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Solubility of hydrogen in ice Ih at pressures up to 8 MPa

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ABSTRACT

Experimental studies of the solubility of hydrogen in ice Ih (usual low-pressure ice) at temperature -1 to -2 °C and pressures up to 8 MPa were carried out. At a pressure equal to 1.90 and 8.04 MPa, hydrogen solubility in the ice was found to be 0.15 and 1.32 cm³/g, respectively (hydrogen volume was reduced to the normal conditions).

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Introduction

The development of new materials that are capable of multiple and reversible sorption/desorption of hydrogen and can be used to store this gas is topical and practically significant research area [1,2]. At present, clathrate hydrates of hydrogen and double clathrate hydrates of hydrogen with various auxiliary components are intensively studied as materials for hydrogen storage [3–10]. Studies in the field of technologies of light gas (helium, hydrogen) separation from gas mixtures are of substantial interest, too [11].

In the binary system hydrogen – water the clathrate hydrate of hydrogen exists at temperatures -25 to 0 °C and at pressures 100–360 MPa [12–14]. At higher pressure, hydrogen hydrates based on ice II and Ic frameworks are stable [15,16]. It should be noted that recently the solid solution of hydrogen in

Ic ice was obtained at a pressure of several tens of MPa and low temperatures [17]. Finally, at pressures below 100 MPa the solid solution of hydrogen in ice Ih is stable. Different crystallographic modifications of ices are discussed in Ref. [18]. In particular, ice Ih is thermodynamically stable low-pressure modification of ice (usual ice), ice Ic is metastable low-pressure modification of ice and ice II is high-pressure ice which exists at temperatures below -17 °C and several hundreds of MPa. Hereafter ice Ih will be referred to as ice, without designations of the structural type. This ice modification is stable under the P-T conditions that are most common in science and technology, so the contact of hydrogen-containing fluid phases with ice is possible not only in laboratory experiments. For instance, the information concerning hydrogen solubility in ice is necessary for design of hydrogen reservoirs in permafrost and gas hydrate hydrogen accumulators for mobile applications. Indeed, smaller or larger

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amounts of ice will be necessarily present in the hydrogen tank if gas hydrates are used for storage (transportation) of hydrogen.

At present only limited information on the properties of hydrogen solutions in ice is available. It is known that hydrogen is capable of rapid diffusion through the crystal framework of ice [19–21]. The spectra of H₂ and D₂ molecules dissolved in the ice matrix were studied in Refs. [22,23]. Hydrogen solubility in ice at pressures higher than 40 MPa was measured in Refs. [24,25]. According to the data reported in Refs. [24], at the pressure of 40–80 MPa hydrogen solubility in ice is ~60% of its solubility in liquid water. According to the data of [25], hydrogen solubility in ice is equal to its solubility in water at the pressure of 50 MPa and exceeds it by a factor of ~2 at the pressure of 100 MPa. Finally, in the recent simulations the solubility of hydrogen in ice was determined to be about one order of magnitude higher than the above values [26]. So, the literature data on hydrogen solubility in ice available at present are contradictory. This determined our interest to this topic.

Materials and methods

The method used to measure the solubility of light gases in ice was described in detail in Ref. [27]. Hydrogen solubility in ice was determined in an autoclave with internal volume $166.4 \pm 0.4 \text{ cm}^3$. Temperature of the thermostat was held with the accuracy $\pm 0.05 \text{ }^\circ\text{C}$. We neglected the volume of the capillary with shutoff valve and manometer arranged outside the thermostat (about 5 cm^3). Pressure was measured with the MIDA-TG-51 pressure sensor (0.1–25 MPa pressure range) calibrated against a reference manometer. The absolute error of the sensor was within 0.1% of the measurement scale, the sensitivity of the sensor to pressure change was at least 0.005 MPa. Experiments were carried out as follows. Ice dust with the characteristic particle size less than 0.1 mm was charged into the autoclave at the temperature of $-30 \text{ }^\circ\text{C}$, the autoclave was evacuated and purged with hydrogen. After that the necessary pressure of hydrogen was set. Commercially available cylinder with compressed hydrogen (>99.9% purity) was used as the hydrogen source. Three stages of experiment were carried out. (1) Thermostat was set at -1 to $-2 \text{ }^\circ\text{C}$, and the sample in the autoclave was kept for 4–8 h until stabilization of hydrogen pressure above powdered ice. (2) The thermostat was heated to $+10 \text{ }^\circ\text{C}$ and kept at this temperature until ice melted completely. After that the thermostat was cooled again to the initial temperature. Liquid water was kept under hydrogen pressure for 4–8 h until complete pressure stabilization. (3) Then the thermostat was set at $-10 \text{ }^\circ\text{C}$ until water was completely frozen. After water freezing, temperature was again set at initial temperature (-1 or $-2 \text{ }^\circ\text{C}$). The piece of ice formed in the autoclave was kept under hydrogen pressure until pressure stabilization. As a rule, pressure was the same at stages (1) and (3); the maximal difference was 0.01 MPa. The solubility of hydrogen in ice was calculated from the difference of hydrogen pressure values above liquid water and above ice using equation $S = (P_1/k_1 - P_2/k_2) V_{\text{total}} / (m_{\text{H}_2\text{O}} P_0) - P_1 / (\rho_{\text{liquid}} P_0 k_1) + P_2 / (\rho_{\text{solid}} P_0 k_2) + S_1$, where S is the solubility of hydrogen in ice (cm^3/g , gas volume was reduced to the

