SYNTHESIS AND COMPOSITION OF THE CLATHRATE PHASE IN THE H_2O-H_2 SYSTEM AT PRESSURES UP TO 1.8 kbar

Barkalov O.I., Klyamkin S.N. [(1)], Efimchenko V.K.*, Antonov V.E.
Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia
[(1)] Moscow State University, Chemical Faculty, 119992 Moscow, Russia
* Факс: 7 096 524 9701, E-mail: efimchen@issp.ac.ru

Introduction

The water-hydrogen system is of fundamental interest primarily because it is composed of the most abundant substances in the universe. Molecular hydrogen frozen into ice is even found in interstellar dust [1]. A DTA investigation [2] revealed anomalies in the curve of decomposition of the H_2O-H_2 solid phase at a pressure of 1 kbar. A hypothesis was proposed that a clathrate phase of hydrogen hydrate is formed in the pressure interval 1 to 4 kbar. A clathrate phase with an *s*II structure was recently synthesized from liquid at a pressure of 2 kbar and a temperature of –24°C [3,4]. The neutron diffraction investigation [4] estimated the composition of that phase as $H_2O/H_2 = 136:(32+X)$, where X can vary from 0 to 16 depending on the pressure and temperature.

The present work was aimed at studying the direct and reverse transition of hexagonal ice I_h to the clathrate phase, and also at studying the transition of the liquid phase to the clathrate one. The points of transitions were located by tracing changes in the solubility of hydrogen in H_2O at pressures from 0.2 to 1.8 kbar. The experimental technique and the calculation methods used are described in [5].

Results and discussion

The specific volumes of different phases of hydrogen hydrate are known from literature [3,4,6]. This allows an *in situ* determination of the hydrogen content of different phases of water. In our experiments, we measured the stationary value of pressure that was reached after varying the temperature or the total amount of hydrogen in the measuring unit. The drift of pressure ceased after about 5 minutes in the absence of phase transitions, after about 1 hour in the course of the $I_h \rightarrow$ *s*II and *s*II $\rightarrow I_h$ transitions, and after about 3–5 minutes when the *s*II phase was synthesized from liquid.

The solubility of hydrogen in the I_h phase of ice at T = –22°C increased from 0.1 wt.% at P = 0.5 kbar to 0.3 wt.% at P = 1 kbar, right before the transition to the *s*II clathrate phase took place (Fig. 1). After this transition, the content of hydrogen in the *s*II phase was about 1.2 wt.%. Further increase in pressure to 1.8 kbar led to the increase in the hydrogen solubility to 2 wt.%.

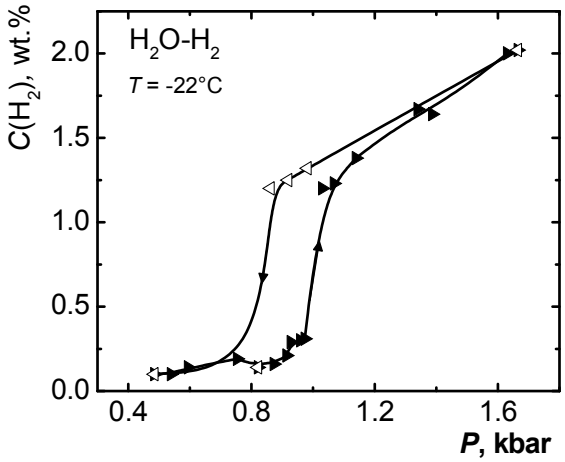

Fig. 1. Hydrogen solubility in H_2O at a temperature of –22°C. Solid triangles – at increasing pressure; open triangles – at decreasing.

On lowering the pressure at each temperature studied, a gradual decrease in the hydrogen content of the clathrate phase was always observed. At T = –22°C, for example, the hydrogen concentration decreased from 2 wt.% at P = 1.8 kbar to 1.2 wt.% at $P \approx$ 0.8 kbar, a transition to the I_h phase of ice occurring at a lower pressure.

Fig. 2 presents an isobar of the hydrogen solubility in liquid water and in the *s*II phase at P = 1.3 kbar. The amount of hydrogen dissolved in the liquid increased from 0.2 wt.% at +16°C to 0.4 wt.% at –18°C. After the transition to the clathrate phase, the hydrogen solubility rose to 1.9–2.0 wt.%.

