

# The Phase Diagram of the Water–Hydrogen System in the Crystallization Field of Solid Solutions Based on Ices Ih and II at High Pressures

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**Abstract.** The decomposition curves of the solid solutions based on ices Ih ( $\alpha$ -solutions) and II ( $\beta$ -solutions) in the water–hydrogen system were studied by the DTA technique at pressures up to 7 kbar. The  $\alpha$ -solution is destabilized by pressure but to a lesser degree than ice Ih and is stable up to 2.3 kbar. The  $\beta$ -solution is stabilized by pressure and at 7 kbar decomposes at about 20 °C. The  $P$ ,  $T$ -phase diagram of the water–hydrogen system in the crystallization range is constructed on the basis of reference [1] and our data. All possible types of stoichiometric interrelationships in the guest–host system are demonstrated by the example of the water–hydrogen system.

**Key words:** Hydrogen–water solid solutions, phase diagram, stoichiometry of clathrates, high pressure.

## 1. Introduction

The  $\text{H}_2\text{O}$ – $\text{H}_2$  system has been studied in the range from 7 to 32 kbar and two hydrates ( $\text{H}_2\cdot\text{H}_2\text{O}$  with the ice Ic framework and  $\text{H}_2\cdot 6\text{H}_2\text{O}$  with the ice II framework) have been found [1]. At pressures up to 2.5 kbar a hydrogen solid solution forms on the basis of the ice Ih framework [2]. So the intermediate part of the diagram has not been studied. While investigating the monovariant liquid–solid–gas equilibrium in the intermediate part of the diagram (2.5–7 kbar) we were interested in discovering whether there are stability fields of ices III, V, VI on the phase diagram with excess hydrogen. Besides, we expected that the study of the phase diagram for this pressure range would allow us to observe all possible types of stoichiometric interrelationships in guest–host systems not only in one system but also in one framework, that of ice II.

## 2. Experimental

The melting points of ices and their hydrogen solid solutions were measured with a chromel–alumel thermocouple (whose operational features are practically pressure

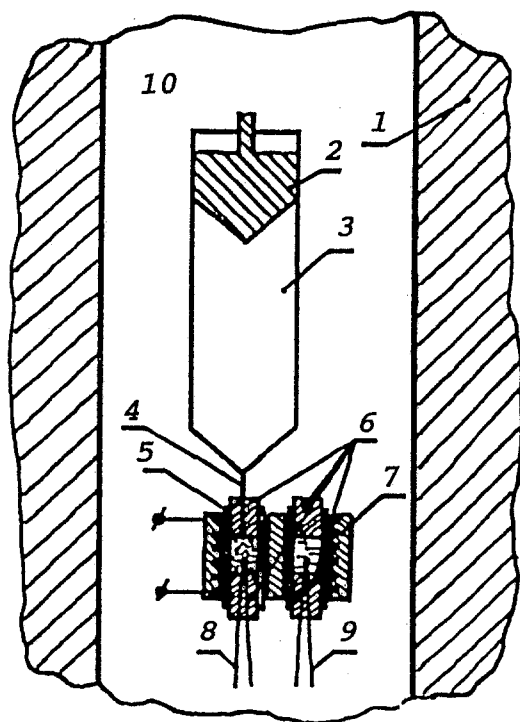


Fig. 1. Scheme of the high pressure cell: 1 – the walls of the high pressure vessel, 2 – piston, 3 – cylinder, 4 – capillary, 5 – organic glass tube, 6 – rubber cork, 7 – electroheater, 8 – thermocouple in the sample, 9 – thermocouple in the standard, 10 – volume of the pressure transmitting medium.

independent in the range considered [3]) by the DTA technique in a piston–cylinder cell for experiments with gases (Figure 1). Cylinder (3) was filled with the gas through capillary (4) at 1 atm and connected with the organic glass ampoule (5) squeezing through the rubber cork (6). Petroleum ether was used as the pressure transmitting medium inside the high pressure zone (10). Pressure was measured with Bourdon (up to 2.5 kbar) and manganin manometers with an accuracy not less than 10 bar, and temperature with an accuracy not less than  $0.2^\circ$ . To speed up the dissolution of the gases, a nonionogenic surface active substance (SAS) was added, whereby its concentration in the solution studied was of the order 0.25% (previously it was shown that such amounts of SAS did not shift the equilibrium in our accuracy range [4]). Similarly, for the same purpose, an inert powder ( $\text{SiO}_2$ -glass,\* SiC) with a grain size of 0.01 cm, was added to water. The inertness of the powder is confirmed by ice Ih and III data. 0.015–0.016 g of distilled water and  $5.5$ – $6.5 \text{ cm}^3$  of the gas at ambient pressure and room temperature were used. The purity of hydrogen was about 99.99%.

