Clathrate formation in Kr–H$_2$O and Xe–H$_2$O systems under pressures up to 15 kbar

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The pressure dependence of the decomposition temperature of krypton and xenon hydrates has been investigated up to 15 kbar; three hydrates have been discovered in the Kr–H$_2$O system whereas CS-I hydrate of Xe is stable under these conditions.

Hydrate formation in the Ar–H$_2$O and Xe–H$_2$O systems differs significantly. Under a comparatively low gas pressure at which clathrate formation begins, in the first system a hydrate of cubic structure II (CS-II) is formed, and in the second system – CS-I.[1] It was shown that xenon hydrate keeps its structure up to 10 kbar at the decomposition temperature[2] and up to 18 kbar at –196 °C,[3] while in the system Ar–H$_2$O in this pressure interval at least three hydrates are formed.[4] The hydrate which is stable at pressures higher than 9.6 kbar (the decomposition temperature at this pressure is 37.5 °C) is significantly denser than hydrates which are formed at lower pressures, as the steep rise of the decomposition temperature shows (75.1 °C at 15 kbar), and cannot be described within the limits of known water clathrate frameworks. As none of the interactions except van der Waals ones are possible in the system being examined, we may surmise that the compactness of structure is achieved only through rather good spatial complementarity of guest and host sub-systems. On the other hand, under this pressure the breaking of hydrogen bonds in water frameworks could hardly be expected, as it proved by high-pressure ice structures.[5] Thus, argon hydrates formed under high pressures are most likely to have a clathrate nature. In this connection the system Kr–H$_2$O is of fundamental importance since the size of the Kr atom is between the sizes of Ar and Xe molecules. To make the comparison more correct we investigate hydrate formation in the Xe–H$_2$O system up to 15 kbar employing our new facilities.

The cell for investigation of hydrate formation and the high pressure apparatus are described in refs. 2,4. Experiments were always carried out under conditions of 50–70 times gas excess.

Pressure was measured with a Bourdon manometer (up to 250 and 2500 bar) and a manganin manometer (up to 15000 bar)
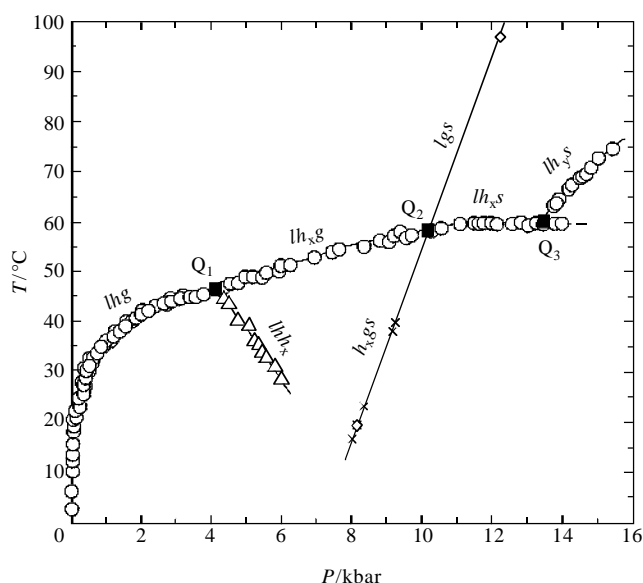
with an accuracy not less than 1%. The melting and decomposition temperatures of the forming phases were measured with a chromel–alumel thermocouple (the readings of which essentially do not depend on pressure in the range under study[6]) by the DTA technique.

In the same manner as for the Xe–H$_2$O[2] and Ar–H$_2$O[4] systems, to speed up gas dissolution non-ionogenic surface-active substance (SAS) with a concentration in the solution of *ca.* 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 accuracy[7,8]). It was shown,[8] that though SAS slows down the hydrate formation in its first stage, nucleation, it speeds up significantly the process of crystal growth on nuclei which results in a speeding up of the reaction under consideration many times. For the same purpose an inert substance was added (SiC powder with grains of the order of 0.01 cm in diameter). The inertness of this substance has been shown before.[2] We used twice-distilled water and gases containing 99.9% of the main substance.

