Clathrate formation in the Ar–H_2O system under pressures up to 15 000 bar

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Under pressure the decomposition curve of argon hydrate passes through a maximum (33.6 °C at *ca.* 6.2 kbar) and undergoes two breaks (at 7.2 and 9.6 kbar), indicating that three hydrates form in the Ar–H_2O system; at 15 kbar the high pressure hydrate decomposes at 75.1 °C.

The argon hydrate Ar·$6H_2O$, the first noble gas compound, was discovered by Villard in 1896,[1] soon after argon itself was discovered by Ramsay and Rayleigh. After Stackelberg[2,3] and Claussen[4] observed two cubic clathrate hydrate structures, argon hydrate was classified as the first structure (CS-I) by analogy with the xenon hydrate (no X-ray experiments were carried out on it). Later it was shown[5] that argon, like three other kinds of small guest-molecules (O_2, N_2, Kr) stabilize cubic structure II (CS-II), filling a considerable number of the small cavities. This explains why the composition of the hydrate is close to that of CS-I hydrates and is the reason why they were classified with hydrates of this structure. The argon hydrate is one of four hydrates whose decomposition was studied at high pressures (up to *ca.* 4000 bar).[6,7] It has been demonstrated that after a sharp rise of the hydrate decomposition temperature caused by the pressure of the gaseous phase among the decomposition products the increase of temperature slows down and there is a tendency towards a maximum.

The study of this system at high pressures is of interest because the hydrate forming there is of CS-II type. The study of the Xe–H_2O system[8] has revealed that xenon hydrate of CS-I type at ambient pressures retains this structure at pressures up to 10 000 bar, indicating that CS-I is denser than CS-II (as will be shown further; with the data available at present it is difficult to predict *a priori* which structure is denser). Since the difference in energy between hydrates of different structures is not large,[5] changing the conditions (in this case pressure) could be expected to result in a conversion from CS-II to CS-I.

The device for creating pressures up to 15 000 bar is shown in Figure 1. Cell (1) (described in detail in ref. 8) with the sample under study was placed into the channel of a high pressure vessel (2). The vessel [thermally insulated with foam plastic jacket (3)] was cooled to the required temperature with liquid nitrogen from a Dewar flask (4). A pressure up to 15 000 bar was created with a booster (5) and measured with a manganin manometer (6). Preliminary pressure up to 2000 bar was delivered into the booster from separator (7) through back valve (8). Low pressure was created with three-plunger pump (9) and through distributor (10) was delivered either into the low pressure cylinder of the booster or into the distributor. Discharge tap (11) makes it possible to decrease pressure. A 2500 bar manometer (12) measures pressure created by the pump. Its productivity can be changed while the device is running from 0 to 18 dm^3 h^{-1}. The packing of the booster stem and high pressure compounds was effected by way of auto tightening. A mixture of polysiloxane oil and benzene in the proportion 1 : 3 was used as a working liquid. It was poured into container (13) and by means of tap (14) was pumped into the distributor while its piston was moved down by a spring. Transformer oil was used as a low pressure liquid.

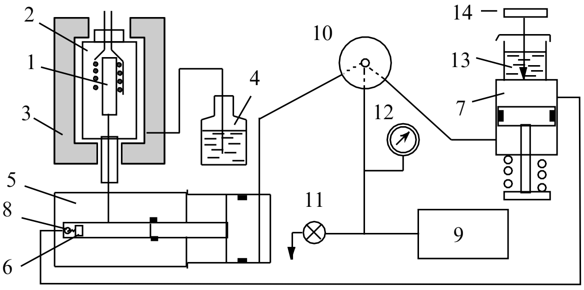

Figure 1 Block diagram of the device creating pressures up to 15 000 bar used in studying the hydrate decomposition (for label descriptions, see text).

Pressure was measured with a Bourdon manometer (up to 250 and 2500 bar) and a manganin manometer (up to 15 000 bar) with an accuracy of not less than 1%. The melting and decomposition temperatures of the forming phases were measured with a chromel–alumel thermocouple (the readings of which essentially do not depend on pressure in the range under study[8]) by the DTA technique.

As in the Xe–H_2O system,[8] to speed up the dissolving of the gas a non-ionogenic surface-active substance (SAS) with a concentration in solution of the order of 0.25% was added to the initial mixture (previously it was shown that such quantities of SAS do not affect the position of the equilibrium within our level of accuracy[9]). For the same purpose an inert substance (SiC powder with grains of the order of 0.01 cm in diameter) was used. The inertness of these substances has been shown before.[8] We used twice-distilled water and argon containing 99.9% of main substance.

