

# Solubility of Helium in Ice Ih at Pressures up to 2000 bar: Experiment and Calculations

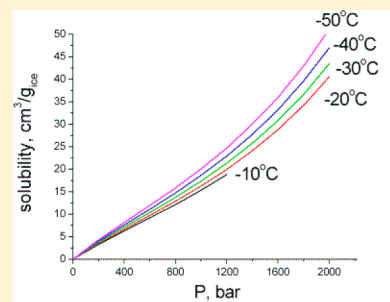
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## Supporting Information

**ABSTRACT:** The solubility of helium in ice Ih has been examined both experimentally and theoretically. It has been demonstrated that the calculations are in good accord with the experimental data. The tested calculation method has been used for deriving the helium solubility in ice Ih at pressures up to 2000 bar and at temperatures of 0–50 °C. Obtained data may be useful in some practical applications (storage of enriched with helium natural gas in permafrost, extraction of helium from natural gas).



## INTRODUCTION

A wide range of materials is currently being considered as potential reversible hydrogen storage media.<sup>1</sup> Significant attention is paid to investigation of double clathrate hydrates of light gases + some organic species that make up a prospective class of hydrogen storage materials (e.g.,<sup>2–6</sup>) and, probably, helium storage materials.<sup>7</sup> Separation of gas mixtures (including hydrogen- and helium-containing mixtures) with the use of clathrate hydrates is also topical. A comprehensive review of recent publications in this field is given in ref 8. An interesting and rather unexpected idea to use ice Ih instead of clathrate hydrates as a hydrogen storage material has been recently suggested and theoretically justified in ref 9. As this modification of ice is widely available, stable under  $P$ – $T$  conditions common in science and industry, and inexpensive, its use in this field is very attractive. The same can be said about helium. All of the above determined our interest to study solubility of helium in ice Ih in a wide range of pressures and temperatures.

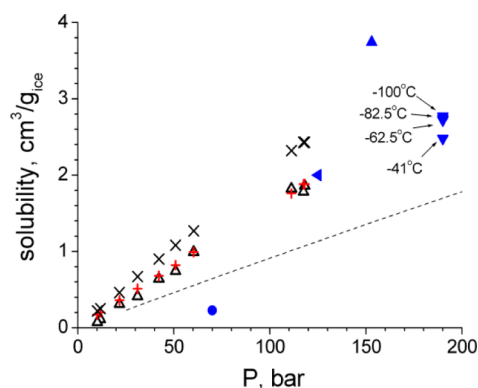
Currently, extensive experimental information has been amassed for hydrates formed by gases with the smallest atomic/molecular sizes (helium, neon, and hydrogen).<sup>10–24</sup> Hydrogen hydrate based on the framework of the metastable ice Ic exists at pressures over 25 kbar.<sup>19,20</sup> At intermediate pressures (1.0–3.6 kbar for hydrogen and 1.9–3.7 kbar for neon), classic polyhedral hydrates exist in the systems  $H_2$ – $H_2O$  and  $Ne$ – $H_2O$ .<sup>16,21–24</sup> Crystal structures of two stable ice polymorphs (Ih and II) have voids large enough to incorporate atoms of helium and neon, as well as hydrogen molecules. Therefore, hydrogen, neon, and helium form solid solutions with ice Ih at pressures below 1000, 1900, and 2100 bar, respectively.<sup>10–18</sup>

Experimental data on the solubility of helium in ice Ih are reported.<sup>10–14</sup> In one study,<sup>12</sup> the solubility of helium in ice was derived from the difference of melting points of pure ice and ice saturated with helium at pressures up to 800 bar. In other works,<sup>10,11,13,14</sup> the solubility of helium in ice Ih was measured using the pressure drop in the experimental chamber caused by dissolution of helium in ice. Reference 25 reports thermodynamic calculations of the solubility of helium in ice, and fragments of the phase diagram for helium–water were constructed for 1000 and 1500 bar. The thermodynamic model of a solid solution of helium in ice Ih took into account deformation of the ice lattice upon inclusion of helium atoms, the energy of interaction of the helium atom with the walls of the cavity, and the change in the entropy of the system upon formation of the solid solution.