The heating curves of krypton–water mixtures always showed endothermic effects whose dependence on pressure is illustrated in Figure 1 by crosses ($\times$). Figure 1 also shows the krypton melting line based on the data.[9] These results indicate that the effects we observed relate to the equilibria accompanying the melting of krypton, and their closeness to the pure krypton melting point at corresponding pressures points indicates the low solubility of the hydrate (at temperatures below 58 °C, see Figure 1) and water (at higher temperatures) in the krypton fluid phase. We have not studied these eqilibria in detail. It was rather interesting as a means of examining the correctness of our measurements.

The decomposition of the krypton hydrates was studied from ambient pressure to 15400 bar. The results obtained are presented in Figure 1. The decomposition temperature rises rapidly from –0.1 °C at 14.3 bar (the lower quadruple point *ilhg*, where *i* is ice Ih, *l* is aqueous solution of krypton, *h* is the initial CS-II hydrate, *g* is gaseous or fluid phase[10]) to 21 °C at 90 bar, and at 4150 bar it reaches 46 °C.[†] At this point the decomposition line undergoes a break. Sometimes during the first recording the heating curves showed endothermic effects whose dependence on pressure is illustrated in Figure 1 ($\triangle$). However, these effects were not observed when the recording was repeated. This indicates that the clathrate formation reaction had not ended during the first experiment (a reminder: we were working with an excess of krypton). This line intersects the hydrate decomposition curve at the same point. We can conclude that this point is Q$_1$ (*lhh$_x$g*, where *h$_x$* is the second hydrate) and the break in the decomposition curve is connected with formation of a new hydrate *h$_x$*. In the pressure range 4150–10000 bar the decomposition temperature of the hydrate rises slowly and reaches 58 °C. Under these conditions, the decomposition line intersects the krypton melting line (more exactly, the lines of the three-phase equilibria *h$_x$gs* and

Figure 1 Fragment of *P,T*-projection of the phase diagram of the Kr–H$_2$O system. $\times$ –melting point of krypton in hydrate *h$_x$* presence; $\diamond$ – melting point of pure krypton;[9] for other designations, see the text.

[†] As well as in the Ar–H$_2$O system[4] we observed a more complicated picture of clathrate formation in this pressure range. On a first recording the heating curves showed endothermic effects at temperatures 1–3 °C lower than given above.
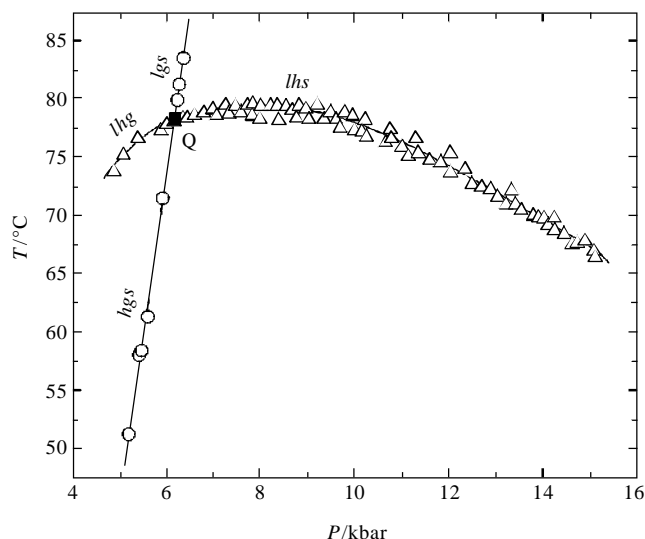
Figure 2 Fragment of P,T-projection of the phase diagram of the Xe–H$_2$O system (for designations, see the text).

lgs, where g is fluid phase, s is solid krypton) in the quadruple point Q$_2$ (lh_xgs). At higher pressures the hydrate decomposes into solid krypton and its saturated aqueous solution (line lh_xs). The process hardly depends on pressure and at 13400 bar the decomposition temperature is 60 °C. At this point the decomposition curve undergoes a break [quadruple point Q$_3$ (lh_xh_ys) where h_y is the third hydrate] and with further pressure increase the curve rises rather steeply. At 15400 bar the hydrate is stable up to 74.8 °C. The resulting picture points to the formation of three hydrates in the Kr–H$_2$O system, just as we observed in the Ar–H$_2$O system.

