

High-Pressure Gas Hydrates of Argon: Compositions and Equations of State

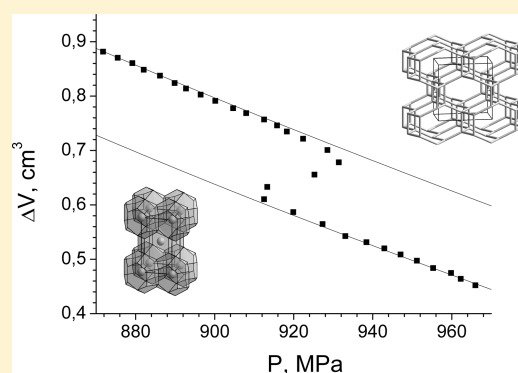
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ABSTRACT: Volume changes corresponding to transitions between different phases of high-pressure argon gas hydrates were studied with a piston–cylinder apparatus at room temperature. Combination of these data with the data taken from the literature allowed us to obtain self-consistent set of data concerning the equations of state and compositions of the high-pressure hydrates of argon.



INTRODUCTION

Gas hydrates are inclusion compounds formed by water and gas (or a volatile liquid), usually under increased pressures and/or low temperatures. The host lattice in gas hydrates is a tetrahedral hydrogen-bonded network, which commonly contains two or more types of polyhedral cavities.^{1,2} A reason for permanent interest in these compounds is the discovery of enormous deposits of gas hydrates in the Earth's crust;³ suggested existence of gas hydrates on some celestial bodies is also of interest.^{4,5} Most gas hydrates formed under pressures close to atmospheric and involving nonpolar or low-polar molecules belong to three structural types: cubic structure I (CS I), cubic structure II (CS II), and hexagonal structure III (HS III, sH or structure H).¹ Various aspects of the structural chemistry and physical chemistry of low-pressure gas hydrates were considered earlier in refs 1, 2, 6, and 7. Investigation of high-pressure gas hydrates formed by methane, argon, and tetrahydrofuran at pressures above 0.5 GPa has revealed new types of hydrate frameworks.^{8–10} Structures of high-pressure gas hydrates as well as phase diagrams of respective systems are discussed in refs 8–28. The distinctive features of high-pressure gas hydrates are the following: (1) multiple occupation of gas hydrate cavities by guest molecules and (2) formation of new types of gas hydrate frameworks including frameworks with space-filling polyhedrons and icelike nonpolyhedral frameworks. In this article, we will denote the structural type of the high-pressure methane hydrate⁹ as orthorhombic structure II (OS-II), high-pressure argon hydrate⁸ as tetragonal structure IV (TS-IV), and high-pressure hydrate of tetrahydrofuran¹⁰ as orthorhombic structure III (OS-III). It should

be noted that different authors use different systems of notations for structural types of gas hydrates. For example, in ref 10 CS-I, HS-III, and OS-II methane hydrates are denoted as SIMH, MH-II, and MH-III, respectively. Authors of ref 26 denoted CS-II, TS-IV, and OS-II hydrates of argon as AH-sII, AH-sT, and AH-IceIIh, respectively.

The phase diagram of the argon–water system has been studied thoroughly. In the early work^{2,5} the decomposition curve of the argon hydrate occurring at the atmospheric pressure has been studied up to pressures of 0.4 GPa. In ref 23, differential-thermal analysis was used at pressures up to 1.5 GPa and the formation of three hydrates (h , h_2 , h_3) was reliably established, though it was noted that a phase transition is very probable at a pressure of about 0.45 GPa; one of the reasons might be the existence of one more hydrate. Subsequent studies confirmed the existence of this phase (h_1) and substantially broadened the range of the investigated pressures;^{24,26–28} no new hydrate phases have been observed in these studies. So, four hydrates have been positively determined on examination of the phase diagram of the argon–water system. Structural data for these hydrates are presented in refs 8, 26, 28, and 29. In ref 8 the studies were carried out on deuterohydrates and in refs 26, 28, and 29 on protium hydrates. The low-pressure phase h is a CS-II hydrate; it is stable up to 0.46 GPa. Powder neutron diffraction studies revealed multiple occupation of large cavities of the CS-II hydrate h ; these cavities

