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Two triple points in the H_2O–H_2 system[†]

V.S. Efimchenko[a]*, V.E. Antonov[a], O.I. Barkalov[a], S.N. Klyamkin[b] and M. Tkacz[c]

[a]*Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow, Russia;* [b]*Moscow State University, Vorob'evy Gory, Moscow, 119992 Russia;* [c]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

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Using a volumetric technique, phase transitions in the H_2O–H_2 system were investigated in the vicinity of two points of an invariant equilibrium, $L + I_h + s\text{II}$ and $L + s\text{II} + C_1$, located at 1.07 kbar and −10 °C and at 3.6 kbar and 1 °C, respectively. Liquid water (L), low-pressure hexagonal ice (I_h) and high-pressure cubic (sII) and rhombohedral (C_1) clathrate hydrates were in equilibrium with gaseous hydrogen taken in excess.

Keywords: hydrogen hydrates; high pressures; phase equilibria

1. Introduction

Compounds of water and hydrogen have been synthesized for the first time by Vos et al. [1]. A rhombohedral hydrate (C_1-phase), described as H-filled ice II with a tentative H_2/H_2O molecular ratio of $X = 1/6$, was shown to form at hydrogen pressures above 7.5 kbar, and the formation of another hydrate (C_2-phase) with a cubic diamond-like H_2O sublattice and $X = 1/1$ was observed at 23 kbar. The occurrence of one more hydrate stable at hydrogen pressures from 1 to 3.6 kbar was later deduced from the behaviour of the melting curve of H_2O ices measured by differential thermal analysis [2]. Further neutron diffraction studies showed that this phase has a cubic clathrate structure of the sII type [3,4] with the concentration of H_2 guest molecules varying with pressure and temperature from $X \approx 0.200$ [5] to $48/136 \approx 0.353$ [4].

Using a volumetric technique [6], the hydrogen [5] and deuterium [7] solubilities in liquid water (L), low-pressure hexagonal ice (I_h), and the sII clathrate phase were studied at pressures up to 1.8 kbar and temperatures from −36 to +20 °C. The investigated T–P range encloses a triple point of the $L + I_h + s\text{II}$ equilibrium. In the H_2O–H_2 system, this point is located at $P = 1.07$ kbar and $T = -10\,°\text{C}$ [5], and the equilibrium hydrogen contents of phases at the triple point are $X_L = 0.017(5)$, $X_{Ih} = 0.011(5)$ and $X_{s\text{II}} = 0.207(5)$ [5,7].

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*Corresponding author. Email: efimchen@issp.ac.ru

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In the present work, using another type of volumetric technique [8], phase transitions in the H_2O–H_2 system were studied at higher pressures, in the vicinity of the second triple point of the $L + s\mathrm{II} + C_1$ equilibrium. Additionally, using the same technique [6] as in [5,7], we examined the process of formation of the sII hydrate from the liquid in more detail than previously, and constructed a metastable extension of the melting line of ice I_h beyond the first $L + I_h + s\mathrm{II}$ triple point.

2. Phase equilibria near the $L + s\mathrm{II} + C_1$ triple point

The upper dash-and-dot curve in Figure 1 shows the melting line in the H_2O–H_2 system according to the DTA measurements [2]. The solid curves at pressures below 1.8 kbar represent phase equilibria established by volumetric measurements [5,7]. Other thick lines and symbols are results of the present work.

The experiments at pressures above 2.2 kbar were carried out in a piston-cylinder high-pressure chamber [8], in which gaseous hydrogen was compressed or decompressed by a movement of the piston. Each studied sample of H_2O was frozen and powdered prior to the high-pressure experiment in order to speed up the kinetics of hydrogen absorption and desorption.

The points of the $s\mathrm{II} \to C_1$ and $C_1 \to s\mathrm{II}$ transitions shown in Figure 1 were determined from a sudden pressure change in the course of a step-wise increase and decrease in the total volume of the H_2O–H_2 system at constant temperature. The dependence of pressures of these transitions on temperature were approximated with thin dashed lines, and the thick solid line representing the $s\mathrm{II} \leftrightarrow C_1$ equilibrium was plotted in the middle between them. This thick line crosses the melting line of ices determined by DTA [2] (dash-dotted curve in Figure 1) exactly at the breakpoint of 3.6 kbar and 1 °C. The breakpoint was assumed [2] to be the point of invariant equilibrium of the L, sII and C_1 phases because the melting temperature of most substances is very close to the temperature of phase equilibrium between the solid and liquid.