normal conditions), V_{total} is the total system volume (ml), $m_{\text{H}_2\text{O}}$ is the mass of water (g), P_1 is gas pressure above liquid water (bar), P_2 is gas pressure above ice (bar), $k_1 = PV/P_0V_0$ above liquid water, $k_2 = PV/P_0V_0$ above ice (P, V are pressure and volume of 1 mole of hydrogen at the given temperature, P_0, V_0 are pressure and volume of 1 mole of hydrogen under normal conditions, $P = 1 \text{ bar}$), ρ_{liquid} is the density of liquid water (g/cm^3), ρ_{solid} is the density of ice (g/cm^3), S_1 is the solubility of hydrogen in water (cm^3/g). The data on the density of liquid water at $-1 \text{ }^\circ\text{C}$ were extrapolated from the data reported in Ref. [28]. The data on ice density at -1 to $-2 \text{ }^\circ\text{C}$ were taken from Ref. [29]. The data on the equation of state for hydrogen were taken from Ref. [30]. The solubility of hydrogen in liquid water at $-1 \text{ }^\circ\text{C}$ was taken from Ref. [31]. Our estimate for the maximal error of the determination of hydrogen solubility in ice is $0.1 \text{ cm}^3/\text{g}$ of ice (gas volume reduced to the normal conditions).

Results and discussion

The numerical data on the solubility of hydrogen in ice at a pressure up to 8 MPa are presented in Table 1. The dependence of solubility on pressure is slightly non-linear though relatively large errors of the measured values do not provide the possibility to discuss the shape of the corresponding curve in more detail. Within the whole pressure range, the solubility of hydrogen in ice is lower than the solubility of hydrogen in liquid water at the same pressure and temperature. The absolute values of hydrogen solubility in ice are the same (within experimental errors) as the values of helium solubility studied by us previously [27]. Comparison with the literature data [24–26] shows a reasonable correspondence between our results and the results of [24] (Fig. 1). The solubility values reported in Ref. [25] and especially in Ref. [26] are substantially higher. Similarly to our case, the data of [24] were obtained at temperatures close to the ice melting point. If we assume that the temperature dependence of hydrogen solubility in ice is close to that for the solubility of helium in ice [27], for experimental temperatures in our work ($-1 \text{ }^\circ\text{C}$) and in Ref. [24] ($-3.5, -5.3, -7.2 \text{ }^\circ\text{C}$ for 40, 60 and 80 MPa, respectively) the temperature shift of solubility appears to be much less than the

Table 1 – Solubility of hydrogen in ice Ih. Volume of dissolved hydrogen was corrected to normal conditions. Symbols \uparrow and \downarrow means that equilibrium solubility was reached starting from lower or higher pressure of hydrogen, respectively.

P, MPa	Temperature, $^\circ\text{C}$	Solubility, cm^3/g
1.90	-1	0.15 \uparrow
2.87	-1	0.31 \uparrow
3.00	-1	0.36 \uparrow
3.56	-1	0.44 \uparrow
3.90	-1	0.49 \uparrow
4.58	-2	0.48 \downarrow
4.90	-1	0.58 \uparrow
5.61	-2	0.71 \uparrow
7.81	-2	1.14 \downarrow
8.04	-2	1.32 \uparrow

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