Clathrate hydrates of hydrogen and neon

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At pressures up to 15 kbar, hydrogen and neon were found to form classical clathrate hydrate structures, whereas argon and krypton, already known as polyhedral clathrate formers, can also form hydrates based on the ice II framework at high pressures.

Small hydrophobic molecules (including monoatomic molecules) are known to form clathrate hydrates; these molecules can be subdivided into two different groups. The smallest molecules, hydrogen, helium and neon, all of linear dimensions less than 3.5 Å, constitute a group that can be incorporated into the small cavities in the lattices of ices Ih, Ic and II, thus forming solid solutions or clathrates very similar to the original ice frameworks.[1–3] Thus, they are not known to form clathrates based on polyhedral structures. The second group includes substances with larger molecular dimensions of 3.8 to 9.2 Å. These do not dissolve in ice frameworks, but form polyhedral clathrate structures, the best known of which are classical cubic structures I and II (CS-I and CS-II), and a hexagonal structure H (HS-III).[4,5]

A study of phase diagrams of the (Ar, Kr, Xe)–H_2O systems at pressures up to 15 kbar showed[6–8] that these gases can form classical clathrate hydrates, which are stable in a wide temperature and pressure range. However, in argon and krypton systems at pressures above 9.6 and 13.4 kbar, respectively, we found new hydrate phases, which are quite dense judging from the fact that their decomposition temperatures rapidly increase with pressure. This high-density packing is impossible in the case of typical clathrate structures where a single guest molecule occupies one cavity in a hydrate framework.[†]

Here, we report the results of studying phase equilibria in the neon–water and hydrogen–water systems. All of the experiments were carried out by differential thermal analysis in an excess of gas. The approximate gas–water molar ratio was 6:1, while the ratio between the components in classical clathrates and ice II structures when every cavity was occupied by one guest molecule was inverse. The temperature was measured with a Chromel–Alumel thermocouple, and the pressure, with a Manganin manometer. The experimental technique was described in detail elsewhere.[6–8]

The results are shown in Figure 1. In both cases, the initial portions of the curves (lines αlg) represent decomposition of solid solutions of the gases in ice Ih.[1] In our case, this manifests itself in a slight increase in the decomposition temperature of the solid solution as compared to the ice melting curve. The final portion of the curve (line βlg) in the hydrogen-containing system corresponds to decomposition of the hydrogen hydrate $H_2{\cdot}6H_2O$ with the ice II framework.[3,9] Note that in both portions of the P–T curves the equilibrium was established rapidly (in about 20 min), and the results were well reproducible.

The most complicated and interesting behaviour is observed in the pressure ranges from 1.0 to 3.6 kbar for hydrogen and from 1.9 to 3.7 kbar for neon systems (lines hlg). In both cases, the equilibria were attained very slowly (in several hours or longer). It is reasonable to suppose that, really, equilibrium states were not achieved in some experiments. The results can be reproduced only with a high excess of gas. We assign these curves to decomposition of the classical hydrogen and neon clathrates. Figure 2 shows the decomposition curves of hydrate phases in the (Ar, Kr, Xe)–H_2O systems[6–8] and those of the systems under discussion. It is evident that in the systems with hard noble gases the decomposition curves of classical structure hydrates (solid lines) are top-shaped, and their sizes regularly decrease from xenon to argon hydrate, *i.e.*, with a decrease in the guest molecule radius. The hydrogen and neon systems are adequately described by this scheme. Kuhs *et al.*[11] showed that every two nitrogen molecules can occupy a large cavity in CS-I and CS-II. This is even more true of the equilibrium in the case of hydrogen and neon molecules.[12] The presence of more than one guest molecules in a cavity, and slow diffusion of hydrogen and neon molecules in the already formed solid compound can result in rather slow establishment of equilibrium in the case of classical hydrate formation.