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contain at average 1.8 and 2.3 argon atoms at 0.34 and 0.43 GPa, respectively.⁸ The unit cell formula of this hydrate may be written as $(8n+16)\text{Ar}\cdot 136\text{H}_2\text{O}$, where n is the average occupation of the large cavity. A phase transition observed for this hydrate at 0.46 GPa corresponds to the transformation of the CS-II hydrate to an HS-III (structure H) hydrate h_1 with large cavities filled with five atoms of argon.⁸ Each of the small cavities is occupied by one argon atom. The unit cell formula of the hydrate h_1 is $10\text{Ar}\cdot 34\text{H}_2\text{O}$. The TS-IV argon hydrate h_2 is formed at pressures above 770 MPa.⁸ This hydrate framework contains the only type of polyhedral cavities; in the case of argon hydrate each of them is occupied by two argon atoms; the unit cell formula of the hydrate is $4\text{Ar}\cdot 12\text{H}_2\text{O}$. Finally, hydrate h_3 has the OS-II structure; polyhedral cavities in this hydrate are connected via octagonal faces forming channels occupied by argon atoms.²⁶ The unit cell formula of this hydrate is $4\text{Ar}\cdot 8\text{H}_2\text{O}$.

The information concerning high-pressure argon hydrates taken from different sources is sometimes contradictory, e.g., no HS-III hydrate has been observed in ref 26. In addition, little information is available on chemical reactions of transitions between different phases of high-pressure argon hydrates, as well as on equations of state of these hydrates. To the best of our knowledge, only a few results related to this subject have appeared in the literature (e.g., ref 24), while numerous studies of this kind have been undertaken for high pressure ices (e.g., refs 30–32). In this contribution, we present our recent results concerning chemical reactions of transitions between different phases of high-pressure argon hydrates and their equations of state.

EXPERIMENTAL METHODS

Volume changes accompanying phase transformations between high-pressure hydrates were measured with a precise high-pressure PVT installation (Figure 1).³³ The installation consists of a high-pressure cylinder (1) with internal diameter 12 mm, obturator (2) assembled with manganin gauge (3) and a movable piston (4). Movement of the piston (4) was controlled by a hydraulic press (5). Shifts of the piston were measured with a mechanical indicator (6). Accuracy of the measurements was ± 0.01 mm providing accuracy of 1 mm^3 in the determination of the volume change. The highest operational pressure was 1.5 GPa. The initial pressure in the apparatus (about 100 MPa) was achieved with a gas compressing device (7), and further raised to the desired value with a press. The pressure was measured with a manganin gauge (3) with accuracy better than ± 4 MPa at pressures up to 1 GPa; resistivity of the manganin gauge (3) was measured with use of a precise resistance gauge (8). Temperature of the high-pressure cylinder was maintained by a liquid thermostat with the accuracy ± 0.5 °C (not shown in Figure 1).

When investigating the argon–water system, the installation precooled to 263 K was loaded with ice powder packed to the sample holder (9, Figure 1). The ice powder was prepared by spraying distilled water in liquid nitrogen (1.5–1.7 g, particle size about 0.05 mm). Then the pressure cell was flushed with argon, and the initial pressure was set (about 100 MPa) and sustained for about 5 h for hydrate formation. During the exposure the pressure was approximately constant, the temperature being within 263–268 K. Afterward, the press was employed to compress the system to the initial pressure of the experiment (0.7–1.1 GPa). The sample chamber was then slowly warmed and kept at room temperature from 2 to 10 days, the final results of the measurements being insensitive to the duration of the

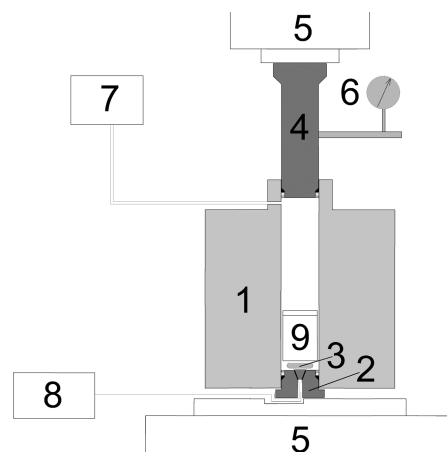


Figure 1. High-pressure PVT installation for measuring volume changes accompanying phase transformations (ref 33): (1) high-pressure cylinder; (2) obturator; (3) manganin gauge; (4) movable piston; (5) hydraulic press; (6) mechanical indicator; (7) gas compressing device; (8) precise resistance gauge; and (9) sample holder.

exposure. Independent studies proved that the procedure provided complete conversion of water into the gas hydrates (ref 35). Internal volume of the pressure cell at the start of experiment was about 12 cm^3 (~ 100 MPa); therefore, the argon gas in the chamber was always in excess during our experiments.

