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Clathrate hydrate of xenon at high pressure

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The decomposition temperature of xenon hydrate rises with pressure from 26.7 °C at 25 bar to 77.3 °C at 6050 bar; at higher pressures the hydrate decomposes into aqueous solution and solid xenon and the decomposition temperature decreases slowly to 75.2 °C at 10080 bar.

The first compound of argon, $Ar \cdot 6H_2O$ (which was found to be of clathrate nature), was discovered in 1896 by Villard,[1] only a little more than a year after Ramsay and Rayleigh had discovered argon. Forcrand discovered krypton and xenon hydrates,[2,3] and studied them at pressures up to several tens of atmospheres. In this connection it should be noted that the noble gas–water systems at high pressures are obviously very valuable as models for the study of clathrate gas hydrates, and this problem has recently been attracting increasingly close attention of researchers due to the discovery of practically inexhaustible natural gas deposits (mainly methane) in the interior of the Earth[4] and at the bottom of the Oceans.[5] However, in spite of the quite intensive studies made on clathrate hydrates at rather high pressures (up to 10 kbar),[6] only four systems with guests which exist in the gaseous state under ordinary conditions have been studied at pressures up to 3.5–4.0 kbar: those with nitrogen, argon,[7] methane[8] and sulfur dioxide.[9] In this paper we report data on the decomposition of xenon hydrate (with an excess of the latter) at pressures up to 10 kbar.

A diagram of the high pressure cell in which measurements were carried out is presented in Figure 1. The studied gas at an initial pressure of up to 20 bar was pumped into a flask made of stainless steel (1).

By means of the steel capillary (2) the flask was connected with a caprolon container (4) situated inside a copper block (3). The container was filled with an inert powder (5, see below). A thermocouple (6) was introduced into the container through a packing system made of rubber and epoxy compound. The packing of the container (4) was brought about by pressing it with a plate spring (7) to a thin rubber ring (8). The standard thermocouple (9) was placed in a specially designed pocket of the copper block (3). Heating was carried out by means of an electrical resistance furnace (10) isolated from the surrounding medium by fluoroplastic articles (11). The whole of the cell was placed into a high hydrostatic pressure vessel, the pressure being produced by a compressor. Light petroleum was used as a pressure-transmitting liquid. Pressure was transmitted into the sample cell through a piston (12) packed with a rubber ring (13). The initial packing of the ring with an article (14) and a flat spring (15) was achieved with the help of a screw (16). The filling of the cell with the gas was carried out through a syringe introduced into the flask (1) along the channel in the piston (12). The needle was packed with a rubber laying (17) pressed with a bolt (18). A complex-shaped screw (19) prevented the moving of the piston out of the flask (1), which might be caused by the initial gas pressure.

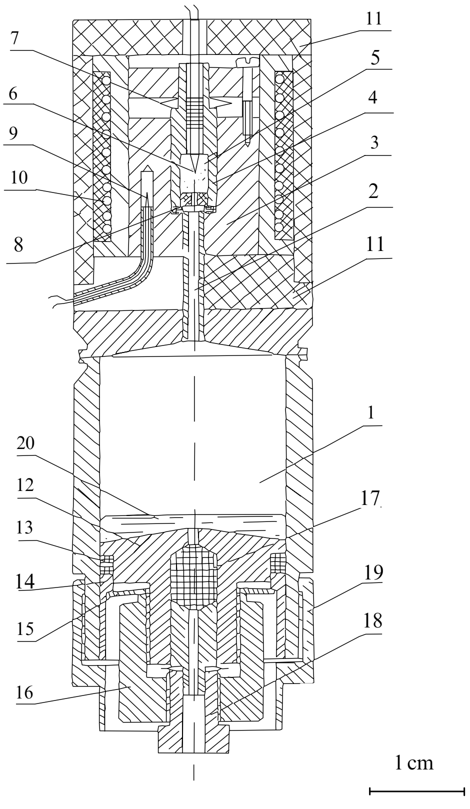

Figure 1 The plan of the cell used for studying the hydrate decomposition at high pressures (see the text for designations).

Mercury (20) was poured into the cell to prevent the leakage of gas through the rubber layings (13 and 17) and to displace the gas into the reaction volume of the container (4) when pressure was exerted.

The pressure inside the cell was measured with Bourdon (up to 250 and 2500 bar) and manganin manometers (up to 10000 bar) with an accuracy of not less than 1%. The melting (decomposition) point temperatures of the forming phases were measured with a chromel-alumel thermocouple (whose response is practically pressure-independent in the range considered) by DTA.

To speed up the dissolution of gases, a nonionogenic surface active substance (SAS) was added, whereby its concentration in the solution studied was of the order 0.25% in water (previously it was shown that within experimental errors such amounts of SAS did not shift the gas–liquid equilibrium).[10] For the same purpose, an inert substance (SiO_2-glass powder, SiC with a grain size of 0.01 cm or filter paper) was added to water. The inertness of these substances was confirmed by the melting curves of their ices and the identical results of the hydrate decomposition curve. Twice distilled water and xenon of 99.99% purity were used.