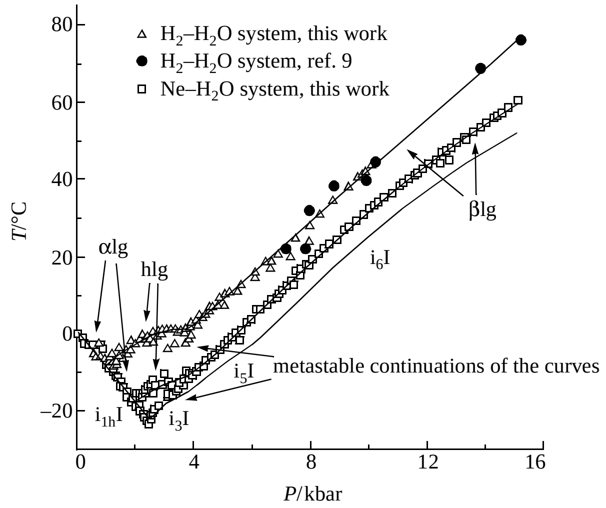

Figure 1 Decomposition curves of hydrates formed in the water–hydrogen and water–neon systems. Melting curves of ices (i_nI) are given for comparison: (α) solid solutions of gases in ice Ih, (β) hydrates of the respective gases based on the ice II crystal framework, (h) classical clathrate hydrate phase, (l) liquid phase, (g) fluid phase.

Figure 2 shows that in all of the systems (except for the xenon system), in addition to the group discussed above, there is a group characterised by similar curves, which go up steeply with increasing pressure (dashed lines). An X-ray study of the compounds formed in the water–hydrogen system showed that this curve branch corresponds to decomposition of a hydrate phase based on the ice II framework. Similar decomposition curves for the systems strongly suggest that, at pressures above 4 kbar in the neon system, 9.6 kbar in the argon system, and 13.4 kbar in the krypton system, hydrates based on the ice II structure are formed. For argon and krypton molecules to be arranged in ice II channel cavities, a slight elongation of hydrogen bonds is required, which is quite realistic. Let us recall that, when the self-clathrate ice VII is formed (two ice Ic frameworks penetrate into each other) at pressures above 20 kbar, the hydrogen bond length increases from 2.76 to 2.96 Å.[13]

Thus, classical clathrate hydrates are formed in aqueous neon,

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[†] It is reasonable to consider the above hydrates as belonging to the same group because, provided that all the cavities are occupied by the same guest, their packing coefficients k[6,10] are similar. For instance, for the CS-I xenon hydrate, $k = 0.584$; for the hypothetical xenon hydrates of other structures, they vary from 0.55 to 0.58, *i.e.*, they are appreciably lower than in the case with the densest packing ($k = 0.74$). Therefore, the effect of pressure on them should be very similar.

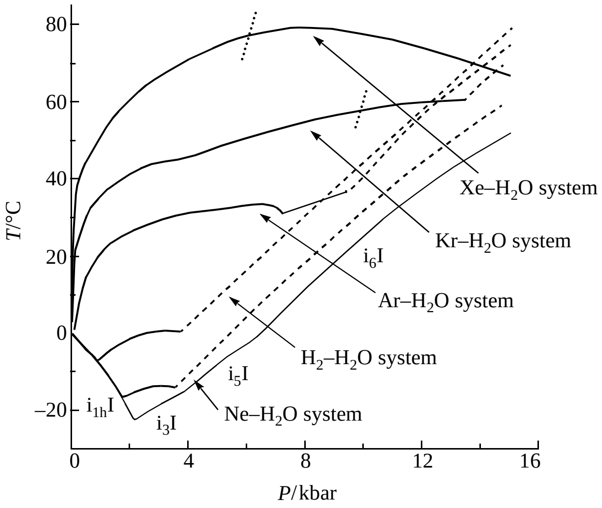

Figure 2 Decomposition curves of hydrates formed in the (Xe, Kr, Ar, H_2, Ne) water systems. Solid lines represent decomposition of polyhedral clathrate hydrates formed in these systems (first portions of decomposition lines in hydrogen and neon systems correspond to decomposition of solid solutions of the gases in ice Ih), dashed lines represent decomposition of hydrates of the gases based on the ice II crystal framework. Dotted lines represent the melting curves of the gases. Melting curves of ices (i_nI) are given for comparison.

hydrogen, argon, krypton and xenon systems. Their stability decreases in the order from xenon to neon. In the first four systems, hydrates are formed on the basis of ice II, and the larger the guest molecules, the higher the pressure required for their formation. A xenon molecule appears to be too bulky to be arranged in an ice II framework cavity, and the CS-I hydrate remains stable at pressures at least up to 15 kbar.

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