Clathrate Hydrates of Sulfur Hexafluoride at High Pressures

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Abstract

The pressure dependence (0.4 MPa–1.3 GPa) of the hydrate decomposition temperatures in the sulfur hexafluoride-water system has been studied. In addition to the known low-pressure hydrate $SF_6 \cdot 17H_2O$ of Cubic Structure II, two new high-pressure hydrates have been found. X-ray analysis *in situ* showed the gas hydrate forming in the sulfur hexafluoride-water system above 50 MPa at room temperature to be of Cubic Structure I. The ability of water to form hydrates whose structures depend on the guest molecule size under normal conditions and at high pressures is discussed.

Introduction

Clathrate formation is an exquisite process affected both by the shape and size of the guest molecule. To distinguish between the above factors we studied water-noble gas systems under high pressures and showed that changing the guest molecule size, provided the shape remains spherical, causes significant differences in clathrate formation [1]. Helium and neon tend to dissolve in ices Ih and II [2–4] (however, most probably neon also forms at least one classic clathrate hydrate [1, 5]). Argon at pressures up to 3 GPa forms four hydrates [6, 7], and krypton at pressures up to 1.5 GPa forms three hydrates [8]. As for xenon, only one hydrate has been found in the pressure range up to 1.5 GPa [9]. The xenon atom is the largest among the above atoms (4.36 Å in diameter). In this connection sulfur hexafluoride is of interest. The molecule is completely inert towards water [10], it is almost spherical in shape, and it is much larger than the xenon atom ($d = 5.96$ Å). At lower pressures sulfur hexafluoride forms a hydrate of Cubic Structure II (CS-II) of composition $SF_6 \cdot 17H_2O$ [11, 12], i.e., a structure with a large number of vacant dodecahedral cavities which results in the destabilization of these hydrates under pressure and formation of new denser hydrate structures [13]. This kind of transformation was first observed in the study discussed in [14] for the water-tetrahydrofuran system where also under pressure the THF·17H₂O hydrate turns into the THF·7H₂O hydrate. The stoichiometry and the decomposition temperature curve of the hydrate verses pressure suggested Cubic Structure I. Further studies [15] showed this hydrate to be of clathrate nature, and a diffraction experiment [16] proved it to be of Cubic Structure I with the parameter $d = 12.08$ Å. However, the authors believed that the experiment was not

conclusive enough. This makes it even more interesting to find out if a similar hydrate forms in the system with SF_6 whose molecules are less suitable for the large CS-I cavities than THF molecules. This paper discusses the data obtained by studying phase equilibria in the water-sulfur hexafluoride system at pressures up to 1.5 GPa and the X-ray data on the hydrate resulting from the original CS-II hydrate under pressure.

Experimental

High pressure device for DTA analysis

The study of the phase equilibria was carried out using differential thermal analysis at high pressures. Temperature was measured with a chromel-alumel thermocouple. The standard Burdon manometer was used to measure pressures up to 250 MPa and a manganine manometer calibrated using mercury, to measure pressures up to 1.5 GPa. This technique, the high-pressure device, and the experimental cell are described in detail in [9].