Data from the cited studies and some results of the present investigation are summarized in Figure 1. The natural trend of larger solubility of helium in ice at higher pressures is evident; however, Henry coefficients calculated for the most different data show almost 10-fold variation. The situation is aggravated by variation of temperatures used for determination of solubility, although it is noteworthy that some studies<sup>11,14,25</sup> report weak dependence of helium solubility on temperature. In general, the consistency of the available data is insufficient. The above considerations have stimulated our interest to acquire precise data on helium solubility in ice Ih.

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**Figure 1.** Solubility of helium in ice Ih at pressures below 200 bar. Dashed line, solubility of He in liquid water at  $-1\text{ }^{\circ}\text{C}$ ;  $\Delta$ , our data at  $-1\text{ }^{\circ}\text{C}$ ;  $+$ , method 1 calculations at  $-1\text{ }^{\circ}\text{C}$ ;  $\times$ , method 1 calculations at  $-41\text{ }^{\circ}\text{C}$ ;  $\blacktriangleleft$ , data from ref 10 ( $-25\text{ }^{\circ}\text{C}$ );  $\blacktriangledown$ , data from ref 11 (four points at temperatures from  $-41$  to  $-100\text{ }^{\circ}\text{C}$ ; the temperatures are marked in the figure);  $\blacktriangle$ , data from ref 13 ( $-25\text{ }^{\circ}\text{C}$ );  $\bullet$ , data from ref 14 ( $-10\text{ }^{\circ}\text{C}$ ). The description of method 1 can be found in the Methods of Calculations section.

## EXPERIMENTAL SECTION

The data for the melting curves of pure ice and helium-saturated ice were obtained by differential thermal analysis (DTA) under high pressure, the technique being described in detail in ref 26. The experiments under the pressure of helium were performed with the use of the following procedure. Samples of inert powder (SiC) wetted with 2–3 drops of distilled water were loaded into the DTA container having a volume of 0.05 mL. The container was hermetically attached to a stainless steel vessel supplied with a movable piston (a volume of 0.5–8 mL, depending on the position of the piston) and a check valve. After that, the vessel was pressurized with helium gas up to the pressure of 20 bar. The assembled cell was placed into a high-pressure hydrostatic chamber filled with a silicon oil–hexane mixture. The pressure was transmitted into the cell by the piston. The experiments were performed in the classical DTA scheme. Temperatures of phase transitions were registered as the moment of maximal difference in temperatures between the reference thermocouple and the thermocouple introduced into the sample container upon quasi-isobaric heating of the DTA cell. Melting temperatures of the pure ice were measured in a hermetically closed Teflon ampule, and the pressure was transmitted into the cell through the walls of the ampule. In typical experiments, the melting points of the samples were measured with a chromel–alumel thermocouple (K-type) at the heating rate of  $1\text{--}2\text{ }^{\circ}\text{C}/\text{min}$ . The thermocouple was calibrated using reference points or a reference thermometer. The error in temperature measurement by the thermocouple did not exceed  $0.3\text{ }^{\circ}\text{C}$ . The pressure was measured with a manganine manometer calibrated against the melting point of mercury. The relative uncertainty of the pressure measurements was about 1% of the measured values. Data on the melting of ice under helium pressure were published by our group about 20 years ago.<sup>27</sup> Now, it turned out that these data contained significant systematic errors caused by imperfection of the experimental cell. The adequacy of the hardware used in this work and the experimental procedures were repeatedly proved by comparison of our experimental data to the data available from the literature (e.g.,

the nitrogen–water system,<sup>28</sup> the methane–water system,<sup>29</sup> and the ethane–water system<sup>30</sup>).

