of such a hydrate studied by neutron diffraction. The isotherms are not very accurate because they were obtained as a linear fit to a few experimental points randomly distributed in the range of helium pressures 2.75−5 kbar and temperatures 21−25 °C.
from -78 to -12 °C. In particular, the difference in the compressibilities of “pure” and He-filled ice II is below the error level. Nevertheless, a comparison of the corresponding isotherms for the helium hydrate and ice II clearly shows a nearly zero volume expansion of ice II with increasing helium content, which reached He/D2O ≈ 1/12 to 1/6 depending on the temperature and helium pressure. This result can be considered as evidence in favor of the assumption discussed above that the molar volume of ice II nearly does not change when the analogues hydrogen hydrate is formed.

The inset to Figure 5 depicts isotherms of the molar volume of D2O ice II measured by piezometry at -35.5 °C and recalculated for -48 °C using the expansivity of D2O ice II. The near position of the isotherms for H2O and D2O ice II at -48 °C shows that the isotopic variation of the molar volume of ice II is negligibly small compared with the uncertainty in the volume effect of hydrogen uptake.

On the grounds of the said, we assumed that the C1 phase in the H2O-H2 system has the same molar volume, V_C1, as ice II containing no hydrogen and that the dependence V_C1(P,T) in a hydrogen atmosphere is described by the equation of state for D2O ice II from ref 15. At pressures from 2.5 to 4.5 kbar and temperatures from -50 to +25 °C, without loss of accuracy, this equation can be approximated as

\[ V_{C1} = 15.59 - 0.106P + 0.0045T \]  

where P is in kbar, T in °C, and V_C1 in cm³/mol H2O. The value of V_C1 at the L + sII + C1 triple point indicated in Table 2 and shown in Figure 5 by the solid star was calculated using this equation.

**Hydrogen Contents of the L and sII Phases near the L + sII + C1 Triple Point.** To immediately obtain the hydrogen contents of phases from volumetric data, it is necessary to know the total amount of each component of the system in addition to the molar volume of each phase. The mass M_{H2O} of water in the condensed phases was always precisely known in our high-pressure experiments, and it did not change with varying the temperature and pressure due to the very low water solubility in the hydrogen gas in the investigated pressure range. At the same time, the total mass M_{H2} of hydrogen in the system could only be estimated with an accuracy no better than 5% that resulted in an unacceptable error of δX ≈ 0.1 in the hydrogen content of the condensed phases. We partly overcame this difficulty by determining the difference in the hydrogen contents of phases that were in equilibrium with each other and by evaluating the possible compositions of these phases from other considerations.

Using the condition that M_{H2} does not change in the course of the sII → L transition and substituting the volume V_L of the liquid phase from eq 1, one gets the equation

\[ X_L = (V_{L0} - V_{sII} - \Delta V_{sII} + V_{H2}X_{sII})/(V_{H2} - \beta) \]  

At the L + sII + C1 triple point, at 3.6 kbar and 1 °C, eq 4 links the compositions of the sII and L phases in a unique fashion because all other parameters are known (V_{L0} = 15.99 cm³/mol; \Delta V_{L→sII} is indicated in Table 1; V_{sII} and V_{H2} in Table 2).

According to ref 6, the hydrogen content of the sII phase reaches its maximum value of X_{sII} = 48/136 ≈ 0.353 at a hydrogen pressure of about 2 kbar when the temperatures is lowered to 50 K. If the sII phase has the same composition at the L + sII + C1 triple point, then eq 4 yields X_L = 0.093 for the liquid at this point. As one can see from Figure 6, such a value of X_L is improbably large.

The solubility of hydrogen in water was earlier measured at temperatures 0–100 °C and hydrogen pressures up to 1000 atm. A linear extrapolation (dashed line in Figure 6) of the experimental isotherm at 1 °C gives X_L = 0.052 at 3.6 kbar. This is the upper limit for X_L at the triple point because the experimental isotherm (solid circles) is convex. In order that the H content of the liquid phase resulting from eq 4 comes down from X_L = 0.093 (open square in Figure 6) to a more feasible value of X_L = 0.04 (solid square), the conjugate sII phase should have X_{sII} = 0.32. An extrapolation of the experimental X(P) isotherms for the H2O–H2 systems to higher pressures demonstrates that X_{sII} = 0.32 is a very likely composition of the sII phase at 3.6 kbar.