Fig. 3 shows a portion of the *T*-*P* diagram constructed according to the results of our measurements. The transition pressure of ice I_h to the *s*II clathrate phase is around 1 kbar and weakly depends on temperature. The pressure of the reverse transition of the *s*II phase to ice I_h decreases with decreasing temperature from 0.9 kbar at –18°C to 0.5 kbar at –36°C. The synthesis of the clathrate phase from liquid occurs by 5 to 7 degrees below the melting temperature of ice I_h at the same pressure.

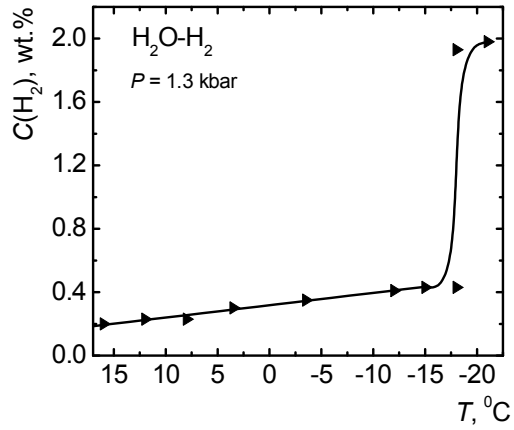

Fig. 2. Hydrogen solubility in H_2O in the course of lowering the temperature at a pressure of 1.3 kbar.

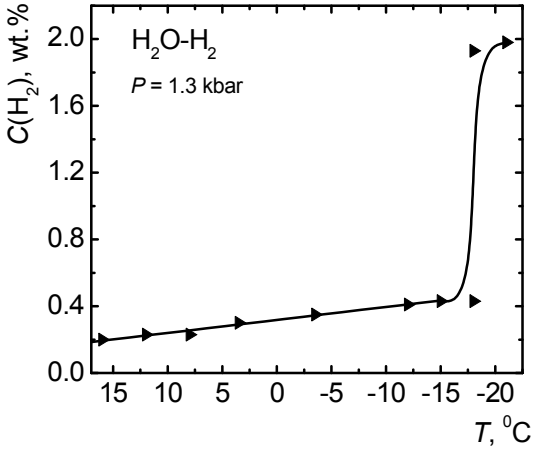

Fig. 3. *T-P* diagram of the H_2O-H_2 system. Solid circles indicate the points of the $I_h \rightarrow sII$ phase transition; open circles – the $sII \rightarrow I_h$ transition; solid triangles show the points of synthesis of the *s*II phase from liquid at decreasing temperature. The dashed line presents the decomposition line of the *s*II clathrate phase determined in [2]; the solid line gives the melting temperature of ice according to [6].

Conclusions

A phase transformation between ice I_h and the *s*II clathrate phase is first discovered and the pressures of the $I_h \rightarrow sII$ and $sII \rightarrow I_h$ phase transitions are determined in the temperature interval from –18 to –36°C. A line of synthesis of the *s*II clathrate phase from liquid is constructed in the pressure interval from 1.0 to 1.8 kbar.

Temperature and pressure dependences of the hydrogen solubility in the *s*II clathrate phase have been also determined *in situ* for the first time. The minimum hydrogen content obtained was 1.2 wt.% and corresponded to the ratio H_2O/H_2 = 136:15. This result contradicts the estimate H_2O/H_2 = 136:32 of Ref. [4] for the minimum hydrogen concentration necessary for the stability of the clathrate structure.

This work was supported by the Program "Physics and Mechanics of Strongly Compressed Matter" of the Russian Academy of Sciences and by the Russian Science Support Foundation.

References

1. Sandford S.A., Alamandola L.J., Geballe T.R. Spectroscopic detection of molecular hydrogen frozen in interstellar ices. Science 1993; 262: 400-402.

2. Dyadin Yu.A., Larionov E.G., Manakov A.Yu. Clathrate formation in the system water – noble gas (hydrogen) at high pressures. Zh. Strukt. Khimii 1999; 40(5): 974-980, in Russian.

3. Mao W.L., Mao H., Goncharov A.F., et al. Hydrogen clusters in clathrate hydrate. Science 2002; 297: 2247-2249.

4. Lokshin K.A., Zhao Y., He D., et al. Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction. Physical Review Letters 2004; 93(12): 125503-125507.

5. Klyamkin S.N., Verbetsky V.N. Interaction of intermetallic compounds with hydrogen at pressures up to 250 MPa: the $LaCo_{5-x}Mn_x$-H_2 and $CeNi_5$-H_2 systems. J. of Alloys and Compounds 1993, 194: 41-45.

6. Tonkov E.Yu. High Pressure Phase Transformations. Vol. 2. Ed. Ponyatovsky E.G. Philadelphia: Gordon & Breach, 1992. P. 448–450.