The solubility of helium in ice Ih was measured in a stainless steel cell with a working pressure up to 150 bar. The temperature of the cell was controlled with a liquid cryostat with a temperature accuracy better than  $\pm 0.1\text{ }^{\circ}\text{C}$ . The internal volume of the cell ( $166.4 \pm 0.4\text{ cm}^3$ ) was determined by weighing after filling with water. The volume beyond the cryostat (an outgoing capillary with a valve and pressure gauge and total volume  $\approx 5\text{ cm}^3$ ) was neglected in calculations. The cell was equipped with a cutoff valve and a tensimetric pressure sensor calibrating against a reference pressure gauge. The absolute specified uncertainty of the tensimetric pressure sensor is better than 0.25 bar, and the sensor sensitivity to the pressure change is better than 0.05 bar. The experiment was conducted in the following way. Ice powder with a particle size below 0.1 mm was prepared by spraying water in liquid nitrogen. Ice particles sizes were determined using a microscope. Then, 70–110 g of the ice powder was loaded in the cell at  $-30\text{ }^{\circ}\text{C}$ , the cell was purged with helium, and then, the pressure of the experiment was set. Three experimental stages were carried out. (I) The thermostat was set to  $-1\text{ }^{\circ}\text{C}$ , and the sample was kept there for 3–4 h until the pressure of helium over the ice powder was constant. (II) Afterward, the thermostat was warmed to  $+10\text{ }^{\circ}\text{C}$ , kept at this temperature until the ice completely melted, and again cooled to  $-1\text{ }^{\circ}\text{C}$ . Liquid water in the cell was kept under helium pressure for 3–4 h until the pressure stabilized. (III) Further, the thermostat was set to  $-10\text{ }^{\circ}\text{C}$ , and the water was allowed to freeze. After freezing, the temperature was returned to  $-1\text{ }^{\circ}\text{C}$ , and the resulting ice monolith was kept under helium pressure until it stabilized. As a rule, the pressures at stages (I) and (III) were the same, with the largest difference of 0.1 bar. The usual duration of the experiment was about 15 h. In all cases, stabilization of the pressure at stage (I) takes less time in comparison with that at stage (III). The solubility of helium in ice was derived from the difference of the helium pressure over liquid water and ice as

$$S = \frac{(P_1/k_1 - P_2/k_2)V_{\text{total}}}{m_{\text{H}_2\text{O}}P_0} - \frac{P_1}{k_1\rho_1P_0} + \frac{P_2}{k_2\rho_2P_0} + S_1$$

where  $S$  is the solubility of helium in ice ( $\text{cm}^3/\text{g}$ ),  $V_{\text{total}}$  is the total volume of the system (mL),  $m_{\text{H}_2\text{O}}$  is the water load (g),  $P_1$  is the gas pressure over liquid water (bar),  $P_2$  is the gas pressure over ice (bar),  $k_1 = PV/P_0V_0$  over liquid water,  $k_2 = PV/P_0V_0$  over ice ( $P$  and  $V$  are the pressure and volume of 1 mol of helium (real gas) at the given temperature,  $P_0$  and  $V_0$  are the pressure and volume of 1 mol of helium under standard conditions, and  $P_0 = 1\text{ bar}$ ),  $\rho_1$  is the density of liquid water ( $\text{g}/\text{cm}^3$ ),  $\rho_2$  is the density of ice ( $\text{g}/\text{cm}^3$ ), and  $S_1$  is the solubility of helium in water ( $\text{cm}^3/\text{g}$ ). The density of water at  $-1\text{ }^{\circ}\text{C}$  was extrapolated from the data of ref 31, and the density of ice at  $-1\text{ }^{\circ}\text{C}$  was taken from ref 32. The constitutive equation for helium was taken from ref 33, and the helium solubility at liquid water at  $-1\text{ }^{\circ}\text{C}$  was extrapolated from the data of ref 34 with use of the Krichevsky–Kazarnovsky equation. The estimated maximal error of solubility of helium in ice is  $0.1\text{ cm}^3/\text{g}_{\text{ice}}$ .