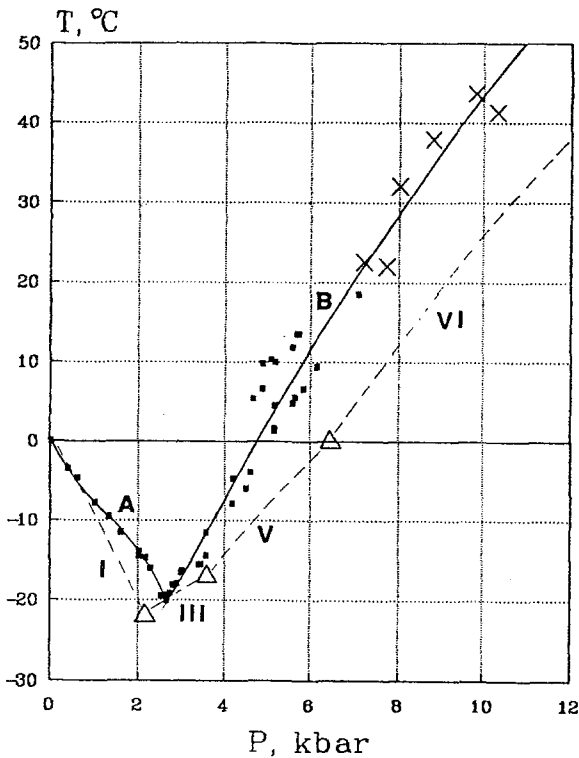


Fig. 2. The pressure dependence of the decomposition temperature of the hydrogen solid solutions in ice Ih (A) and ice II (B).  $\times$  - data from [1];  $\blacksquare$  - our data; - - - - melting point lines of ices under pressure;  $\Delta$  - nonvariant triple points in the water system.

### 3. Results and Discussion

The results of the decomposition of hydrogen solid solution in ice Ih and II are presented in Figure 2. Curve A, representing the monovariant equilibrium of the decomposition of hydrogen solid solution in ice Ih (the ' $\alpha$ -solution'), occupies the space up to 2.3 kbar which is somewhat higher (by approximately 0.2 kbar) than the pressure at which ice Ih is stable. Pressure destabilizes the  $\alpha$ -solution just as for ice Ih, which shows that the thickening of the structure due to the inclusion of hydrogen molecules in the ice Ih cavities is not sufficient for the phase of the solid solutions formed to be stabilized by pressure.

At approximately the same pressure endothermic effects appeared on the heating curves which on the basis of the data of references [1, 6, 7] can be attributed to the monovariant equilibrium of the decomposition of the solid solution based on ice II ( $\beta$ -solution) into the liquid phase rich in water ( $l$ ) and the fluid one rich in hydrogen ( $g$ ). As illustrated in Figure 2, our data agree satisfactorily with those of reference [1]. This has led to attempts to display the conditions of the water-hydrogen system as a  $P,T$ -phase diagram (Figure 3), using the data of references [1-3]. Since the