The isotherms in refs 5, 7, and 8 looked similar at all investigated temperatures, from -40 to -10 °C. For illustration (Figure 7) we chose one of the D2O–D2 isotherms because those had been measured more accurately than the H2O–H2 isotherms. The portion of the isotherm at pressures above 1 kbar represents the dependence of the equilibrium hydrogen solubility in the sII phase. A linear extrapolation of this dependence to 3.6 kbar gives X_{sII} ≈ 0.35, nearly coinciding with the maximum value of X_{sII} = 48/136 that the sII phase can have. However, there are no reasons to think that 3.6 kbar is a singular point of the X_{sII}(P) dependence, at which X_{sII} reaches the maximum value and then stops changing. It is much more likely that this dependence approaches X_{sII} asymptotically.

As seen from Figure 7a, a smooth prolongation of the experimental X_{sII}(P) dependence so as to asymptotically approach X_{sII} = 48/136 (horizontal dashed line) at increasing pressure requires that 0.32 ≤ X_{sII}(3.6 kbar) ≤ 0.34. This interval of the admissible X_{sII}(3.6 kbar) values was the same for every X_{sII}(P) isotherm measured at temperatures from -40 to -10 °C and could therefore be extrapolated without change to a temperature of +1 °C of the L + sII + C1 triple point. We adopted X_{sII}(3.6 kbar) = 0.32 as the hydrogen content of the sII phase in equilibrium with the L phase at the triple point in order to get a plausible value of X_L = 0.04 from eq 4.

It should be emphasized that the achieved consistency of the X_{sII} and X_L values linked with eq 4 is only possible if \Delta V_{L→sII}...
is equal to 0.35 cm$^3$/mol as in Table 1 or has a larger positive value. For example, $\Delta V_{\text{sII}} = 0$ would require $X_{\text{sII}}(3.6 \text{ kbar}) = 0.30$ to get $X_C = 0.04$. As seen from Figure 7a, this $X_{\text{sII}}$ value is too low for the $X_{\text{sII}}(P)$ dependence to smoothly approach the $X_{\text{all}} = 48/136$ asymptote at increasing pressure. Since $\Delta V_{\text{sII}} > 0$ requires $(dT/dP)_{T<\text{sII}} < 0$ at the triple point, this justifies the occurrence of a maximum on the equilibrium melting curve of the sII phase (see Figure 2), in excellent agreement with DTA results of ref 2.

**Hydrogen Content of the C1 Phase near the L + sII + C1 Triple Point.** On the basis of results of Raman studies, the C1 phase was earlier assumed to be a stoichiometric compound with the maximum hydrogen content $X_C = 1/6 \approx 0.167$ possible from crystallographic considerations. Our estimates showed that the hydrogen content of the C1 phase at the L + sII + C1 triple point is smaller and its most likely value is $X_C = 0.1$.

The estimates were based on the equation

$$X_{\text{sII}} = X_C + (V_{\text{sII}} - V_C + \Delta V_{\text{sII} - C1})/V_{H_2}$$  \hspace{1cm} (5)

resulting from the invariance of the total mass $M_{H_2}$ of hydrogen in the course of the sII $\rightarrow$ C1 transition. Using $\Delta V_{\text{sII} - C1}$ from Table 1, $V_{\text{H2}}$, $V_C$, and $V_C$ from Table 2, and $X_C = 1/6$ suggested in ref 3, eq 5 yields $X_{\text{sII}} = 0.39$ at the L + sII + C1 triple point. This significantly exceeds $X_{\text{H2}}^{\text{cmax}} = 48/136 \approx 0.353$ assessed in ref 6.

There are two variables in eq 5, $V_C$ and $X_C$, whose values are not known with certainty. If $X_C = 1/6$ is assumed to be correct, eq 5 will require $V_C = 15.90$ and 16.58 cm$^3$/mol to get $X_{\text{sII}} = 0.353$ and 0.32, respectively, at 3.6 kbar and 1 °C. If the

$V_C(P)$ dependence is further assumed to obey a Birch–Murnaghan equation with the same $K_0$ and $K'_0$ as ice II, an extrapolation to 21 kbar and 22 °C will transform the two $V_C$ values to those shown in Figure 5 with the half-blackened squares. As one can see from Figure 5, both points thus calculated are inconsistent with experiment (solid square), and the discrepancy is so large that it cannot be eliminated by changing the extrapolation method within reasonable limits.