## METHODS OF CALCULATIONS

As noticed above, helium can intercalate in the voids of ice Ih, affording a solid solution. Admitting total occupation of all voids, there are two water molecules per one helium atom, that is, the ultimate composition of the solution is  $\text{He}\cdot 2\text{H}_2\text{O}$ . Let us

consider the solid solution as an ideal mixture of empty ( $2\text{H}_2\text{O}$ ) and filled voids ( $\text{He}\cdot 2\text{H}_2\text{O}$ ). Hereafter, all quantities related to water are marked with subscript “w”, and those related to helium are designated with “He”. The Gibbs energy of a solution formed from  $N_w$  water molecules and  $N_{\text{He}}$  atoms is formulated as

$$G = \frac{1}{2}N_w(1 - \theta)g_e + \frac{1}{2}N_{\text{He}}\theta g_f + N_wRT [\theta \ln \theta + (1 - \theta) \ln(1 - \theta)] \quad (1)$$

Here,  $g_e$  and  $g_f$  are the Gibbs energies of the empty and filled voids,  $\theta = 2N_{\text{He}}/N_w$  is the occupation of the voids depending on the mole fraction of helium in the solid solution,  $x = N_{\text{He}}/(N_w + N_{\text{He}})$ , as  $\theta = 2x/(1 - x)$ . Differentiating this expression against  $N_w$  and  $N_{\text{He}}$  affords expressions for chemical potentials of the components in the solid solution (superscript “s”)

$$\mu_{\text{He}}^s = (g_f - g_e) + RT \ln \frac{\theta}{1 - \theta} = \mu_{\text{He}}^{s0} + RT \ln \frac{2x}{1 - 3x} \quad (2)$$

$$\mu_w^s = \frac{g_e}{2} + \frac{RT}{2} \ln \frac{(N_A - \nu N_B)}{N_A} = \frac{g_e}{2} + \frac{RT}{2} R T \ln(1 - \theta) = \mu_w^{s0} + \frac{RT}{2} \ln \frac{1 - 3x}{1 - x} \quad (3)$$

For dilute solutions with  $x \ll 1$ , the following approximations are valid:

$$\mu_{\text{He}}^s = \mu_{\text{He}}^{s0} + RT \ln x \quad \mu_w^s = \mu_w^{s0} - RTx \quad (4)$$

Here,  $\mu_{\text{He}}^{s0}$  and  $\mu_w^{s0}$  are the standard contributions in the chemical potentials. To standardize the state of  $\text{H}_2\text{O}$  in the solid solution, we used Gibbs molar energy of ice for a given pressure  $P$  and temperature  $T$ ; hence,  $\mu_w^{s0} = 0$ .

For an equilibrium gas–solid solution, in this particular  $P$ – $T$  field, the partial pressure of water is small; therefore, the gas in the first approximation can be considered as single-component. In this case, the equilibrium gas–solid solution is described as

$$\mu_{\text{He}}^{s0}(P, T) + RT \ln \frac{2x}{1 - 3x} = \mu_{\text{He}}^{g0}(P, T) + RT \ln f(P, T) \quad (5)$$

Here,  $f$  is the fugacity of helium. The value of  $\Delta\mu_{\text{He}}^{sg0} = \mu_{\text{He}}^{s0} - \mu_{\text{He}}^{g0}$  equals the work of the transition of helium from the solid solution to gas. Its calculation is described in ref 25. Here,  $\Delta\mu_{\text{He}}^{sg0} = \Delta g_{\text{def}} - \Delta g_{\text{He}}$ , where  $\Delta g_{\text{def}}$  is the work of extension of the ice Ih crystalline framework from starting unit cell parameters  $a_0, c_0$  to  $a_1, c_1$  ( $\theta = 0$ ).  $\Delta g_{\text{He}}$  is the work of helium transfer from the deformed cell to gas at a given pressure and temperature. Quasiharmonic approximation was used for calculation of  $\Delta g_{\text{def}} = \Delta u_{\text{def}} + P\Delta v_{\text{def}} - T\Delta s_{\text{def}}$ . The energies of the hydrogen bonds in the ice lattice were calculated with the use of data from ref 35. The calculation procedure was described in ref 36. He– $\text{H}_2\text{O}$  interaction energies were calculated with use of the 6–12 potential. Parameters of the potential were taken from ref 37. The value  $\Delta g_{\text{He}}$  was calculated with the use of a liquid cell model and a helium equation of state in the form of Redlich–Kwong. The described model is a close to approximation of van der Waals and Platteeuw<sup>38</sup> modified for a stable lattice of the host, except for an assumption about invariance of properties of a host lattice in the case of implementation of guest molecules. It is convenient to reformulate eq 5 as

$$f = \frac{2x}{1 - 3x} \exp\left(\frac{\mu_{\text{He}}^{s0} - \mu_{\text{He}}^{g0}}{RT}\right) = \mu_{\text{He}}^{sg}(P, T) \frac{x}{1 - 3x} \quad (6)$$