X-ray experiment

The diffraction study was carried out in a specially designed high-pressure piston-cylinder device using synchrotron radiation from the VEPP-3 accelerator (Institute of Nuclear Physics, Siberian Branch of the Russian Academy of Sciences). The gas hydrate sample resided in a thick wall beryllium capsule. Compressing hydrate former (SF_6) taken in excess created hydrostatic pressure. The study was carried out at room temperature (about 22 °C). The general scheme of the device is shown in Figure 1. The sample is placed into the channel in the beryllium capsule (1), which is 1–1.5 mm
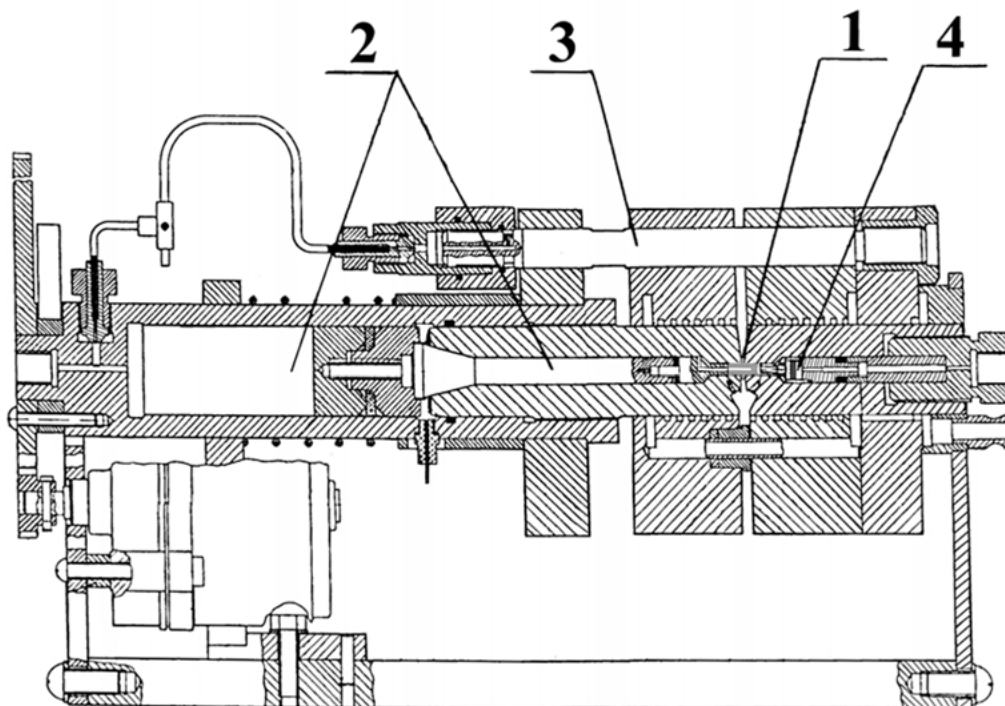
† Deceased.

Figure 1. Principal scheme of the apparatus for investigation of the powder diffraction patterns of gas hydrates at high pressures. 1 – beryllium capsule, 2 – multiplicator, 3 – compressing device, 4 – backward flap.

in diameter. The walls are 3 mm thick. The multiplicator (2) with the piston area ratio of 1 : 10 creates gas pressure in the capsule. The compressing device (3) provides a hermetic connection between the beryllium capsule (1) and the high-pressure part of the multiplicator (2) and supports the capsule. The device is filled with the gas hydrate former through the backward flap (4). The gas hydrate sample forms from ice powder and hydrate former loaded into the capsule (1) at high pressure. The X-Ray experiment was carried out according to the Debye–Scherrer scheme. The powder diffraction patterns were recorded using a one-coordinate detector, calibrated against α-quartz. A BAS-SR (FUDJI-FILM) image-plate was used at 650 MPa. The diffractogram was extracted from the image-plate data by numerical integration with use of a specially designed computer program. The sector of the row image was used for integration. Short-wave synchrotron radiation ($\lambda = 0.3635$ Å) was used.

Results and discussion

Decomposition curves of the SF$_6$ hydrates

The decomposition curves of the sulfur hexafluoride hydrates at pressures up to 1.3 GPa are shown in Figure 2, numerical data are summarized in Table 1. At least three hydrates form in this pressure interval. Hydrate h_1 (CS-II hydrate [11] with the composition SF$_6 \cdot$17H$_2$O [12]) is stable up to 33 MPa (quadruple point Q_1^h in Table 2). Metastable continuation of the decomposition curve of this hydrate was registered up to a pressure of 58 MPa (10.5 °C) in experiments performed by stepwise increase of pressure. An-

other solid phase h_2 crystallizes in this region after several melting-crystallization cycles or after prolonged standing of the system (CS-I hydrate as will be discussed below). The decomposition curve of this hydrate can be subdivided into two parts; 33–101 MPa: the hydrate decomposes to two liquids (curve $l_1h_2l_2$), and 101–132 MPa: the hydrate decomposes to aqueous rich liquid and solid SF$_6$ (curve l_1h_2s). The location of the corresponding quadruple point Q_3 is shown in Table 2. Incongruent melting of the hydrate h_2 was observed up to a pressure of 202 MPa (which significantly exceeds the highest pressure of the hydrate stability). Hydrate h_3 is stable in the pressure interval 132 Mpa–1.3 GPa. Despite the fact that our equipment allows work at pressures up to 1.5 GPa, we could not register the decomposition temperature of the hydrate by the DTA method at higher pressures because of the fast decrease of the DTA signal (which is proportional to the heat of hydrate decomposition) with the pressure increase. Two points of the h_2h_3s curve (originated from the quadruple point Q_2^h) were observed.