This result evidences that $X_C$ is significantly less than 1/6 at the L + sII + C1 triple point. There is only one analogue of the C1 phase, the He-filled ice II. Its composition was earlier studied by neutron diffraction and shown to vary from He/D$_2$O $\approx 1/12$ to 1/6 depending on temperature and pressure, while the molar volume practically coincided with that of pure ice II. We therefore examined the effect of varying the hydrogen content of the C1 phase from $X_C = 1/12$ to 1/6 on the composition of the sII phase assuming that the C1 phase had the same molar volume as ice II.

The open stars in Figure 7 show results for the sII phase at the triple point calculated using eq 5. As one can see, the compositions $1/10 < X_C < 1/8$ of the C1 phase are most likely. The value of $X_C = 1/10$ corresponds to $X_{\text{sII}} = 0.32$ which gives an acceptable value of $X_C = 0.04$ if substituted in eq 4. The three compositions satisfy every constraint resulting from extrapolation of the known properties of H$_2$O–H$_2$ phases to the vicinity of the L + sII + C1 triple point. These compositions are indicated in Table 2 together with the corresponding molar volumes.

As an additional test for self-consistency of the obtained results, we examined one more relation between the compositions of an H$_2$O–H$_2$ sample in two single-phase states, sII and C1, at different hydrogen pressures.

$$X_{\text{sII}}^3 = X_{\text{sII}}^{4/136} - V_{\text{sys}}^s - V_{\text{sys}}^c \frac{\mu_{\text{H}_2}^c}{M_{\text{H}_2}^c} + \frac{1 - V_{\text{H}_2}^{s} M_{\text{H}_2}^c \mu_{\text{H}_2}^c}{V_{\text{H}_2}^{s} M_{\text{H}_2}^c \mu_{\text{H}_2}^c} + V_{\text{sII}}^s - V_{\text{sII}}^c$$  \hspace{1cm} (6)

In this equation, variables with the superscripts “c” and “s” refer respectively to the point $(P_{\text{H}_2},T)$ where the C1 phase is stable and to the point $(P_{\text{H}_2},T)$ with the stable sII phase; $V_{\text{sys}} - V_{\text{sys}}^c$ is the experimental difference between the two volumes of the H$_2$O–H$_2$ system; $M_{\text{H}_2}^c$ is the water mass; $M_{\text{H}_2}$ is the mass of the H$_2$ gas at the $(P_{\text{H}_2},T)$ point; $\mu_{\text{H}_2}^c = 18.015$ and $\mu_{\text{H}_2} = 2.016$ are the molecular masses of H$_2$O and H$_2$.

To make use of eq 6, we proceeded on the assumptions that while constructing the isotherms of the hydrogen solubility in ice: (i) each of our H$_2$O–H$_2$ samples completely transformed to the C1 phase when the pressure was increased to the maximum value; (ii) the hydrogen content of the C1 phase did not change on further increase in pressure until the C1 $\rightarrow$ sII transition began; (iii) the sample completely transformed to the sII phase immediately after the C1 $\rightarrow$ sII transition. Pressure dependences of the molar volumes of the sII and C1 phase were approximated by eq 2 and eq 3, respectively.

The mass $M_{\text{H}_2}$ of the H$_2$ gas in equilibrium with the C1 phase was determined by a least-squares fit of the equation of state of molecular hydrogen$^{11}$ to the difference $(V_{\text{sys}} - V_{\text{sys}}^c) - (V_C - V_C^c)$ for the experimental points of the C1 phase on each $V(P)$ isotherm measured at decreasing pressure. One of the points located at $(P_{\text{H}_2}^c, T)$ was arbitrary taken as the computing
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origin. The typical quality of the fits is illustrated by the solid left triangles in Figure 3b.