The results are presented in Figure 2. At ambient pressure xenon forms a hydrate of cubic structure I (CS-I).[11,12] As the pressure is increased, its decomposition temperature rises rapidly from 0 °C at 1.52 bar [11] to 35 °C at 60 bar, and at 6050 bar it reaches 77.3 °C. Under these conditions the decomposition curve of the hydrate (lhg) (Figure 2) intersects the crystallization line of xenon[†] at the quadruple point (lhgs). Our experimental data on the phase transition are plotted as triangles in Figure 2, and the melting curve of xenon is drawn in accordance with data taken from literature.[13]

At higher pressures the hydrate decomposes into solid xenon and its saturated aqueous solution (line lhs), the process being accompanied by a small temperature decrease (to 75.2 °C at 10080 bar).

The curve lhg, which passes through 87 experimental points, is described by equations (1) and (2) ($T/°C$; P/bar)

$$T = -117.68 + 87.414\ln P - 16.8389\ln^2 P + 1.12525\ln^3 P \qquad (1)$$

with the root-mean-square error of $\sigma = 0.38$ in the calculation of temperature in the pressure range 25–575 bar.

In the range 80–6050 bar equation (2)

$$T = 80.25 - 21.2556\ln P + 2.8350\ln^2 P + 0.049857\ln^3 P \qquad (2)$$

is also suited for this purpose ($\sigma = 0.44$).

The curve of the hydrate decomposition into solid xenon and aqueous solution over the entire studied range (6050–10080 bar, 16 experimental points) is well approximated by equation (3).

$$T = 68.40 + (2.658 \times 10^{-3})P - (1.9678 \times 10^{-7})P^2 \qquad (3)$$

The curves in Figure 2 are based on these equations, and it is evident that the empirical fits are quite satisfactory.

Even at ambient pressure the degree of filling of the large (y_l) and small (y_s) cavities in the xenon hydrate is rather high and $y_l = 0.980$ and $y_s = 0.716$.[12] The xenon atom is one whose dimensions and shape fit both the large and the small cavities of the framework CS-I well, which explains the rather high packing coefficient ($k = 0.564$) of its clathrate hydrate.[6] If the rather good capacity of xenon for dispersion interaction is taken into account, the reason for the extremely high decomposition temperature of the hydrate becomes clear. However, since the compressibility of xenon is very good (with a pressure increase from 1 to 6000 bar along the melting curve the volume of the fluid phase decreases by 13.5% and the solid phase by 6.4%, while the temperature increases from –111.7° to 77.3 °C [13]), the volume of the decomposition products of the hydrate becomes practically equal to that of the hydrate at pressures close to 6000 bar (as judged by the pressure dependence of the hydrate decomposition curve). With the jumpwise decrease in xenon molar volume (by 6% [13]) on going from the fluid to the solid state, the volume of the hydrate decomposition products becomes smaller than that of the hydrate and, as the pressure increases, the decomposition temperature goes down. If a denser hydrate does not form in the system at even higher pressures, one might expect the decomposition curve of the hydrate to intersect the melting line of the water eutectic (which, due to the relatively low solubility of xenon in water, practically coincides with the ice VI melting curve) at 16–18 kbar, after which for known reasons the line of the hydrate decomposition into solid xenon and ice VI falls off even more steeply. Therefore, we might expect to find an upper (pressure) limit in the stability of the classic gas hydrates in this region, and in the case of the majority of hydrates it should be located below the stability limit of xenon hydrate.

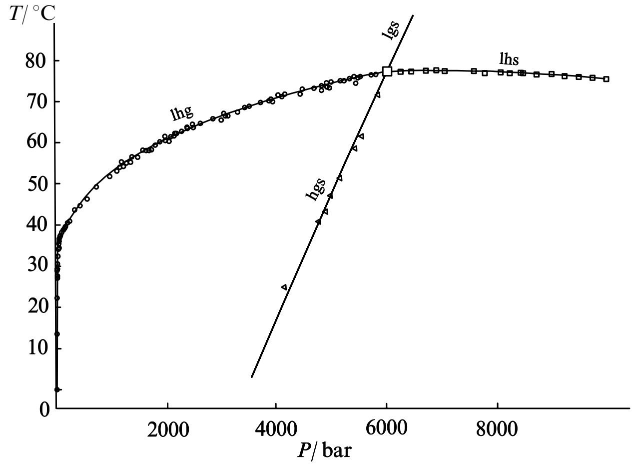

Figure 2 Fragment of the phase diagram of the xenon–water system on the xenon-rich side: l – water-rich liquid phase, g – xenon-rich gas (fluid) phase, h – hydrate, s – solid xenon.

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[†] To be more exact, the lines of the three-phase equilibria (hgs) and (lgs), which are practically degenerate, coincide with the crystallization line of xenon because of the low solubility of the hydrate and water in xenon.