This equation is equivalent to the Henry’s law for equilibrium between gaseous helium and a solid solution of helium in ice Ih;  $H_{\text{He}}^{sg}$  is Henry’s constant. For diluted solutions, eq 6 approaches the canonical form of the Henry’s rule, where the fugacity of helium is proportional to its concentration in the solid solution

$$f = H_{\text{He}}^{sg}(P, T)x \quad (7)$$

The solubility of helium in ice was derived using equation states of ice<sup>32</sup> and helium.<sup>33</sup> The results of the calculations are summarized in Table 1 and Tables s1 and s2 in the Supporting Information.

**Table 1. Calculated Solubility of Helium in Ice Ih ( $\text{cm}^3$  of He at Normal Conditions per 1 g of Ice Ih)<sup>a</sup>**

P (bar)	0 °C	−10 °C	−20 °C
200	3.10(i) 1.76(liq)	3.28	3.48
400	5.93(i) 3.37(liq)	6.27	6.65
600	8.67(i) 4.82(liq)	9.18	9.75
800	11.48(i) 6.12(liq)	12.13	12.91
1000	14.49(i) 7.26(liq)	15.31	16.26
1200	17.74(i) 8.24(liq)	18.79	19.95
1400	21.43(i) 9.08(liq)	22.65(i) 9.12(liq)	24.10
1600	22.65(i) 9.77(liq)	27.04(i) 9.66(liq)	28.77
1800	30.48(i) 10.30(liq)	32.14(i) 10.02(liq)	34.20
2000	36.06(i) 10.67(liq)	38.02(i) 10.19(liq)	40.55
P (bar)	−30 °C	−40 °C	−50 °C
200	3.70	3.98	4.28
400	7.10	7.59	8.17
600	10.38	11.12	11.94
800	13.74	14.72	15.85
1000	17.34	18.62	20.04
1200	21.33	22.91	24.72
1400	25.76	27.73	29.99
1600	30.83	33.19	35.98
1800	36.64	39.63	42.95
2000	43.45	46.99	51.17

<sup>a</sup>(i) is the extrapolated value of the solubility calculated for pressures and temperatures in which liquid water is the thermodynamically stable phase (these values are given for convenience of interpolation). (liq) is the solubility of helium in liquid water at these conditions.

For the equilibrium gas–liquid solution, experimental data evidence low solubility of noble gases in water, and hence, the equilibrium between the liquid and the gas phase can be described by the Henry’s rule in the form

$$f = H_{\text{He}}^{\text{wg}}y \quad (8)$$

Here,  $H_{\text{He}}^{\text{wg}}$  is the Henry constant for the equilibrium water–gas, and  $y$  is the mole fraction of the guest component in the aqueous solution. The necessary data were taken from ref 34 reporting the helium solubility in liquid water at pressures up to 1000 bar and temperatures 0 °C and above. Extrapolation to higher pressures and temperatures below 0 °C was made with the Krichevsky–Kazarnovsky equation. Extrapolation to subzero temperatures was made using the helium solubility in water at 0 and 25 °C; the resulting corrections appeared to be small in all cases.