Phase diagram of the SF$_6$-H$_2$O system

The above observations and the data of [12] suggest the following interpretation of the SF$_6$-H$_2$O phase diagram: the monovariant curve (ih_1g) of the SF$_6$-H$_2$O hydrate decomposition (h_1) into ice (i) and gas phase (g) has been studied in the pressure range from 0.055 MPa (-9 °C) up to the point Q_1 at 0.0 °C and 0.09 MPa (Table 2). At higher temperatures the hydrate decomposes into a liquid water phase (l_1) and gas (curve l_1h_1g) which goes up to the upper quadruple point Q_2 (14.0 °C, 2.02 MPa). Further pressure increase results

Table 1. Decomposition temperatures of gas hydrates in the sulfur hexafluoride-water system at different pressures

P (MPa)	T (°C)		P (MPa)	T (°C)		P (MPa)	T (°C)		P (MPa)	T (°C)	
0.4	8.2	h_1	111	27.4	–	608	79.4	–	37	15.2	m.c. h_1
0.5	9.0	–	120	26.8	–	626	80.0	–	38	15.3	–
1	12.0	–	130	28.0	–	651	80.8	–	40	15.2	–
2	14.3	–	137	30.2	h_3	668	81.8	–	45	15.0	–
6	14.8	–	138	30.0	–	694	82.3	–	50	13.8	–
10	14.9	–	145	32.2	–	698	81.4	–	54	12.5	–
12	15.2	–	155	35.0	–	701	82.6	–	58	10.5	–
20	15.2	–	162	3606	–	706	82.8	–			
28	15.0	-	163	38.2	–	724	83.7	–	120	18.0	m.c. h_3
30	15.2	–	173	39.2	–	746	85.3	–	130	25.0	–
32	15.4	–	178	40.0	–	751	85.4	–			
34	15.6	h_2	182	40.6	-	760	85.5	–	1340	28.4	m.c. h_2
35.5	15.8	–	202	44.2	–	762	86.0	–	1720	30.6	–
37	16.3	–	214	45.7	–	780	86.6	–	1820	31.6	–
38	17.1	–	214	45.6	–	781	87.0	–	2015	32.5	–
40	17.5	–	230	48.0	–	802	86.8	–	2500	34.6	–
45	18.0	–	250	50.2	–	808	88.2	–			
47	18.1	–	262	51.2	–	822	88.2	–			
48	18.1	–	278	53.4	–	842	88.6	–			
50	18.8	–	299	56.0	–	855	89.8	–			
52	19.0	–	325	57.6	–	865	90.3	–			
54	19.7	–	361	61.3	–	870	90.4	–			
59	19.8	–	388	63.6	–	872	90.5	–			
60	20.0	–	402	65.6	–	923	92.0	–			
67	21.0	–	421	66.5	–	1010	94.3	–			
75	22.2	–	450	68.7	–	1115	97.6	–			
90	23.9	–	483	71.7	–	1210	100.5	–			
100	24.6	–	532	75.0	–	1300	96.5	–			

h_1, gas hydrate of cubic structure II.
h_2, gas hydrate of cubic structure I.
h_3, gas hydrate with unknown structure.
m.c., metastable continuation of the respective line.

Table 2. Quadruple points in the SF_6-H_2O system

Point	Coexisting phrases*	T (°C)	P (MPa)	Ref.
Q_1	il_1h_1g	0.0	0.09	[12]
Q_2	$l_1h_1l_2g$	14.0	2.02	[12]
Q_3	$l_1h_2l_2s$	25.5	101	This work
Q_1^h	$l_1h_1h_2l_2$	15.2	33	This work
Q_2^h	$l_1h_2h_3s$	28.2	132	This work

* I and s, ice and solid SF_6, l_1 and l_2, liquid aqueous and SF_6 phases, h_1, h_2, h_3, CS-II hydrate phase $SF_6 \cdot 17H_2O$, CS-I hydrate with probable stoichiometry $SF_6 \cdot 7\frac{2}{3}H_2O$, hydrate phase with unknown structure, Respectively, g, gas phase. All the phases are arranged from left to right in the order determined by increase of the SF_6 content in the phase.