To measure volume changes accompanying the hydrate–hydrate transformation at a constant temperature, the piston (4) was shifted upward in a stepwise manner. Each step of the piston shift corresponded to a pressure drop of 5–10 MPa in the high-pressure cylinder. At each pressure the system was kept for 5–15 min, longer delays being experimentally unfeasible. As a rule, the pressure settled in 2–3 min and did not show observable evolution. Values of the piston shift were measured with the indicator (6); volume changes of the high-pressure cylinder (ΔV) were calculated from these data (zero volume change at the start of experiments, maximal volume changes at the end of experiments). Values of the pressure at the end of each step as well as corresponding ΔV were recorded. The data obtained in our experiments were presented as ΔV versus pressure plots (Figure 2).

Preparation of the samples of high-pressure argon hydrates and determination of their compositions was described elsewhere.³⁵ The CS-II argon hydrate was synthesized in a high-pressure piston–cylinder apparatus from thoroughly ground ice and an excess of argon at pressures close to 250 and 400 MPa. To equilibrate the system, the mixture was kept at this pressure from 2 to 3 weeks. After that the whole apparatus was cooled to 77 K in liquid nitrogen and a quenched sample of high-pressure hydrate was recovered. The sample was kept in liquid nitrogen no longer than 24 h before the measurements; no appreciable changes in the gas hydrate composition were observed within this period of time. The release of gas from the studied samples was monitored as a function of temperature by collecting the gas into a calibrated buret filled with a saturated aqueous solution of NaCl. The weight of water that remained after the decomposition of hydrate was calculated as a difference between the weight of the empty cell and the weight after the experiment. The estimated size of particles in the main fraction of the hydrate was about 0.1 mm as determined by microscopic observations. The weight of the hydrate samples used for the analyses was within 0.3–0.5 g. The measured gas volumes were corrected for vapor pressure over the NaCl

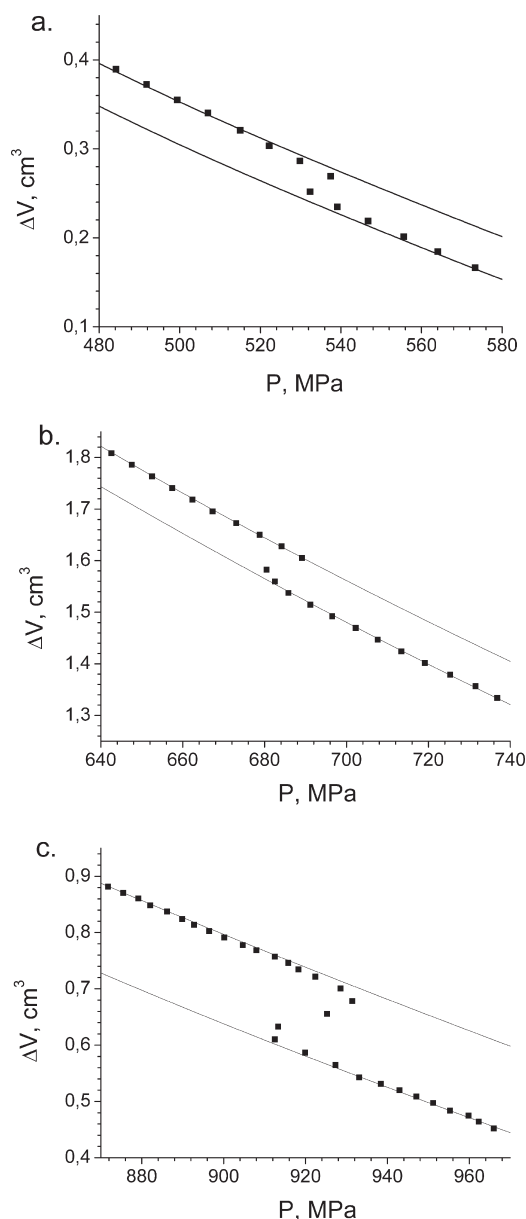


Figure 2. Typical experimental curves: (a) transformation HS-III \rightarrow CS-II, $T = 296$ K, (b) transformation TS-IV \rightarrow HS-III, $T = 296$ K, and (c) transformation OS-II \rightarrow TS-IV, $T = 300$ K.