The results obtained are presented in Figure 2. It is clear from the Figure, that the data are in good agreement with the data from other studies[6,7] in which the decomposition curve of

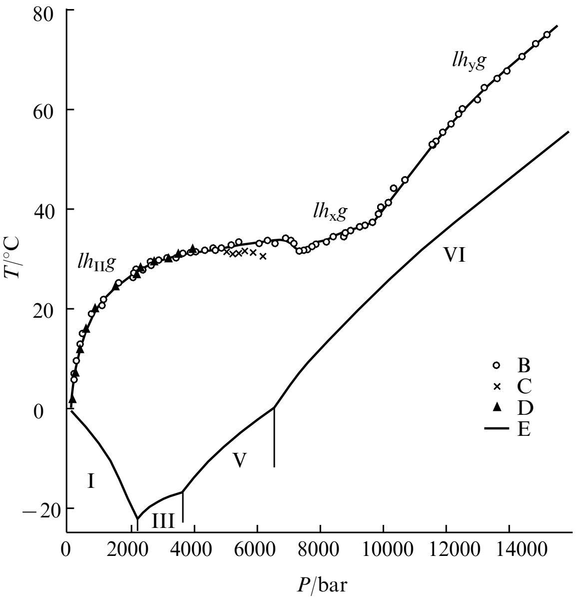

Figure 2 Pressure dependence of the decomposition points of argon hydrates in comparison with the melting point curves of ice. B, C: decomposition of stable and metastable phases (our data); D: data from refs. 6,7; E: melting points of ice. *l, g,* h_{II}, h_x, h_y: liquid aqueous phase, gaseous (fluid) phase, hydrates of CS-II and unknown structures X and Y, respectively, I, III, V, VI: ice modifications.

the argon hydrate was studied up to 3830 bar. In the pressure range from 88 bar (pressure in the lower quadruple point[10]) to 7200 bar the decomposition of the hydrate can be described as one smooth curve[†] with a very gentle maximum (33.4 °C) at pressures *ca.* 6100–6300 bar. After that the decomposition curve goes down slightly to 31.5 at 7.200 bar. At this point it undergoes a break. In the pressure range 7200–9600 bar the decomposition temperature of the hydrate goes up slowly and reaches 37.5 °C. Another fracture of the curve is observed under these conditions, and with further pressure increase the curve goes upward rather steeply. At 15 040 bar the hydrate is stable up to 75.1 °C. The resulting picture points to the formation of at least three hydrates in the Ar–H_2O system. Since there is no reason to suspect any chemical interactions among the components of the system, the observed diversity is due to the packing factor. Judging from the most abundant (and suitable for argon) water frameworks of CS-I and CS-II types, one can assume the formation of the hydrate of CS-I type at high pressures. The fact that CS-I and CS-II water clathrate frameworks are the most common and suitable for argon suggests the formation of a CS-I hydrate at high pressures. Since the packing coefficients of these structures are very close provided the cavities are fully occupied (under these pressures this condition should be met to a good approximation), a change to a structure that might be somewhat denser is quite probable.[‡] At present we lack data that could show accurately which of the above structures is denser. However, since the xenon hydrate of CS-I retains its structure at pressures at least up to 10 000 bar[§] at its decomposition temperature[8] and up to 18 000 bar at −196 °C,[11] one may conclude that hydrates of CS-I type with the same type of guests are somewhat denser than those of CS-II. At ambient pressure the argon hydrate, as has already been mentioned, is of CS-II type; with packing coefficient $k = 0.515$[¶] (on condition that all cavities are occupied by the guest molecules). Therefore, for the argon hydrate of CS-I to be more stable under pressure its packing coefficient k ($k = \Sigma v_i/V$, where v_i is the total volume of the molecules constituting a phase with the volume V [12]) should be greater than the above value. Hence, the parameter of the unit cell of the assumed CS-I argon hydrate should be $a < 11.98$ A at 0 °C. This condition seems to be quite reasonable. Thus, the change of a CS-II argon hydrate under pressure can be considered to be a well-substantiated preliminary hypothesis.

As for the structure of the hydrate that is stable at pressures above 9600 bar, this cannot be explained in terms of the known water clathrate frameworks. We can only conclude, judging by the slope of the hydrate decomposition curve,[14] that it is a very dense structure with a packing coefficient not lower than that of ice VI.

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[†] It is possible that the curve consists of two curves that cross at appromaxitely 4500 bar and hence belong to different hydrates (or modifications). This was suggested by the fact that in the pressure range 4900–6050 bar with an increase of pressure the points of the hydrate decomposition that we obtained were located in the range of low temperatures (designated with crosses in the Figure). These effects were not observed during repeated recognizing of the heating curves of the samples, and they could be ascribed to the decomposition of the hydrate that is stable up to 4500 bar in the range of its metastability. However, we will reserve our further judgment because we believe that additional studies should be carried out on the subject.

[‡] This conclusion is true if we assume the free energies of the hydrates of both structures to be close at ambient pressures, which has been shown by the study in ref. 5.

[§] At present we found that the CS-I xenon hydrate retained this structure up to 15000 bar at a decomposition temperatute 66.7 °C.

[¶] To calculate the packing coefficient we used the following reference value: van der Waals radii of oxygen $R_O = 1.29$ A, hydrogen $R_H = 1.16$ A, $R_{Ar} = 1.92$ A, $a = 17.22$ A at 0 °C,[13] the length of the H-bond $l_H = 2.80$ A. Based on these initial data, the volume occupied by a water molecule in the hydrate $v_{H_2O} = 14.12$ A^3,[14] and the volume of molecule $v_{Ar} = 29.65$ A^3.