in liquefaction of sulfur hexafluoride and the monovariant equilibrium $l_1g_1l_2$. The other two monovariant curves, h_1l_2g and l_1l_2g, starting at point Q_2 do not appear. However, for the known reason the latter should essentially coincide with the SF_6 boiling curve under pressure. Of particular interest is the temperature dependence of the hydrate decomposition into two liquids under pressure. In all the CS-II systems with the stoichiometry G·17H₂O (G = trimethylene oxide, 1,4-dioxane, 1,3-dioxolane) [13] studied so far at high pressures the guest was liquid under normal conditions (the hydrates of "liquids" according to [11]), i.e., the so called upper quadruple point Q_2 was detected at $P < 1$ atm.[1]

Since in hydrates of CS-II the proportion of the vacant dodecahedral cavities is large, they are all destabilized by pressure (i.e., for the melting curve $dt/dp < 0$). At some point (always at $P < 300$ MPa) CS-II hydrates inevitably change to hydrates of a denser structure [13]. In the system concerned, which is obvious from Table 1 and Figure 2, the decomposition temperature of the hydrate in the monovariant equilibrium $l_1h_1l_2$ first increases slowly with pressure increase in the range Q_2–12.0 MPa from 14.0 to 15.2 °C, does not essentially change up to 40 MPa, and only at 58 MPa decreases to 10.5 °C, (a significant part of the curve at $P > 33.2$ MPa being located in the interval of the hydrate h_1 metastability). Such an unusual run of the decomposition curve of the CS-II hydrate is due to the ability of the liquid SF_6 to be compressed considerably which in turn is explained by its low "internal pressure".[2]

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[1] Gas hydrate research workers use the following commonly accepted designations: $Q_1(il_1hg)$ is the lower quadruple point and $Q_2(l_1hl_2g)$ is the upper quadruple point, where i is ice, l_1 and l_2 are aqueous and guest (in this case, SF_6) liquid phases, respectively, h and g are hydrate and gas phases, respectively. The phases appear from the left to the right in the order of guest content increase.

[2] The internal pressure $P = \Delta H / V$, where ΔH is the evaporation heat and V is the molar volume of the liquid [10]. For water this value is of the order of 2.5 GPa while for SF_6 it is one order lower.
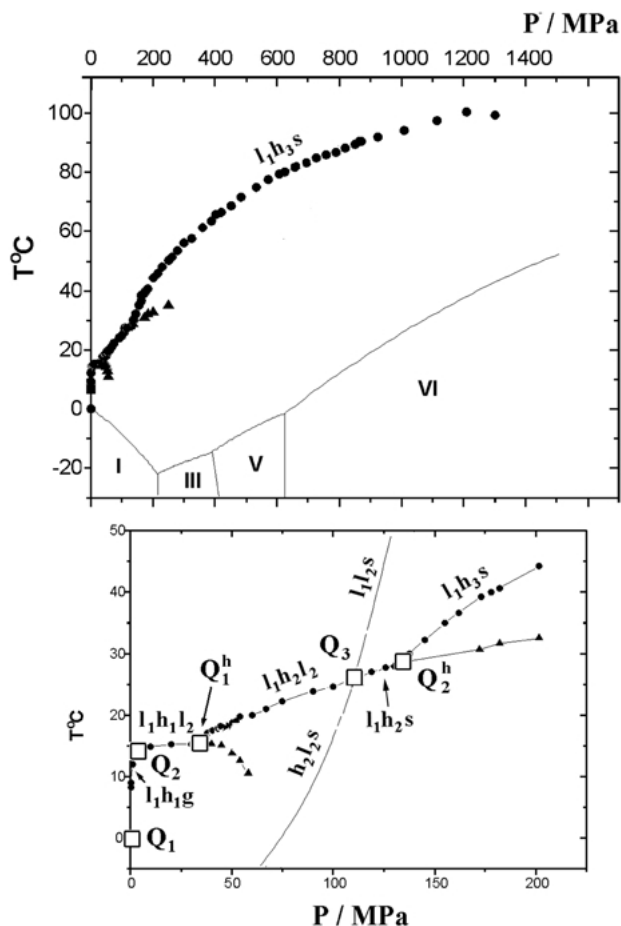
Figure 2. Decomposition curves of gas hydrates in the SF_6-H_2O system. i and s, ice and solid SF_6, l_1 and l_2, liquid aqueous and SF_6 phases; h_1, h_2, h_3, CS-II hydrate phase $SF_6 \cdot 17H_2O$, CS-I hydrate with probable stoichiometry $SF_6 \cdot 7\frac{2}{3}H_2O$, hydrate phase with unknown structure, respectively; g, gas phase. Lower: the 0–225 MPa region of the upper one in more detail. Equilibrium points are given by the solid rings, metastable continuations of the equilibrium lines are given by the solid triangles.