We also constructed two isochors $P(T)$ in the vicinity of the $L + s\mathrm{II} + C_1$ triple point. The slanted bar in Figure 1 shows the position of the step in one of those isochors caused by melting

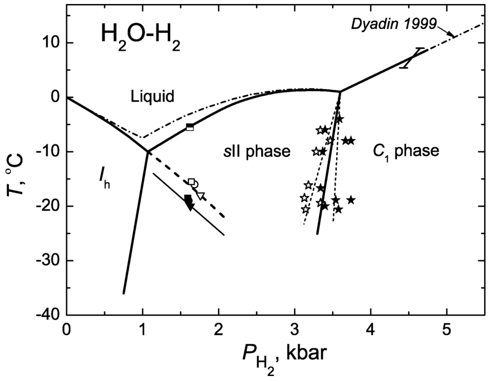

Figure 1. T–P diagram of the H_2O–H_2 system. The dash-and-dot curve shows the melting line of water ices in a hydrogen atmosphere determined by DTA [2]. The thick solid lines represent phase equilibria between pairs of condensed H_2O–H_2 phases (data from [5,7] and the present work). The solid and open stars stand, respectively, for the $s\mathrm{II} \to C_1$ and $C_1 \to s\mathrm{II}$ transitions. The slanted bar indicates the interval of isochoric melting of the C_1 phase. The solid and open symbols at pressures below 2 kbar show the starting points of metastable crystallization and melting of ice I_h in an atmosphere of gaseous hydrogen; the half-blackened square shows the starting point of melting of the sII phase (see Figure 2). The thick dashed curve represents the melting line of ice I_h in the absence of hydrogen [9] and can be regarded as a metastable extension of the melting line of ice I_h in hydrogen beyond the triple point. The thin solid line underneath is for the crystallization of the sII phase from the liquid in a H_2 atmosphere [5].

of the C_1 phase. The bar falls onto the melting curve of the C_1 phase constructed by DTA [2]. This good agreement between the melting conditions determined by different techniques together with the fact that the melting curves of the sII and C_1 phases and the line of the $s\text{II} \leftrightarrow C_1$ transformation intersect at one point suggest that the melting curves of both hydrates measured in [2] should accurately reproduce the equilibria near the $L + s\text{II} + C_1$ triple point.

Our second isochor crossed the melting line, $T_\text{m}(P)$, of the sII phase at 3.3 kbar. The isochor was nearly linear and showed no step-wise anomalies. This implies a zero volume effect, ΔV_m, of melting and therefore justifies the occurrence of a maximum on the melting curve (Clapeyron's equation gives $\text{d}T_\text{m}/\text{d}P = \Delta V_\text{m}/\Delta S_\text{m} = 0$ with $\Delta V_\text{m} = 0$, because the change in entropy, ΔS_m, is always positive on melting). Correspondingly, we extended the equilibrium melting curve from [5] up to the $L + s\text{II} + C_1$ triple point (thick solid line in Figure 1) so that it asymptotically approached the melting line determined in [2] near its maximum.

3. Crystallization of the sII phase from the liquid near the $L + I_\text{h} + s\text{II}$ triple point

The volumetric investigation of the D_2O–D_2 system showed [7] that the formation of the sII phase from the liquid at decreasing temperature can only occur together with the formation of a metastable phase of ice I_h. The experiments were carried out in an autoclave filled with deuterium gas using an external pump [6].

In the present work, the same technique [6] was applied to construct isochors crossing the ranges of melting and crystallization of the sII and I_h phases in the H_2O–H_2 system. The results are presented in Figure 2. After equilibrating with gaseous hydrogen in a closed autoclave at 1.7 kbar and −1 °C, the liquid was slowly cooled (route 1 → 2) that led to a phase transition causing a steep increase in pressure typical of the ice I_h crystallization. On subsequent heating (route 2 → 4), this ice I_h melted, giving rise to a step-wise pressure decrease. As seen from Figure 1, the crystallization and melting of ice I_h in a hydrogen atmosphere occur at approximately the same temperature and pressure as in the absence of hydrogen. Further cycling across the temperature range of these transitions decreased the magnitude of the steps in the isochors.

The volume effects of the $L \rightarrow s\text{II}$ and $L \rightarrow I_\text{h}$ transitions are of opposite sign, and the magnitude of the steps in the isochors corresponds to the presence of 20, 55 and 75% of the sII phase in the $I_\text{h} + s\text{II}$ mixtures formed after the first, second and third cycles of cooling. This means that 20% of the starting liquid was transformed to the sII phase in the course of the first cooling and

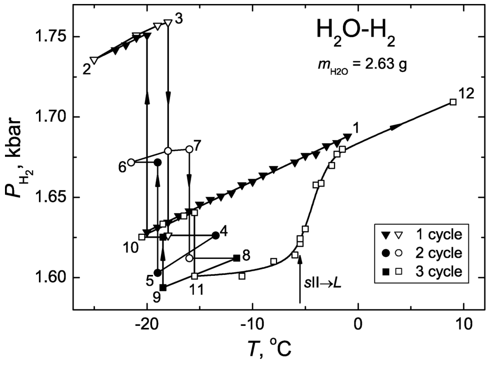

Figure 2. Variation of pressure in the closed autoclave that was heated and cooled in the succession of 1 to 12. The starting points of the step-wise increase and decrease in pressure are shown in Figure 1 with the corresponding symbols.

about 44% of the liquid produced by melting of the remaining ice I_h was additionally converted to sII hydrate in each of the further two cycles. Interestingly, the small difference in the hydrogen solubilities in liquid H_2O and ice I_h was only sufficient for the formation of 3–4% of the sII phase on cooling the liquid. Therefore, most hydrogen required to form the observed 20–44% of the sII phase should have come from the gas phase. This suggests a high rate of hydrogen diffusion through the condensed H_2O–H_2 phases because the thickness of their layer at the bottom of the autoclave exceeded 30 mm, whereas the crystallization of the $I_h + s$II mixtures was completed in less than 15 min.

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