Substituting the obtained $M_{b}$, value together with the values of $V_{sys}$, $V_{liq}$, and $V_{g}$ for one of the fitting points in eq 6 gives a unique correspondence between the hydrogen content of the $C_{1}$ phase and the hydrogen content of the $sII$ phase at every point of the $V(P)$ isotherm below the pressure of the $C_{1} \rightarrow sII$ transition. Using eq 6, the $X_{sII}(P)$ dependences were calculated for all $V(P)$ isotherms and, within the experimental scatter, proved to be independent of the measuring temperature. The $X_{sII}(P)$ points calculated for two compositions of $X_{C_{1}} = 1/6$ and 1/10 at all temperatures are presented by two clusters of circles in Figure 7b. The solid thin curves in this figure show polynomial fits to the experimental $X_{sII}(P)$ dependence (open left triangles) and clusters of the $X_{sII}(P)$ points calculated for different values of $X_{C_{1}}$. As one can see, the fitting line for $X_{C_{1}} = 1/10$ is close to the point $X_{sII}(3.6 \text{ kbar}) = 0.32$ shown by the open star and calculated for $X_{C_{1}} = 1/10$ more accurately using eq 5. Assuming that the $X_{sII}(P)$ dependence should asymptotically approach $X_{sII}^{lim} = 48/136$ at increasing pressure, the behavior of the fitting lines confirms that the hydrogen content of $X_{C_{1}} \approx 0.1$ is most likely for the $C_{1}$ phase.

$X_{C_{1}} = 0.1$ corresponds to a concentration of 9.1 mol % H$_{2}$ in the $C_{1}$ phase that is below the bottom limit of the interval 10–20 mol % H$_{2}$ established for the $C_{1}$ phase in ref 3. Nevertheless, we are not inclined to consider this as a serious discrepancy because the estimate of ref 3 was based on the intensities of peaks in the Raman spectra, and such a method can overestimate the hydrogen concentration in hydrates. For example, the preliminary estimate of the hydrogen content of the $sII$ phase using this method$^{4}$ proved later to be overestimated by 33%$^{,5}$.

The inset in Figure 7b shows the behavior of the equilibrium hydrogen solubility in ices that should be observed at temperatures below the $L + 2I$ or $sII$ triple point according to results of refs 5 and 8 and the present work. An interesting effect is the decrease in the hydrogen content of ice after the $sII \rightarrow C_{1}$ phase transition. In most systems with gaseous hydrogen, an increase in the H$_{2}$ pressure leads to the increase in the hydrogen solubility in the condensed phases. The reverse effect accompanying the $sII \rightarrow C_{1}$ transition is a consequence of the loosening of clathrate structure of the $sII$ phase. The molar volume of this phase is by 2.01 cm$^{3}$/mol higher than the total volume of the $C_{1}$ phase and gaseous hydrogen liberated from the $sII$ phase in the course of the transition (see Table 1). The negative change in volume, $\Delta V$, gives rise to the thermodynamic driving force $f\Delta V \delta P$ causing the phase transition at increasing pressure in accordance with Le Chatelier’s principle.

Conclusions

With the line of the $sII \leftrightarrow C_{1}$ transformation constructed in the present work, the limits of the stability region of the $sII$ phase are fully identified (Figure 2). The melting lines of the $sII$ and $C_{1}$ phases determined by DTA in ref 2 are re-examined and shown to accurately represent the phase equilibria near the $L + sII + C_{1}$ triple point. In particular, the negative slope of the $sII \leftrightarrow L$ curve near the triple point and therefore the occurrence of a maximum on this curve at a lower pressure proved to be a requisite for the consistency of hydrogen contents of the $sII$ and $L$ phases. To our knowledge, among the $T$–$P$ diagrams of a large body of gas–water systems studied so far, the diagram of the H$_{2}O$–H$_{2}$ system is the first, in which equilibrium lines of phase transformations between solid phases have been constructed.

The obtained volumetric data also allowed a reliable determination of the volume and entropy effects of phase transitions near the $L + sII + C_{1}$ triple point (Table 1). The analysis of the available literature data gave plausible values of the molar volumes of the $sII$ and $L$ phases and a reasonable estimate of the volume of the $C_{1}$ phase (Table 2). Combining these values of the molar volumes with results of the volumetric measurements, the hydrogen content of each condensed phase at the triple point was estimated (Table 2).

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References and Notes