Thus, we can see that the SF_6-H_2O system in many respects resembles that with hydrophilic guests, such as tetrahydrofuran, dioxanes, acetone and others that under lower pressures form CS-II hydrates [13]. Several hydrates have also been found in each of these systems. As has been mentioned above, they differ in the temperature dependence of the decomposition pressure of the CS-II hydrate at the origin of the curve. The other difference is that at high pressures the thermal effects of the decomposition of the hydrate are not observed. In all the systems studied earlier the thermal effects decreased with pressure increase. However, they were still large enough (at least 1.5 GPa) to be detected by the DTA technique we used.

X-ray experiments

For the pressure range 50–650 MPa (room temperature) we obtained X-ray diffraction patterns of the SF_6 hydrate samples that exist under these conditions. In the pressure range studied the diffraction pattern is consistent with the hydrate of Cubic Structure I described in the literature [11] with the exception of the reflections corresponding to sulfur

hexafluoride and the beryllium capsule whose locations are known (see below). The powder diffraction pattern obtained at 650 MPa is shown in Figure 3 and the location and interpretation of the diffraction peaks are presented in Table 3. All the peaks of the experimental diffraction pattern can be divided into three groups. The diffraction peaks of the first group are caused by the fact that certain parts of the high-pressure device and the beryllium capsule are exposed to synchrotron radiation. These diffraction peaks are unequivocally determined by a blank experiment. Another group of diffraction peaks corresponds to the solid sulfur hexafluoride phase and exists only in the range of the existence of the phase [17]. These peaks are in good agreement with those calculated for the cubic cell of solid SF_6 [18, 19]. The rest of the diffraction peaks (the third group) can be interpreted on the basis of the literature data on gas hydrates of Cubic Structure I (CS-I). In the studied pressure range the gas hydrate of sulfur hexafluoride retains its structure (CS-I), the parameter a of the unit cell changing from 12.06(1) Å at 50 ± 2 MPa to 11.85(2) Å at 650 ± 50 MPa (values of standard deviations, which are given in parentheses, are obtained on least-squares refinement of the parameter a). Uncertainty in the value of the unit cell parameter a arising from the pressure determination error is about 0.02 Å. To calculate the hydrate unit cell parameters, at least ten (five at 50 MPa) strongest peaks were used. At the maximum pressure (650 ± 50 MPa) the diffraction pattern was obtained by two independent techniques: one-coordinate detector and image plate. The values of the parameter a obtained coincided within experimental error (11.84(2) and 11.859(7) Å, respectively). To confirm that the phase being studied is hydrate h_2 the pressure in the system was gradually decreased below 50 MPa until the hydrate melted. After pressure was increased again above the hydrate formation pressure the hydrate being formed gave the same diffraction pattern (Figure 4). Our results did not show the transition of hydrate h_2 into hydrate h_3 which was suggested by the phase diagram. Most probably the reason for this is that the transition is very slow since all three products of the equilibrium h_2h_3s are solid substances (note that we used excess SF_6), while the equilibrium $l_1h_2h_3$ is only possible at temperatures above our experimental temperature.

Thus, based on the data of differential thermal analysis and X-ray diffraction *in situ* we concluded that in the sulfur hexafluoride – water system at pressures up to 1.3 GPa at least three hydrates form, and hydrate h_2 (see Figure 2) belongs to CS-I.

Guest molecule size and hydrate formation under pressure

Water, like all substances whose atoms (molecules) are of tetrahedral coordination, can form similar energy framework structures. Of all these structures only those whose cavities are best suited to the guest molecules in size and shape are stabilized. For the same reason changing thermodynamic parameters (temperature, composition, and pressure) can also result in a phase transition connected with the formation of clathrate structures.