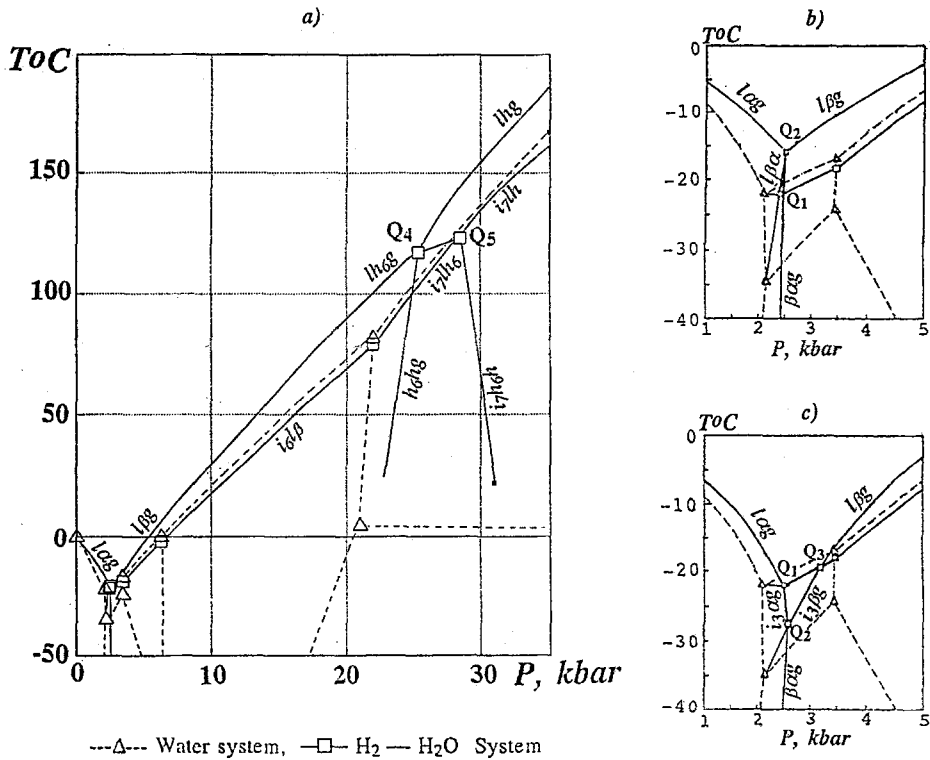


Fig. 3.  $P, T$ -projection of the water-hydrogen system. (a) Possible versions of the phase equilibria in the  $H_2O-H_2$  system at average pressures: (b) the ice crystallization fields are completely overlapped by the solid solution crystallization fields; (c) there is some crystallization field of ice III ( $Q_1Q_2Q_3$ ),  $Q$  is the quadruple point,  $l, g, i, \alpha, \beta$  are liquid, gas, corresponding ice, solid solutions based on ice Ih and ice II, respectively.

lines  $A$  (the monovariant equilibrium  $l\alpha g$ ) and  $B$  ( $l\beta g$ ) cross near the line of the melting of ice III, with the given experimental accuracy it is impossible to say which of the two versions of the equilibria (Figure 3b, c) occurs in the system. As helium dissolves in ice Ih more readily [2] and its solubility in ice II does not seem to be lower [6, 7], we believe that the most likely version of the phase equilibria in the helium-water system is that shown in Figure 3b. However, in the case where hydrogen is the guest one can see that the excess gas causes complete overlapping of the crystallization fields of ices V and VI and probably complete overlapping of the ice III crystallization field. The water-hydrogen system is unique in that it is a vivid and unique illustration of the three types of the stoichiometric interrelationships and their interconversions in the guest-host system.

(1) Ischoric solutions (solid solutions of the guest component in the host framework forming due to the variable occupation of the cavities [8]) of the first type form when the guest dissolves in the thermodynamically stable host modification. We observed this phenomenon for  $\alpha$ -solutions up to a pressure of 2.1 kbar, i.e. a

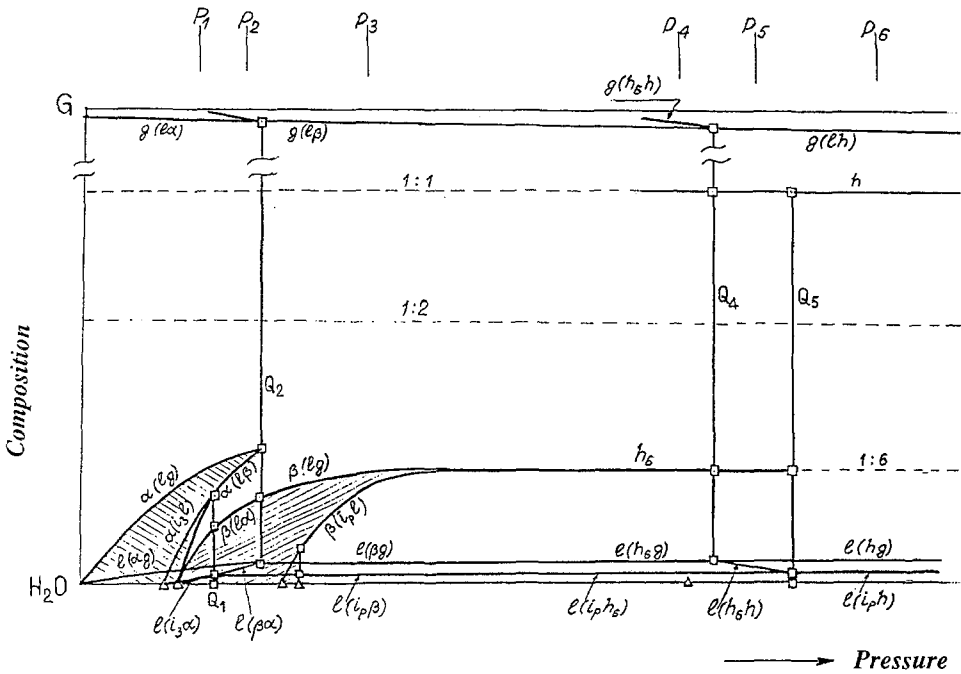


Fig. 4.  $P, X$ -projection (scheme) of the water-hydrogen system (version b, see Figure 3).  $i_3, i_p$  are ice III and high pressure ices, respectively.  $\alpha(l, g)$  means that the  $\alpha$ -phase is in equilibrium with  $l$  and  $g$ -phases. The phases are arranged in the order of increasing guest component. (This  $P, X$ -projection does not show the whole of its subsolidus part.)

pressure at which ice Ih is still stable and for  $\beta$ -solutions at pressures of the ice II stability range (Figure 4).