solution and were reduced to normal conditions. The composition of hydrates was calculated from the measured quantities of gas and water. The X-ray diffraction study was performed using synchrotron radiation at the 4th beamline of the VEPP-3 storage ring (Siberian Synchrotron and Terahertz Radiation Center, Budker Institute of Nuclear Physics SB RAS), at $\lambda = 0.3685$ Å. An image plate detector MAR3450 (pixel dimension $100\ \mu\text{m}$) was used to register the diffraction pattern. The distance between the sample and the detector calibrated against the diffraction pattern of sodium chloride was 391.0 mm. Experimental procedure is described elsewhere.³⁵

RESULTS AND DISCUSSION

The numerical results of our experiments are listed in Table 1; typical experimental P – V curves are shown in Figure 2. The shape

of the experimental curves between the phase transition regions was indistinguishable from the isotherm of pure argon³⁶ due to following reasons: (1) the amount of argon in the experimental cell was several times larger than the amount of the hydrate in the experimental cell and (2) compressibility of fluid argon is higher than that of solid substances. The differences observed in some cases most likely can be attributed to insignificant argon loss during sealing. The value of the volume change during the phase transition was calculated as the difference between the volumes corresponding to the isotherms drawn at the neighboring regions of the curve, determined at the given pressure. The hydrate–hydrate phase transformations proceeded slowly in all the cases (up to an hour), sometimes in several stages. Pressure rise in the system, caused by the transformations of the hydrates, reached 100 MPa in some cases. Transition pressure values determined in different experiments substantially differed from each other.

Attempts to synthesize the hydrate OS-II at the temperature of 297 K and pressure above 1 GPa were unsuccessful. In this case, the volume rise occurred at the pressure of 0.955 GPa, which corresponds to melting of ice VI. So, under these conditions the formation of the hydrate from ice VI and argon does not take place. For this reason, we studied the transformation of hydrate OS-II into hydrate TS-IV at a temperature of 300 K. Under these conditions, all operations took place in the P – T region corresponding to the existence of liquid water. In this case, the formation and decomposition of the hydrate occurred without any hindrance.

In order to calculate the volume rise during the transformations of high-pressure hydrates, one needs the information about (1) the equations of state for all phases existing in the system, and (2) the composition of these phases. The compositions of hydrates OS-II, TS-IV, and HS-III were studied in refs 8, 28, and 35 and the corresponding data are presented in Table 1. It follows from structural and thermodynamic considerations that varying occupation of argon positions in these hydrates is unlikely. In addition, occurrence of the “empty” (not filled with guest molecules) space in the hydrate framework under high-pressure conditions is rather improbable from the thermodynamic point of view. We speculate that argon hydrates OS-II, TS-IV, and HS-III are stoichiometric compounds. This assumption will be supported by our experimental data as discussed below. The CS-II argon hydrate has variable composition; at the pressure of 0.43 GPa the number of argon atoms residing in the large cavity of the hydrate framework can reach 2.3 .⁸ These data were obtained on the basis of refinement of the powder neutron diffraction patterns of the hydrates, and thus, they are to be verified by use of an independent method. In order to do this, we used the direct determination of the composition of quenched samples of high-pressure hydrates; previously, we used this procedure to study the composition of the HS-III argon hydrate. According to the data of powder X-ray diffraction, a quenched sample taken out of the apparatus was pure hydrate CS-II (Figure 3). The composition of the hydrate was calculated on the basis of the volume of gas evolved during sample decomposition and the mass of the residual water. We assume that all the small cavities are filled with one argon atom (double filling is impossible here, as suggested by geometric considerations;⁸ the existence of vacant cavities at such a high pressure is very doubtful). The number of argon atoms in the large cavity, calculated under these assumptions, is shown in Figure 4; the results of ref 8 are shown there, too. The sets of data obtained using different methods are in good agreement. Extrapolation to the pressure of 0.479 GPa gives 2.44 argon atoms per large cavity. It is difficult