Table 3. Interplanar spacing, indexing and interpretation of reflections on a powder diffraction pattern of a sulfur hexafluoride gas hydrate at a pressure of 650 ± 50 MPa at room temperature

2θ (°)	d_{expt} (Å)	$d_{\text{calc.}}$ (Å)	Phase	*hkl*	2θ (°)	d_{expt} (Å)	$d_{\text{calc.}}$ (Å)	Phase	*hkl*
2.49	8.336	8.386	CS-I	110	8.78	2.374	2.372	CS-I	430
3.82	5.910	5.930	CS-I	200	9.31	2.327		CS-I + SF$_6$ (s)	510, 431
3.95	5.284	5.303	CS-I	210	9.47	2.202	2.202	CS-I	520, 432
4.31	4.829	4.841	CS-I	211	9.72	2.147	2.165	CS-I	521
4.99	4.179	4.193	CS-I	220	10.25	2.034		app. + CS-I	433, 530
5.16	4.038		SF$_6$ (s)		10.40	2.005		CS-I + SF$_6$ (s)	531
5.57	3.742	3.750	CS-I	310	10.56	1.972		Be + CS-I	600, 442
6.09	3.417	3.423	CS-I	222	10.71	1.947		Be + CS-I	610
6.35	3.282	3.289	CS-I	320	10.82	1.927	1.924	CS-I	532, 611
6.59	3.164	3.170	CS-I	321	11.12	1.876	1.875	CS-I	620
7.02	2.961	2.965	CS-I	400	11.23	1.856	1.852	CS-I	540, 621
7.25	2.874	2.876	CS-I	410	11.43	1.824	1.830	CS-I	621
7.36	2.828		SF$_6$ (s)		11.62	1.795		Be + SF$_6$ (s)	
7.48	2.787	2.795	CS-I	330, 411	11.71	1.782		Be + CS-I	622
7.87	2.647	2.652	CS-I	420	11.81	1.766		CS-I	630, 542
8.05	2.585	2.588	CS-I	421	12.12	1.722		Be + CS-I	444
8.24	2.528	2.528	CS-I	332	12.25	1.704		Be + CS-I	632, 710
8.61	2.420	2.421	CS-I	422					

CS-I, sulfur hexafluoride cubic structure I gas hydrate, SF$_6$(s), solid sulfur hexafluoride, app., Be, the parts of the high-pressure apparatus (Be, beryllium capsule).
The interplanar spacing was calculated for the CS-I gas hydrate with the unit-cell parameter 11.859 Å (space group Pm3n). Only reflections that did not interfere with the reflections of other substances were taken into account in the calculation of the unit-cell parameter. The reflections of beryllium were split because of diffraction by different walls of the beryllium capsule.
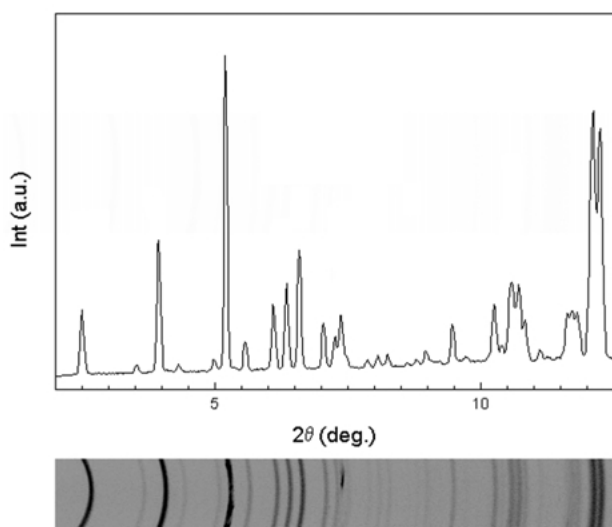

Figure 3. Powder diffraction pattern of the CS-I high-pressure gas hydrate phase in the sulfur hexafluoride-water system at 650 MPa obtained with use of an *Image-Plate*. The full image obtained is given in the bottom part of the figure, with the exception of the low-angle part which does not contain diffraction peaks.

The ability of the large cavities of clathrate frameworks to accommodate more than one molecule [20] results in an even greater diversity of phases that can be made up from water and guest molecules depending on their size. Let us see how changing the size of the hydrophobic guest molecules at relatively low pressures affects clathrate formation (paragraphs 2-5 overlapping with the consideration given in Chapter 2 [21]).

(1) In the first group are the smallest guest-species (d < 3.5 Å, where d is the van der Waals diameter of the guest), i.e., hydrogen, helium and neon which form solid solutions based on ice Ih [2] and, at high pressures, hydrates based on ice II and Ic [22, 23].

(2) Slightly larger species (argon, krypton, oxygen and nitrogen, d < 4.2 Å) form CS-II hydrates, filling both "large" and "small" pentagon dodecahedral D-cavities [24], with each H-cavity accommodating two nitrogen molecules [20].

