

Clathrate formation in Kr–H₂O and Xe–H₂O 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–H₂O system whereas CS-I hydrate of Xe is stable under these conditions.

Hydrate formation in the Ar–H₂O and Xe–H₂O 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 temperature² and up to 18 kbar at –196 °C,³ while in the system Ar–H₂O 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–H₂O 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–H₂O 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)

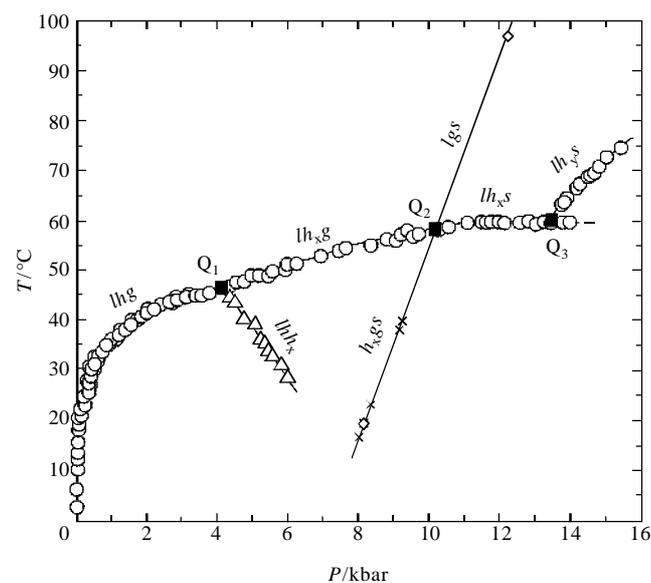


Figure 1 Fragment of P,T -projection of the phase diagram of the Kr–H₂O system. × – melting point of krypton in hydrate h_x presence; ◇ – melting point of pure krypton;⁹ for other designations, see the text.

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 study⁶) by the DTA technique.

In the same manner as for the Xe–H₂O² and Ar–H₂O⁴ 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 (×). 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 equilibria 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 ilh_g , where i is ice Ih, l is aqueous solution of krypton, h is the initial CS-II hydrate, g is gaseous or fluid phase¹⁰) 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 (Δ). 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 (ilh_xg , 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_xgs and

[†] As well as in the Ar–H₂O system⁴ 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.