The data received on xenon hydrate decomposition in the range from 5000 to 15000 bar are given in Figure 2. They are rather satisfactory, conforming to the results received earlier[2] in the corresponding pressure interval. The temperature of hydrate decomposition into solid xenon and its water solution (78–79 °C) hardly depends on the pressure in the range from 6150 bar (quadruple point Q) to 9400 bar, and, further, smoothly decreases to 67 °C at 15000 bar. From this data and ref. 2 we may conclude that xenon hydrate of cubic structure I is formed at ambient pressure and that the temperature of decomposition is stable at least up to 15000 bar and at a liquid nitrogen temperature up to 18000 bar.[3]

One can assume – much as we do in ref. 4 – that the phase transition in the Kr–H$_2$O system at 4150 bar is conditioned by the transformation of the CS-II hydrate into the CS-I hydrate. Indeed, the packing coefficient of the krypton CS-II hydrate is equal to 0.528.[‡] For the assumed krypton hydrate of CS-I to be more stable under pressure its packing coefficient should be greater than the above value and therefore the unit cell parameter of the assumed CS-I krypton hydrate should be $a < 11.99$ Å at 0 °C. This assumption seems to be quite reasonable (for the methane hydrate with a similar guest molecular size $a = 11.74$ Å at 5.2 K[1] and one can expect the parameter a to be about 11.90Å at 0°C,[1,14] for the xenon hydrate $a = 11.97$ Å[11]). The explanation of the first phase transformation by the transition of the hydrate CS-II into CS-I is supported by the fact that the difference between the slopes of the hydrate decomposition curves is relatively low. This is to be expected under such an assumption, because the heats of

decomposition and packing coefficients are not very different, as follows from the above. Besides, it was recently shown[16] that at relatively low pressures one can observe the formation of nitrogen hydrate both in the CS-I and the CS-II structures, which is evidence of the energetic similarity of these structures. Thus, one phase transformation with a certain degree of confidence could be explained by the transition of the hydrate CS-II into the CS-I one.

Speaking of the high density which is formed at pressures exceeding 13400 bar, it is hard to explain this phenomenon within the limits of known water frameworks. It is tempting to link this with the ability of such small guest molecules as Ar and Kr to insert into large cavities in pairs (by analogy with N$_2$[16]). However, this phenomenon with nitrogen as a guest is already observed at moderate pressures (about several hundred bars) and is more likely to be linked with anomalies being observed in these systems at moderate pressures.

Thus, the Kr–H$_2$O system resembles the argon system in many ways, and significantly differs from the xenon system. The question of whether this type of diagram is typical of hydrates with a small guest molecule can be answered to some extent by an investigation of the N$_2$–H$_2$O system, in which CS-II hydrate is also formed at moderate pressure.

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[‡] The packing coefficient $k = \Sigma v_i / V$, where Σv_i is the total volume of the molecules constituting a phase with volume V.[12] To calculate it we used the following reference value: van der Waals radii of oxygen $R_O = 1.29$Å, hydrogen $R_H = 1.16$Å, $R_{Kr} = 1.98$Å,[13] $a = 17.23$ Å at 0 °C,[14] the length of the H-bond $l_H = 2.80$Å. Based on these initial data, the volume occupied by a water molecule in the hydrate $v_{H_2O} = 14.12$Å^3,[3,15] and the volume of krypton molecule $v_{Kr} = 32.52$Å^3.[3]