Table 1. Comparison of the Measured and Calculated Volume Changes in Reactions 1, 2, and 3^a

reaction	OS-II → TS-IV (reaction 1)	TS-IV → HS-III (reaction 2)	HS-III → CS-II (reaction 3)
Experimental Data			
$\Delta V_{\text{exptl}}, \text{cm}^3/\text{g}_{\text{H}_2\text{O}} (P_{\text{transformn}}, \text{GPa})$	0.107 (0.931) 0.099 (0.940) 0.093 (0.959)	0.056 (0.689) 0.055 (0.668) 0.055 (0.750)	0.030 (0.407) 0.024 (0.537) 0.041 (0.494)
averaged values: $\Delta V_{\text{exptl}}, \text{cm}^3/\text{g}_{\text{H}_2\text{O}} (P_{\text{transformn}}, \text{GPa})$	0.100(4) (0.943)	0.055(1) (0.702)	0.032(5) (0.479)
Calculated Volume Changes			
$B_0, \text{GPa}; V_0, \text{\AA}^3$	OS-II: $B_0 = 13.8, V_0 = 323.1$; TS-IV: $B_0 = 9.0; V_0 = 463.4$ HS-III: $B_0 = 9.0, V_0 = 1314.7$; CS-II: $B_0 = 11.0, V_0 = 5103.7$		
molar volume of phases at $P_{\text{transformn}}, \text{cm}^3/\text{mol}$	OS-II: 183.190 TS-IV: 255.659 Ar: 22.585	TS-IV: 260.357 HS-III: 738.784 Ar: 23.931	HS-III: 754.626 CS-II: 2953.326 Ar: 26.219
$\Delta V_{\text{calcd}}, \text{cm}^3/\text{g}_{\text{H}_2\text{O}}$	0.121	0.054	0.021
Volume Changes Calculated with Use of Corrected Birch–Murnaghan EOS for TS-IV and HS-III Hydrates (See Text)			
$B_0, \text{GPa}; V_0, \text{\AA}^3$	OS-II: $B_0 = 13.8, V_0 = 323.1$; TS-IV: $B_0 = 9.0; V_0 = 455.3$ HS-III: $B_0 = 9.0, V_0 = 1292.0$; CS-II: $B_0 = 11.0, V_0 = 5103.7$		
molar volume of phases at $P_{\text{transformn}}, \text{cm}^3/\text{mol}$	OS-II: 183.190 TS-IV: 251.227 Ar: 22.585	TS-IV: 255.845 HS-III: 725.999 Ar: 23.931	HS-III: 741.578 CS-II: 2953.326 Ar: 26.219
$\Delta V_{\text{calcd}}, \text{cm}^3/\text{g}_{\text{H}_2\text{O}}$	0.100	0.054	0.040

^a 1 mol of hydrate was taken as (4Ar*8H₂O), (4Ar*12H₂O), (10Ar*34H₂O), and (35.52Ar*136H₂O) for OS-II, TS-IV, HS-III, and CS-II, respectively.^{8,28,35} Unit cell volumes of gas hydrates were described with use of Birch–Murnaghan equation $P = 1.5B_0((V_0/V)^{7/3} - (V_0/V)^{5/3})(1 + 0.75(B_0' - 4)((V_0/V)^{2/3} - 1))$ ($B_0' = 4$ in all cases); coefficients of this equation are shown in the table. Molar volume of argon at different pressures was taken from ref 36. Reaction 1 was studied at 300 K, reactions 2 and 3 at 296 K.

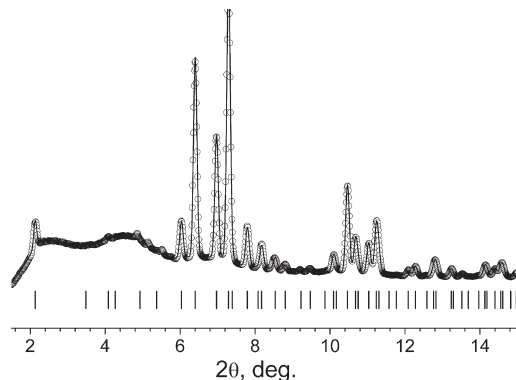


Figure 3. X-ray powder diffraction pattern of the CS-II argon hydrate synthesized at 250 MPa. The pattern was taken at 105 K.