The equilibrium for the liquid solution–solid solution is described as

$$\mu_{\text{He}}^{\text{lo}} + RT \ln y = \mu_{\text{He}}^{\text{so}} + RT \frac{2x}{1-3x} \quad (9)$$

$$\mu_{\text{w}}^{\text{lo}} + RT \ln(1-y) = \mu_{\text{w}}^{\text{so}} + \frac{1}{2}RT \ln \frac{1-3x}{1-x} \quad (10)$$

Here,  $\mu_{\text{w}}^{\text{lo}}(P, T)$  is the molar Gibbs energy of liquid water. For diluted solutions, these equations can be rewritten as a dependence of distribution coefficients of the components between the solid and liquid solutions on temperature

$$\kappa_{\text{He}} = \frac{x}{y} = \frac{1}{2} \exp \left( \frac{\mu_{\text{He}}^{\text{lo}} - \mu_{\text{He}}^{\text{so}}}{RT} \right) \quad (11)$$

$$\kappa_{\text{w}} = y - x = \frac{\mu_{\text{w}}^{\text{lo}} - \mu_{\text{w}}^{\text{so}}}{RT} \quad (12)$$

Distribution coefficient of helium can be expressed using Henry's constants for the equilibria between gas and solid and liquid solutions

$$\kappa_{\text{He}} = \frac{H_{\text{He}}^{\text{wg}}}{H_{\text{He}}^{\text{sg}}} \quad (13)$$

In eq 12

$$\mu_{\text{w}}^{\text{lo}} - \mu_{\text{w}}^{\text{so}} = h_{\text{w}}^{\text{sl}} - T s_{\text{w}}^{\text{sl}} \quad (14)$$

where  $\mu_{\text{w}}^{\text{sl}}(P, T)$  and  $s_{\text{w}}^{\text{sl}}(P, T)$  are the enthalpy and the entropy of nonequilibrium ice melting for given  $T$  and  $P$ . As the equilibrium between the solid and the liquid solutions of helium in ice Ih occurs in a narrow temperature range, it can be considered as temperature-independent. Hence,  $h_{\text{w}}^{\text{sl}} = T_0 s_{\text{w}}^{\text{sl}}$ , where  $T_0$  is the melting point of ice at pressure  $P$  and  $h_{\text{w}}^{\text{sl}}$  is the enthalpy of ice melting at this pressure. In this approximation

$$\kappa_{\text{w}} = \frac{h_{\text{w}}^{\text{sl}}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (15)$$

Ice melting enthalpies at varying pressures are given in ref 39. To the first approximation, melting enthalpy is linearly related to pressure as

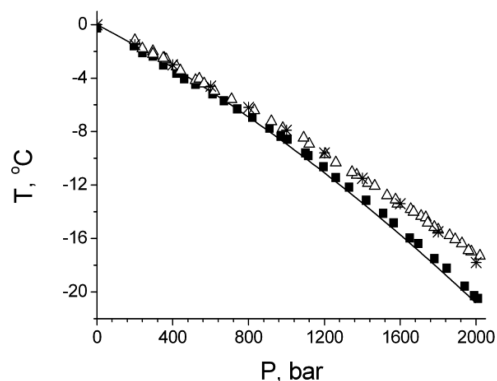
$$h_{\text{w}}^{\text{sl}} = u_{\text{w}}^{\text{sl}} + v_{\text{w}}^{\text{sl}} P \quad (19)$$

where  $u_{\text{w}}^{\text{sl}}$  and  $v_{\text{w}}^{\text{sl}}$  are the changes in internal energy and molar volume upon ice melting. Therefore, the data of ref 39 were approximated with a linear equation. Hereafter, this approach will be referenced as “calculation method 1” or “method 1”. Examples of calculations with this method are given in ref 25. One should note that the method is purely theoretical.