(2) Ischoric solutions of the second type form on the basis of the discussed frameworks at higher pressures where the host itself becomes metastable, while its solid solutions are still stable. Thus, in our case ischoric  $\alpha$ -solutions of the second type are observed from 2.1 to 2.3 kbar and ischoric  $\beta$ -solutions of the second type, at pressures above 4 kbar.

(3) Finally, compounds of stable composition are observed when the host framework is absolutely unstable in the absence of the guest. Exactly the same conditions were discovered in the studied system for the phase based on the ice II framework. As has already been mentioned, at average pressures (4–6 kbar) these were  $\beta$ -solutions whose homogeneous range narrows with the pressure increase and approaches the composition which corresponds to the complete filling of the cavities. It is evident that at a pressure of 26 kbar and a temperature of 115 °C (i.e. 20 kbar and 140° higher than those at which ice II is stable) ice II is absolutely unstable: and in the absence of the guest any fragment of this structure will be immediately destroyed. Therefore, the only stable structure is the one whose

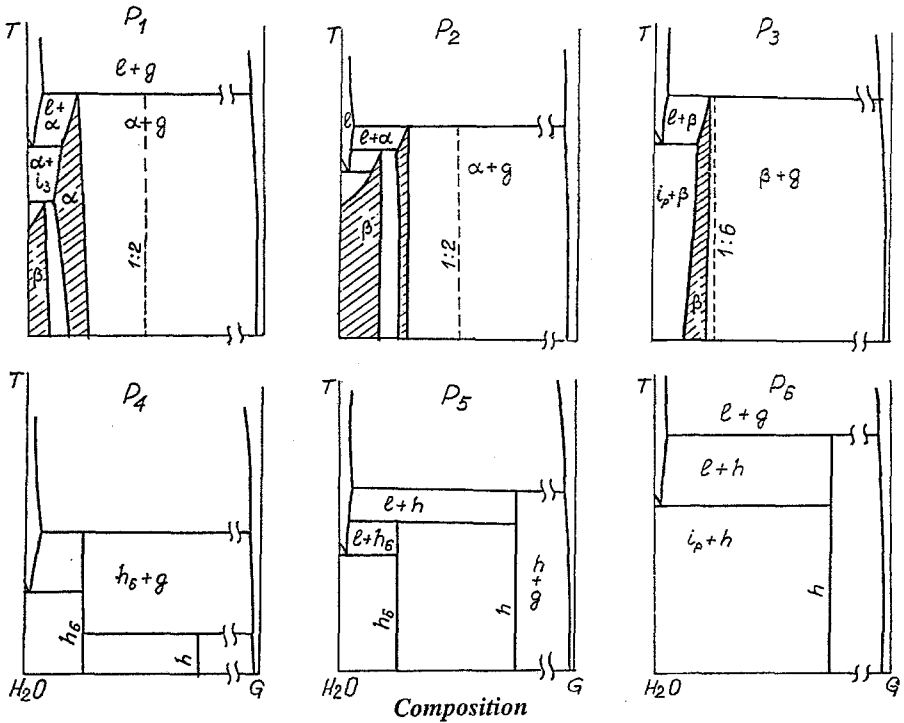


Fig. 5. Characteristic isobaric sections in the water-hydrogen system (schematic).

cavities are all filled with the guest, in our case,  $\text{H}_2 \cdot 6\text{H}_2\text{O}$ . This reasoning is all the more true of the ice Ic and its hydrate  $\text{H}_2 \cdot \text{H}_2\text{O}$  [1].

In other words, using the phase of hydrogen inclusion in the ice II framework as an example, the transition from the type I ischoric solutions to the type II solutions and to a compound of constant composition which occurred with the pressure increase, i.e. all possible kinds of stoichiometric interrelations in various guest-host system were observed.

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### Note

\*The rather high solubility and diffusion of helium in silica glass [5] seem to result in speeding up the solution of helium in ice. It is assumed that the behaviour of hydrogen is similar.

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