to determine the error of this value; a rough estimation gives ± 0.3 atoms per cavity. The composition of the unit cell corresponding to this value for CS-II hydrate is presented in Table 1. It should be noted that the data of ref 37 concerning occupancy of small cavities with argon atoms partially contradict the above considerations. According to the information presented in this reference, about 80% of the small cavities are occupied at the pressure of 300 MPa. We believe that the latest data presented in the ref 8 are more consistent with general physicochemical regularities related to the occupation of clathrate cavities with guest molecules. In any case, calculation of occupancy of large cavities taking into account 80% occupancy of small cavities increases the content of the argon atoms by ~ 0.4 . This value is close to our experimental error. On the basis of the above

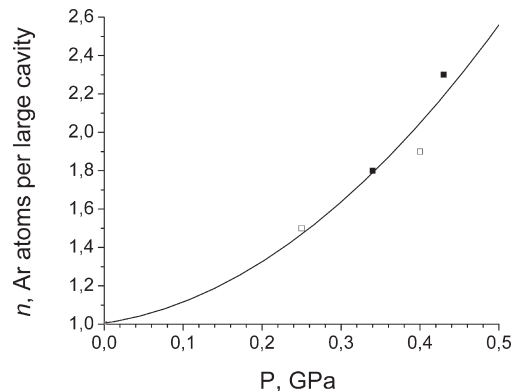
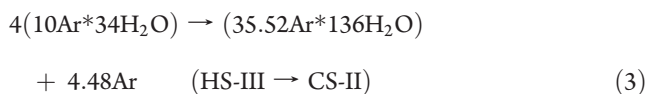
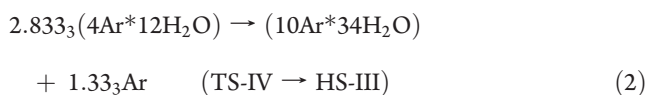
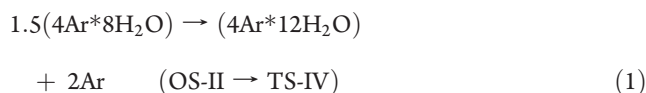


Figure 4. Number of guest argon atoms in the CS-II argon hydrate at different pressures. Open symbols, our data; solid symbols, data of ref 8.

considerations, the following reactions describing transformations of the high-pressure hydrates of argon may be written:



A set of the experimental X-ray data allowing determination of the coefficients of the Birch–Murnaghan equation of state $P = 1.5B_0((V_0/V)^{7/3} - (V_0/V)^{5/3})(1 + 0.75(B_0' - 4)((V_0/V)^{2/3} - 1))$ is currently available only for the OS-II hydrate.²⁸ This set of data is rather reliable because the sample under investigation contained not only the hydrate but also ice VIII, for which the calculated cell parameters are in good agreement with the literature data. Starting from the primary experimental data reported in this work, we calculated the parameters B_0 and V_0 for this phase (Table 1), assuming B_0' to be equal to 4. In ref 38 we analyzed the available data on compressibility of gas hydrates within different pressure ranges. It was shown that compressibility of the hydrates existing at moderate pressures is determined mainly by the compression of hydrogen-bonded framework (except for the cases when a guest molecule tightly fits into the hydrate cavity). It turned out that in the majority of cases the use of the cubic Birch–Murnaghan equation with $B_0' = 4$ allows satisfactory description of the compression curves for gas hydrates at pressures up to 1.5–2 GPa. At pressures below 0.5 GPa, the bulk modulus of gas hydrates is close to 9 ± 2 GPa ($B_0' = 4$); in the hydrates with single filling of cavities and relatively small guest molecules (weak guest–host interactions), B_0 is close to the lower limit, while in the gas hydrates with variable occupation of cavities it is close to the upper limit. Within the pressure range 0.5–2 GPa, the value of B_0 is close to 9 GPa ($B_0' = 4$) in all cases. On the basis of these data, it is possible to state that the most probable values for the argon hydrates under consideration will be the following: for CS-II hydrate $B_0 = 11$, $B_0' = 4$; for HS-III hydrate $B_0 = 9$, $B_0' = 4$; for TS-IV hydrate $B_0 = 9$, $B_0' = 4$.