## RESULTS AND DISCUSSION

The results of our experiments on the solubility of helium in ice Ih at −1 °C and pressures up to 130 bar are shown in Figure 1, numerical data being presented in Table s1 in the Supporting Information. In this range of pressures, the solubility depends on the pressure practically linearly; the solubility of helium on ice is higher than that in liquid water for the same temperature and pressure. For comparison, we have calculated the solubility of helium in ice Ih at the same pressures using method 1.<sup>25</sup> Calculations were performed for two temperatures, −1 and −41 °C (Figure 1, Table s1 in the Supporting Information). For −1 °C, the calculated solubilities generally exceed measured ones. However, the average difference between calculated and measured solubilities is 0.05(5) cm<sup>3</sup>/g. Hence, statistically, the difference between calculated and measured values falls within uncertainty. It is noteworthy that the trend of calculated values (method 1) to exceed experimental ones is more pronounced at lower pressures, which can be related to incomplete achievement of equilibrium at these conditions. Therefore, the agreement between the calculated and our experimental data is good for this pressure range. Our data allow estimation of a dependence of the solubility of helium in ice Ih on the temperature (Table s1 in the Supporting Information). One can conclude that our experimental and calculated solubilities are in satisfactory agreement with experimental data obtained at −25<sup>10</sup> and −41 °C<sup>11</sup> (Figure 1). The difference with the data of refs 13 and 14 is significant.

Pressure dependences of melting of pure ice Ih and ice Ih pressurized with helium are shown in Figure 2 and Table s3 in

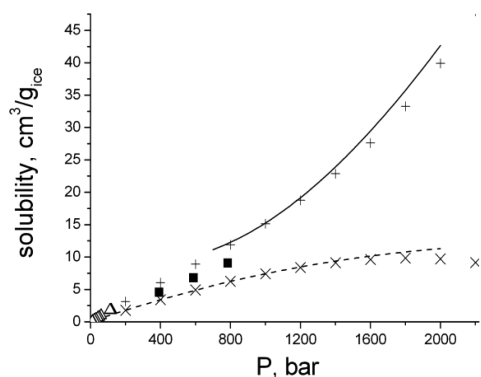


**Figure 2.** Pressure dependence of melting temperatures of pure ice Ih and ice Ih pressurized with helium. Solid line, melting of ice, data from ref 40; ■, melting of ice, our data; \*, melting of ice under He pressure, method 1 calculations; Δ, melting of ice under He pressure, our experimental data.

the Supporting Information. Three series of experiments have been carried out for each curve, the precision being good. The obtained melting curve of ice Ih satisfactory matches the literature data,<sup>40</sup> although there is a systematic shift equal to the maximum estimated experimental error. As we were primarily interested in the difference between two curves, we have not attempted to enhance convergence between our data and that from the literature. The data sets were interpolated with second-order polynomials further used in calculations. Only data for pressures above 700 bar were used as at lower pressures, the difference in melting points falls within the measurement uncertainty.



The concentration of helium dissolved in ice was derived from the difference in the melting temperature of pure ice and ice under helium pressure with use of eq 15 (hereafter “calculation method 2” or “method 2”). Method 2 differs from method 1 by use of experimental melting temperatures of pure ice and ice under helium pressure instead of calculations. The solid and liquid solutions were supposed to be in equilibrium. As in calculations by method 1, enthalpies of ice melting at different pressures were taken from ref 39 and approximated with a linear equation. Extrapolation of the helium solubility in water to higher pressures and temperatures below 0 °C<sup>34</sup> was made with the Krichevsky–Kazarnovski equation. Figure 3

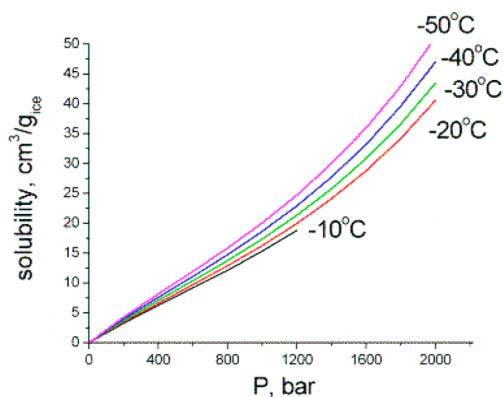


**Figure 3.** Solubilities of helium in ice Ih at high pressures. Solid line, solubility of He in ice Ih along its melting curve calculated with the use of the method 2; +, solubility of He in ice Ih along its melting curve calculated with use of method 1; dashed line, solubility of He in liquid water along the ice melting curve, experiment and extrapolation; x, solubility of He in liquid water along the ice melting curve calculated with the use of method 1; Δ, solubility of helium in ice at low pressures, our data at −1 °C; ■, solubility of helium in ice, data of ref 12.