(3) The third group includes several substances (CH$_4$, H$_2$S, SO$_2$, CO$_2$, Xe, C$_2$H$_6$ and others) whose size is between 4.3 and 5.6 Å. These substances and water produce hydrates of CS-I where in addition to the D-cavities there are also "large" 14-hedral T-cavities.

(4) Guest molecules 5.8–7.2 Å in size produce hydrates with the stoichiometry G·17H$_2$O of CS-II where only H-cavities are occupied. The D-cavities are all vacant. Sulfur hexafluoride belongs to this group.

(5) If the guest-molecules are bigger (for example, methylcyclohexane, cyclohexanone, etc), they form only hydrates of hexagonal structure III (HS-III or structure H) (only in the presence of a help-gas, like H$_2$S, Xe and others) [25]. In hydrates of this structure in addition to two kinds of 12-hedral cavities accommodating help-gas species there are also 20-hedral E-cavities [25] accommodating the main guest species mentioned above.
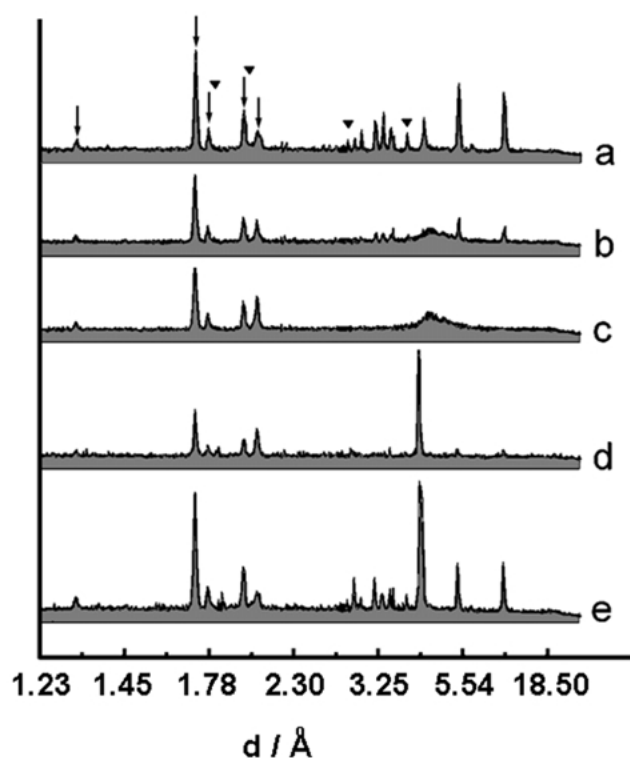
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Figure 4. Powder diffraction patterns (a) of CS-I gas hydrate of SF$_6$ at 100 MPa, (b) at 50 MPa during decomposition of the hydrate, (c) at 50 MPa after decomposition of the hydrate; diffuse peak is due to diffraction by the liquid water-liquid SF$_6$ mixture, (d) after pressure increase to 100 MPa (crystallization of SF$_6$), (e) after further pressure increase to 150 MPa (crystallization of CS-I hydrate). Some reflections are due to parts of the experimental apparatus + beryllium cell (marked by arrows) and solid SF$_6$ (marked by triangles).

The data obtained at high pressure show that the differences in the way hydrate formation occurs for different groups of guests are not so remarkable. Thus, the guests of the first group (at least hydrogen and neon) are most probably also capable of stabilizing hydrates of classic structure [1, 5] while the guests of the second group (at least argon and krypton) seem to form hydrates on the basis of ices II [1, 5, 26]. Already at a pressure of about 100 MPa methane (group three guest) can form CS-II hydrates [27] filling all types of cavities, which makes it almost suitable for group two. The guests of the fourth group, such as tetrahydrofuran [16] and SF$_6$ (the present work), are capable of producing CS-I hydrates at pressures above 23.5 and 33.2 MPa, respectively. This suggests that at high pressures the molecules concerned are located in the 14-hedral T-cavities, while at normal pressure they would rather occupy 16-hedral H-cavities.

An interesting fact has recently been found: methane produces HS-III hydrates [27] at pressures above 630 MPa. Undoubtedly, 20-hedral E-cavities can only be stabilized (also at high pressure) if they accommodate several methane molecules each. Thus, for the first time at high pressures the authors of the work [27] succeeded in obtaining HS-III hydrate where methane acts as both the main and auxiliary guest.

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