In order to determine the coefficient V_0 in the Birch–Murnaghan equation of state, it is necessary to know the data on the parameters of their unit cell, at least at one pressure value. The data of this kind were reported in refs 8, 26, 28, 29, and 39, and among these works, ref 26 presents one set of values for each of the hydrates CS-II, TS-IV, and OS-II; in ref 8 one set of values for each of the hydrates CS-II, HS-III, and TS-IV is reported; values of the unit cell parameter for CS-II are reported in refs 8, 28, 29, and 39. The data on the unit cell parameter of the hydrate CS-II at atmospheric pressure and the temperature about 100 K were reported in refs 28 and 29. These values may be easily recalculated to the room temperature using the results reported in ref 40. As we have mentioned above, the data on the pressure dependence of the unit cell parameters of hydrate OS-II presented in ref 28 seem to be correct due to presence of ice VII reflections in the powder diffraction pattern. In this case, ice VII plays the role of internal standard that makes these data reliable. Their comparison with the values presented in ref 26 shows that the results reported in ref 26 are most probably overestimated. Taking into account the features of diffraction experiments in diamond anvils, we may expect that the unit cell parameters for other hydrates studied in that work are overestimated, too. For this reason, we excluded the data of ref 26 from consideration. The heterogeneous character of the available data should also be mentioned. The data reported in refs 8 and 39 were obtained by means of neutron diffraction on the samples with heavy water, while usual water was used for obtaining hydrates in refs 26, 28, and 29. According to the data reported in refs 41 and 42 (ice Ih and methane hydrate), we calculated the averaged ratio of unit cell parameters for the compounds based on light and heavy water; the ratio turned out to be equal to 0.99879. In our calculations, the unit cell parameters of deuterohydrates were multiplied by this factor. The V_0 values in the Birch–Murnaghan

equation of state, obtained on the basis of the above-considered literature data, are listed in Table 1.

The calculated ΔV values for mutual transformations of argon hydrates existing at different pressures are presented in Table 1. Molar volumes of argon at different pressures were taken from ref 36. One can see that there is a satisfactory agreement between the calculated and experimental data. Attention should be paid to the fact that the calculated value for reaction 1 is overestimated, while that for reaction 3 is underestimated. It is clear from the considerations presented in the previous paragraph that the equations of state for hydrates CS-II and OS-II are rather reliable, while for hydrates HS-III and TS-IV the coefficients V_0 were determined using a sole experimental point available for each hydrate. It seems reasonable to introduce corrections into the equations of state for hydrates HS-III and TS-IV, which will result in a better agreement between the calculated and experimental values. To introduce corrections, we assumed that the value determined experimentally for reaction 1, $\Delta V = 0.100 \text{ cm}^3/\text{g}_{\text{H}_2\text{O}}$, is absolutely accurate. Corrections into the equations of state for hydrates HS-III and TS-IV were introduced in such a manner that the calculated ΔV value for reaction 1 was exactly $0.100 \text{ cm}^3/\text{g}_{\text{H}_2\text{O}}$, while ΔV for reaction 2 did not change. The results of recalculation are listed in Table 1. In this case experimental and calculated values of ΔV are almost identical. The only exception is reaction 3. One can see that for reaction 3 $\Delta V = 0.040 \text{ cm}^3/\text{g}_{\text{H}_2\text{O}}$, which is somewhat more than the value obtained experimentally. At the same time, if the large cavity of hydrate CS-II contains not 2.44 but 2.57 argon atoms at average, the calculated ΔV value for reaction 3 becomes exactly equal to the value measured experimentally. This value surely does not exceed the error in determination of the composition of the CS-II hydrate (see above). So, the second data set presented in Table 1 is currently the best self-consistent set of data about the equations of state and compositions of the high-pressure hydrates of argon.

CONCLUSIONS

In this work, we presented numerical data concerning changes of volume accompanying transitions between different phases of high-pressure argon gas hydrates. Analysis of our data in combination with available data taken from the literature allowed us to obtain self-consistent set of data concerning the equations of state and compositions of the high-pressure hydrates of argon. Self-consistency of the data obtained by different experimental methods as well as by different authors is a sound argument supporting (within experimental errors) the correctness of our hypothesis concerning (1) equations of state of different phases of high-pressure gas hydrates of argon (Table 1); (2) stoichiometric nature of OS-II, RS-IV, and HS-III argon hydrates; (3) non-stoichiometric nature of CS-II argon hydrate; and (4) specific compositions of these phases.

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