illustrates experimental and extrapolated solubilities of helium in liquid water at temperatures and pressures corresponding to the monovariant equilibrium liquid solution of helium in a water–solid solution of helium in ice–gaseous helium. Solubilities of helium in ice Ih calculated with method 2 are given in Table S2 (Supporting Information) and Figure 3. These results are in satisfactory agreement with our experimental data on solubility at low pressures but are appreciably higher than the literature data obtained in the same way<sup>12</sup> (Figure 3). The data on the solubility of He in ice and liquid water show significant divergence especially at high pressures (Figure 3). An increase of the He solubility in ice with a pressure increase may be explained by (a) a temperature drop along this curve and (b) the nonlinear dependence of the He solubility on the pressure according to eq 6. The occurrence of a maximum on the pressure dependence of the He solubility in liquid water may be rationalized in terms of breaking of the open structure of liquid water caused by a pressure increase.<sup>41</sup>

Using method 1, we have calculated the monovariant curve of melting of ice Ih pressurized with helium, as well as the solubilities of helium in liquid water and ice Ih at selected points of this curve. Numerical data are given in Table S2 in the Supporting Information. The comparison of theoretical data derived by method 1 to other results of this study is illustrated in Figures 2 and 3. It is evident that there is good accord between data sets obtained by different methods. The solubility of helium in ice Ih shows the average discrepancy between

different methods within 5%. In all cases, the largest differences between the calculations and the experiment occur at the highest pressures. In general, one can conclude that the data on helium solubility in ice Ih at pressures up to 2000 bar obtained by three independent methods (direct measurements, calculation from the melting temperature of ice pressurized with helium, and thermodynamic calculations) are in good accord. It is possible to conclude that thermodynamic calculations by method 1 afford correct values of the solubility of helium in ice Ih in a wide range of temperatures and pressures. Hence, we concluded that it would be useful to calculate solubilities for pressure ranging up to 2000 bar and temperatures from 0 to −50 °C. Corresponding values are collected in Table 1 and Figure 4. For convenience of deriving solubilities at



**Figure 4.** Solubility of helium in ice Ih at different pressures and temperatures.

intermediate temperatures and pressures, Table 1 gives the supposed solubility of helium in ice Ih for temperatures and pressures where ice Ih is unstable. The calculated solubility of helium in liquid water under the same  $P$ – $T$  conditions is also given. The nonlinear shape of all curves is related to the nonlinear character of eq 6, which allowed us to calculate the solubility of helium in ice Ih. The temperature decrease results in an increase of the helium solubility because the enthalpy of helium transfer from solid solution to gas is positive.

## CONCLUSION

This study presents three independent data sets on the solubility of helium in ice Ih. (1) Solubility was experimentally measured at −1 °C and pressures below 120 bar. (2) The difference between melting points of pure ice Ih and ice Ih pressurized with helium was used to derive the solubility of helium for pressure in the range of 700–2000 bar. (3) Under the same  $P$ – $T$  conditions, the solubility of helium in ice Ih was calculated by thermodynamic modeling. The comparison of the data obtained has revealed good convergence of the results, that is, the suggested calculation method is correct. Using this method, we have calculated solubilities of helium in ice Ih for pressures up to 2000 bar and temperatures of 0–50 °C. To summarize, this study for the first time presents reliable data on the solubility of helium in ice Ih for a wide range of temperatures and pressures. One may assume several fields in which our data may be applied. First of all, helium is the most commonly used gas for dead space measurement in adsorption studies. It is necessary to be able to evaluate the systematic error when those kinds of experiments are done on ice with

helium as the calibration gas. Information about helium solubility in ice may be useful for underground storage of natural gas containing helium (especially in permafrost regions) and in high-pressure studies where helium is often used as pressure-transmitting media. Finally, these data may be used in studies directed to design new methods of helium separation from natural gas.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

(1) Experimental and calculated data on the solubility of helium in ice Ih at different temperatures. (2) High-pressure solubility of helium in ice Ih and liquid water. (3) Experimental melting temperatures of pure ice Ih and ice Ih under different pressures of helium. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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